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Plasticity and creep in thin free-standing nanocrystalline Pd films

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Crystals are like people: it is the defects in them that make them interesting.

Sir Charles Frank

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 $^{^{1}}$ Même si l'alu flue, il est cool aussi!

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- M. Coulombier, G. Guisbiers, **M.S. Colla**, R. Vayrette, J.P. Raskin, T. Pardoen. *On-chip stress relaxation testing method for freestanding thin film materials*. Review of Scientific Instruments, 83 (10): 105004-105009, 2012.
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Acronyms

FCC	Face centered cubic
BCC	Body-centered cubic
HCP	Hexagonal close packed
PVD	Physical vapour deposition
nc	Nanocrystalline
ufc	Ultra-fine crystalline
mc	Microcrystalline
ns	Nanostructured
nt	Nanotwinned
H-P	Hall-Petch
GB	Grain boundary
TB	Twin boundary
TEM	Transmission electron microscope
SEM	Scanning electron microscope
FEG	Field emission gun
XRD	X-ray diffraction
MD	Molecular dynamics
GBAZ	Grain boundary affected zone
TBAZ	Twin boundary affected zone
SGP	Strain gradient plasticity
MEMS	Micro-electro mechanical system
FIB	Focused ion beam
BF	Bright field
DF	Dark field
ACOMTEM	Automated crystallographic orientation indexation in a TEM
EBSD	Electron backscattered diffraction
HRTEM	High resolution TEM
\mathbf{FFT}	Fast Fourier transform
GPA	Geometrical phase analysis
EELS	Electron energy loss spectroscopy

EFTEM	Energy filtering TEM
EDX	Energy dispersive X-ray
AFM	Atomic force microscopy
SADP	Selected area diffraction pattern
ICP-OES	Inductive coupled plasma - optical emission spectrometry
SPD	Shockley partial dislocation
FD	Frank disclocation
LAGB	Low angle grain boundary
HAGB	High angle grain boundary
FWHM	Full width at half maximum
NURBS	Non-uniform b-spline
SFE	Stacking fault energy
GND	Geometrically necessary dislocation
SSD	Statistically stored dislocation

_____ Part I _____

Introduction and background

In the constant race towards miniaturization, new scientific challenges continuously emerge. This context has motivated the scientific community to study the properties of thin films for more than 30 years. Thin films are materials presenting one extremely reduced dimension, from a few microns to a few nanometres. While thin films are often used for their functional properties (semiconductors, conductors, ...), the question of their mechanical integrity is a key for the reliability of the devices under interest. Indeed, this reduced dimension proved to be the origin of new and improved properties of thin films as compared to their bulk counterpart, for example an increased mechanical strength. Of course, other mechanical properties of thin films suffer from this size reduction like the ductility. A first scientific challenge is thus to understand the origin of the mechanical properties in order to isolate the key microstructural features that can lead to improved properties.

Palladium (Pd) is the material studied in this thesis. Two main reasons have lead us to consider this unusual material as a good candidate to study and resolve the scientific challenges presented before.

The first reason for selecting Pd is historical. This thesis was preceded by the master thesis and the PhD work of Renaud Delmelle on the hydriding kinetics of Pd thin films and by my master thesis on the effect of hydrogen on the mechanical response of Pd thin films. The deposition of Pd films was thus already controlled at UCL. Furthermore, the study of the mechanical properties of the Pd film itself was missing in the previous works. Also, through the study of the effect of hydrogen on the properties of Pd, a fundamental interest for studying this nanocrystalline material, which turned out to involve nanotwins as well, provided an additional motivation for the present thesis. Pd will thus be used here as a model material to study the mechanical properties of FCC nanocrystalline metallic thin films. It means that the results and observations obtained in this work should help to understand the mechanical behaviour of other FCC materials presenting similar nanocrystalline microstructure with, possibly, nanotwins, like Cu, Ag, Ni². Moreover, the use of Pd made possible to broaden the scope of the thesis and to close the loop by investigating how hydriding cycles alter the mechanical properties of thin palladium films.

The second reason is the industrial interest for this material. Thanks to its specific properties (e.g. good corrosion and oxidation resistance, chemical stability, electrical conductivity, erosion resistance), Pd is widely used in the industry as catalyst, in electronics, for hydrogen storage or detection, and in jewellery. The electronics industry begun to intensively study the properties of thin palladium films in the 1970s. At this time, the price of gold increased so much that it crea-

 $^{^{2}}$ One has to keep in mind that these materials are not perfectly comparable. For instance, their stacking fault energy affects i.e. the presence of twins and the extent of stacking faults which can, in turn, affect the mechanical properties.

ted a need to find a more viable material for electrical connectors and contact finishes. Palladium films proved to be one of the best candidates [1]. The exceptional affinity of palladium for hydrogen also made this material essential in a variety of hydrogen based technologies: thin palladium membranes constitute an enabling material for hydrogen storage [2], sensing [3], purification and separation technologies [4].

At the micro- and nano-scale, the second scientific challenge is to build an experimental set-up able to deform in a controlled way and to quantitatively measure the mechanical response of free-standing thin films [5]. The reduced dimensions of the samples require a test method that allows imposing very small forces (of the order of the μ N). The related drift control is thus also very important to produce an exploitable signal/noise ratio.

The main testing method used in this thesis consists in internal stress actuated on-chip tensile structures. The method has been developed at UCL in the years 2005-2006 [6,7] and has been upgraded since then, e.g. [8,9]. The idea is to use the internal stress present in a thin film to deform the material of interest.

To sum up, the objectives of this thesis are the following:

- to develop the on-chip microtensile method to obtain a stable process for the testing of free-standing Pd films;
- to characterize on-chip the yield stress, the ductility, the hardening behaviour and the strain rate sensitivity as a function of the deposition conditions and of a prior hydrogen loading;
- to compare the results of on-chip testing with nanoindentation;
- to identify the fundamental deformation and failure mechanisms using advanced microscopy techniques (SEM, TEM, HRTEM, ACOMTEM);
- to understand and model the link between the microstructure (e.g. grain size, twin density, texture), the mechanisms and the strength-ductility-creep properties;
- to propose routes to optimize the mechanical properties.

The work performed to reach these objectives was performed in a highly active collaboration framework involving different teams in different universities. Conventional and advanced TEM was carried out at the Universiteit Antwerpen by the team of Prof. D. Schryvers, while ACOMTEM was performed at the Université libre de Bruxelles by the team of Prof. S. Godet. The microscopy competences of these two teams have significantly contributed to this thesis. I have effectively participated to a few microscopy runs but the generation of the micrographs and the analysis of the observed defects was essentially performed by the colleagues from Antwerp and Brussels. Moreover, international collaborations have also lead to acquire an improved knowledge of the topic. Together with the team of Prof. H. Van Swygenhoven at the Paul Scherrer Institute (Switzerland) we were able to perform a first campaign of synchrotron X-ray diffraction experiments on our specimens. Also, a short stay at the University of Illinois at Urbana-Champaign (USA) in the team of Prof. T. Saif has allowed the mechanical testing of Pd films under cyclic conditions.

This thesis is organized as follows. First, the thin film problematic will be introduced in chapter 1. Therein, a literature overview of the deformation mechanisms in small-scale metallic materials will be provided in addition to a literature review of the different experimental techniques developed to characterize this kind of materials, see chapter 2. The second part of the thesis will detail the experimental techniques used during this work, and will expose some basics about Pd as well as the as-deposited microstructure of the studied Pd films (chapters 3 and 4). The process parameters used to modify the Pd microstructure will also be discussed in this chapter. Finally, in the third part, the results will be shown and discussed. The effect of the film thickness on the strength, the strain hardening and the ductility will be first presented and modelled (chapter 5). The next chapter (6) contains additional results showing the effect of different Pd configurations and microstructure on the strength, strain hardening and ductility. Then, in chapter 7, the rate dependent plasticity and the related relaxation mechanisms in the Pd films will be studied. And finally, the hydriding effect on the mechanical and relaxation properties will be considered in chapter 8.

Chapter 1

Background I: Mechanics of thin metallic films

The study of the mechanical properties and the understanding of the related deformation mechanisms for small scale materials does not only concern fundamental research but is also a concern for the microelectronics industry and the surface functionalization industry. For them, the knowledge of the mechanical limits of the small scale materials, which are submitted to e.g. internal stresses, tension and wear, is of primary importance.

The miniaturization has motivated the production of materials with a so small characteristic length scale that their deformation mechanisms were not anymore comparable to the classical bulk materials. The miniaturization leads on one hand to the reduction of the structure dimension ($< 1 \mu$ m), and on the other hand to the possibility to point out the microstructure characteristics (e.g. grain and twin size) which are reduced to much less than 1 µm. This has pushed the scientific community to understand such nanoscale materials as some properties are enhanced at the nanoscale and others, like ductility, are deteriorated.

This chapter is divided in two sections. First, the characteristics related to the confinement of one direction of the material will be presented. More specifically, attention will be paid to the size effects and the processing techniques. As thin films exhibit one reduced dimension and are processed on a substrate, i.e. differently than bulk materials, they often involve very small grains of the order of tens of nanometres and non negligible internal stress. A short overview of the different origins of the internal stress is also given is this section. The second section will thus present the effect of a reduced grain size on the mechanical

properties and on the deformation mechanisms of nanocrystalline materials. This last section will not be restricted to the study on nanocrystalline thin films but will also include the results and the understanding of bulk nanocrystalline materials.

1.1 State-of-the-art: thin metallic films

Thin films present the particularity to have one reduced dimension compared to the two others. This section will successively present the size effects generated by the size reduction, the processing routes commonly used to prepare thin metallic films, and finally the origins of the internal stresses present in thin films.

1.1.1 Size effects

The main difference between bulk materials and thin film materials is related to the increased surface/volume ratio of thin films. The difficulty in this work is to understand and to separate the size effects coming from the reduced dimension of the nano- or microstructure and those coming from the reduced dimension of the sample.

The particularity of thin films is that their behaviour results in a combination of both intrinsic size effects and extrinsic size effects. As a matter of fact, the grain size is usually dependent on the film thickness [10]. Very small film thicknesses thus lead to a nanocrystalline structure. A reduced grain size will affect the properties of the material through what is called *intrinsic size effects*. Moreover, the geometry of thin films, with one direction (the thickness) much smaller than the two others, increases the surface/volume ratio with comparison to bulk materials. This contributes to the *extrinsic size effects*.

Intrinsic size effects occur when microsctructural length scale governs the mechanical properties. The properties are dependent on the grain size but not on the size of the sample. On the contrary, extrinsic size effects are related to how the sample size and the boundary conditions affect the mechanical properties of the material [11,12].

Experimentally, monocrystalline samples with different geometrical size are used to assess the extrinsic size effects while nanocrystalline materials, where the grain size is much lower than the sample size, are used to evaluate the intrinsic size effects. Thin films involve a combination of both size effects due to the small thickness which is often similar to the grain size.



Figure 1.1: Global view of extrinsic and intrinsic size effects. Picture taken from [11].

Figure 1.1 presents on a 3-D plot, a summary of combined intrinsic and extrinsic size effects on Ni or Ni-based alloys [11]. See [13–16] for the respective experimental data. The experimental points have been obtained in tension and in compression. The authors considered that for mostly all crystalline materials (except body-centered cubic materials and ordered compounds) the deformation behaviour is the same in tension than in compression [11].

This section will focus on the extrinsic size effects. The intrinsic size effects will be detailed in section 1.2.

Extrinsic size effects have been mostly studied using micro-compression due to an easier experimental implementation (see e.g. [17]). But progressively some research groups begun to explore these effects in tension like Espinosa et al. [18] who investigated Au, Cu and Al membranes using their home made membrane deflection tensile technique (see section 2.3). The major issue in prospecting extrinsic size effects in tension is the use of thin film materials where the grain size often depends on the film thickness. This point is still problematic since Xiang et al. attributed the film thickness effect observed on the mechanical properties to a change of grain size [19].

The effect of a boundary layer around a film can be included as part of the extrinsic size effects. Vlassak et al. have experimentally pointed out the role of a passivation layer on Cu and Al films [20]. Firstly, they observed a film thickness effect for passivated films and succeeded in modelizing it [21]. The passivated films are significantly stronger than the unpassivated one. Secondly,



Figure 1.2: Schematic view of the dislocation channelling theory of Nix. *Picture taken from [10].*

they observed a strong Bauschinger effect under the presence of a passivation layer due to the dislocation barrier created at the film surface. Dislocations are not free to escape from the surface of passivated films, generating back-stress which is known to be responsible of the presence of the Bauschinger effect [20]. A more detailed description of the Bauschinger effect will be presented below in section 1.2.1.

A model was proposed by Nix [10] to understand the thickness effect and the boundary layer effect on the mechanical properties of thin films. He interprets the effect using a dislocation channelling theory, see figure 1.2.

1.1.2 Processing

The two most used techniques to deposit metallic thin films are electrodeposition and physical vapour deposition (PVD). Other methods have been used during the last three decades but they are less interesting in a mechanical point of view due to the porosity they induce inside the films (e.g. inert gas condensation). This section will focus on the two most important PVD deposition methods related to this thesis, namely the evaporation and the sputtering. More information on other deposition processes can be found in [22, 23].

The PVD appellation gathers the methods able to deposit a film by the condensation of a vapour atmosphere of the material. The deposition is done only via the transfer of atoms from a source to a substrate. No chemical reactions enter into the deposition process.

The microstructure of a film depends on the processing technique and on the parameters used. Thornton has summarized the different reachable morphologies in sputtering, see figure 1.3 [24]. The propensity to create columnar grains can be avoided by regularly interrupting the deposition, as proposed by Chen et al. on Al thin films [25].

Finally, it is worth noting that films deposited by PVD often exhibit a texture due to the preferential growth of grains oriented in the lowest surface energy



Figure 1.3: Microstructure map for different argon pressure and substrate temperatures. Zone 1 is characterized by a porous structure with tapered crystallites separated by voids, zone T is a transition zone where the grains are fibrous but condensely packed, zone 2 consists in columnar grains and zone 3 generates a recrystallized grain structure. Figure taken from [24].

configuration [18]. Indeed, the (111) orientation has the lowest interface energy and the highest biaxial elastic stiffness, while the (100) has the lowest biaxial modulus and thus the lowest strain energy at a given elastic strain [26].

Evaporation

During evaporation, atoms are thermally removed from the source and condensate on a substrate located in front of the source. Metals can be classified into two categories depending on whether the vapour effectively emanates from a liquid or from a solid source:

- metals that can be evaporated only when the source is sufficiently heated to become liquid (most metals belong to this category),
- metals that can reach sufficiently high vapour pressures below the melting point, i.e. metals which sublime (like e.g. Ti, Cr, Mo, Fe).

One advantage of evaporation is the prospective high deposition rate and the high vacuum conditions (around 10^{-7} mbar inside the chamber). These two characteristics lead to a high purity of the deposited films. The high vacuum is crucial to increase the mean free-path of the evaporated atoms and to prevent the incorporation of impurities into the deposit. This is highly valuable as for instance gaseous impurities like oxygen or nitrogen are responsible for an increase of the hardness of Al thin films [22].

Two different techniques exist to evaporate the material from the source. The first way consists in using resistively heated sources made either in refractory metals alone, or in a combination with inert oxide or ceramic compound crucibles. The main disadvantages of this resistive evaporation are the contamination of the evaporated material by the crucibles, by the heaters and by the surrounding materials, and the limitation of the resistive heating which makes difficult to evaporate materials with a high melting point under a decent rate.

The second technique to evaporate materials is by using an electron beam to locally heat the source. The heating of a tungsten filament emits electrons that are then accelerated by a magnetic field. This is often the preferred evaporation route today as it allows theoretically the evaporation of all materials at any rate. Moreover, as the charge to evaporate is placed in a water-cooled crucible and due to the very local heating of the source by the beam, only a small amount of the charge melts or sublimes. This improves the already good purity of the deposited films. In this thesis, the e-beam evaporation technique was used to deposit the Pd films.

The evaporation process does not allow playing with a wide range of deposition parameters. Usually, only the deposition rate can be varied. This limits the achievable microstructure range.

Sputtering

In sputtering, atoms are removed from a solid target through impact of energetic ions. The target is connected to the negative terminal of a direct current (DC) or radio frequency (RF) power supply. The target is playing the role of the cathode. Typically, several kilovolts are applied to it. The substrate that faces the cathode may be grounded, electrically floating, biased positively or negatively, heated, cooled, or some combination of these. After the vacuum is made in the chamber, a gas, typically argon, is introduced and serves as the medium in which a plasma is initiated and sustained. Gas pressures usually range from a few to 100 mTorr [22].

Since sputtered atoms carry more energy than evaporated atoms, the density of sputtered films is generally higher than for evaporated films. However, an important issue of sputtering is the temperature rise of the substrate during film deposition.

Different categories of sputtering methods exist:

• DC sputtering: a continuous current is applied between the anode and the cathode,

- RF sputtering: thanks to the polarization variation of the voltage source, RF sputtering can be used to deposit insulating films. Indeed, without this alternating voltage, the accumulation of positive or negative charges on insulating targets will prevent further material deposition.
- Magnetron sputtering: the electrons emitted from the cathode are accelerated via a magnetic field. Higher deposition rates are thus possible and it allows a decrease of the pressure chamber. This will improve the purity of the deposit.
- Reactive sputtering: deposition of compounds from metallic targets in the presence of a reactive gas usually mixed with Ar. The most common compounds produced by reactive sputtering are oxides, nitrides, carbides, or sulfides.

On the contrary to evaporation, sputtering is more flexible regarding the deposition parameters (e.g. the Ar pressure, the sputtering category and the temperature of the substrate). They have a large impact on the microstructure of the deposited film compared to evaporation, see the Thornton diagram in figure 1.3.

1.1.3 The origin of internal stresses

When resting on a substrate, most thin films and coatings involve a certain amount of internal stress¹. Internal stresses can induce different undesirable effects in the film/substrate system including film delamination, fracture, buckling and cracks in the film and/or in the substrate, and can drive microstructure evolution. Their control is thus of primary importance for the production of reliable industrial devices.

Internal stresses can be classified into three categories depending on their origins.

The first category involves *thermal stresses* which develop due to a thermal mismatch between the film and the substrate as a result of a difference in thermal expansion coefficient. This can happen for instance when a film is deposited on a substrate at high temperature in a stress-free state and when the system cools down to room temperature [10]. In this case, the related film stress can be written:

 $^{^1\}mathrm{The}$ term 'residual stress' is also often found in the literature as a synonym of 'internal stress'.



Figure 1.4: Typical evolution of the internal stress during the film growth as a function of the deposited thickness. Figure adapted from [27].

$$\sigma_{th} = \frac{E_f}{1 - \nu_f} \Delta \alpha \Delta T, \qquad (1.1)$$

where E_f and ν_f are the Young's modulus and Poisson ratio of the film, $\Delta \alpha$ is the thermal expansion coefficient mismatch between the film and the substrate, and ΔT is the temperature difference between deposition temperature and room temperature.

The second type of internal stress is called *growth stress* or *intrinsic stress*. These stresses arise during the growth process of the film on the substrate. In the initial stage of deposition, the material forms islands (or crystallites) on the substrate, see figure 1.4. This leads to the creation of compressive internal stress due to the action of surface and/or interface energy. By increasing the thickness, the crystallites begin to coalesce, which causes a switch to a tensile state of stress, see figure 1.4. By increasing further the thickness of the film, some relaxation phenomena appear due to the incorporation of new atoms in the lattice, inducing the reduction of the tensile stresses or even the apparition of compressive stresses.

Finally, the last possible origin for the presence of internal stress is related to epitaxial growth. *Epitaxial stresses* are the result of the constraint of a crystalline substrate on a crystalline film dictated by coherency requirement between the two crystalline lattices. Epitaxial growth involves the coherency between the film and the substrate lattice. However, the lattice parameter mismatch between them leads to internal stresses in the film, see figure 1.5. Misfit dislocations are sometimes generated to relax the elastic strain in the film.



Figure 1.5: Schematic origin of tensile epitaxial stress in thin films. a_f and a_s are the lattice parameters of the films and the substrate, respectively.



Figure 1.6: Evolution of the stress.thickness product as a function of the deposited thickness for various argon sputtering pressures. Picture taken from [28].

In this thesis, the Pd films were deposited by e-beam evaporation. This deposition process does not provide high degree of freedom to vary and/or control the internal stress level in the films. In this work, for e-beam evaporated Pd, only tensile stresses have been produced, as explained later in section 4.4. It is interesting to note that sputter deposition does not suffer from this limitation in the control of the internal stress level thanks to the high kinetic energy of atoms arriving at the growth surface and to the fact that the argon atmosphere in the deposition chamber can be modified. The bombardment of the growth surface is depending on the energy of the arriving atoms and on the argon pressure. For instance, the effect of the argon pressure on the internal stress of Pd films deposited by DC magnetron sputtering at a power of 120 W has been measured by Delmelle et al. [28], see figure 1.6. The internal stress has been monitored in-situ during film growth, see [29] for more details. The internal stress in thin films can be measured using different methods, e.g. by substrate curvature measurements, by optical measurement of the substrate curvature, or by dedicated on-chip structures. These listed methods will be detailed in sections 2.1, 4.3 and 3.2, respectively.

1.2 Nanocrystalline materials

The usual classification of materials found in the literature is the following (e.g. [30]): for a grain size lower than 100 nm, the material is called nanocrystalline (nc). When the grain size ranges between 100 nm and 1 µm, it is considered as ultra-fine crystalline (ufc). For grain size bigger than 1 µm, the term microcrystalline (mc) is used. Some authors have added a last category of nanostructured materials (ns) for which one or more internal dimensions are smaller than 100 nm [31–33]. The lower bounds in terms of grain size for nanocrystalline materials are amorphous materials [34].

The limited ductility but high strength of nanocrystalline materials has opened new challenges to optimize their mechanical properties by playing with the microstructure and with the architecture of the materials. The classical methods used to strengthen and to improve the mechanical properties of classical coarse-grained bulk materials (e.g. alloying, solid solution strengthening or precipitation hardening) cannot be easily transposed to nanocrystalline materials [11]. The point is that due to the high grain boundary density of nanocrystalline materials, their deformation mechanisms are more affected by grain boundaries than microcrystalline materials. Also, a huge challenge is to deal with microstructural and stability problems like porosity or grain growth that are frequent in nanocrystalline materials [35].

In this part, nanocrystalline materials either in bulk or thin film forms will be considered. There exists various processing routes to produce nanocrystalline materials. They can be classified into two main categories: the bottom-up and the top-down approaches [35]. The first category includes the deposition methods where the nanocrystalline material is produced by adding atoms to a substrate. This bottom-up approach is mainly used to produce thin films. The different ways to grow a film have been presented in the section 1.1.2. The second category consists in breaking the bulk microstructure into a nanostructure to produce bulk nanocrystalline materials (e.g. via severe plastic deformation [31] or mechanical milling/alloying [36]).

When studying nanocrystalline materials, a major issue is to compare results that are comparable. The porosity, the defect density, the grain size distribution, the residual stresses, the distribution of interface misorientation angles,



Figure 1.7: Effect of the porosity on the Young's modulus and on the yield strength of nanocrystalline materials. Figures taken from [39] on the basis of [37, 38].

the impurities content constitute a non exhaustive list of parameters that can influence the mechanical properties.

The following sections will present first how the elastic and plastic properties are affected by the reduced grain size of nanocrystalline materials and second, which deformation mechanisms are active in presence of very small grains? This will open roads to possibly improve the ductility of nanocrystalline materials.

1.2.1 Mechanical properties of nanocrystalline materials

The understanding of the mechanical properties of nanocrystalline materials is of prime importance before trying to optimize these properties. This section will present and compare the mechanical properties of nanocrystalline materials with those observed for microcrystalline materials. Only the case of fully dense FCC nanocrystalline materials will be addressed. Actually, the issue of porosity has been intensively explored and it is now accepted that the porosity artificially decreases the yield strength and the Young's modulus of nanocrystalline materials, see figure 1.7 [37,38].

Young's modulus

The Young's modulus is a mechanical property linked to the strength of the atomic bonds. For classical coarse grained materials, the Young's modulus is a function of the chemical composition and of the crystallography of the material but not a function of the other microstructure specifications. This assumption is invalid for nanocrystalline materials where the percentage of grain boundary atoms is not anymore negligible [40]. The first studies reported a decrease of

the Young's modulus when the grain size becomes lower than 20 nm [41–43]. Although this observation was later related to the low density of those samples and that a strong dependence of the elastic modulus and the porosity was established [38], other studies on porosity-free nanocrystalline metals revealed the same tendency both experimentally [44] and numerically [45]. Some authors suggest that the magnitude of this effect is linked to the anharmonicity of the potential energy curve [46].

Yield Strength

The yield strength is the stress at which a material begins to deform plastically. For conventional coarse grained materials, this criterion is relatively easy to define and an empirical criterion is often used: the engineering yield strength is the stress necessary to induced a permanent deformation of 0.2%. This corresponds to the transition from microscopic yielding to macroscopic yielding. The microplastic regime begins when at least one grain is deforming plastically, while the macroplastic regime starts when all the grains are deforming plastically. For nanocrystalline materials, this definition is not so obvious. Nanocrystalline materials often present a smooth stress-strain curve and a long elasto-plastic transition for which the macroscopic yielding appears at around 2-10% of deformation, far from the 0.2% of coarse grained materials [47, 48]. Some authors used a tangent modulus approach where the macroscopic yield stress is defined as the point where the tangent modulus θ ($\theta = d\sigma/d\varepsilon$) is less than one third of the Young's modulus [49]. Others are less accurate but mention that at $\sim 1\%$ of plastic strain, all the grains have been sheared by at least one dislocation, which is the requirement to claim a macroyielding regime [48]. Saada and co-workers proposed to determine the large spreading of the microplastic regime by the extraction of the plastic strain rate from the stress-strain curve [47]. This value is however dependent on the strain rate. Ames and co-workers established the macrovield strength by linearly extrapolating the normalized strain hardening rate versus the applied stress to cross the abscissa [50].

The Hall-Petch (H-P) semi-empirical law predicts an increase of yield strength when the material grain size decreases (equation 1.2) [51, 52]:

$$\sigma_y = \sigma_0 + k d^{n_d} \tag{1.2}$$

where σ_y is the yield stress, σ_0 and k are material constants, d is the grain size and n_d is an exponent comprised between -1 and -0.4. The mostly used value of n_d is equal to -1/2 but is not always well accepted, see for instance in [53]. The physical interpretation of this law will be presented in section 1.2.2 in the next paragraph discussing the dislocation nucleation and activity. Note that the strengthening effect with the grain size reduction is less marked in BCC and HCP materials than in FCC materials [54].

Nanocrystalline materials follow the H-P trend down to a grain size of ~ 10 -20 nm. Below that limit, dislocations sources cease to operate due to the too small grain size. Some authors proposed new deformation mechanisms by grain boundary sliding, grain boundary migration or diffusion and an evolution of the yield strength scaling with 1/d under the critical grain size of 15 nm. Other groups observe an inverse Hall-Petch effect, i.e. a decrease of yield strength under this critical grain size [55, 56]. The mechanisms involved at this critical grain size are not yet understood and are still under debate due to the difficulty of sample preparation and analysis, see section 1.2.2 for more details.

Decreasing the grain size is not the unique way to improve the yield strength. During the last decade, people have found that nanoscale growth twins were, like grain boundaries, strong obstacles for dislocation motion. By reducing the twin boundary spacing, both the yield strength and the ductility are increased (as discussed in the next item). As for the grain boundaries, a critical twin boundary spacing exists under which this trend is not valid anymore. This critical spacing arises when the pile-up and cutting of twin boundaries by dislocations becomes impossible due to the reduced length scale, and when it switches in a dislocation nucleation controlled softening mechanism [57]. The critical twin boundary spacing is a function of grain size. The smaller the grain size, the lower the critical spacing and then the higher the maximum strength [57].

In some nanocrystalline materials, the yield strength is seen to decrease with time for long or slow mechanical loadings due to dynamic grain growth [35,58]. This comes from the far from equilibrium nanocrystalline structure. The stress applied during a mechanical test can be sufficient to promote the relaxation of the high excess energy associated with the high density of boundaries. This effect can be delayed by the presence of impurities in grain boundaries [59].

Furthermore, some authors have shown using numerical simulations that a solid solution can increase the strength of nanocrystalline nickel [60].

Finally, Shao et al. have highlighted the stochastic character of the yield stress in nanocrystalline materials [61]. They have demonstrated that the onset of plasticity is stochastic in small volumes containing a small density of dislocations because of the statistical variation of the initial dislocation content.

Ductility

The ductility represents the ability for a material to deform plastically without failure. Two mechanisms control the amount of ductility: the plastic localization in the form of diffused or localized necking due to the low strain hardening capacity (see next point), or the damage controlled mechanism which appears most often at the grain boundaries due to porosity, impurities or stress concentrations [62]. Contrarily to their coarse grained counterpart, nanocrystalline materials are known to exhibit a low ductility. This was attributed to the small length scale of the grains which allows only few dislocation movements and storage. Huge effort has been done these last 20 years to understand how to improve the ductility without deteriorating the high strength of nc materials to make those nc materials industrially viable.

The first studies reported a very small ductility. This was partly due to a material processing artefact, namely the porosity [30,63].

There exists an empirical criterion established by Considère to quantify the amount of ductility. The Considère's criterion predicts the onset of unstable flow when the strain is equal to the strain hardening exponent: $\varepsilon_u = n$ [64]. This criterion has been extended by Hart to include the strain rate sensitivity effect: $\varepsilon_u = \frac{n}{1-m}$ [65] where ε is the ultimate strain, n is the strain hardening exponent and m is the strain rate sensitivity. Note that the Hart's criterion is only qualitative as it largely underestimates the effect of the strain rate sensitivity on the ductility. A more exact approach, proposed first by Neale and Hutchinson, relies on a localisation analysis taking into account the imperfection magnitude [66,67]. This more accurate analysis leads to a more pronounced dependence of the ultimate strain regarding the strain rate sensitivity exponent, see figure 1.8.

Some years ago, people succeeded in producing nanocrystalline material with high strength and high ductility thanks to high quality samples without porosity (see [68] for nc Cu, and [69] for nc Ni and Ni-Fe alloys). But the mechanisms still need to be identified because they probably do not involve classical dislocation based mechanisms due to their very small grain size.

The ductility of nanocrystalline thin films is usually smaller than for nc bulk materials due to their increased sensitivity to propagate surface cracks which leads to instabilities or failure [35]. Indeed, the lower density of free surfaces in bulk nc materials prevents the easy cracks propagation. Huge effort is made today to improve the ductility and new insights have been proposed for that [33]. Only the routes of improvements which can be used for pure metallic films will be presented below.

A first way to increase the ductility is to mix up length scales by creating a


Figure 1.8: Variation of the strain at localisation ε_{inst} as a function of the strain hardening exponent n and of the strain rate sensitivity exponent m for an imperfection f of 0.999. Figure taken from [67].

controlled grain size distribution. A bimodal grain size distribution imparts high strength thanks to the heterogeneity of the micro- and nanocrystalline grains. This induces strain hardening mechanisms (kinematic hardening origin mainly) through the high strain gradients between adjacent grains which stabilise the deformation [70].

The same ductility improvement is observed when nanoscale growth twins are present inside materials [71–73]. In addition to create a multimodal length scale distribution, coherent twin boundaries, which are low energy defects, constitute strong obstacles to dislocation motion. Morevover, they do not permit dynamic recovery like grain boundaries or dislocation cells [71,73,74]. We will come back to plastic strain recovery later.

The last improvement route is to increase the strain hardening capacity or/and the strain rate sensitivity. As exposed in figure 1.8 and in [75], a high strain hardening exponent n coupled with a high rate sensitivity m will lead to a higher fracture strain. In nanocrystalline materials, as grain boundary mediated mechanisms are promoted, a high m value is not surprising [75]. However, it is concomitant to a reduced strain hardening capacity due to the absence of dislocation nucleation and storage. Those properties will be discussed here under.

Strain hardening

Efficient isotropic strain hardening mechanisms are usually not observed in nc materials with grain size below $\sim 100 \text{ nm}$ [76], unless deformation is performed

under high pressure [77]. The limited strain hardening leads to plastic instability and causes localized deformation at low plastic strain [30]. Conventional strain hardening mechanisms like forest hardening have never been observed in standard conditions (room temperature and atmospheric pressure).

The nucleation of dislocations in nanocrystalline materials most often arises at grain boundaries due to the very small grain size which prevents intragrain nucleation sources [39] and because of the disordered structure of grain boundaries. In the same time, grain boundaries have also been seen to act as dislocation sinks. Dislocations then emerge at GB, cross the grain and disappear in the opposite GB [78]. This mechanism does not lead to dislocation storage. Furthermore, dynamic recovery decreases the already low dislocation density [39].

Nevertheless, significant kinematic hardening is observed in nc materials. Indeed, during the long microplastic regime, interfacial deformation probably takes place to accommodate the deformation between adjacent grains [50, 79]. It results in a high deformation heterogeneity inside the material as well as in the creation of long-range back stresses² [80]. The physical mechanisms related to strain hardening will be described in section 1.2.2. Note that the presence of twins increases the strain hardening rate [81].

Strain rate sensitivity

As explained before, the control of the strain rate sensitivity provides a way to improve the ductility. Two parameters are of primary importance to understand the kinematics of plastic deformation: the activation volume V_{act} and the strain rate sensitivity coefficient m. The theoretical foundations needed to interpret these two properties will first be recalled in this sub-section, inspired by publications of Argon [82], Poirier [83] and Kocks et al. [84].

A theoretical thermodynamic framework can be used to express these two parameters and their dependence on temperature and applied stress. Before detailing the relations, it is interesting to recall some basics of thermodynamics. The two quantities used to describe the properties of a closed system are the internal energy U and the entropy S. The first and the second laws of thermodynamics restrict the way the system can change under an increment of work ΔW and an increment of heat ΔQ :

$$\Delta U = \Delta Q + \Delta W, \tag{1.3}$$

 $^{^{2}}$ The notion of long-range stress will be introduced in the next paragraph.



Figure 1.9: State evolution of a system deformed from A to B. (a) Helmholtz free energy ΔF as a function of the applied shear strain γ , and (b) evolution of the shear resistance τ as a function of the shear strain γ . Figure taken from [82].

$$\Delta S \ge \frac{\Delta Q}{T}.\tag{1.4}$$

As the analysis only considers properties and variations at constant temperature only, it is useful to define another property of the system: the Helmholtz free energy F:

$$\Delta F = \Delta U - T \Delta S. \tag{1.5}$$

If we now consider an experiment in which the overall system is deformed by small increments of shear strain $d\gamma$ from $\gamma = 0$ (state A) to $\gamma = \Delta \gamma_0$ (state B), the expected Helmholtz free energy evolution of the system should look like to the energy profile presented in figure 1.9.

By taking V as the volume of the system, the shear resistance is defined as:

$$\tau \equiv \frac{1}{V} \frac{\partial \Delta F}{\partial \gamma}.$$
 (1.6)

Under an applied shear stress σ , it should be possible to deform the system from $\gamma = 0$ to $\gamma = \Delta \gamma_0$. On two points in figure 1.9(b), σ is in equilibrium with the shear resistance: at γ_s where $\Delta F > \Delta W$ (stable position) and at γ_u where $\Delta F < \Delta W$ (unstable position).

The energy barrier to overcome in figure 1.9(b) is equal to:

$$\Delta G^* = \Delta F^* - \Delta W^*,$$

= $V \int_{\gamma_s}^{\gamma_u} \tau(\gamma) d\gamma - V \sigma(\gamma_u - \gamma_s),$ (1.7)

where the asterisks are used to denote the quantities related to the activation process. ΔG^* is thus the required activation free energy that must be provided by thermal fluctuations to transform the system from the stable position s to the unstable one u under an applied stress σ^3 . Once the barrier is overcome, the system spontaneously reaches the next stable position s'. An increase in the strain rate produces the same effect on this energy barrier as a decrease of temperature, i.e. it requires a higher effective stress to overcome the barrier.

Note that after the overcoming of the barrier, the energy ΔF at state B is often higher than the one at the initial state A. It means that a part of the applied stress σ must serve to this free-energy storage. The component of the stress available to assist the system over the thermally penetrable obstacles is $\sigma_{eff} = \sigma - \sigma_i$, where σ_{eff} is called the effective stress and σ_i the internal stress⁴. Another view of the internal and the effective stress is that mobile dislocations in polycrystals experience resistance due to forces arising from their long-range elastic interactions, also called 'back-stress', which exhibit longwavelength spatial fluctuations (σ_i) and due to short-range interactions with localized obstacles such as impurities, forest dislocations or grain boundary structures which exhibit short-range fluctuations (σ_{eff}) [79, 85, 86]. σ_i is thus athermal and depends only on the strain, whereas σ_{eff} in combination with thermal fluctuations is needed to overcome the short-range obstacles. It has been found that σ_i is roughly equal to three times σ_{eff} in some nanocrystalline materials [85]. The σ used in the following should thus be taken as the effective part of the applied stress.

The activation rate R for the inelastic process is equal to

 $^{{}^{3}\}Delta G^{*}$ can be associated to the Gibbs free energy used in classical thermodynamics, with the difference that the work considered here involves the global stress tensor and not only its normal components constituting the pressure.

 $^{^4\}mathrm{The}$ term 'internal stress' used here has to be distinguished from the appellation used in section 1.1.3.

$$R = \nu_G \exp\left(\frac{-\Delta G^*}{kT}\right),\tag{1.8}$$

where ν_G is a characteristic normal mode frequency of the defect type taking place in the activation process, k is the Boltzmann constant and T is the absolute temperature. The exponential factor gives the probability that a thermal fluctuation provides the extra energy required to overcome the barrier at a temperature T. As we are interested in the net inelastic strain rate $\dot{\gamma}$ here, it is possible to transform equation (1.8) to:

$$\dot{\gamma} = Rc_f \Delta \gamma^T = \nu_G c_f \Delta \gamma^T \exp\left(\frac{-\Delta G^*}{kT}\right),\tag{1.9}$$

where c_f is the volume fraction of material that can take part to the relaxation process, with an associated shear strain $\Delta \gamma^T$. We can now define the shear activation volume as

$$\begin{aligned} V_{act} &\equiv -\left(\frac{\partial(\Delta G^*)}{\partial\sigma}\right)_{p,T}, \\ &= kT\left(\frac{\partial\ln\dot{\gamma}}{\partial\sigma} - \frac{\partial\ln\dot{\gamma_0}}{\partial\sigma}\right), \\ &\simeq kT\frac{\partial\ln\dot{\gamma}}{\partial\sigma}, \end{aligned} \tag{1.10}$$

where $\dot{\gamma_0}$ is equal to $(\nu_G c_f \Delta \gamma^T)$. This is the general form of the activation volume, regardless of the involved mechanism. This expression can be translated in terms of a tensile stress and tensile strain by using the Taylor factor M: $V_{act} = MkT \frac{\partial \ln \dot{\gamma}}{\partial \sigma}$. The Taylor factor value depends on the deformation mechanisms and its value is still under debate for nanocrystalline materials as some authors used a Taylor factor equal to 3 or $\sqrt{3}$ [86–88]. A detailed discussion about the Taylor factor value can be found in appendix A. The activation volume is usually expressed in b^3 where b is the Burgers vector of the slip system under interest for dislocation based deformation, or, by extension, the volume of a vacancy for a diffusion based mechanism.

If the relaxation mechanism is based on dislocation glide, equation (1.10) can be simplified by using and integrating equation (1.7). This gives

$$V_{act} = b\lambda \Delta y^*, \tag{1.11}$$



Figure 1.10: (a) Schematic view of a dislocation of length 2λ pressing, under an applied force σb against an obstacle located at O. (b) Zoom on the obstacle region. Figure taken from [82].

where b is the Burgers vector, λ is the spacing between obstacles in the glide plane and Δy^* is the activation distance, see figure 1.10 for a schematic description.

Many authors also use the empirical strain rate sensitivity exponent $m = \frac{\partial \ln \sigma}{\partial \ln \dot{\epsilon}}$ to describe thermally activated phenomena. This parameter originally comes from the fact that it is often experimentally observed that $\dot{\epsilon} \propto \sigma^{1/m}$. V_{act} and m are linked through $V_{act} = \frac{MkT}{\sigma m}$.

Experimentally, V_{act} and m can be measured by different methods such as nanoindentation [89], tensile strain rate jump tests [90], nanoindentation strain rate jump tests [91], strain dip tests [83,85] or direct tensile testing [73]. The main issues in experimental tests are to test materials without any variation of microstructure at different rates to be able to extract the true activation volume and to separate the effective stress from the long-range stresses. For instance, for strain rate jump tests and strain dip tests, it is possible to separate experimentally σ_i and σ_{eff} .

A high m (or equivalently a small V_{act}) implies also an increased temperature dependence of the stress [74]. Small activation volumes bring up to an easier thermal activation of the mechanisms.

The strain rate sensitivity coefficient and the activation volume are directly related to the rate controlling plastic deformation mechanisms in materials. In nanocrystalline materials, it is then not surprising to find an increased strain rate sensitivity as compared to conventional materials because dislocation based mechanisms ($V_{act} \sim 10^2 - 10^3 b^3$) are progressively replaced by grain boundary-dislocation interaction mechanisms ($V_{act} \sim 1 - 10 b^3$) [39, 92]. Figure 1.11 presents the evolution of the strain rate sensitivity with the grain size d and the twin lamellar spacing λ [35]. Nanoscale twins play an identical role as grain



Figure 1.11: Evolution of m with the grain size and twin lamellar spacing. Picture taken from [35] and references therein.

boundaries leading to an increased strain rate sensitivity [73,89,93,94]. Some authors have established an analytical relation between V_{act} and the grain size d leading to the same conclusion [95]. Note that the enhanced strain rate sensitivity of metals when reducing the grain size is only observed for face centered cubic (FCC) materials. Indeed, in body-centered cubic materials, the rate-limiting mechanism is the rather strong Peierls barrier to dislocation motion in the lattice itself [90].

The *m* values reported in figure 1.11 are four times higher when the grain size is decreased to the nanoscale. This is still too low to be a signature of grain boundary sliding (m = 0.5) or Coble creep (m = 1) mechanisms [35,95]. The corresponding activation volume for grain boundary sliding and Coble creep is of the order of atomic volume, i.e. $\sim 1 b^3$. It indicates that grain boundary diffusion mechanisms are not the dominant deformation modes for nanocrystalline materials with d > 10 nm. A mix between GB diffusion and dislocation-GB interaction probably happens. Sanders and co-workers attributed that value of *m* to the high fraction of low energy grain boundaries (growth twins) and to the low dislocation activity due to the small grain size [96]. Others attributed the higher strain rate sensitivity to the smaller volume needed for dislocation to escape from grain boundaries [90,97].

Hirakata et al. have investigated the film thickness effect on the rate sensitivity of nc Al [98]. When the film thickness decreases, the diffusion creep is enhanced due to the lower ratio between grain interior and grain boundaries. If the grain boundary density increases, more fast diffusion paths are available. But at a critical film thickness of around 100-200 nm, the driving force to reduce the surface area due to surface tension becomes dominant, leading to a decrease in the creep rate. Dislocation creep is generally dominant in high stress regions, while diffusion creep is dominant in low stress regions.

The creation of materials with a controlled grain size distribution is also valuable for the strain rate sensitivity. Guo et al. have prepared Cu film with a bimodal grain size (40 and 220 nm). They observed that the loading history significantly affect the creep behaviour of their bimodal grain size distributed Cu films [99]. Moreover, faster loading rates result in greater primary creep strain rate and smaller steady state creep rate.

Finally, the accumulation of plastic strain in a material can influence the strain rate sensitivity exponent m [100] and the relaxation mechanisms. Karanjgaokar and his team have confirmed that nanocrystalline materials subjected to a constant applied stress will relax following different creep mechanisms depending on the level of applied stress [101]. Usually, grain boundary sliding is the likely mechanism but it can be accommodated either by elastic and diffusional mechanisms at low stress, either by dislocation based mechanisms at higher stresses. Low and high stresses are relative to the elastic limit. The diffusional creep mechanisms are also divided into different categories: the Coble creep and the Nabarro-Herring creep. See references [102–104] for more details.

Bauschinger effect

During a loading-unloading cycle, an asymmetry between the tensile yield stress and the compressive yield stress can appear, see figure 1.12. This effect, called the *Bauschinger effect*, is associated in bulk materials to the creation of deformation structures which induce long-range stresses, called *back-stresses*. The notion of long-range stress has already been introduced in the previous section. As a matter of fact, the deformation history of a material is important as, for a material plastically deformed in one direction, its yield stress in the reverse direction is often lower [20]. The increased density of interfaces and free surfaces will strongly affect the mechanical behaviour of thin films [20]. Initially, the Bauschinger effect in thin films was only predicted numerically [105, 106] due to the difficulty to apply cyclic loadings to thin films without the buckling of the film. Recently, different groups succeeded to investigate the Bauschinger effect of nanoscale materials thanks to dedicated testing methods, i.e. the bulge test [20, 21], uniaxial testing devices [49] and micropillars [107], see chapter 2 for a brief description of these techniques.

The heterogeneity of nc materials highly affects the Bauschinger effect. Indeed,



Figure 1.12: Schematic view of the stress-strain curve of a metallic material presenting a Bauschinger effect. Figure taken from [20].

as reported by Rajagopalan et al., the Bauschinger effect is more pronounced for heterogeneous nc Au thin films than for homogeneous nc Al thin films due to the build-up of internal stresses during deformation [49]. This group also attributed the plastic strain recovery of nc films to the inhomogeneities in their microstructure [108].

Also, the presence of a passivation layer influences the Bauschinger effect. Xiang et al. observed and modelized the asymmetry of the yield stress during cyclic loading of thin Cu films passivated on 0, 1 or 2 sides [20,21]. They found an increased Bauschinger effect when the confinement of the film was increased. This passivation effect has also been observed through the compression of Cu micropillars [107, 109].

Finally, note that Zhu et al. showed numerically that a tension-compression cycle can be different than a compression-tension cycle [110]. They also analysed and compared the strength of the Bauschinger effect induced by the presence of grain boundaries, twin boundaries or the absence of boundaries. They reported that the Bauschinger effect exists in systems containing grain boundaries and that grain boundaries lead to a stronger Bauschinger effect than twin boundaries. But, an even stronger Bauschinger effect appears in single crystals.

1.2.2 Deformation mechanisms in nanocrystalline materials

The identification of the nanoscale deformation mechanisms of nanocrystalline materials is a prerequisite for pushing further the optimization of mechanical properties of those small scale materials. In this context, a close coupling between experimental observation and numerical study has proved to be powerful. The first one gives the evidence of certain mechanisms while the second one allows the prediction of scenarios that are beyond the limits of microscopy observation.

Despite the small grain size, dislocations have been observed by transmission electron microscope (TEM) in nanocrystalline materials (see e.g. [111] for dislocations in nc Ni). Note that it is not clear if TEM observation of deformation mechanisms in nc thin films are representative of those in bulk nc materials [112]. Nevertheless, it is clear that dislocations are not expected to be the only vector of plastic deformation of nc materials as the dislocation density left after a tensile test is not sufficient to explain the high level of plastic strain reached during the experiment. A severe lack of dislocation storage capacity is often observed in nc materials [78].

Moreover, owing to image forces from the free surfaces, isolated small particles tend to be free of dislocations. An analogous argument would suggest that dislocations are not relevant for the deformation of nanocrystalline materials [112]. Of course, some types of grain boundaries inside nc materials can act differently than free surfaces and can stabilize dislocations due to the microstrain fields created by grain boundaries.

The few dislocations-based deformation mechanisms observed in nc materials are in good concordance with their moderate strain hardening and with the emergence of new mechanisms, namely grain boundary sliding [112]. The emergence of new deformation mechanisms is also probably the reason of the increased strain rate sensitivity of nc materials.

This section will present some of the main deformation mechanisms inherent to nanocrystalline materials. This section does not aim to be exhaustive. More detailed information about the deformation mechanisms acting in nc materials can be found in, e.g., [113].

Pile-up theory validity

In classical coarse grained materials, a high increase of dislocation density is observed during plastic deformation [82]. These dislocations accumulate, or pile-up, against obstacles such as grain boundaries or Lomer-Cottrell locks which prevent their glide. Note that Lomer-Cottrell locks are rarely observed in nc materials. The effect of the grain size on this pile-up mechanism is captured by the empirical Hall-Petch relation which predicts an initial yield stress proportional to the inverse square root of the grain size (see equation (1.2)). Different ways exist to physically and theoretically justify this law [114–117]:

- grain boundaries act as barriers to dislocations, which leads to dislocation pile-ups at the boundaries and to the creation of stress concentration which activates dislocation emission and motion in the adjacent grains;
- grain boundaries act as dislocation sources and can thus initiate plastic deformation;
- the mismatch of slip at the boundaries between grains with different orientation can result in gradients of plastic strain, which subsequently results in the formation of *geometrically necessary dislocations* (GND)⁵ to ensure compatible deformation between adjacent grains.

In nanocrystalline materials on the contrary, very little dislocation debris are found in nanocrystalline materials after deformation and the classical theory breaks down. This absence of dislocation storage has been observed by TEM [111, 120] and also by X-ray diffraction (XRD) [78]. Therefore, investigations started to point out if dislocations are the actual carrier of plastic deformation in nanocrystalline materials. In-situ TEM [111, 121] as well as MD simulations [122, 123] have shown that once nucleated, dislocations cross the grain and are absorbed in the opposite grain boundary.

For these reasons, deviations from the Hall-Petch strengthening has been recorded for nanocrystalline materials. Different alternative laws can be found in the literature [124]. For instance, Misra and co-workers considered that the plastic flow is governed by the motion of single dislocations located on closely spaced glide planes [125, 126]. This mechanism is different from what happens in bulk polycrystals where Frank-Read sources operate and flow occurs by dislocation pile-ups on planes separated by about 1 μ m [125]. The authors associated the confined layer slip of single dislocation to the Orowan bowing of dislocations with grain boundaries as obstacles. The related grain size dependence is

$$\sigma_y \propto \frac{1}{d} \ln\left(\frac{d}{b}\right),$$
 (1.12)

where b is the Burgers vector. A moving dislocation pinned at opposite grain boundaries will thus move parallel to the boundaries by bowing, leaving behind

 $^{{}^{5}}$ GNDs, which are present due to the presence of plastic strain gradients in materials, have to be distinguished from statistically stored dislocations (SSD), which simply accumulate at random as a result of the obstacles to dislocation motion created by dislocation intersections and elastic interactions [117, 118]. The notion of GNDs used to explain the accommodation of strain gradients has been first introduced by Ashby [119]. The GNDs do not contribute to the plastic strain of the deformed material but they contribute to its strain hardening as they constitute obstacles to the motion of the SSDs. GNDs can thus be viewed as contributing to an extra storage of dislocations in the presence of plastic strain gradients [116].

misfit dislocations in the grain boundaries. The logarithmic term of equation (1.12) is sometimes not considered, giving a linear dependence on 1/d.

Dislocation nucleation and activity

Dislocation nucleation mechanisms in nanocrystalline materials differ from those in microcrystalline materials. Due to the small grain size of nc materials, conventional intragrain Frank-Read sources cease to operate and grain boundary assisted nucleation and accommodation prevail [39]. In nanocrystalline materials, grain boundaries are most of the time high energy non-equilibrium boundaries which contain a much higher density of dislocations compared to equilibrium. These dislocations in excess are good candidate to be at the origin of the emission inside the nanograins [39]. Moreover, the high distortions present near non-equilibrium grain boundaries induce high stress concentrations which can lead to the nucleation of partial dislocations and twins [127].

The difference between mc and nc materials appears also in the fact that plasticity is governed by dislocation glide for mc materials and by dislocation nucleation for nc materials [86]. As a matter of fact, in coarse-grained materials, each grain contains a high number of dislocations and dislocation sources. When the grain size falls down, the source density is reduced, which drives the preexisting dislocations out of the system during deformation [128]. This means that the dislocations escape from the crystal or the grains more rapidly than they are multiplied by the sources. This is called a 'dislocation starvation' state [129]. This state requires a continual dislocation nucleation during deformation leading to a nucleation-limited plasticity and to an increase of the flow stress.

From classical intragranular slip, the minimum shear stress needed to generate and expand dislocations is equal to $\alpha\mu b/L$ where α is a geometrical parameter, μ is the shear modulus, b is the magnitude of the Burgers vector and L the dislocation length. The α parameter has been determined as comprised between 0.5 and 1.5 by Hirth and Lothe [130]. For very small grain size, L should be smaller than the grain diameter d and has been evaluated as smaller than one third of the grain size [130]. This leads for a 1 µm grained Pd to a minimum stress barrier of around 40.5 MPa if one takes α equal to 1 like in [25]. This value increases up to 1822.5 MPa when the grain size is reduced to 20 nm. The level of required stress for this mechanism is thus too high in nc materials to be considered as the active mechanism.

Asaro and Suresh have built an energetic based model to find the stress needed for perfect or partial dislocation nucleation [97]. By using the fact that grain boundaries act as dislocation sources and sinks, they balanced the energy of the



Figure 1.13: Schematic view of the model used by Asaro and Suresh [97] for the emission of partial or perfect dislocations from a grain boundary.

dislocation segment with the work done by the two residual segments created in the GB side, see figure 1.13. Doing that, they found a scaling proportional to d^{-1} for the stress instead of the $d^{-1/2}$ for the classical Hall-Petch law.

Contrarily to what was reported earlier, perfect dislocations are highly active in nanocrystalline materials [120, 131]. But partial dislocation activity is not absent as presented by Liao et al. for nc Al containing stacking faults bounded by partial dislocations much wider than expected [132]. Furthermore, they predict the same behaviour for other FCC materials with high stacking faults energy like Ni or Pd. The high stacking fault energy is a requirement, in their work, for wide stacking faults in a nc material to ensure a sufficient driving force for the trailing partial dislocation emission. In low stacking fault energy materials, the tendency will be to produce deformation twins and stacking faults. The role of twins will be discussed below. Moreover, Yamakov et al. have predicted by molecular dynamics that in columnar nanocrystalline Al, the plasticity is fully determined by dislocation activity [133].

Grain boundary sliding

Grain boundary sliding has been proposed as a potential deformation mechanism for nanocrystalline materials by molecular dynamics (MD) simulation studies (see e.g. [134–136]) but clear experimental evidences of this mechanism are difficult to obtain. Note that Shan et al. have observed grain rotation during in-situ TEM straining [137]. In fact, no direct observation during deformation is available without altering the grain boundary structures. For TEM observation, the sample often needs to be thinned down which leads to grain boundary structure modification and relaxation [138]. Grain boundary sliding is also the proposed mechanism to explain superplasticity in materials [139].

Many groups suggested that GB sliding and grain rotation also contribute to deform plastically nc materials [111, 121, 140] but no direct experimental observation of these mechanisms has been provided. Only indirect evidence of GB sliding has been found, e.g. the lack of texture formation and the retention of equiaxed grains [139]. Though, some authors used grain boundary sliding mechanism to explain the observed grain boundary aligning [139, 141].

It has been observed that at high strain rate, the grain boundary sliding process is viscous [142]. Fu et al. also considered a viscous term for the grain boundary sliding accommodation [114].

Grain boundary sliding can be a useful mechanism to improve some mechanical properties. For instance, in front of a crack tip, grain boundary sliding and stress-driven grain boundary motion increase the fracture toughness of nc materials [143].

Schiotz and Jacobsen found a maximum in the strength of nc materials around 10 nm grain size [144]. They attribute it to a change in deformation mechanisms from dislocation-based mechanisms to grain boundary sliding when the grain size falls below 10 nm. By decreasing the grain size, their MD simulations show an increased plastic activity at grain boundaries although at higher grain size, this activity was present both at GBs and at glide planes in the interior of the grains. Other authors have observed the same change of mechanisms [145]. It is noting that the grain boundary sliding mechanism has been used to explain the inverse Hall-Petch effect.

Grain boundary sliding alone is geometrically insufficient to explain the total plasticity in nanocrystalline materials [88]. This mechanism needs to be accompanied by dislocation movement or atom shuffling to ensure the geometric compatibility [88]. Fu et al. [114] addressed this geometric compatibility using the perspective proposed by Ashby [119] that deformation gradients are accommodated by geometrically necessary dislocations.

Grain coarsening

Nanocrystalline materials are not thermodynamically stable and a high excess of grain boundary is present. This argument was used by some groups to explain grain coarsening through grain boundary migration in nanocrystalline materials at room temperature [146] or under stress [147, 148]. The understanding of this effect is of primary importance to ensure no degradation of the enhanced mechanical properties of nc materials and because it is linked to the absence of deformation sub-structure. For instance, Gianola et al. [149] revealed an enhanced ductility coupled with a reduced strength of nc Al thin films due to stress-assisted grain growth.

Grain growth is responsible of an important hardness drop during indentation creep tests [147,148]. Zhu et al. have modelled the hardness decrease appearing during nanoindentation creep of Ni and Cu by considering grain growth in their equations [150]. Their results were in accordance with the work done by Zhang et al. but they do not predict a saturation of the stress-induced grain growth mechanism [150]. Ovid'ko et al. investigated the boundary motion [151] but no study fully understands yet this phenomenon.

Grain coarsening can also arise from grain rotation where adjacent grains rotate to align their own orientation. This process produces larger grains where the previously existing grain boundaries are replaced by high density dislocation areas [137, 152]. This mechanism can be related to local sliding at the grain boundary of individual grains.

To stabilize grain boundaries, adding some impurities has been seen useful (e.g. [13]). Indeed, Ames and co-workers were able to unravel the rapid grain coarsening at room temperature of nc Pd prepared by inert gas condensation [146]. They discovered that a saturation segregation of Zr at the Pd grain boundaries can efficiently stabilize the grain size. Also, the addition of 10% at. of Au during the preparation of nc Pd improves the thermal stability of the grains [153]. The same observations have been made on nc Cu by introducing a solid solution of Fe which segregates at GBs and retards grain growth [154,155]. Such a feature was also supported by MD simulations [156].

The role of twins

The presence of twins has a positive impact on the mechanical properties (see above). In classical coarse grained bulk materials, two types of twins are distinguished: annealing and mechanical twins. Annealing twins appear during heat treatment to minimize the internal stresses in the material. Mechanical twins develop during the deformation of materials either to compensate the lack of slip systems (as in HCP materials), either as a competitive mechanism with dislocation glide when the stacking fault energy of the material is sufficiently low to allow extended partial dislocations. In nanocrystalline thin films, the terminology used in the literature is slightly different. In this case, the two different kinds of twins considered are growth twins and deformation twins. The former appears during the processing and the microstructure genesis albeit the later is produced during the deformation of the material. This sub-section will mainly focus on the effect of growth twins.



Figure 1.14: Twin boundary affected zone representation as imagined by [73].

Most of the experiments were performed on copper with nanoscale growth twins [71,72,74,89,157,158]. The open questions are why nanoscale twins give an enhanced strength like nanoscale grains in addition to a good ductility, and why twins have an impact on the strain rate sensitivity of materials?

The presence of twin boundaries (TBs) significantly increases the dislocation storage capacity of nanocrystalline materials [113]. The TB-dislocations interactions seem to be of primary importance to explain the deformation mechanisms in nanotwinned (nt) materials as a lot of dislocation debris have been found after deformation in nt materials [89]. This accumulation of debris can, in turn, induce elastic strains in the lattice area next to TB [73]. TEM analysis have shown that the dislocation pile-up against TB is the principal vector of plastic deformation. TBs are then able to sustain much more shear strain than the grain interior. But, despite the blocking properties of TBs, dislocations have been seen, both experimentally [159] and numerically [160–162], to be able to propagate across those TBs, leaving defects on the twin boundaries. Zhu et al. have systematically investigated all the possible reactions when dislocations arise at a twin boundary [163] and Ni et al. included the effect of the dislocation density to the dislocation-TB reactions [164]. Note that caution should be brought here due to the numerous studies dedicated to the dislocation-TB reactions on plenty of various materials with different microstructural features.

Other authors have modelled the mechanical behaviour of nt-materials by transposing to TBs the concept of grain boundary affected zone proposed by Schwaiger [165]. In this case, one will talk about twin boundary affected zone (TBAZ), see figure 1.14. The idea is that atoms lying next to TBs are differently involved in plastic deformation (e.g. this zone is plastically softer and more rate



Figure 1.15: (a) Experimental stress-strain curves of different Cu specimens showing the effect of the twin density on strength and ductility, and the increased strain rate sensitivity with the twin density. (b) Simulation results obtained using the concept of TBAZ. The crosses on the curves indicate the predicted failure point. The simulation results are in good agreement with the experimental results. Graphs taken from [73].

sensitive than the grain interiors) and their constitutive equation is different from the one for grain interior atoms [73]. In agreement with experimental observation, this model was able to predict the enhanced ductility, strength and strain rate sensitivity brought by an increased TB density, see fig 1.15 (a) and (b).

The twins are often initially coherent. Recently, Morris Wang et al. have demonstrated the inherently defective state of coherent twin boundaries in nanotwinned copper [166]. Zhu et al. have observed that the initially coherent TBs loose their coherency during deformation [88]. The same authors have studied, by atomistic simulations, the reaction between dislocations and twin boundaries. They attributed the high ductility of nanotwinned copper to the hardening produced by the progressive loss of coherency of the twin boundaries. They found that TBs act as sources and sinks for dislocations but can also play the role of strong obstacles against dislocation transmission across TBs. The strain rate sensitivity was also extracted and a good match with experimental values was observed when the rate-controlling mechanism is TBmediated slip transfer reactions. Absorption of dislocations by TB is more favourable than transmission and desorption which induce an accumulation of interfacial residual dislocations. They also found that materials with TBs are more hardenable than those containing only grain boundaries because of the gradual loss of coherency of the TBs. In fact, the slip transfer of dislocation across TB leaves, in the TB, dislocation debris which accumulate and provide an increased back stress. For further slip transfer across this TB, an increased

applied stress is required, and strain hardening is obtained.

Note that in some cases, the coherency loss of the TBs induces twin coarsening and leads to the material softening as observed by Niu et al. on nt Cu [167].

Another advantage of nanotwinned materials is lying in the good thermal stability of nanotwins [168]. Coherent and incoherent twin boundaries contain less stored energy than high angle boundaries. It leads to a lower driving force to coarsen the twins, then to an increased thermal stability. This observation designates nt-materials as the ideal candidates for high temperature applications because they do not suffer from coarsening and guaranty no loss of the enhanced properties thanks to the nanoscale microstructural dimensions [168].

Material science textbooks usually present that deformation twinning only occurs when the stacking fault energy of the material is low enough to be energetically favourable and that a decrease in grain size will make deformation twinning more difficult. But surprisingly, MD study on nc materials predicted the formation of deformation twins in nc materials [169]. The confined volume of nanograins makes the nucleation of trailing partial less favourable which leads to higher activity of partial dislocations and twins [162]. Later, experimental observation of deformation twins was made in nc Al, confirming this deformation mechanism in real nc materials [25] but raising the question of why this process can happen in materials with high stacking fault energy like aluminium ($\gamma_{sf} = \sim 142 \ mJ/m^2$ [169]). The same experimental observation was made on nc Cu where the twins were formed during GB migration via the emission of partial dislocations [170]. As a matter of fact, in nanocrystalline FCC materials, it is energetically favourable to nucleate partial dislocations which results in the preferential formation of stacking faults and twins compared to perfect dislocations [25]. Below a critical grain size, this affirmation becomes invalid and an inverse grain size effect on twinning is obtained [113]. Wu et al. demonstrated that mechanical twinning is promoted at low deformation temperature [113] and at high strain rates and/or large plastic strain to create large stress concentration which is favourable for twinning [171]. Furthermore, Wu et al. have highlighted the importance of non-equilibrium GBs which favours the nucleation of partial dislocations, stacking faults and twins [127].

Even if deformation twinning was observed for materials with a high stacking fault energy like Al, reducing this energy will theoretically favours the formation of twins during deformation. This reduction can be obtained via the presence of impurities [172, 173] or by alloying materials, e.g. by adding Ag in Pd, one is able to reduce the stacking fault energy of Pd [174].

When comparing materials with nanotwins, one should be careful as a distinction has to be made between nc materials and nt materials where the later contains usually large grains but nanoscale twins. Indeed, the deformation mechanisms of nt materials involve hard and soft modes for dislocation glide due to the two different length scales [162].

A last observation has to be made before finishing this section. Even if it was discovered in Mg, an HCP material, it is integrated in this thesis as it can open new strategies to produce mechanically improved materials: Nie et al. observed a segregation of solute atoms in fully coherent twin boundaries of Mg. The segregation provides a pinning effect of the twin boundaries and hence a large strengthening effect [175]. Note that to enhance the radiation tolerance of metals (e.g. Ag), maintaining the mobility of twin boundaries is beneficial [176].

Grain aggregate models

Intensive XRD and TEM observations have revealed microstructure details coupled with statistical analysis. These are important inputs for physicallybased models. This section will provide an overview of the different existing models.

The influence of the grain size distribution has been highlighted to contribute to the overall mechanical properties for a fixed average grain size experimentally [177] and then numerically [150]. The narrower is the grain size distribution, the larger is the strength and strain hardening rate. One has to pay attention to the fact that the largest grains dominate the volume fraction. In addition to consider the grain size distribution, Zhu et al. have proposed a model where grain interiors deform either by nucleation of perfect/partial dislocations or by grain boundary sliding [178]. They were able to quantify the relative importance of each mechanism, see figure 1.16.

Conrad and Narayan focused on the grain boundary sliding mechanisms and extracted the associated plastic strain rate [145,179]. Wei and co-workers established a more complex model with a rate dependent amorphous grain boundary to represent e.g. cavitation phenomenon at triple junctions, and with a classical crystal plasticity behaviour for the grain interiors [180]. Using a finite-element-based model, they concluded that a transition from intragrain shearing mechanisms to grain boundary shearing occurs when the grain size falls from 50 nm down to 10 nm.

Another type of model involves the so called phase mixture models [114, 181, 182] and grain boundary affected zone (GBAZ) models [165]. They both consider a different behaviour between intragrain regions and boundary regions. Grain boundary regions are able to harden more than the grain interior re-



Figure 1.16: Evolution of the contributions to the overall plastic deformation of the three mechanisms envisioned by [178] at room temperature in nc Ni.

gions and when the grain size is reduced, the grain boundary layer becomes increasingly important. These models capture the grain size and strain rate dependence of nanocrystalline materials. Furthermore, Fu et al. incorporated the concept of strain gradient plasticity (SGP) in their model [114]. The drawback of usual SGP models is that they do not consider a different behaviour of the grain boundary regions and they do not predict an effect of the grain size on the yield stress.

To go one scale down, researchers have used molecular dynamics simulation to model the microstructure at the atomic level. The two pioneer groups are led by Van Swygenhoven (see e.g. [138, 183–186]) and by Yamakov (see e.g. [122, 133, 169, 187, 188]).

The MD simulation concept is to consider that interactions between two atoms is dictated by a force which is represented by a potential function determined by quantum mechanical modelling of small systems. But one have to know that MD simulations are not the panacea and are subject to different limitations:

- The time scale is highly restricted, which leads to deform at much higher strain rate than in real experiments to reach sufficient level of plastic deformation. This prevents internal relaxation and can result in artefacts in terms of yield strength [186].
- The size of the system which can be simulated is very small. From one point of view, this is not a drawback for nc materials as it still allows the modellisation of a few grains. But it makes impossible to directly compare the numerical results with those of coarse grained materials [39].

• To be in equilibrium, the initial state cannot contain defects such as grain boundaries or stacking faults. People used relaxation methods to approach equilibrium when introducing this kind of perturbations [189].

On the contrary to the physically-based models, MD simulation was used for prediction or validation of the possible deformation mechanisms in nanocrystalline materials. Furthermore, MD simulation does not suffer from the continuum hypothesis made in finite element models, which leads to consider no intrinsic length scale. In nanocrystalline materials, this hypothesis becomes invalid due to their specific deformation mechanisms [39].

1.3 Conclusion

Through this chapter, the scientific challenges and issues to understand and to optimize the properties of nanocrystalline thin films appear obvious. Thin films do not specially involve nanocrystalline grains, but it is often the case. As explained in the chapter, important changes in the mechanical properties appears when the grain size is of tens of nanometers. This chapter also points out that the number of papers in the literature on that topic is non negligible and that attention should be paid when comparing different results together due to the highly different reachable microstructures and their huge impact on the mechanical properties.

Chapter 2

Background II: Nano-mechanical testing - a review

During the last ten years, a wide variety of testing methods has been adapted or created for the mechanical characterization of thin metallic films. On the contrary to the macroworld, mechanical testing of submicron sized samples is recent and does not benefit from extensive practice and from standardisation procedures (e.g. ASTM standards). The review proposed in this chapter will mostly cover the methods named 'on-chip' but some widely used techniques like nanoindentation will also be briefly described. When the method is used in this thesis to characterize the mechanical properties of the Pd films, then it will be specifically mentioned. On-chip means here that the material is characterized directly on the substrate on which it is deposited thus without needing a complex handling to remove it from the substrate, and with the loading system and the measurement device partly or totally embedded on the substrate.

The characterization methods can be classified into various categories:

- methods requiring a transfer of the sample versus methods testing the sample without removing it from the substrate;
- methods deforming thin films lying on a substrate versus methods testing free-standing films. The sample preparation process for the first category is usually easier than for the second;
- methods requiring external actuation and measurements versus partly on-chip methods (on-chip deformation and external measurement) versus totally on-chip methods;

- methods inducing complex loading of the sample versus uniaxial testing loading methods;
- in-situ versus ex-situ methods.

The ideal configuration is a method allowing the testing of a free-standing film without the need for transfer, using on-chip uniaxial deformation and on-chip measurement and dedicated for in-situ observation, while being easy to produce and implement. Of course, all these characteristics are impossible to gather, which explains the emergence of so many different testing techniques.

Methods allowing the co-fabrication of the sample and of the tensile testing system are very attractive when possible because it circumvents transfer, gripping and alignment problems [190]. Also, uniaxial testing methods give a direct access to the mechanical properties such as Young's modulus without requiring a complex model like for multi-axial testing methods. Furthermore, when available, in-situ testing is preferable as a direct link between deformation mechanisms and the global mechanical response is possible. And finally, when the film is free-standing, the results are representative of the film behaviour without artefacts coming from the confinement of the film by the substrate.

Uniaxial testing methods are thus powerful but more difficult to carry out due to [191]:

- the complex fabrication and handling of free-standing samples,
- the difficulty to apply small forces,
- the need for high resolution stress and strain measurement,
- the difficulty to grip the samples,
- the difficulty to ensure a purely uniaxial test.

The last item of the list has been extensively studied by Saif's group [192].

This chapter will first present the main methods used to assess the mechanical properties of thin films lying directly on a substrate. Then, an overview of the methods implying complex loading of free-standing films will be exposed. After that, methods designed for on-chip uniaxial testing of free-standing films will be presented and finally, some methods dedicated to in-situ TEM loading experiments will be introduced.



Figure 2.1: Schematic load-displacement curve obtained by nanoindentation. The different information that can be extracted is shown on the graph. Image taken from [10].

2.1 Deformation of samples lying on a substrate

One of the most common method used to characterize the mechanical properties of thin films is nanoindentation. It gives access to the Young's modulus [41], the hardness [193, 194], the strain rate sensitivity [89, 195, 196] and, in some circumstances, to the fracture toughness [197] of thin films, see figure 2.1. During the indentation, both load and displacement of the indenter are recorded and the analysis of this load versus displacement curve provides the properties [198, 199]. The main limitation of this technique is related to the substrate effect [200]. It renders the interpretation of the results of very thin films difficult and the prediction of the effect is laborious because of the complex stress distribution under the indenter [201]. Also, it does not provide the strength and the strain hardening of the films except with sophisticated inverse identification procedures [5]. Beside these disadvantages, this technique is very easy to implement and does not require long sample preparation time. Moreover, the applied strain rate can be varied over four orders of magnitude and the experimentally affordable strains are much higher than the one used in uniaxial tension. Nanoindentation was used in this work to characterize the Young's modulus, the hardness and the strain rate sensitivity exponent of the Pd films.

Another simple technique to implement is the **wafer curvature measurement**. The principle is to follow the change of curvature of a film/substrate system during heating or cooling for instance, and to calculate the stress variations inside the film thanks to the Stoney formula [10]. Depending on the thermal expansion coefficient mismatch between the film and the substrate, a tensile or compressive stress is generated in the film upon cooling or heating. The Stoney formula links the change of curvature to the biaxial stress σ_f inside the film through the hypothesis that the film stiffness $E_f t_f$ is small in comparison to the substrate stiffness $E_s t_s$ and that the substrate deforms elastically:

$$\sigma_f = \frac{1}{6} \frac{E_s}{(1 - \nu_s)} \frac{t_s^2}{t_f} (\frac{1}{R} - \frac{1}{R_0})$$
(2.1)

where E_s is the Young's modulus of the substrate, ν_s is the Poisson ratio of the substrate, and R_0 and R the curvature of the substrate before and after the change of temperature considered.

Among the advantages of this technique, one can observe that it does not require the knowledge of the Young's modulus of the film and that it allows the study of the yield stress and its thermal evolution, as well as the time-dependent plastic flow by holding the temperature and observing the stress variation. On the other hand, a few drawbacks are to be raised: first it does not provide information about the stress distribution in the film but only a global value [26]; second it is impossible to obtain an isothermal stress-strain curve; third, the results are difficult to interpret when large microstructural changes occur due to heating [10], and finally, the confinement associated with the substrate is playing a non negligible role and makes the results difficult to compare with what occurs in free-standing films. Wafer curvature measurements were used in this thesis to quantify the internal stress in the Pd films after deposition, the internal stress evolution upon annealing and ageing, and finally to measure the internal stress variation during the hydriding of the films.

Microcompression of pillars is also a widely used technique to study the mechanical properties. The pioneer work was made by Nix's group [17,128,202] who used focus ion beam (FIB) to fabricate pillars inside bulk single-crystalline materials with different dimensions, and who compressed the pillars using a flat punch nanoindentation tip. They were able to investigate the external size effects of a wide variety of materials [17]. Later, micropillar compression has been combined with in-situ microdiffraction by e.g. the group of Van Swygenhoven [203]. This technique presents different advantages: it allows the testing of single-crystalline materials (classical thin film deposition methods only provided micro-/nanocrystalline films) and thanks to the compression nature of testing, it circumvents the limit of low ductility of nanocrystalline materials (see section 1.2.1). But, unfortunately, each method is always accompanied by a few

drawbacks. First, it constitutes a big challenge to perfectly align the pillar to ensure uniaxial compression, to avoid buckling, to remove the substrate effect if the pillar is not made in the bulk and to control the constraint effect of the indenter/pillar contact [5]. Second, pillars are most of the time prepared using FIB milling. This preparation method is known to alter the initial microstructure in four different ways: (1) the purity of the material changes due to the implantation of some gallium ions used to process the pillar, (2) an amorphous layer is created on the surface, (3) the roughness of the FIB defined surface is non negligible and (4) defects like dislocations or precipitates appear in the ion irradiated zone which leads to apparent hardening [204]. This method was not used in this work.

2.2 Multi-axial loading of free-standing thin films

This section will present the different methods reported in the literature for the multi-axial testing of free-standing films. None of the methods presented in this section have been used in this thesis.

Nix and co-workers have demonstrated that **microcantilever beam bending** under a nanoindenter tip allows the study of the elastic and plastic properties of thin films, see figure 2.2 [205]. More recently, they used triangular beams instead of rectangular beams to impose a uniform plane strain state to the film during the test [206]. The main drawback of this technique is that in the plastic regime, the fracture and localization properties can depend on the volume of tested material which is intrinsically small in bending experiments [5]. Also, the results can be influenced by the boundary conditions and by the geometry of the beam. Note that Haque and Saif have extended this technique by replacing the external actuation of the indenter by a MEMS (micro-electro mechanical system) based actuation system [207].



Figure 2.2: Schematic view of the microcantilever beam bending method developed by the Nix's group to characterize the elastic and plastic properties of thin films. Picture taken from [10].



Figure 2.3: Schematic view of the bulge test technique on rectangular membranes. Picture taken from [19].

The **bulge test** is another method developed to study the elastic and plastic behaviour of free-standing thin films, see figure 2.3. It consists of a clamped free-standing membrane loaded by applying uniform pressure to one side of the film. The stress-strain relation is obtained by linking the deflection observed to the applied pressure [208]. Bulge testing has revealed some difficulties like the need of complex models for the boundary conditions and the sensitivity of the results to slight variations of the sample dimensions [5]. Vlassak and colleagues improved this technique. They changed the shape of the membrane from circular to rectangular or squared shapes and defined geometries to obtain plane strain conditions in the center of the membrane [20, 21]. This method is frequently used in the material science community, see e.g. [209] for the extraction of the fracture toughness or [210] for the study of size effects.

The last method exposed in this section has been imagined by de Boer et al. It consists in **MEMS test structures** dedicated to study fracture and fatigue strength of thin films [211, 212]. The force is applied electrostatically on the film, see figure 2.4.



Figure 2.4: Top and cross section views of the testing method proposed by de Boer et al. Figures taken from [211].

2.3 On-chip uniaxial tensile testing of free-standing films

The first microtensile mechanical testing system has been imagined by **Sharpe** et al. [213]. The free-standing sample lies in the middle of a Si frame and the tensile test is performed by gripping the device to an external tensile apparatus (see figure 2.5). Later, Lin et al. have extended this technique to test the temperature dependency of the mechanical properties of thin films up to 400°C [214].

Haque and Saif have developed a more sophisticated tensile system (but still easy to build) for accurate stress-strain measurement, see figure 2.6. They designed the device to minimize a possible misalignment using U-shaped springs [192]. They intensively studied the alignment issue, see [215,216]. An external piezo-actuator system is used to pull on the sample. The stress and strain state of the sample is extracted by imaging the gap between the corresponding gauges and by calibrating post-mortem the rigidity of the force sensing beams [217]. This technique is suitable for quantitative in-situ TEM deformation [218]. Thanks to a collaboration with the team of Prof. Saif, this method has been applied in this thesis to deform Pd thin films. The results are presented later in appendix C.

The tensile stage as presented in figure 2.6 allows only the testing of thin films that can be produced by classical deposition methods. Moreover, the tensile experiment begins at a non-zero stress due to the internal stresses built in the film during its deposition. Kang and Saif have modified the stage by adopting



Figure 2.5: Schematic view of the first microtensile test developed by the Sharpe's group. Figure taken from [214].



Figure 2.6: Schematic view of the in-situ SEM or TEM tensile device designed by the Saif's group. The sample is deformed by a piezo-actuator pulling on the moving end of the device.



Figure 2.7: Improvement of the device presented in figure 2.6 allowing the testing of a much larger variety of materials that cannot be co-fabricated with the loading frame. Figure taken from [215].



Figure 2.8: Uniaxial testing method developed by Espinosa et al. The deformation is applied using a nanoindenter at the center of the beam. Figure taken from [220].

an assembly approach to test materials that cannot be co-deposited with the loading stage, see figure 2.7. This improvement allows the testing of a broad variety of materials and sample geometries [191, 215, 216]. However, it adds new challenges to achieve uniaxial loading as any irregularity in the sample can alter the point of contact and thus induce off-axis loading [216].

Espinosa and co-workers have built a nanoindentation based method to test free-standing clamped beams in purely uniaxial tensile conditions, see figure 2.8 [18,219,220]. This experiment is coupled with interferometry measurements to obtain the stress and the strain in the sample.

Kraft's group has investigated the tensile testing of nanocrystalline materials deposited on compliant polyimide substrate [221]. Later, they coupled it with simultaneous in-situ X-ray diffraction experiments [222, 223]. X-ray diffraction



Figure 2.9: Uniaxial testing stage designed for on-chip measurement of the mechanical properties of thin films. The system is compatible for in-situ observation during deformation. Figure from [225].

gives insights on e.g. the dislocation density, the grain size and the microstrain by studying the diffraction peak shift/broadening/shape variations during deformation and by comparing it with models. The presence of the substrate, even if it is compliant, has to be taken into account in the analysis as the film cannot be considered as free-standing. The method is also limited to crystalline materials because it is based on diffraction. But this technique should become increasingly important due to the contemporary flexible electronics development [5].

The next method that will be presented here gathers uniaxial testing and insitu imaging (SEM, TEM, XRD). It was also built by the **Espinosa**'s group. It consists in a MEMS providing both the actuation (thermally or electrostatically activated) and the load sensing (based on differential capacitive measurements), see figure 2.9 [224–226]. This technique is called 'on-chip' as all the required parts, actuation and sensing, are directly built on the Si wafer and do not need external actuation. This technique allows the testing of nanostructures like nanowires or carbon nanotubes using nano-manipulators to handle and attach the sample [227, 228].

Other groups have imagined compact on-chip microtensile test systems, like e.g. the group of **de Boer** [229, 230], see figure 2.10. Note that the group of **Vlassak** also designed a tensile technique. This technique cannot be qualified as 'on-chip' but the actuation and sensing systems are embedded in the system [231], see figure 2.11.

Finally, a microtensile on-chip technique was proposed at **UCL**. This method is able to deform, through unixial tensile testing, free-standing thin films and enables in-situ observation. The idea is to use the internal stress present in one film to deform another film, see figure 3.1 coming later on page 63. Chapter 3 extensively describes this technique as it constitutes the main testing method used in this thesis to characterize Pd thin films. The microtensile on-chip



Figure 2.10: (a) Schematic view of the on-chip tensile test developed by the group of de Boer. (b) SEM micrograph of the same system. Figure from [230]



Figure 2.11: Schematic view of the tensile test developed by the group of Vlassak. Figure coming from [231].

method has been developed in the years 2005-2006 [6, 7, 232] and has been upgraded since then [8, 9]. This testing technique has provided information about the mechanical properties of Al thin films [6, 233], AlSi films [9], silicon nitride films [234] and monocrystalline silicon beams [235].

2.4 In-situ TEM loading techniques

Conventional in-situ TEM straining does not provide stress-strain measurements and always remains qualitative due to large frictional force on the tensile stage, to the inaccurately measurable cross-section of the sample and to the difficulties to perfectly grip the sample [236]. Only in certain situations where the same sample area is recorded during the tensile test, the strain can be deduced by image correlation of the moving points of the image [237]. Quantitative in-situ TEM deformation methods are thus very attractive to allow a control of the strain rate.

The very small sample size of nanocrystalline materials or thin films is challenging for the mechanical characterization but, at the same time, it opens a way for in-situ characterization due to this intrinsic small size. As a matter of fact, the testing instruments often scale with the size of the samples. In-situ TEM testing is particularly attractive owing to the possibility to monitor the overall macroscopic response while simultaneously observing the underlying deformation mechanisms [191]. Such in-situ studies are tedious to perform but give invaluable information, especially with the current interest to understand the size effects of nanocrystalline materials [238]. With the recent technological advances in high-resolution and fast digital imaging, microactuators, and highfidelity sensors, TEM has opened new horizons toward acquiring quantitative data during in-situ straining [239]. This section will thus briefly summarize the existing methods for in-situ experiments. It will be specified in the dedicated paragraph when the method has been used in this work.

The first developed methods were not as sophisticated as today. For instance, **Legros** et al. developed in-situ straining method by exploiting the thermal expansion mismatch between the studied film and the substrate which induces tensile or compressive stress inside the film [240]. The samples are wedge-shaped in a special way to retain the constraint of the Si substrate. The heating of the system is performed in the TEM and a qualitative evolution of the deformation mechanisms is obtained in-situ. Unfortunately, this method is not suited for the study of free-standing films.

Another kind of in-situ testing consists in nanoindentation of wedge-shaped samples, as proposed by **Stach**, see figure 2.12 [58, 59, 241]. A wide variety



Figure 2.12: In-situ TEM nanoindentation developed by Stach et al. [241]. Picture taken from [58].

of materials can be tested as it only implies the use of the classical thin film deposition methods. The thickness of the film has to be chosen carefully to ensure the electron transparency of the top of the wedge. This technique is specially powerful to understand grain growth [58], dislocation movements, the interaction between dislocations and grain/twin boundaries, and the effect of solute atoms on those mechanisms [59].

Based on the concept of microcompression, **Kiener** et al. have developed a quantitative FIB-based microtensile testing technique [242]. A tungsten gripper attached to a microindenter tip located in a SEM allows the pulling of a previously FIB milled sample, see figure 2.13. The microindenter system is designed for forward and reverse loading. Note that this prospective study was performed in-situ inside a scanning electron microscope (SEM). The same idea of in-situ tensile testing was improved for TEM straining [243]. **Han** et al. have also developed a method to bend or to pull on nanowires located on TEM grids [244]

Another testing test developed for in-situ TEM tensile test consists in pushing on a frame with a specific design using a pico-indenter designed for in-situ TEM indentation tests, to pull on a sample, see figure 2.14. The **push-to-pull** method has proved to be powerful to investigate the deformation mechanisms at the nanoscale [245]. This technique has been used to deform Pd films in this thesis but without success due to problems during the transfer of the Pd specimens to the push-to-pull sample holder.

Finally, **Mompiou** et al. were able to investigate the inter- and intragranular plasticity mechanisms in ultra-fine grained Al thin films using in-situ TEM uniaxial tensile straining [246]. The tensile stages were prepared at the UCL and will be described in section 3.2 in the next chapter. In this work, some



Figure 2.13: In-situ SEM tension experiments of miniaturized samples developed by Kiener et al. Figure taken from [242].



Figure 2.14: (a) Tip of the TEM holder containing the pico-indenter. (b) The indenter is pushing on the area indicated by an arrow to pull on the sample (c). The specimen width is around $2 \ \mu m$. Figure taken from [245].
trials using this in-situ technique were performed but were unsuccessful due to fabrication process problems. Note that these problems could be overcome with some additional efforts, but a lack of time here prevented the optimization of the fabrication process.

2.5 Conclusion

This chapter has provided a short overview of the several existing methods to deform materials with reduced dimensions. This overview is far from being exhaustive but covers the main specific techniques. What is clear is that the ideal testing method does not exist. As each method contains its own advantages and limitations, it is often pertinent to carry out the same experiments of the same material using different techniques. In this thesis, a combination between the UCL-made on-chip microtensile testing method and nanoindentation was performed to provide a better understanding of the experimental results.

_____ Part II _____

Testing procedures and materials

Chapter 3

On-chip method to deform freestanding Pd films

Micro- and nanofabrication techniques were primarily used in the microelectronics industry. Thanks to their maturity and stability, they are now widely used in a variety of other miniaturized applications. For example, in the glass and steel industries, major effort is made to functionalize the materials through the deposition of specific thin layers on top of the steel or glass surfaces. This opens new research domains e.g. to understand the mechanical behaviour of these layers and to predict their mechanical behaviour to ensure the reliability of the systems.

Motivated by these new challenges, the scientific community has imagined new testing devices able to characterize the mechanical properties of materials with reduced dimensions, see e.g. the methods presented in chapter 2.

The nano-mechanical testing method developed at UCL to measure the tensile response of thin Pd films relies on these micro-fabrication techniques [6,7]. In this chapter, the concept of the testing method will be presented as well as the different testing configurations. Then, the data reduction scheme will be detailed, followed by the fabrication process exclusively performed in class 100 cleanroom. It is noting that some other testing methods, e.g. nanoindentation, were used during this thesis, but only the principal method used in this thesis is presented in the present chapter.

3.1 On-chip internal stress based actuation test: the concept

The first idea underlying the concept of on-chip nanomechanical testing is to use the internal stresses created during the deposition of a film on a substrate to deform another film (see figure 3.1). This concept benefits from the microfabrication techniques which provide the possibility to reproduce easily a high number of elementary structures. It also allows the control and the progressive variation of the deformation state inside different specimens without the need to build a complex multi-purpose testing stage. The present testing method differs thus from those exposed in chapter 2 as it multiplies elementary testing elements, each elementary structure providing one point of the stress-strain curve. By extracting a stress-strain curve from different specimens, the method takes into account the material scattering. One 3" silicon wafer contains more than a thousand different elementary test structures. The main disadvantage of the technique is that the loading rate is not controlled and that the specimen is always analysed after the test while some relaxation might already take place. Note that, although the loading rate was not controlled using the structure design of figure 3.1, some improvements of the technique are planned as, for instance, the use of tapered actuators instead of the initially designed rectangular actuators.

In this thesis, only elementary uniaxial tensile testing structures were used but many other loading configurations can be imagined like, e.g., compression or shear. Some tensile structures were dedicated for in-situ TEM observation and in-situ TEM straining. For these two specific cases, the process was slightly different than for the classical one as windows have to be opened under the structures.

An elementary tensile testing stage is built on a silicon wafer (see fig 3.2). First, a sacrificial layer is deposited. On top of it, the actuator layer is deposited. The material of this layer involves high tensile internal stresses. The next step is to pattern the actuator. Then, the specimen layer is deposited and also patterned, see figure 3.2(f). At this point, the process for the classical structures differs from the one for TEM structures. If no window needs to be opened, the sacrificial layer is etched to release the structure, with the actuator beam pulling on the specimen beam to deform the specimen layer, see figure 3.2(g). On the contrary, if the transparency is required for TEM analysis, a window is opened under the structure from the back face of the wafer with a plasma etching, see figure 3.2(g'). The sacrificial layer is finally removed after this back-etching, see figure 3.2(h). Once the structure is released, the stress and the mechanical strain in the specimen can be directly inferred from the displacement u measured between a moving and a fixed cursor (see figure On-chip internal stress based actuation test: the concept



Figure 3.1: Elementary internal stress actuated uniaxial tensile test structure, (a) before release, (b) after release. One elementary structure provides one point of the stress-strain curve thanks to the displacement measurement performed using dedicated cursors.



Figure 3.2: Process steps used to prepare tensile structures. Two routes have been used, one for classical structures (a to g) and one which allows direct TEM observation by etching the substrate lying under the structures of interest (a to h').

3.1(b)) and from the knowledge of the mismatch strain of both the actuator and test specimen, and of the Young's modulus of the actuator.

The selection of the material of each layer is important. Here, the specifications for each layer will be presented. The true choice made to prepare the tensile stages used in this thesis is presented in section 3.3. For the sacrificial layer, the requirement is the possibility to find a selective etching solution which can remove this layer without damaging the actuator and specimen layers. Also, in the case of TEM dedicated structures, this layer has to contain a low level of internal stress to avoid buckling or cracking of the sacrificial membrane containing the specimens after the back-etching, see figure 3.2(g').

The actuator material requires also specific characteristics. As said before, it has to contain a high level of tensile internal stress or, equivalently, a high mis-



Figure 3.3: (a) Set of elementary test structures with different lengths and leading to different imposed deformation to the test specimen. (b) Idem for *TEM* observation.

match strain. But, at the same time, the internal stress gradient in the thickness has to be as small as possible to avoid out-of-plane deformation. The actuator layer must also involve a high fracture stress to ensure that the specimen will break first. Finally, the actuator has to present a linear elastic behaviour and a reproducible Young's modulus to provide an accurate mechanical analysis.

The choice of the specimen layer is dictated by scientific or practical interest. It can contain tensile or compressive internal stresses. The internal stress has to be known for the mechanical analysis, see section 3.4. The specimen and the actuator can be made of the same material if it respects all the requirements.

Different strains can be imposed by changing the length or the width of the actuator and/or of the test specimen, allowing the determination of a full stress strain curve. As a consequence, the design includes series of test structures with varying dimensions. Typical widths are 10-15 μ m and 1-4 μ m for the actuator and specimen beams, respectively. The total length of the structure (actuator and specimen) is between 500 and 2000 μ m. For classical structures, a high number of adjacent sets of structures as presented in figure 3.3(a) can be found on the Si wafer. For TEM dedicated structures, only one set is present in the center of a 3 mm in diameter silicon ring to fit inside TEM holders, see figure 3.3(b). The structures presented in figure 3.3(b) are useful to directly link the deformation mechanisms to the overall macroscopic response of the specimen. This is especially interesting for micro and nanoscale specimens due to the expected size effects.

3.2 Other test configurations

This section will present other structures that are located next to the uniaxial tensile testing structures and that are useful to determine the internal stress in the specimen and in the actuator or to complete the analysis of the deformation mechanisms. Two main classes of structures will be presented here: first the structures allowing the internal stress extraction, and then the structures designed for in-situ TEM straining.

As said before, the internal stress of the actuator and of the specimen have to be known. In section 2.1 of chapter 2, the substrate curvature method has been introduced. This method gives access to a global measurement of the internal stresses of a film via the Stoney formula. Some on-chip structures were designed on our masks to extract this information locally in an area close to the tensile testing structures of interest. This gives the opportunity to compare, to valid the measurement and to evaluate the homogeneity of the layer properties on the substrate. The accuracy on the internal stress measurement has a major impact on the accuracy of the determination of the specimen stress, see section $3.4.^1$

The first structures that can be used to measure the local internal stress are the rotating sensors, see figure 3.4(a). On this figure, the structure is not yet released and the central beam is perpendicular to the two clamped arms. When the structure is free to move, the angle of the central beam is a function of the internal stress. Using analytical analysis or finite element simulations, one can obtain the exact internal stress of the material assuming that its Young's modulus is known [247,248]. Different geometries can be found in the literature [249] but they all rely on the same principle of rotation.

The second kind of structures used to locally measure the internal stress of a material are free actuators, see figure 3.4(b). When the sacrificial layer is etched, the beam expands or contracts, for compressive or tensile internal stresses, respectively. By measuring the displacement of the structure after release, the mismatch strain or equivalently the internal stress can be easily calculated by equation (3.1) where ε^{mis} is the mismatch strain, L_0^{free} the length of the unreleased beam and u_{free} the measured displacement after release. The main drawback of this structure is the difficulty to avoid out-of-plane displacements due to internal stress gradient in the material thickness.

¹In the present chapter, to simplify the notations, the mismatch strain will be used in the mathematical equations instead of the internal stress. The mismatch strain ε^{mis} is related to σ_{int} by $\sigma_{int} = E\varepsilon^{mis}$, where E is the Young's modulus of the considered film. It is worth mentioning that in this work, we only measure the elastic part of the internal stress. It will however not affect the mechanical analysis as only the elastic part of the mismatch strain is of interest in the mechanical analysis presented in section 3.4.



Figure 3.4: Two structures allowing the local internal stress extraction. The red (green) arrows represent the movement of the structure after a release of a film in compression (tension). (a) Schematic view of an unreleased rotating sensor, (b) schematic view of an unreleased free actuator.

$$\varepsilon^{mis} = \ln\left(\frac{L_0^{free} - u_{free}}{L_0^{free}}\right). \tag{3.1}$$

The last family of structures dedicated to the local internal stress calculation are the self-actuated tensile testing structures. They are designed identically as the uniaxial tensile testing devices but the specimen and the actuator are made of the same material, see figure 3.5(a). These structures can then only be used for materials which respect the requirements of both actuator and specimen materials presented in section 3.1. Like for classical uniaxial tensile structures, the properties are extracted through the displacement measurement. The mechanical analysis of self-actuated structures is presented in the section 3.4 as the approach is similar to the stress and strain extraction for the classical uniaxial tensile test structures.

Finally, another structure differing from the elementary tensile testing stages presented above is designed to allow in-situ straining inside a TEM, see figure 3.5(b). It is composed of a silicon frame containing the specimen which is prepared using the same microfabrication methods needed to produce elementary tensile testing. This silicon frame is then glued on a copper grid. The copper grid presents two holes where the pins of a special TEM straining holder fit. The two lateral springs on the silicon frame have two functions. First, they facilitate the handling without breaking the films during the transfer from the Si wafer to the Cu grid. Second, they allow the film deformation during in-situ straining. The strain control during deformation is qualitative and only one specimen is needed to cover a classical deformation range. To quantitatively





Figure 3.5: (a) Self-actuated tensile structure to extract the mismatch strain of a material. (b) Structure dedicated for in-situ TEM straining.

determine the imposed deformation, an envisaged solution could be to design stress and strain cursors on the sides of the specimen as proposed by Saif's group [49,217].

The loading profile is different than for the elementary tensile testing because only one specimen is used to cover the full deformation range and because the strain rate is controlled and is much lower than for the elementary tensile structures. However, the comparison of both methods can give insights about the mechanisms that take place during the deformation of thin films. This kind of in-situ TEM straining structures has been used to analyse inter- and intragranular plasticity in Al thin films [246].

3.3 Fabrication process and material selection

The details of the process used to produce structures dedicated to Pd testing are described in this section. Figure 3.2 illustrates the description. Each step will be detailed but the related microfabrication techniques will not be detailed here. More information on these techniques can be found in [22,23].

The substrate. The choice of the substrate is influenced by the type of structures under interest. The substrates classically used in the UCL cleanrooms are {100} monocrystalline silicon wafers with a diameter of 3 inches. For classical structures, a 380 µm-thick wafer polished on one side is used. For TEM dedicated structures, a 180 µm-thick doubled side polished silicon wafer is preferred for two reasons. First, the smaller thickness facilitates the back-etching process

that will take place at the end of the process, see figure 3.2. Second, the backetching step requires a polished back face to ensure a good etching quality. In order to generate accurate curvature measurements, the wafer has to show a monotonic curvature in order to provide a smooth, as constant as possible, radius of curvature. In order to properly select the wafers with initially constant curvatures, they are scanned over the diameter using a profilometer.

The sacrificial layer. The nature of this layer is a function of the etching selectivity. The sacrificial layer has to be etched using wet or dry etching without damaging the actuator and the specimen layer. Also, the nature of this layer has to be compatible with the subsequent processing steps for example, to resist to temperature if the actuator is deposited at high temperature. In this work, the choice was to use a silicon dioxide sacrificial layer and a wet release using hydrofluoric acid (see the release part for more information). Some tests were performed using a polyimide sacrificial layer to avoid the wet etching and the manipulation of dangerous acids but the polyimide limits the temperature deposition of the other layers. The best compromise between layer quality and etching time is to use plasma enhanced chemical vapour deposition (PECVD) to deposit the SiO_2 layer. The precursor gases were composed of 100 sccm of SiH_4 , 700 sccm of N_2O and 350 sccm of N_2 . The deposition was made at 300°C and was densified during 20 minutes at 800°C to provide optimum control of the etching rate (i.e. an etching time of about one minute to release 15 µmwide beams) and to avoid any modification of this layer during the following steps of the process. The typical thickness of the sacrificial layer is 1 µm. With this recipe, the internal compressive stress is about 100 MPa. This level is sufficiently low to avoid damage in the SiO_2 membrane created for TEM dedicated structures.

The actuator layer. As said before, this layer has to contain a high level of tensile internal stresses and to be as uniform as possible over the entire wafer. To achieve these requirements, a low pressure chemical vapour deposition (LPCVD) Si_3N_4 layer was deposited at 800°C on top of the SiO₂ layer. The precursor gases were 30 sccm of SiH_2Cl_2 and 120 sccm of NH_3 at a pressure of 35 Pa in the tube. This recipe induces around 1 GPa of tensile internal stresses. As the LPCVD deposition method is used, Si_3N_4 is deposited on both sides of the wafers. Prior to the actuator patterning on the front face, this layer is totally etched on the back face. Then a classical photolithography (see table 3.1 for the parameters) followed by a SF_6 plasma etching is used for the front face patterning. The thickness of the Si_3N_4 actuator material is related to the thickness of the specimen film. Usually, the actuator thickness is half the specimen thickness to create an overlap of the two layers strong enough to avoid premature fracture in this area. The last specific property that the actuator must present is a mechanical stability, i.e. this material cannot relax. This criterion is fulfilled by the Si_3N_4 layer.

Classical positive photolithography	Reversal lift-off photolithography
1. Spin coating of resist AZ6612 at 4000 rpm	1. Spin coating of resist AZ5214E at 4000 rpm
2. Prebake at 110°C for 90 sec	2. Prebake at 110°C for 90 sec
3. Exposure with mask during 3.2 sec^*	3. Exposure with mask during 2 sec [*]
4. Development in AZ 726 MIF during 60 sec	4. Reversal bake at 120°C for 90 sec
5. Postbake at 130°C for 90 sec	5. Flood exposure without mask during 6 sec [*]
	6. Development in AZ 726 MIF during 105 sec
* (7) 1 1 1 1 1 1 1 1 1 1	

* The UV lamp used delivers $10 \text{ mJ}/(\text{s.cm}^2)$

 Table 3.1: Parameters used for the lithography steps.
 Parameters uset used for the lit

The specimen layer. In this thesis, only pure Pd was investigated. Pd films were deposited using e-beam evaporation. To ensure a good adhesion to the underneath layers, Pd was deposited on top of a thin Ti or Cr adhesion layer. In order to vary the Pd microstructure, different deposition rates, ranging between 0.3 and 10 Å/s were used, see section 4.4.4. The Pd films were patterned using lift-off photolithography (see table 3.1 for the parameters). In contrast to classical photolithography, the photoresist is first deposited on the substrate and patterned. The target material (here Pd) is then deposited non-conformally over the resist to leave the side of the resist free. The target material lying on the photoresist is lifted off by dissolving the resist with a solvent, e.g. acetone, while the material deposited between the resist pattern remains on the substrate [23]. The accuracy of patterning using lift-off is a little bit lower than with classical photolithography followed with selective etching but the lift-off patterning method is much softer for the film as it is only exposed to acetone.

Back-etching. For TEM dedicated structures, windows must be opened under the beams of interest prior to release. The process step includes thus a first photolithography using thick photoresist on the back face of the wafer to define a resist mask containing the windows to open. The choice of the photoresist is important as it will be exposed during a long time to plasma during the deep silicon etching. Some researchers use an aluminium mask instead of a resist mask because Al is totally resistant to the plasma used to etch Si [250]. As an Al mask renders the process longer and more complex, the resist mask was preferred here. After the creation of the resist mask, the Si substrate is etched using deep reactive ion etching (RIE). This etching process is highly anisotropic and thus allows the opening of deep trenches with high aspect ratio in silicon. Here, the Bosch method was applied, i.e. a rapid switch between a highly directional isotropic plasma etching using SF_6 and a deposition step of C_4F_8 . The C₄F₈ step is used to passivate and to protect the sides of the trenches from further etching. The etch/passivation process is repeated many times to pass through the entire silicon wafer. The use of thin wafers is thus valuable here to reduce the number of needed cycles. The Bosch process presents a good selectivity against SiO₂. It means that our sacrificial layer will play the role of a stop layer and will protect the Pd film from plasma exposure which can alter



Figure 3.6: *SEM images presenting the displacement measurement procedure based on the observation of multiple cursors.*

its properties.

Release. This final processing step allows the loading of the Pd beams by releasing the structures from the constraint of the substrate. The release is performed at room temperature by etching the SiO₂ sacrificial layer with hydrofluoric acid (HF 73 %). The etching time has been optimized through the study of the SiO₂ deposition and densification parameters. A 1 minute release is the compromise chosen between reducing the time to improve the selectivity and increasing the time to allow a reproducible and manually feasible etching. Prior selectivity studies carried out in the same conditions have shown almost no alteration of the Si₃N₄ and Pd layers by the HF etchant. As the release is made in a wet environment, it has to be followed by supercritical drying to avoid the stiction phenomenon due to capillarity forces.

Measurement of parameters for data reduction. After each process step, it is important to characterize the layers. Ellipsometry was used to measure the thickness of transparent layers, i.e. the actuator and sacrificial layers. A profilometer was used to evaluate the curvature of the system after each deposition (in order to estimate the internal stress using the Stoney method) and to measure the thickness of the non-transparent layers, i.e. the Pd layer here. Measurements of the displacements and of all the geometric parameters were carried out in a field emission gun (FEG) SEM. Several cursors are located on the sides of the structures for displacement measurements. Four measurements are performed for each structure (on each side of the cursor using at least one cursor on each side of the beam), see figure 3.6. All structures are labelled based on their position on the wafer. This labelling is important for the subsequent relaxation analysis to ensure the measurement of exactly the same structure each time, see section 3.5.



Figure 3.7: Schematic illustration of the notations used to extract the stress and strain state of an elementary tensile structure.

3.4 Mechanical analysis

In the case of uniaxial tension, the stress σ and the mechanical strain ε^{mech} in the specimen can be directly inferred from the displacement u measured between a moving and a fixed cursor using scanning electron microscopy, from the knowledge of the Young's modulus of the actuator, and from the mismatch strain of both the actuator ε_a^{mis} and the test specimen ε^{mis} ². The experimental approach will be presented in this section.

Some notations are given first, see also figure 3.7:

u and u_{free}	Displacement measured at the end of the actuator after
	the release for a constrained and a free actuator respec-
	tively $(u < u_{free})$. The displacement is taken as positive
	when the actuator is contracting.
ε_a^{mis}	Mismatch strain of the actuator.
E_a and ν_a	Young's modulus and Poisson ratio of the actuator res-
	pectively.
L_{a0}^{free} and L_{a0}	Initial length (i.e. before release) of a constrained and a
	free actuator respectively.
S_{a0} and S_a	Cross section area of the actuator before and after release
	respectively.

 $^{^2 {\}rm The}$ link between ε^{mis} and σ_{int} has already been presented in section 3.2.

$\sigma_a, \varepsilon_a \text{ and } \varepsilon_a^{mech}$	Stress, strain and mechanical strain in the actuator res-
	pectively.
ε^{mis}	Mismatch strain of the specimen.
E and ν	Young's modulus and Poisson ratio of the specimen.
L_0	Initial length (i.e. before release) of the specimen.
S_0 and S	Cross section area of the actuator before and after re-
	lease.
$\sigma, \varepsilon \text{ and } \varepsilon^{mech}$	Stress, strain and mechanical strain in the specimen.

The mechanical analysis will start by considering the actuator. Then, the analysis of the stress state in the specimen subjected to uniaxial tension will be presented.

The total strain in the actuator is the addition of the mechanical strain and the mismatch strain, see equation (3.2).

$$\varepsilon_a = \varepsilon_a^{mech} + \varepsilon_a^{mis}. \tag{3.2}$$

The strain in the actuator is obtained from equation (3.3). In our convention, a contraction of the actuator is associated to a positive displacement, hence, using the small strain assumption, the strain writes

$$\varepsilon_a = \frac{-u}{L_{a0}},\tag{3.3}$$

because a contraction is associated to negative strain. As the actuator has been chosen such as it deforms only elastically, it is possible to determine the stress from the elastic strain ε_a^{elast} being equal to the mechanical strain:

$$\sigma_a = E_a \varepsilon_a^{elast} = E_a \varepsilon_a^{mech}. \tag{3.4}$$

Using for instance free actuators to determine the mismatch strain inside the actuator, equation (3.1) becomes:

$$\varepsilon_a^{mis} = \frac{-u_{free}}{L_{a0}^{free}}.$$
(3.5)

As a matter of fact, in the case of a free actuator, as no external loading is applied, the mechanical stress is zero and the total strain after release is exactly equal to the mismatch strain. Note that the mismatch strain can also be determined using the dedicated structures presented in section 3.2 or using wafer curvature measurements (see the Stoney equation (2.1)). Care must be taken here as the Stoney method relates to equibiaxial loading conditions. To obtain the uniaxial mismatch strain from wafer curvature measurement, one has to use Hooke's law leading to

$$\varepsilon_a^{mis} = \sigma_{Stoney} \frac{1 - \nu_a}{E_a}.$$
(3.6)

Using equation (3.4), it is possible to calculate the load F corresponding to a constrained actuator:

$$F = S_a \sigma_a = S_a E_a \varepsilon_a^{mech} = S_a E_a \left(\varepsilon_a - \varepsilon_a^{mis}\right) = S_a E_a \left(\frac{-u}{L_{a0}} + \frac{u_{free}}{L_{a0}^{free}}\right). \quad (3.7)$$

If we now consider uniaxial tension in the specimen, the total deformation of the specimen is given by:

$$\varepsilon = \varepsilon^{mech} + \varepsilon^{mis} = ln\left(\frac{L_0 + u}{L_0}\right).$$
 (3.8)

The small strain definition is not used for the specimen as it can undergo large deformation and a logarithmic strain definition is more physical. The mismatch strain of the specimen can be calculated in the same way than for the actuator.

The stress inside the specimen can be inferred directly from the force equilibrium, i.e. $F = \sigma_a S_a = \sigma S$. This leads to:

$$\sigma = \frac{F}{S} = \frac{S_a}{S} E_a \left(\frac{-u}{L_{a0}} + \frac{u_{free}}{L_{a0}^{free}} \right).$$
(3.9)

Equations (3.8) and (3.9) provide one point of the specimen stress-strain curve. By varying the geometrical dimensions of the system, it is possible to cover a large range of stresses and strains in the specimen, giving access to the full stress-strain curve of the specimen.

If the actuator material is identical to the specimen material, i.e. for selfactuated structures (see section 3.2), the mechanical analysis gives a way to identify the mismatch strain of the layer under interest. The analytical development is similar to the one used for the bi-material uniaxial tensile structures up to equation (3.7). We assume here that the entire self-actuated structure behaves elastically (actuator part and specimen part). This leads to express the stress inside the specimen as $\sigma = E\varepsilon^{mech}$. Then, it comes:

$$\sigma_a S_a = S_a E_a \left(\frac{-u}{L_{a0}} - \varepsilon_a^{mis} \right),$$

$$\sigma S = SE \left(\ln \left(\frac{L_0 + u}{L_0} \right) - \varepsilon^{mis} \right).$$
(3.10)

As $F = \sigma_a S_a = \sigma S$, $E \equiv E_a$ and $\varepsilon_a^{mis} \equiv \varepsilon^{mis}$, and after combining with the corresponding terms of equation (3.10), the only unknown parameter that remains is $\varepsilon_a^{mis} \equiv \varepsilon^{mis}$, and

$$\varepsilon_a^{mis} = \frac{S\ln\left(\frac{L_0+u}{L_0}\right) + S_a \frac{u}{L_{a0}}}{S - S_a}.$$
(3.11)

The design and error analysis have been detailed in [7]. The most important sources of error on the stress extraction comes from the errors on the measurement of u and ε_a^{mis} . The accuracy on the displacement measurement is considered to be less than 50 nm when using high magnification SEM FEG micrographs (see for instance figure 3.6). The current accuracy estimation of the mismatch strain is about 5% using dedicated test structures near the set of tensile structures, such as rotating sensors, free actuators and self-actuators, see section 3.2. This leads to an error on the stress of around 10%. Regarding the measurement of the strain, only the error on u is critical. Considering the dimensions of the test structures, it results in less than 5% relative error on the strain.³

3.5 Relaxation analysis

Only a limited number of methods have been used to characterize the creep or relaxation behaviour at the nanoscale, involving nanoindentation [89], tensile strain rate jump tests [90], nanoindentation strain rate jump tests [91], strain dip tests [85] or direct tensile testing [73]. The main shortcomings are the difficulty to impose very small strain rates typical of real applications and to

 $^{^{3}}$ Note that an alternative approach to extract the stress in the actuator and in the test specimen has been proposed by S. Houri based on the measurement of the vibration frequencies of the structures [251].

perform in-situ relaxation tests in order to characterize the deformation mechanisms. Also, the sensitivity to drift is increased when dealing with very small loads and displacements, which prevents imposing a constant load during long periods of time. A technique consisting in stress evolution measurement during thermal cycling and allowing in-situ observation has been proposed in the literature but the interpretation and high resolution observation are difficult [252]. The on-chip tensile testing used in this thesis circumvents the limitations encountered by the classical methods [9,253]. Moreover, it allows in-situ observation of the relaxation mechanisms when using the TEM dedicated tensile test structures.

The relaxation experiment is performed by measuring at different time intervals the displacement of the specimens. Note that here, both the stress and the strain vary during relaxation experiments. The strain rate sensitivity parameters can be extracted following the methodology presented in [9]. The methodology will also be exposed in this section.

The strain rate sensitivity exponent m and the activation volume V_{act} are related to the stress and strain evolution of the specimen beams through:

$$m = \frac{\partial \ln \sigma}{\partial \ln \dot{\varepsilon}_p},\tag{3.12}$$

$$V_{act} = M k_B T \frac{\partial \ln \dot{\varepsilon}_p}{\partial \sigma}, \qquad (3.13)$$

where σ is the stress in the beam, $\dot{\varepsilon}_p$ the plastic strain rate, M the Taylor factor, k_B the Boltzmann constant, and T the temperature. Section 1.2.1 has introduced these two formulas.

The experimental procedure is the following. First, consider the behaviour of one elementary tensile testing structure, see figure 3.8. Before the release step, the stress inside the actuator is maximal. If this actuator is released alone without being attached to a specimen beam, the stress inside is zero. When the system actuator-specimen is released, it reaches a force equilibrium. As the actuator does not relax (this was a prerequisite for the selection of the actuator material), the way this equilibrium is modified is due to the relaxation of the Pd specimen, see figure 3.8. LPCVD Si₃N₄ has been used in this study for the actuator material and preliminary tests have proven that this material does not relax.

The displacement evolution of the structures with time is recorded thanks to successive SEM observations and measurements of the cursor position. The displacement versus time curve is smoothed using cubic splines, see figure 3.9.



Figure 3.8: Stress versus strain diagram for the actuator (blue dashed line) and the specimen beam (grey curve) with the equilibrium point attained during the release and a few relaxation points.



Figure 3.9: Methodology applied to extract the strain rate sensitivity parameters from one elementary tensile testing structure.

Based on this curve, the plastic strain and stress evolution can be obtained and by taking the derivatives, the strain rate sensitivity evolution and the activation volume of this specimen beam are extracted. The procedure is repeated to compare the values of different beams with different initial stress level.

3.6 Conclusion

This chapter has introduced the homemade on-chip microtensile testing technique. This technique has been first introduced as well as the other specific structures dedicated to supplementary measurements. Then, the fabrication process has been detailed, followed by the mechanical and relaxation analysis descriptions. This technique will be central in the rest of the thesis. Some of the results generated in this thesis were obtained using other techniques. When it will be the case, the techniques will be directly described in the related result parts.

On-chip tensile testing has proved to be an efficient tool to extract the mechanical properties of various thin films and to perform in-situ relaxation analysis. This will be presented later in chapters 5 to 8.

Finally, to summarize, the key assumptions underlying the use of the method are:

- the actuator behaviour is linear elastic and its Young's modulus is known,
- the actuator does not relax,
- the internal stress of the actuator is highly tensile and the internal stress of the specimen and of the actuator are known,
- the layers have to be compatible from a chemical selectivity point of view;

while the main sources of errors come from:

- the displacement measurement,
- the mismatch strain measurements.

Chapter 4

Processing, hydriding and initial microstructure characterization

The structure of this chapter is the following. First, a short overview of the Pd general properties will be provided. After, the parameters used to deposit the Pd films by e-beam evaporation will be presented. This section will be followed by the presentation of the hydriding and annealing experimental setup used in this thesis. Then, a rapid description of the microscopy methods used in this work will be presented. After that, the reference microstructure of an as-deposited reference Pd film will be detailed. Finally, the effect of different parameters on the microstructure of the as-deposited Pd films, like the thickness of the films, the deposition rate or the temperature, will be described. It will serve as a basis to make comparison with the deformed microstructure, see part III of this thesis. The microstructure after hydriding will be addressed later in chapter 8.

This chapter is inspired from several published papers connected to the present thesis work [8,9,253–257]. Most of the figures come from these papers.

4.1 General properties of Pd

Palladium is the material studied in this thesis. This section provides some basics about Pd and about its properties.

Palladium has been identified in 1803 by Wollaston. He named it *palladium* to make reference to Pallas, an asteroid discovered at the same period. Pd can be

extracted from copper and nickel ores and can also be isolated during copper recycling. Pd resources are mainly located in Russia, South Africa, Canada and United States. Russia is the top producer of Pd. Over 50% of the world Pd production is used for catalytic converters which transform harmful gases coming from vehicles into less-harmful gases. Pd is also used in electronics (for instance for electronic connectors), in jewellery, and finally for hydrogen based-applications as hydrogen storage, hydrogen purification and hydrogen sensing [1–4]. The properties of the Pd/H system will be presented in chapter 8.

Palladium belongs to the platinum group metals (PGMs) which gathers metals (Pt, Rh, Ru, Ir and Os) having similar properties. In the PGMs, Pd is the least dense metal (12,023 g/cm³) and presents the lowest melting point (1554.9°C). Pd is a face-centered cubic (FCC) metal with a lattice constant of 3.89 Å. Its coefficient of linear thermal expansion is equal to 11.2 10^{-6} K⁻¹ [258]. In standard atmospheric conditions, no oxide layer is formed at the Pd surface [259].

The stacking fault energy and the unstable stacking fault energy of Pd, which are indicators of the twinnability of a material, are respectively equal to 175-180 mJ/m² and 265 mJ/m² [260, 261]. These values predict that the growth of twins can be, under specific circumstances, energetically favourable in Pd [261]. The Burgers vector of Pd is equal to 0,275 nm [262].

The elastic constants of Pd are $C_{11} = 227.1$ GPa, $C_{12} = 176.1$ GPa and $C_{44} = 30$ GPa [194, 263]. These constants allow the calculation of the anisotropy ratio $A = \frac{2C_{44}}{C_{11}-C_{12}}$ of Pd. This gives A = 3 for Pd, which indicates a high elastic anisotropy [264]. Indeed, a perfectly isotropic material is characterized by A = 1. If Pd is textured in any of the three following crystallographic directions, one should obtain for its Young's modulus $E_{111} = 162$ GPa, $E_{110} = 137$ GPa, $E_{100} = 111$ GPa [194]. For a randomly textured Pd sample, the Young's modulus should be comprised between E_{100} and E_{111} . The Young's modulus of Pd is reduced when the grain size is decreasing under 10 nm [262] or when the porosity inside Pd is important [38]. The shear modulus of Pd is related to its Young's modulus as $\mu = 3/8$ E. This gives a shear modulus of around 45 GPa, in agreement with the value reported in [265].

The tensile yield strength of bulk coarse-grained Pd is around 250 MPa [38] with, obviously, a dependence on the grain size. This value is highly increased (up to 400-500 MPa) when dealing with nanoscale grains, in agreement with the Hall-Petch effect (see section 1.2.1). The compressive yield strength of nanocrystalline Pd prepared by inert gas condensation is around 1 GPa [37]. Note that this value is affected by the porosity of the material [37].

Deformation mechanisms and mechanical properties of nc Pd have been widely

studied over the last twenty years. However, most of the experimental studies focused on Pd prepared by inert gas condensation (IGC). As explained in section 1.1.2, this preparation method induces a high porosity in the material. The results of these studies will thus not be summarized here as only fully dense Pd is investigated in this work. Nevertheless, more information on IGC Pd can be found in the following papers [55, 92, 112, 141, 146, 266–268].

Numerical studies have also been performed on nanocrystalline Pd to study e.g. the inverse Hall-Petch effect [134], the critical resolved shear stress necessary to nucleate partial dislocations for varying grain size [97] or the presence of new deformation mechanisms like grain boundary sliding for nanocrystalline Pd [187].

4.2 Deposition method

The Pd films studied in this thesis exclusively consist of e-beam evaporated films, see section 1.1.2 for more details about this deposition technique¹. This physical vapour deposition (PVD) method is compatible with the process requirements (temperature, conformality) for preparing uniaxial tensile testing devices. Different film thicknesses ranging from 50 to 500 nm have been deposited at different rates (between 0.3 and 10 \dot{A}/s). The mechanical tests require a good adhesion between Pd and the underlying layers. An adhesion layer (Ti or Cr) is thus always used. The Pd is evaporated using a high purity target (>99.95 %) under a high vacuum (at least 4 x 10⁻⁷ mbar) produced by a cryogenic pump inside the deposition chamber. Hence, no pollution effect is expected inside the Pd films. Section 4.4.2 will present the analysis that confirms the absence of impurities in the Pd thin films.

The substrate is not heated during deposition but some heating can occur due to the evaporation process. However, the temperature of the substrate during the deposition is lower than 100°C. This low temperature avoids the burning of the photoresist used for the lift-off photolithography.

4.3 Hydriding and annealing set-up

The experimental set-up used both for the annealing experiments and for the hydriding of the Pd films will be described in this section. The system allows the

¹Note that sputter deposition was used by R. Delmelle in his thesis leading to films with different microstructure characteristics compared to the evaporated films. These differences will be briefly mentioned later when useful for a better understanding of our own data.



Figure 4.1: Schematic view of the experimental set-up used for the annealing and hydriding experiments. The sample is clamped in a quartz wagon.

in-situ measurement of the internal stress inside films subjected to temperature or hydrogen cycles. The system has been built during the PhD of R. Delmelle to study various chemical, thermal or coupled effects on the properties of thin films via in-situ monitoring of the internal stress inside the films [3, 28, 29]. In this section, the chamber and its overall environment will first be explained. Then, the in-situ internal stress measurement system will be presented. Some paragraphs are inspired from [3].

Figure 4.1 schematically presents the experimental system. The chamber consists of a quartz tube embedded in an heating environment. The sample, consisting of a Si cantilever covered by a Pd film with a size of around 0.5 x 3 cm², is clamped into a quartz wagon. The quartz ensures the compatibility with high temperature treatments. Two pumps, a primary pump and a turbo pump, can act on the chamber to create high vacuum working conditions (at least 10^{-6} mbar). Various gases can be injected into the chamber. The pressure inside the chamber is continuously measured via two electronic gauges, working on different pressure ranges.

A high resolution curvature measurement set-up, including a laser and a CCD camera (kSA Multi-beam Optical Sensor from k-Space Associates), is mounted onto the chamber. It continuously detects the position of 5 laser beams reflected off the cantilevered sample, thus allowing the monitoring of the sample curvature $\Delta \kappa$ in real-time [3]:

$$\Delta \kappa = \frac{\cos \alpha}{2L} \frac{\Delta D}{D_0},\tag{4.1}$$

where $\frac{\Delta D}{D_0}$ is the mean differential spacing between the reflected spots in the CCD, and $\frac{\cos\alpha}{2L}$ is a calibration factor equal to 1.336 m and linked to the geometrical distance and to the angle between the sample, the laser spots and the CCD. The resolution of the curvature measurement is around 10 km while the time resolution is better than 100 ms. The internal stress in the film can be easily derived from the Stoney formula as already exposed in equation (2.1) in chapter 2:

$$\Delta \sigma = \frac{1}{6} \frac{E_s}{(1 - \nu_s)} \frac{t_s^2}{t_f} \Delta \kappa, \qquad (4.2)$$

where $\frac{E_s}{(1-\nu_s)}$ is the biaxial elastic modulus of the substrate, t_s the substrate thickness and t_f the film thickness.

The annealing cycles were made in this work under high vacuum conditions while the hydrogen cycles were performed using Ar/H_2 mixtures with 1% and 10% of H₂ to inject accurately different hydrogen partial pressures.

4.4 Microstructure characterization of the as-deposited films

4.4.1 Microstructure characterization methods

Many TEM techniques have been used to characterize the microstructure of the Pd films studied in this thesis. This section will expose successively the different techniques and their technical details. The related microstructure characterizations of the as-deposited Pd films will be presented in the next sections.

Due to the submicron dimensions of the studied Pd films, samples for TEM characterization were prepared by **focused ion beam (FIB)** with the 'liftout' method. The main advantage of the lift-out technique is that the TEM samples can be made directly from the desired location. Most of the TEM samples were cross-sectional views of the films, although, in some cases, planview TEM samples were produced. Figure 4.2 shows an example of one of these cross-sectional slices. The lift-out procedure is the following: first, a protective platinum layer is deposited on the Pd area of interest prior to FIB milling. This prevents radiation damage of the Pd film surface by the incident Ga^+ ions. Second, the TEM sample is prepared by cutting a thin slice perpendicularly to the surface, see figure 4.2. Then, the thin slice is transferred and glued



Figure 4.2: SEM image of a cross-sectional slice cut from a Pd beam by FIB. The schematic illustration on the right presents the lift-out procedure to prepare a TEM sample.

onto a modified TEM copper grid and thinned to obtain the needed electron transparency. A FEI dual beam xT Nova Nanolab 200 system which combines ultra-high resolution field emission scanning electron microscopy (SEM) and precise FIB for etching and deposition is employed. An ion beam of 30 kV/3 nA and 30 kV/0.3 nA was used for sample cutting and early stage milling, with a probe size of 81 nm and 33 nm, respectively. For the final step, an ion beam of 5 kV/14pA was employed to achieve the final milling and to minimize the presence of amorphous layers generated during high voltage FIB milling.

Conventional TEM characterization in bright field (BF) and dark field (DF) conditions was carried out in a CM20 microscope (LaB₆, 200 kV) to observe the overall microstructure at low TEM magnification. This technique allows a statistical analysis of the grain height, the grain diameter, the grain size distribution and the twin density in the Pd films.

It should be noticed that, although the use of FIB cross-section foils was essential to observe the microstructure of the films throughout their thickness (in particular to evaluate the aspect ratio and the number of grains in the thickness), in some cases, due to the small grain size and the random orientation of these grains, stereological effects associated to the FIB cross-sectioning process could lead to an apparent grain size and orientation distribution in BF and DF images different from the real one. Indeed, some columnar grains will appear smaller than others because of their initial position inside the FIB thin lamella, e.g. some grains are sectioned in the middle while others are sectioned close to an edge. Also, a small misalignment of the cross-section FIB lamellas could yield FIB samples containing slices from several columnar grains in the direction perpendicular to the surface of the films, thus slightly affecting the statistical measurements of grain size distribution. In order to avoid these FIB artefacts and to improve the statistics, ACOMTEM was performed on plan-view FIB samples.

Automated crystallographic orientation indexation in a TEM (ACOM-TEM) has been performed in a Philips CM20 microscope (LaB₆, 200 kV) to characterize the evolution of the grain size distribution, the crystallographic texture and the character of grain boundaries. This technique is very powerful to study nanocrystalline materials since it can provide a quantitative and accurate estimation of the grain size distribution and of the crystallographic texture for a large number of grains in the 10-100 nm range in relatively short times compared to conventional BF and DF techniques. Only plan-view FIB samples were observed using ACOMTEM. Note that the resolution of a LaB₆ TEM is worse than the resolution of a FEG TEM. This thus excludes the possibility to observe all the twins, especially the thinner twins with dimensions smaller than 10 nm. For this reason, BF and DF TEM was always performed in addition to ACOMTEM.

This technique which uses small probe diffraction spot patterns in TEM is an effective method for mapping phase and crystal orientation, and is an alternative to more conventional electron backscattered diffraction (EBSD) in SEM based on Kikuchi line patterns. When using FEG TEM, the ACOMTEM technique has a spatial resolution up to 4 nm, much better than EBSD which has a spatial resolution in the range of 30-50 nm depending on the material type [269–271]. A selected area is scanned with a small probe and the electron diffraction spot patterns are collected using an external CCD camera. Off-line, every diffraction pattern is compared to the pre-calculated templates of selected phases and the best match is selected [272]. In order to eliminate the ambiguity that can exist for highly symmetric orientations, a build-in data clean-up procedure in the OIM TSL software from EDAX Inc. has been used. By using this clean-up procedure, a single orientation for each ambiguous situation is selected.

The ACOMTEM orientation maps are 250x250 pixels in size and were obtained using a spot size of 8 or 13 nm, a step size of 4 or 8 nm, and with an acquisition frequency around 70 frames per second. In order to avoid ambiguities for the measurement of the grain size distribution, $\Sigma 3$ TBs were excluded. To determine the grain size, the histograms were fitted using a log-normal distribution [273, 274].

High Resolution TEM (HRTEM) was used to characterize the crystallographic defects (e.g. dislocation density, dislocation reactions with twin boundaries) at the nanoscale in a TECNAI G2 microscope (Field Emission Gun, 200 kV). In order to allow easy visualization of single dislocations, fast Fourier transforms (FFTs) and geometrical phase analysis (GPA) maps were used on the HRTEM images. GPA is an image processing technique which is sensitive to small displacements of the lattice fringes in HRTEM images. A mask is applied in the Fourier transform of the HRTEM image centered on the periodicity of interest [275].

Finally, **analytical microscopy** was also used to investigate the presence of impurities and of a native oxide layer in the Pd films. For that, electron energy loss spectroscopy (EELS), energy filtering TEM (EFTEM) and energy dispersive X-ray (EDX) studies were performed using a CM30 (Field Emission Gun, 300 kV). Extensive EDX analysis on the as-deposited Pd films were performed in the grain interior and along the TBs and GBs in order to reveal a possible segregation of impurities on these defects. With careful measurements and analysis, EDX can detect levels of elements down to 0.1%at. The absorption of low-energy X-rays is a severe problem for elements with a low atomic mass (Z < 11) and this can make light elements quantification extremely unreliable. The analysis of a possible native oxide layer on the Pd films therefore required the use of EELS and EFTEM, which are better suited for the investigation of light elements.

4.4.2 Reference microstructure

The microstructure which will constitute the 'master case' for the analysis and discussions is a 310 nm-thick Pd film deposited at 1 Å/s on a 5 nm-thick Cr adhesion layer. The Pd film exhibits a morphological texture with columnar grains elongated parallel to the growth direction (bottom to top in figure 4.3). The ring shaped selected area diffraction patterns (SADPs), taken from the entire cross-section and shown as insets, reveal the expected face centered cubic crystalline structure. No clear preferential crystallographic orientation of the grains is detected from the SADP of figure 4.3, indicating the absence of a marked crystallographic texture.

Based on the analysis of BF (figure 4.3) and DF micrographs, the statistical distribution of the in-plane grain size and of the aspect ratio of the grains (grain height/in-plane grain size) in the 310-nm thick as-deposited film yields an average grain diameter of 25.6 ± 7.3 nm with an aspect ratio equal to around 7. About 200 grains have been analysed to obtain statistically representative results. Note that as said before, stereological effects associated with the FIB cross-sectioning process can lead to an under-estimation of the mean grain size.

In order to avoid stereological effects during the measurement of the grain size distribution and in order to analyse the crystallographic texture, ACOMTEM has been used. Figure 4.4 shows the ACOMTEM results including the orientation map, the grain size distribution and the crystallographic texture of a plane-view FIB sample. From this figure, it can be clearly seen that the grain size distribution is relatively narrow with an average grain size of 24.4 ± 1.1 nm,

Microstructure characterization of the as-deposited films



Figure 4.3: Cross-sectional BF image of the as-deposited 310 nm-thick Pd film. White arrows indicate the position of growth twins. Figure taken from [256].

in very good agreement with the results extracted from BF and DF images (figure 4.3). The investigation of the crystallographic texture reveals a low $\langle 101 \rangle$ fiber texture normal to the film surface (see figure 4.4), not detected in the diffraction patterns of figure 4.3. The origin of this $\langle 101 \rangle$ texture remains unclear since FCC metallic films often exhibit a $\langle 111 \rangle$ texture related to the minimum surface energy [18, 26]. The misorientation angle between adjacent grains has been extracted from the ACOMTEM maps, see figure 4.5. The GBs are divided in low angle (LAGBs) and high angle grain boundaries (HAGBs). A low angle GB is a GB with a misorientation angle of lower than 15°. HAGBs have a misorientation angle higher than 15°. During atomic deposition of Pd films, it can be expected that twins have more chance to be formed from HAGBs since these have higher driving forces (in terms of stress) to form the twins.

A significant density of planar defects was observed inside the grains of the asdeposited Pd films as indicated by white arrows in the BF micrograph of figure 4.3. These defects were identified as {111} nanotwins using the nanodiffraction patterns provided in the lower part of figure 4.3. Indeed, the diffraction pattern obtained from the TB region indicated by a white circle in figure 4.3 and oriented along a $\langle 110 \rangle$ zone axis reveals the typical superposition of two mirrored $\langle 110 \rangle$ diffraction patterns with respect to the {111} plane. Tsiaoussis et al. have also observed twins in Pd thin films despite the high stacking fault energy of Pd [276]. Figure 4.3 also shows that most twins are not parallel to the surface of the films and that their orientation changes randomly from one grain to another, confirming the absence of a clear crystallographic texture. The twins are heterogeneously distributed within the grains and over the film thickness. The distance between two subsequent TBs ranges from 1-2 nm to 20 nm. About 20 % to 30 % of the grains are estimated to contain 1 or 2 TBs.



Figure 4.4: Orientation mapping, grain size distribution and crystallographic texture of a plan-view FIB sample prepared from the as-deposited 310-nm thick Pd film. Figure taken from [255].



Figure 4.5: Grain boundary analysis of the plan-view image of the reference Pd film. $\Sigma 3$ {111} TBs have been excluded in the measurements to improve the statistics of the GB character.



Figure 4.6: *HRTEM image obtained in the as-deposited 310 nm-thick Pd film showing a coherent twin boundary. The inserted fast Fourier transform (FFT) shows a typical twin relationship for {111} twins in the FCC structure. Figure taken from [255].*

It can be shown that the observed twins correspond to growth twins. In order to ensure that no twins were missed, the sample was tilted up to 30° along two perpendicular directions with BF images taken after each 1° of tilting. However, it is worth noting that, due to the random orientation of the grains and to the size of some twin domains, the observation of the twins using BF and DF techniques as well as the resulting statistical measurement of these defects was not trivial. As a consequence, the twin density given here is probably an under-estimation. Moreover, due to the ACOMTEM resolution of 10 nm (a LaB₆ TEM was used in this work) and due to the nanoscale twin domains, statistical measurement of the twin density using ACOMTEM was impossible.

Figure 4.6 shows a HRTEM image of a typical Σ 3 {111} type TB in the asdeposited 310 nm thick Pd film. The TB appears perfectly coherent and atomically sharp without steps indicating the absence of dislocations in the twinning plane. This result was confirmed by further HRTEM analysis of several TBs in the as-deposited film. Taking into account the high stacking fault energy of Pd ($\gamma_{sf} = 180 \text{ mJ}/m^2$ [277]), it was surprising to observe the formation of this relatively high density of growth nanotwins. By comparing the microstructure of a highly textured film without twins deposited by sputtering (see the thesis of R. Delmelle [29]), it can be anticipated that the absence of a strong crystallographic texture in the present 310 nm-thick e-beam evaporated Pd film has an effect on the formation of twins [256]. A careful analysis of the twin/matrix interfaces using HRTEM has been performed and confirmed that the weak crystallographic texture resulting in large misorientation between the grains provides the driving force required for the formation of nanoscale growth twins via the GB splitting and migration mechanism. This mechanism helps to decrease the total interfacial energy. This twin formation mechanism does not involve the nucleation and the glide of Shockley partial dislocations (SPDs)



Figure 4.7: *HRTEM image showing the presence of incoherent twin boundaries (ITBs). (a) Pd film produced in this work showing coherent TBs (CTBs) bounded by ITBs. (b) Same observation made on other Pd films studied in [278].*

and can thus explain the exact lattice coherency of the TBs in the as-deposited films (see figure 4.6). However, deeper HRTEM analysis of the GBs resulting from the twin formation has revealed that the twin formation mechanism showed similarities regarding the GB splitting but that the mechanisms involved the coordinated movement of $\Sigma 3$ {112} incoherent twin boundaries [278], see figure 4.7. The initial analysis of the twin formation mechanism in the present Pd films have been studied in lots of details by the team in the University of Antwerp in order to propose a sound scenario for the growth of the twins. This has been published in [256]. The role of the {112} incoherent twin boundaries was not detected at that time. The analysis of this paper should thus be partly corrected owing to this new observation. It is worth noting that the internal stress might also enhance the formation of twins. Furthermore, as presented in the next paragraphs, due to the absence of contaminations in Pd, the role of impurities for the enhancement of twin formation by reducing the stacking fault energy was excluded.

In the as-deposited state, the observed grains do not reveal significant dislocation density. Indeed, the HRTEM image of figure 4.8 taken in one nanograin exhibits a homogeneous contrast free from dislocations. Only one dislocation in the upper left part of figure 4.8 can be observed (see the high magnification insert). A dislocation density of $(2.4 - 3.4) \times 10^{15} \text{ m}^{-2}$ was measured using inverse FFT from high quality HRTEM images of various grains. On some occasions the distortions in the inverse FFT did not perfectly reveal a dislocation. As a result of this uncertainty, only an interval of the density can be obtained, the lower bound referring to all clearly visible dislocations, the upper bound referring to the extra sites potentially corresponding to dislocations.



Figure 4.8: *HRTEM image showing the low dislocation activity in the asdeposited 310 nm-thick Pd film. Only one dislocation in the upper left part of the figure can be observed in the high magnification insert. Figure taken from [255].*



Figure 4.9: *EDX analysis performed on the as-deposited 310 nm-thick Pd films showing low amounts of contaminants. Figure taken from [255].*

The purity of the Pd films has been analysed using EDX on a FIB crosssectional sample, see figure 4.9. No presence of foreign chemical elements in the form of precipitates was observed along the GBs and/or in the grain interiors. However, small amounts of impurities could exist in the form of solid solution which would affect GB energy and SF energy. From literature, it is well known that it can influence the related grain boundary mediated processes such as GB migration [154, 156] and the formation of deformation twins [172]. The EDX spectrum presented in figure 4.9 reveals low amounts of Si (0.9%), Cu (12.2%), and C (9.2%). These contamination elements are often observed in thin foils prepared by FIB and their origin is attributed to sputtering from the substrate (Si), the support (Cu) or the protecting layer (C). From these results, it can be concluded that, except for these FIB contaminants, the TEM foils do not contain any significant concentration of impurities originating from the manufacturing and/or deposition process. It is also worth noting that multiple EDX spectra were obtained on several TBs and GBs confirming the absence (at the detection limit of the EDX technique) of any enrichment of these boundaries with impurities. Further extensive analysis of the Pd films using EELS did not reveal the presence of other impurities within the matrix or along the GBs.

To confirm the purity of the Pd films, inductive coupled plasma - optical emission spectrometry (ICP-OES) was carried out after dissolution of the Pd film in an acid solution mixed from 177 parts water : 20 parts HNO₃ (68%) : 2 parts HCl (37%) : 1 part CH₃COOH (100%). No contaminants were detected at the resolution limit of this technique, i.e. no impurities with a concentration higher than 25 ppb have been found.

The analysis of oxygen contamination on the Pd film surface region was performed using EFTEM. The oxygen concentration on the surface reflects the
Microstructure characterization of the as-deposited films



Figure 4.10: (a) TEM and (b) EFTEM on the Pt/Pd interface showing the absence of a native oxide layer on the surface of the Pd film.

presence of a native oxide layer which could affect the confinement of the plastic deformation by acting as obstacle for deformation dislocations [279]. Also, this layer could affect the ductility of Pd films by acting as a preferential site for the nucleation of cracks, thus accelerating the failure of the films. Oxygen atoms can also segregate along GBs and modify the energy of planar defects such as GBs and TBs. Figure 4.10 shows a BF TEM micrograph of one Pd/Pt interface. The Pt protective layer was deposited with an electron beam (5 kV/0.4 nA) to avoid surface damage from incident ions during FIB thinning. EFTEM maps of palladium, carbon and oxygen are displayed in figure 4.10(b). The carbon signal originates from the Pt protective layer as this layer contains a high density of carbon. The oxygen map in figure 4.10 indicates that no oxide layer is detected on the Pd thin film surface (i.e., between the Pd film and Pt protective layer) in agreement with other results on Pd films performed in standard atmospheric conditions [259]. The only oxygen atoms observed in figure 4.10(b) result from the omnipresent contamination layer on the surface of the entire FIB sample which cannot be avoided even using plasma cleaning prior to TEM characterization.

The internal stress σ_{int} in the reference Pd film has been measured by the wafer curvature technique, see section 2.1. For this reference Pd film with a thickness of 310 nm, $\sigma_{int} = 420 \pm 20$ MPa. The convention in this thesis is that a tensile stress is positive and a compressive stress is negative, following the classical mechanics definitions. The value given here is for the system Cr/Pd as it was impossible to measure the internal stresses of the Pd layer alone. Even though the Cr adhesion layer is only 5 nm-thick, it involves a very high internal stress level which can significantly affect the overall measurement of the internal stress. The impact of the Cr layer increases when the film thickness decreases. Considering a Cr layer with 3 ± 0.5 GPa of tensile internal stress as

justified in references [22, 280], the internal stress in Pd films can be estimated as equal to 375 ± 20 MPa.

Finally, the roughness of the Pd film, measured by atomic force microscopy (AFM), is very small and comes from the roughness of the underneath PECVD SiO₂ layer. Indeed, the roughness R_q of the Si substrate is around 0.3 nm while the roughness R_q of the SiO₂ and Pd films is around 2 nm.

4.4.3 Variations of initial microstructure with film thickness

Pd films with thicknesses ranging between 80 and 310 nm have been deposited at 1 Å/s by e-beam evaporation. Three film thicknesses are compared here but many other deposits were prepared to generate the results of chapters 5 to 8. Some of the films presented later do not involve exactly the same microstructural details or internal stress. This comes from the variation in the deposition date. For instance, the quartz that measures the deposition rate and the deposited thickness evolves with the thickness of the materials previously deposited in the chamber. This can cause slight changes in the deposition conditions, and especially here as the depositions were made during four years and by different operators. However, the trends reported in this section and in sections 4.4.4 and 4.4.5 are always respected.

The thickness of the Pd film influences the microstructure of the films and the internal stress. As presented in figure 4.11, the columnar shape of the grains remains whatever the thickness of the film (see the inserts on the figure). This figure also shows the narrow grain size distributions of the different films. The mean values are presented in table 4.1. The statistical analysis of the grain size was performed on more than 200 grains across each cross-section obtained by BF and DF TEM imaging. The distributions shown in figure 4.11 should be taken as qualitative due to stereological effects related to the FIB cross-sectioning. Nevertheless, the in-plane grain size does not significantly vary among the different film thicknesses.

All films contain nanotwins but nanotwins are not observed in all grains. Table 4.1 gathers averaged percentage of twinned grains and number of twins per twinned grain. However, although samples were observed along different crystallographic orientations in order to capture as many twins as possible, it should be noticed that, due to the random and non-textured orientation of the nano-grains, these measured twin densities are still underestimated.

The internal stresses of the different films are shown in table 4.1. As explained before, the Cr layer can contribute to the global internal stress. The internal stress value extracted from direct wafer curvature measurements is presented



Figure 4.11: (a-c) Grain width distributions of the three film thicknesses derived from the cross-section analysis without stereological correction. (d-f) Grain height distributions derived from the same cross-section samples. (Inserts a-c) TEM dark field images of the cross-section of the 80, 160 and 310 nm-thick Pd films, respectively. Average values are given with the standard errors. Figure taken from [254].

	310 nm-thick	160 nm-thick	80 nm-thick
Grain size (width and	26 ± 1 and 184 ± 8	33 ± 2 and 100 ± 4	35 ± 2 and 57 ± 2
heigth)(nm)			
Twinned grains (%)	26	13	8
Number of twins per	1.4	1.5	1
twinned grain			
σ_{int} in the Pd/Cr bi-	420 ± 20	730 ± 40	850 ± 80
layer (MPa)			
σ_{int} estimated in Pd	375 ± 20	655 ± 30	705 ± 70
(MPa)			

Table 4.1: Characteristic features of the Pd films with different thick-nesses.

Chapter 4. Processing, hydriding and initial microstructure characterization



Figure 4.12: BF image and corresponding diffraction pattern of the three Pd films deposited at a) 0.3 Å/s, b) 1 Å/s and c) 5 Å/s. Figure taken from [257].

as well as the internal stress of the Pd alone assuming that the 5-nm thick Cr film contains 3 GPa of tensile internal stress. The internal stress is increasing when the film thickness decreases. This thickness-dependence of the internal stresses has already been observed numerically for hetero-epitaxially grown thin films [281].

4.4.4 Influence of the deposition rate

The impact of the deposition rate is summarized in this section. The microstructural features of three Pd films deposited at different rates (0.3, 1 and 5 Å/s) are compared. Some results concerning a Pd film deposited at 10 Å/s will be presented in part III but this film will not enter in the comparison here for a sake of simplicity. The next paragraphs will consecutively detail the effect of the deposition rate on the grain size, grain size distribution, twin density, twin coherency, crystallographic texture, dislocation density, internal stresses, and grain boundary character. This analysis has been published in reference [257] and performed by the team of the University of Antwerp.

Figure 4.12 shows the BF TEM micrographs of cross-sectional samples deposited at 0.3, 1 and 5 Å/s respectively. All the films exhibit a morphological texture with columnar grains elongated parallel to the growth direction (bottom to top of the figures). The ring shaped selected area diffraction patterns inserted on the figures reveal the expected face centered cubic Pd structure. The grain size of the three films has been statistically measured based on these images, and are presented in table 4.2. ACOMTEM was also performed at the University of Brussels to investigate the grain size distribution without the stereological artefacts present when using cross-sectional samples like for conventional TEM. The obtained grain size distributions are relatively narrow (see figure 4.13) with an average value equal to 23.7 ± 0.5 nm, 34.4 ± 0.4 nm,

Microstructure characterization of the as-deposited films

Deposition rate $(Å/s)$	0.3	1	5
Grain width (nm)	14 - 32 ± 2	$15 - 40 \pm 2$	$18 - 40 \pm 2$
Grain height (nm)	$41 - 105 \pm 2$	45 - 100 \pm 2	$45 - 112 \pm 2$
TB density (m^{-3})	$6.1 - 6.7 \ge 10^{21}$	$9.4 - 10.3 \ge 10^{21}$	$12 - 13.2 \ge 10^{21}$
TB spacing (nm)	$2 - 12 \pm 2$	$2 - 13 \pm 2$	$2 - 10 \pm 2$
TB length (nm)	$14 - 35 \pm 2$	$13 - 40 \pm 2$	$10 - 50 \pm 2$
Grains containing TB (%)	25 - 30	35 - 40	50 - 54
Grains containing more than 2	4	10	20
TB (%)			
Dislocation density (m^{-2})	$2.5 - 3.5 \ge 10^{15}$	$2.4 - 3.4 \ge 10^{15}$	$6.25 - 7.75 \ge 10^{16}$
σ_{int} (MPa)	420 ± 20	730 ± 40	850 ± 80

Table 4.2: Statistical measurements of the three nanocrystalline Pd films from BF TEM images.



Figure 4.13: ACOMTEM grain size distribution of plan-view FIB samples of the three Pd films deposited at (a) 0.3 Å/s, (b) 1 Å/s and (c) 5 Å/s. Figure taken from [257].

and 32.5 ± 0.4 nm for the films deposited at 0.3 Å/s, 1 Å/s and 5 Å/s, respectively. These values fall within the ranges observed by conventional TEM (table 4.2). The increased precision of the ACOMTEM technique confirms that there is a true increase of the grain size when the deposition rate increases from 0.3 to 1 Å/s, whereas for 5 Å/s, the grain size does not change much compared to 1 Å/s.

Statistical measurements of $\Sigma 3$ {111} TB densities and of the volume fraction of grains containing twins have been performed using BF TEM images and are exposed in table 4.2. It is clear that the TB density and the volume fraction of grains containing twins increase with increasing the deposition rate. This link between twin density and deposition rate has been already observed in the literature [282].

HRTEM was performed to analyse the coherency of the twins and the dislocation density for the different deposition rates. As shown in the HRTEM images of figure 4.14, most of the TBs are fully coherent without any residual dislocations for the lowest deposition rates (0.3 and 1 Å/s). However, for the highest deposition rate (5 Å/s), the coherency of the TBs decreased significantly. In this figure, it can be clearly seen that the atomic structure of the TBs is highly distorted. The dislocation density is also affected by the deposition rate. The dislocation density increases when the deposition rate increases over 1 Å/s, see



Figure 4.14: (a) HRTEM image showing the TB structure of the Pd film deposited at 0.3 Å/s. Note the coherency of the TB and the lack of dislocation contrast. Similar behaviour was observed in the film deposited at 1 Å/s. (b) Incoherent TBs are observed in the film deposited at 5 Å/s. Figure taken from [257].

table 4.2. The dislocation positions are indicated by white arrows in figure 4.14. No dislocation is observed in figure 4.14(a) while several dislocations are detected in figure 4.14(b). The strong loss of coherency of the TBs in the film produced at the highest deposition rate (5 Å/s) is thus in agreement with the increase of the lattice dislocation density in this film. The increase of dislocation density can be attributed to the increase of internal stress upon deposition. Indeed, the internal stress measured using the wafer curvature method in the film deposited at 1 Å/s was equal to 300 MPa and increases up to 600 MPa for the film deposited at 5 Å/s. It can thus be expected that some dislocation activity took place in the majority of the grains during the deposition of the films deposited at 5 Å/s (the equivalent plastic strain corresponding to a yield strength of 600 MPa is about 0.5%) while only few dislocations will nucleate in the film deposited at 1 Å/s.

Based on the coarsening of the spots of the (111) ring observed in the diffraction patterns of figure 4.12, it can be concluded that, qualitatively, a {111} crystal-lographic texture component is appearing with increasing the deposition rate. ACOMTEM was also used here to analyse more accurately the crystallographic texture evolution with the deposition rate. The ACOMTEM results show that the Pd film deposited at the lowest deposition rate of 0.3 Å/s involves a {101} texture, which decreases with increasing deposition rate, see figure 4.15. In the same time, the {111} texture component is seen to increase as qualitatively described by the SADP of figure 4.12.

The pole figures corresponding to Pd films deposited at different rates are displayed in figure 4.16. The results show that the Pd film deposited at the lowest deposition rate of 0.3 Å/s involves a strong $\{101\}$ texture component, which Microstructure characterization of the as-deposited films



Figure 4.15: ACOMTEM orientation mapping and crystallographic texture of plan-view FIB samples of Pd thin films deposited at various rates: (a) 0.3 Å/s, (b) 1 Å/s and (c) 5 Å/s. Figure taken from [257].



Figure 4.16: {101} and {111} pole figures of plan-view FIB specimens for Pd thin films deposited at various rates of (a) 0.3 Å/s, (b) 1 Å/s and (c) 5 Å/s. Figure taken from [257].

decreases with increasing deposition rate. This is consistent with the XRD measurements performed by Castrup et al. [283]. The $\{111\}$ texture component becomes sharper with increasing deposition rate. However, a detailed analysis of the pole figures shows that a full $\{111\}$ fiber texture has not been formed and that the $\{101\}$ texture is still dominant.

As explained in section 4.4.2 and in [256], the absence of crystallographic texture seems to be at the origin of the formation of growth twins via a mechanism similar to GB migration through the coordinate move of SPDs. It means that an increased deposition rate is expected to favour the possibility of formation of growth twins as the $\{101\}$ texture component is weakening when increasing the deposition rate, leading to a more random texture and resulting in a higher twin density. This is in good agreement with the TB densities extracted from BF and DF images. The type of GB can also play a role in the formation mechanism of twins during deposition or in the deformation mechanisms. The GB character of the Pd films deposited at various rates has been extracted from the ACOMTEM maps. Although both high angle and low angle GBs are detected in the Pd films obtained with different deposition rates, the fraction of different types of HAGBs plays an important role to understand the differences among the microstructures. The statistical measurements show that the fraction of HAGBs in the range of $55-65^{\circ}$ is 19%, 22% and 25% for Pd thin films deposited at the respective rates of 0.3 Å/s, 1 Å/s and 5 Å/s. On the other hand, the fractions of HAGBs in the range of 15–55° are almost independent of deposition rate. The increase of the fraction of HAGBs in the range of 55–65° with increasing deposition rate is possibly related to the observed decrease of the dominant {101} texture discussed above. Indeed, although a relatively strong texture does not automatically imply a small fraction of HAGBs, a loss of texture provides more freedom for the occurrence of HAGBs as seen in the present observations. And, as mentioned in section 4.4.2, twins have more chance to be formed from HAGBs.

Based on these results, it can be concluded that the GB character and texture of thin Pd films can be controlled by optimizing the deposition conditions. Consequently, TB density and coherency of TBs can be controlled by optimizing the GB character or the texture through the selection of the deposition rate.

4.4.5 Thermal stability of the initial microstructure

An in-situ TEM annealing experiment was performed on a FIB thinned crosssectional sample in order to directly observe any variation in twin density and morphology during grain growth. Such an experiment provides additional information concerning the thermal stability of the growth twins which can affect the mechanical properties of the films at elevated temperatures.

Figure 4.17 reveals the evolution of the microstructure of the 310 nm-thick Pd film deposited by electron-beam evaporation at 1 Å/s, observed during insitu TEM heating. Figure 4.17(a) shows the initial microstructure of the film. In this figure, growth twins can be clearly observed within several nanograins. Grain A has a diameter of 70 nm and contains diverse growth twins on different families of $\{111\}$ planes. The thicknesses of the twins labelled T1 and T2 are 10.8 and 5.3 nm, respectively. In the same figure, grain B has a diameter of 26 nm and contains several growth nanotwins shown by a small white arrow. The latter are less visible than those observed in grain A because of the difference between the diffraction conditions in the two grains.

Figure 4.17(b) shows the same region as figure 4.17(a) but after an annealing

Microstructure characterization of the as-deposited films



Figure 4.17: Microstructure evolution of the 310 nm-thick Pd film during in-situ heating at 500°C for 20 min. Figure taken from [256].

at 500°C during 20 minutes. Figure 4.17(b) clearly shows that grain A has undergone significant growth during annealing. Its diameter increased from approximately 70 to 130 nm. However, no variation in the twin thickness inside this grain was detected. The initial thickness of the twins T1 and T2 remains unchanged before and after annealing, while the length of the twin lamellae increased following the grain growth. Furthermore, emission of Shockley partial dislocations (SPDs) from TB-GB intersection and glide of pre-existing SPDs in the twin plane were not observed during the in-situ TEM heating. The correlation between the change of the grain size and the length expansion of the twin lamellae indicates that this expansion is controlled by a mechanism similar to GB migration which is also the mechanism found to be responsible for the twin formation. The present observations confirm the above conclusions on the formation mechanism of the TBs.

In addition, it is worth mentioning that the twin density considerably decreases after annealing. For example, the growth twins of grain B in figure 4.17(a) were eliminated due to the shrinking and final disappearance of grain B after annealing at 500°C.

Note that all the observations here were made on a thin TEM foil containing only one grain over the thickness of the sample. The behaviour of an asdeposited film under annealing is different as the constraint of the surrounded grains delays the grain growth mechanism, as exposed in the next paragraph.

The internal stress of a 400 nm thick Pd film deposited on a Cr adhesion layer at 1 Å/s has been recorded in-situ during thermal annealing thanks to the experimental set-up described in section 4.3. The applied annealing profile is shown in figure 4.18(a). It consists of a heating rate of 15°C/min followed by a temperature plateau of 1 hour and finally by a cooling rate determined



Figure 4.18: Annealing cycles performed on a 400 nm thick Pd film deposited on Cr. (a) Temperature profile. (b) Evolution of the internal stress in the Pd film during the first annealing cycle as a function of the temperature. This graph can be compared to the one presented in (c) and taken from ref [10] for an $AlSi_{1\%}Ti_{2.5\%}$ film.

Conclusion



Figure 4.19: Microstructure evolution of the 310 nm-thick Pd film during in-situ heating at 500°C for 20 min.

by the inertia of the experimental set-up and thus uncontrolled. The first annealing cycle is presented in terms of the internal stress inside the Pd film versus the temperature, see figure 4.18(b). The arrows indicate the history line of the cycle. The beginning of the cycle should be linear but it is not the case here, probably due to a bad clamping of the sample. During the heating, the thermal expansion helped fixing this problem, as at around 170° C the linearity appeared. The internal stress evolution was not continuously recorded until the system reached the ambient temperature because the in-situ internal stress measurement cannot be active for more than three consecutive hours. Thus, a last measurement point was taken after the system cooled down to room temperature.

This cycle can be compared to literature data, see figure 4.18(c) [10]. The temperature at which grain growth should appear lies around 380°C on the graph 4.18(b). But when looking at the in-plane grain size using SEM, no clear effect of annealing on grain growth nor hillocking is observed, see figure 4.19. Thus, the annealing has probably removed here the lattice defects such as dislocations or vacancies, explaining the higher internal stress present in the Pd film after annealing.

This confirms that attention has to be paid when comparing experiments on thin FIB foils or on a film constrained by the substrate.

4.5 Conclusion

This chapter has introduced some basics about palladium. After, the deposition conditions of the Pd film as well as the annealing and hydriding experimental set-up have been presented. To conclude, a brief summary of the main observations made on the as-deposited Pd films will be provided. The use of a variety of characterization methods has allowed an extensive study of the initial Pd microstructure prior to external deformation. The reference film presents columnar grains containing $\Sigma 3$ {111} growth nanotwins. The grain diameter is around 25 nm and the aspect ratio of the grains is equal to around 7. A low $\langle 101 \rangle$ fiber texture is observed perpendicularly to the film surface. The twins were observed in about 25% of the grains and are coherent in the as-deposited state, in agreement with the absence of dislocation activity in the grains and with the formation mechanism of the twins. Moreover, no impurities nor surface contamination of the films were found.

When the thickness of the film is modified, the grain size is unchanged but the twin density decreases with the thickness. Also, the internal stress of the film increases when the thickness decreases. When comparing films deposited at different rates, some effects on the microstructure have been observed. First, the grain size increases with the deposition rate, as well as the twin density. But the coherency of the TBs is degraded and the dislocation activity is enhanced when increasing the deposition rate. The higher twin density has been linked to a more random texture when the deposition rate is higher. Finally, the thermal stability of the films has been studied. From that, it is clear that attention should be paid when comparing the behaviour of FIB thinned lamellas with the behaviour of the entire as-deposited film. Indeed, grain growth clearly appears during the heating of a thin FIB sample, but no grain growth is detected when performing annealing cycles on the as-deposited film.

_____ Part III _____

Results and discussion

Chapter 5

Strength, strain hardening and ductility - Thickness effect and modelling

This chapter encloses the paper "*High strength-ductility of thin nanocrystalline palladium films with nanoscale twins: on-chip testing and grain aggregate model*" published in Acta Materialia [254]. This paper is focusing on the mechanical aspects of the paper published in Advanced Materials [8] which presents the baseline understanding of the results. For the sake of simplicity, the content of the Acta Materialia paper is almost exactly duplicated here. The results acquired after the publication of this paper are presented in chapter 6 and have contradicted or modified some of the assumptions made in this paper, even if the general conclusions remain correct. A discussion about the validity of the hypotheses made in the paper (thus in this chapter) will be provided in the conclusion of chapter 6.

To understand the effect of each microstructural detail, different Pd films have been analysed and compared using the on-chip tensile testing method presented in chapter 3. The chapter here will present the mechanical properties of the Pd films measured immediately after the release step to avoid any relaxation effect on the results. More specifically, the mechanical measurements are made approximately 1 hour after the release due to the required step of supercritical drying (see section 3.3). Also, the release was carried out directly after the Pd film deposition. This avoids the relaxation of the Pd film on the substrate as it contains a relatively high level of tensile internal stress. The relaxation behaviour of the Pd films will be presented later in chapter 7. The present chapter will only expose the effect of the thickness of the Pd films on their mechanical properties. A grain aggregate model has been developed to explain some microstructural effects. In addition to the thickness effect, other effects will be presented in chapters 6 and 8 and could sometimes question the validity of some hypotheses considered in the present model. Also, some information can be redundant regarding what was exposed in the part II of this thesis.

The outline of this chapter is the following. The experimental conditions and the on-chip tensile testing method will be presented first. Then, the stressstrain curves of Pd thin films and the main transmission electron microscopy observations will be summarized. The elementary grain aggregate model will be described next, followed by the parameters identification, the parameters assessment and a parametric study.

5.1 Abstract

The mechanical behaviour of thin nanocrystalline palladium films with ~ 30 nm grain size has been characterized on-chip under uniaxial tension. The films exhibit a large strain hardening capacity and a significant increase of the strength with decreasing thickness. Transmission electron microscopy has revealed the presence of a moderate density of growth nanotwins interacting with dislocations. A semi-analytical grain aggregate model is proposed to investigate the impact of different contributions to the flow behaviour, involving the effect of the twins, of the grain size, and of the presence of a thin surface layer. This model provides guidelines towards optimizing the strength/ductility ratio of the films.

5.2 Introduction

Thin palladium membranes constitute an enabling material in hydrogen storage [2], sensing [3], purification and separation technologies [4]. These membranes must be as thin as possible to ensure a good hydrogen permeance while remaining mechanically stable [4]. The lack of ductility of thin Pd films [30], as for most metallic thin films, is a key issue for these applications [284]. From a more fundamental perspective, the mechanical behaviour of nanocrystalline Pd has received attention in the recent literature dealing with several interesting scientific questions related to the deformation mechanisms and the connection to the microstructure, see [141,153,267] for experimental studies, and [285,286] for numerical modelling. Regarding the general lack of ductility of thin films, the presence of nanotwins appears to be a very attractive way to enhance the ductility of nanocrystalline metals without altering the high strength, such as demonstrated first for Cu, see [71, 157, 287–289]. Kulkarni and Asaro studied theoretically the deformation mechanisms in nanotwinned FCC metals like Pd, Cu, Al and Ag addressing the problem from a more general perspective [260]. These authors found for instance a transition in the deformation mechanism which is a function of the twin lamella spacing, except for Pd.

The Pd films studied in [8] exhibit a large strength related to the nanometer size of the grains, a moderate ductility between 3 and 6%, and a high strain hardening capacity. The high strain hardening capacity of the films was understood to possibly result of dislocation/twin interactions based on detailed transmission electron microscopy (TEM) characterizations of the individual deformation mechanisms and defect interactions though other contributions were invoked such as kinematic hardening. The free-standing films were deformed on-chip by a microtensile testing technique [6, 7, 232]. In this chapter, the mechanical response of Pd films is analysed in more details and a semi-analytical model is developed to improve the understanding of the relationship between the heterogeneous nanostructure and the overall flow behaviour. The model is based on the collective response of an aggregate of grains with different twin densities. This model confirms the potentially large impact of the twins on the high strain hardening capacity but also accounts for a long elasto-plastic transition, and highlights the effect of a residual surface layer on one side of the test structures.

5.3 Experimental study

5.3.1 Materials and methods

The principle of on-chip tensile testing has been already detailed in chapter 3 (page 61) and will not be repeated here. The films studied consist in 80, 160 and 310 nm-thick Pd films deposited on a thin Cr adhesion layer. The microscopy analysis was performed using the tools presented in section 4.4.1 (page 83).

5.3.2 Results and discussion

Figure 5.1 shows the raw stress-strain curves of the three film thicknesses (80, 160 and 310 nm). Structures with different actuator and specimen widths have been measured in order to evaluate the reproducibility of the method and to account for material variations over the wafer. The repeatability is acceptable

and is improved when the film thickness increases. The overall experimental data set involves more than three different film thicknesses deposited under similar conditions. But for a sake of simplicity, only three are selected here. All the obtained curves are presented in the next chapter and follow the trend of the three selected curves.

One of the stress-strain curves shown in figure 5.1 has been selected for each film thickness, i.e. the T15_2, T10_2 and T10_2 curves have been selected for the 80, 160 and 310 nm-thick films respectively. The representative curves have been smoothed and interpolated using cubic splines, see figure 5.2(a). As the stress-strain data are calculated from the same displacement measurements, the interpolation is performed directly on the displacement versus beam length data in order to avoid the propagation of errors during the mechanical analysis. The elastic line drawn in figure 5.2(a) corresponds to the Young's modulus measured by nanoindentation as being equal to 120 GPa. Table 5.1 collects all the numerical values related to the results plotted in figure 5.2.

The yield stress defined at 0.2% offset strain (σ_0) is equal to 450 ± 39 , 690 ± 386 and 1030 ± 3149 MPa for the 310, 160 and 80 nm-thick films, respectively. The error has been calculated by analysing the error propagation [290] in the equation (3.9) presented in the section 3.4 of this thesis. Another criterion based on the tangent modulus [49,291] was also used, giving essentially the same values (see table 5.1). The tangent modulus approach is often used for materials presenting a long elasto-plastic transition, and defines the yield stress as the stress at which the strain hardening rate $\Theta = d\sigma/d\varepsilon^{pl}$ becomes smaller than one third of the Young's modulus [291].

The increase of the yield strength with decreasing thickness has often been reported in the literature and related to a Hall-Petch type effect associated to the constraint induced by grain boundaries on the plastic flow [30, 292] (the grain size often decreases with decreasing film thickness) or from the presence of surface layers putting an additional constraint on the dislocations and preventing the dislocations to escape [21, 293]. Here, the in-plane grain size does not significantly vary among the different film thicknesses, see table 4.1 of section 4.4.3. Furthermore, no oxide is present on the Pd surface, as confirmed by the high resolution electron energy loss spectroscopy (HREELS) measurements presented in section 4.4.2 and in agreement with other literature reports for standard atmospheric conditions [259].

It is worth noting that, for the three films compared here, the thin Cr adhesion layer is still present along one of the sides of the test specimens during the tensile test. This thin Cr layer can be viewed as a passivation layer which confines one free surface of the Pd specimen. The impact of this Cr layer will be discussed in a model presented in the next section, and will also be analysed



Figure 5.1: Stress-strain curves of the raw data for the (a) 80, (b) 160 and (c) 310 nm-thick films. The straight line corresponds to the elastic regime of the Pd samples with a slope of 120 GPa, as measured by nanoindentation. The notation TX_Y used here means that the samples are tested in tension (T), with X representing the actuator width in microns and Y the sample width, also in microns.



Figure 5.2: (a) Stress-strain curves after smoothing and interpolation with cubic splines. Nanoindentation was used to determine the elastic modulus of the films. (b) The incremental strain hardening has been computed based on the smoothed data in (a). The straight line represents the Considère's criterion. The arrows represent the end of the first maximum. The dashed arrow for the thinnest film is showing the expected end of the maximum. (c) Evolution of the strain hardening rate versus the difference between the stress and the yield stress.

	310 nm-thick	160 nm-thick	80 nm-thick
$\sigma_0 (MPa)$			
0.2% offset strain criterion	450 ± 39	690 ± 86	1030 ± 149
Tangent modulus approach	500 ± 43	690 ± 86	1100 ± 159
σ_{int} estimated in Pd (MPa)	375 ± 20	655 ± 30	705 ± 70
ε^f maximum (/)	0.04	0.05	0.02
Θ_0 (GPa)	~ 60	~ 60	~ 200

Table 5.1: Summary of the properties extracted for each film thickness by on-chip microtensile testing.

experimentally in the next chapter, in section 6.5.

The internal stresses σ_{int} of the as-deposited films provided in table 4.1 have been recalled here in table 5.1. Wafer curvature measurements were used to extract the internal stress of the films. As said in section 4.4.2, only a measure of the internal stress of the Pd/Cr bilayer can be obtained but the internal stress inside the Pd film can be estimated. Only the estimated values in the Pd films are presented in table 5.1. They are in good agreement with the internal stress values reported in [294], except for the 310 nm-thick film which exhibits here a lower level of internal stress. A parallel can be make between the yield stress and the internal stress. Indeed, the observed yield stress is each time slightly higher than the internal stress, both lying in the same range. It somehow validates the data as, physically, the internal stress of a film cannot exceed its yield stress value.

Concerning the ability of the films to deform plastically, the fracture strain presented in table 5.1 shows that the ductility is highly reduced when the film thickness decreases. This can be explained by the fact that the thinner the film, the larger the relative magnitude of imperfections leading to premature fracture [62].

The stress-strain curves of figure 5.2(a) show a very large apparent strain hardening capacity, leading to a strength increase on the order of 0.5 GPa over a few percent of deformation. The strain hardening capacity has been quantified in terms of the incremental strain hardening exponent,

$$n_{incr} = \frac{d\ln\sigma}{d\ln\varepsilon^{pl}},\tag{5.1}$$

and in terms of the strain hardening rate

$$\Theta = \frac{d\sigma}{d\varepsilon^{pl}},\tag{5.2}$$

where σ is the stress and ε^{pl} is the plastic strain. Figures 5.2(b) and (c) present

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the smoothed data and the evolution of n_{incr} and Θ according to the plastic strain ε^{pl} or to the stress minus the initial yield stress $(\sigma - \sigma_0)$, respectively. Note that, as can be deduced from the error analysis, the error on the extracted stress σ increases with decreasing the specimen thickness. The variation of n_{incr} first increases with deformation and then progressively decreases. This graph reveals that the Considère criterion, predicting that necking starts when $n_{incr} =$ σ , is not attained. That means that fracture occurs earlier. Imperfections such as roughness or grain boundary grooving and/or cracking of the Cr layer, can induce an early localization or fracture of the Pd films [233]. In figure 5.2(c), the initial hardening rate Θ_0 obtained by interpolating linearly the initial response down to $(\sigma - \sigma_0) = 0$, is equal to about 60 GPa for the 310 and 160 nm-thick films. The maximum expected hardening rate is about E/50 for a polycrystal with micron-size grains [295]. This value should be equal to 2.4 GPa for Pd, i.e. more than one order of magnitude lower than the value measured in the present study, see figure 5.2(c) or table 5.1. Such a high Θ_0 means that some regions of the material behave elastically while other parts are already deforming plastically, inducing a significant kinematic hardening contribution. A long elasto-plastic transition can thus constitute a first explanation for the high apparent strain hardening capacity of the films and justifies to consider the tangent modulus approach to define the yield stress. Similar long elasto-plastic transitions were observed in other nanocrystalline materials [49, 296–298]. The Θ_0 value for the 80 nm-thick film is even larger but it should be considered with caution due to the large error associated with this specimen thickness. Note that in [296], similar increase of the hardening rate is observed when the thickness of Al films is decreased down to 100 nm.

Another possible origin of the high strain hardening capacity related to dislocation mechanisms has been addressed by extensive TEM and HRTEM analysis, see [8, 255] for the fully detailed study. As presented in chapter 4, all films contain nanotwins but nanotwins are not observed in all grains. This means that twins are present before deformation, appearing during the deposition of the films. Table 5.2 gives the microstructure information presented before. Although samples were observed along different crystallographic orientations to capture as many twins as possible, it should be noticed that, due to the random and non-textured orientation of the nanograins, these measured twin densities are possibly still an underestimation.

HRTEM was performed on two different specimens coming from the 310 nmthick Pd film: one undeformed (as-deposited) specimen and another one deformed up to 4%, see figure 5.3 showing the twin boundary evolution regarding the imposed strain. Initially, in figure 5.3(a), the twin boundaries are perfectly coherent. A loss of coherency of the twin boundaries takes place during plastic deformation (figure 5.3(b)). Twin boundaries act as barriers to dislocation motion as well as sources of dislocations. The dislocation/twin interaction

Grain aggregate model

	310 nm-thick	160 nm-thick	80 nm-thick
Grain size (width and	$26 \pm 1 \text{ and } 184 \pm 8$	33 ± 2 and 100 ± 4	35 ± 2 and 57 ± 2
heigth)(nm)			
Twinned grains (%)	26	13	8
Number of twins per	1.4	1.5	1
twinned grain			

Table 5.2: Characteristic dimensions of the microstructure of the three Pd films based on TEM observations.



Figure 5.3: *HRTEM image showing typical twin boundary structures in two different 310 nm-thick Pd samples. (a) Coherent parallel twin boundaries observed before release. (b) Another nanoscale twin boundary distorted after a strain of 4% has been applied to the sample.*

mechanisms constitute a second possible factor, here an isotropic hardening contribution, explaining the large strain hardening capacity of the films. The mechanisms of interaction between dislocations and TBs will be detailed in section 6.3 of the next chapter. The fact that all the grains do not have the same twin density also participates to the heterogeneity of the microstructure and contributes to the long elasto-plastic transition.

5.4 Grain aggregate model

5.4.1 Presentation

In order to better understand the relative contribution of the strain hardening mechanisms proposed in the previous section, a semi-analytical grain aggregate model has been developed for representing the plastic flow behaviour of



Figure 5.4: Schematic view of the film used for the grain aggregate model. The number of grains within the Pd sample thickness and the proportion of twins are chosen for the model in accordance to the TEM observations.

the Pd films as well as the potential impact of the Cr layer. This model is based on the idea that the grain behaviour depends on the number of twin boundaries inside the grains as well as on its position with respect to the upper free surface or lower constrained surface. The objective was to limit, at this stage, the complexity and to focus on the physics through developing a simple 1D empirical model in the spirit of the so-called tangent modulus models [49]. More sophisticated numerical models applied to Cu can be found in [287,299]. The model proposed in [287] relies on crystal plasticity theory, probably not applicable here considering the very small grain size. And the study presented in [299] is based on 3D molecular dynamic simulations, requiring representative volume elements much smaller than those of interest in this study. Figure 5.4 shows the schematic model used to describe the microstructure of the films. The presence of the Cr adhesion layer is taken into account. It influences the strength and the hardening of the Pd films by adding a barrier to dislocation motion. This barrier prevents the dislocations to escape [279]. The Cr layer can also crack, inducing a local stress concentration in the Pd film and relaxing the confinement on the dislocations.

More precisely, a Pd film is described as an aggregate of columns, each column being made of m grains (figure 5.4). There are l different types of grains depending on the number i of twins per grain, i varying between 0 and l-1. The volume fraction of each type of grain is defined as f_i . There are l^m types of columns. The position p of a grain in a column is important in order to take into account the nature of the upper and lower interfaces of the grain (free surface, grain boundary or Cr layer). The vertical interfaces are grain boundaries (no effect of free lateral surfaces is taken into account, the specimen width being much larger than the grain size). Each type of column k has a volume fraction f_k , k varying between 1 and l^m . The information regarding the microstructure is known from experimental characterization (see above). The objective of the model is to calculate the evolution of the overall uniaxial stress σ applied to the film as a function of the overall applied strain ε .

Each grain is modelled as a uniformly deforming entity characterized by an isotropic elastic-plastic behaviour. The Young's modulus E relates the stress to the elastic strain, ε^{el} as $\sigma = E\varepsilon^{el}$, hence $\sigma = E(\varepsilon - \varepsilon^{pl})$. The hardening law describing the variation of the flow stress σ_y of a grain containing *i* twins with the accumulated plastic strain $\overline{\varepsilon}^{pl}$ is described by a power law of the form

$$\sigma_{y,i}^{p} = \underbrace{\left(\sigma_{00} + M\alpha\mu bK^{p}\left(\frac{1}{d_{eff}} + \frac{1}{\lambda_{i}}\right)\right)}_{A_{i}^{p}: initial yield stress} \left(1 + \beta_{i}\overline{\varepsilon}^{pl}\right)^{n_{i}}.$$
(5.3)

The first bracket of equation (5.3) represents the initial yield stress, involving the following parameters:

- the Peierls stress σ_{00} which expresses the lattice resistance against dislocation motion;
- the stress needed to activate a dislocation source: $M \alpha \mu b K^p \left(\frac{1}{d_{eff}}\right)$ where M is the Taylor factor, α is a parameter, μ is the shear modulus, b is the Burgers vector, K^p is a constant depending on the confinement of the grain and, thus, on its position p, and d_{eff} is the effective grain size of the film. This term is directly based on the Taylor's theory [295, 300]. The grains are so small that classical forest hardening is impossible¹. Plastic deformation is carried by dislocations which nucleate at grain boundaries, cross the grain and sink in the opposite grain boundary or interface, or escape from the free surface. The larger the grain boundary area, the larger the probability to nucleate dislocations. The twin density does not influence this term. The non-dimensional K^p parameter is influenced by the presence of the Cr adhesive layer which adds a supplementary barrier to dislocation motion, reflected in an increased K^p . The identification of K^p will be explained later. The $1/d_{eff}$ dependence comes from the fact that the stress needed to activate a source is inversely proportional to the distance between the pinning points which, in nanograins, is imposed by the grain size [298]. This distance is taken as the effective grain size, as in [301]. The effective grain size is calculated by averaging the three dimensions of the grain, i.e.

$$d_{eff} = \frac{H + 2R}{3},\tag{5.4}$$

¹It will be experimentally shown in chapter 6, that this assumption is incorrect here as dislocation storage is observed in the Pd films after deformation.

where H is the height of the grain and R is the in-plane size.

• The influence of twins on the yield stress is taken into account through the term $\left(\frac{1}{\lambda_i}\right)$ where λ_i is the twin spacing. As proposed in [302], the flow stress varies as a function of the inverse of the twin spacing for the same reason as for the grain size. The twin spacing is taken here as the height of the grain divided by the number of twins. Note that no specific behaviour was attributed to the nanotwin domains; only the number of twins was considered here with twins viewed as grain boundaries.

The second bracket of (5.3) is the plastic part of the isotropic phenomenological Swift law where β_i is a parameter depending on the number of twins in the grain and n_i is the strain hardening exponent. The use of an isotropic law is justified here as the specimens are always tested in the same direction under uniaxial tension. The parameter n_i is taken constant and very low for grains containing no twins (i = 0) as no sources of strain hardening are available. The strain hardening capacity of grains involving twins $(i \neq 0)$ is initially high because, when plastic deformation proceeds, twin boundaries become incoherent with the presence of sessile and partial dislocations accumulating along the interfaces and become more impenetrable to dislocations, see e.g. [73,88]. This increasing strength of the interface leads to a high strain hardening exponent. After a few percent of deformation, the interface reaches a fully incoherent state and its strength does not increase anymore. The source of strain hardening becomes then exhausted. This is translated mathematically by assuming that the exponent n_i decreases with plastic deformation: $n_i = n_{init} - \kappa \varepsilon^{pl}$ where n_{init} is the initial strain hardening exponent in twinned grains and κ is a parameter to be identified.

The following strategy is used to estimate and homogenize the overall response of the film during deformation. The film is a two-layer system composed of one Pd film on top of a Cr film undergoing the same strain. The response is computed incrementally by imposing a total strain increment $d\varepsilon$, with the objective to calculate the corresponding total stress increment $d\sigma$. The relationship between $d\varepsilon$ and the strain increment in the columns of Pd grains $d\varepsilon_k$ writes

$$d\varepsilon = \sum_{k=1}^{l^n} f_k d\varepsilon_k.$$
(5.5)

Then, the iso-energy assumption is enforced in order to homogenize the behaviour among different columns. The iso-energy assumption has been shown to provide a realistic intermediate response in a 1D problem compared to the iso-stress and iso-strain bounds [303]. Iso-energy means that

$$\sigma_1 d\varepsilon_1 = \sigma_2 d\varepsilon_2 = \dots = \sigma_{l^m} d\varepsilon_{l^m}, \tag{5.6}$$

where σ_k is the stress in column k. Based on (5.5) and (5.6), the strain in each column can be expressed as

$$d\varepsilon_k = \frac{d\varepsilon}{\sigma_k} \left(\frac{1}{\frac{f_1}{\sigma_1} + \frac{f_2}{\sigma_2} + \dots + \frac{f_{l^m}}{\sigma_{l^m}}} \right).$$
(5.7)

Motivated by the aligned configuration of the grains in each column, iso-strain is assumed for averaging the response within each column, i.e. the strain increment in a grain of type *i* located in a column of type *k*, $d\varepsilon_{ik}$, is equal to $d\varepsilon_k$.

The stress increment in a grain of type i in a column of type k writes as follows:

$$d\sigma_{ik} = E_{Pd} d\varepsilon_{ik}^{el} = E_{Pd} \left(d\varepsilon_k - \gamma_i d\varepsilon_{ik}^{pl} \right), \tag{5.8}$$

where $d\varepsilon_{ik}^{el}$ and $d\varepsilon_{ik}^{pl}$ are the elastic and plastic strain increments in the grain *i* of column *k*, respectively, γ_i is a constant equal to 0 if $\sigma_{ik} < \sigma_{y,ik}$ and equal to 1 otherwise, with $\sigma_{y,ik}$ being the current yield stress of the grain *i* in the column *k*. The Young's modulus is considered here as the films are not highly textured and as the stress is considered uniaxial in each grain. After some elementary algebra implying the use of the hardening law (5.3), the plastic strain increment in the Pd film can be written as

$$d\varepsilon_{ik}^{pl} = \frac{d\sigma_{ik}}{A_i^p n_i \beta_i} \left(\frac{\sigma_{ik}}{A_i^p}\right)^{\frac{1-n_i}{n_i}},\tag{5.9}$$

where A_i^p represents the first bracket of equation (5.3). Combining (5.8) and (5.9) provides a solution for the stress and the plastic strain increment in each grain. The stress increment in each column $d\sigma_k$ is given by

$$d\sigma_k = \sum_{i=0}^{l-1} f_{ik} d\sigma_{ik}, \qquad (5.10)$$

and the total stress increment in the Pd film is given by

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$$d\sigma|_{in\ Pd} = \sum_{k=1}^{l^n} f_k d\sigma_k.$$
(5.11)

When adding the contribution of the Cr layer to the overall mechanical response, equation (5.11) becomes:

$$d\sigma = w_{Pd} \sum_{k=1}^{l^n} f_k d\sigma_k + (1 - w_{Pd}) \, d\sigma_{Cr}, \qquad (5.12)$$

where w_{Pd} is the proportion of Pd in the total thickness of the two-layer system.

The stress increment in the Cr layer is calculated as follows, under the hypothesis that Cr behaves elastically, the thickness being too small to allow any plastic deformation mechanisms [11], and that the Cr layer softens as a result of damage by transverse cracking:

$$d\sigma_{Cr} = E_{Cr} d\varepsilon_{Cr} \left(1 - D\right) = E_{Cr} d\varepsilon \left(1 - D\right), \qquad (5.13)$$

where D represents the damage in the layer and E_{Cr} is the Young's modulus of Cr. D is assumed to evolve linearly with ε such as $D = \zeta \varepsilon$ (ζ is a parameter identified hereafter).

5.4.2 Parameters identification

There exists four different categories of parameters: microstructure parameters determined from TEM observations, material parameters defined by the literature, parameters arbitrarily fixed and parameters identified such as to optimize the agreement between the model and the experimental results. The parameters of the model have been identified in the following way. First, the microstructure parameters coming from TEM observations will be presented, see table 5.3. Two grains are considered over the thickness (m = 2) for each film as the average grain size along the thickness direction is equal to 184 ± 8 nm for the 310 nm-thick film, 100 ± 4 nm for the 160 nm-thick film, and $57 \pm$ 2 nm for the 80 nm-thick film. As a matter of fact, a preliminary parametric study has shown that the predictions are only weakly affected by the choice of m. The number of twins i per grain depends on the film thickness: for the 310 and 160 nm-thick films, grains contain 0, 1 or 2 twins while the 80-nm thick film contains only 0 or 1 twin per grain. The volume fraction of each type of grain f_{ki} is found owing to a statistical analysis of many TEM observations and

Grain aggregate model

Pd film	310 nm-thick	160 nm-thick	80 nm-thick
Number of grains over the	2	2	2
film thickness m			
Number of grain types k	3	3	2
d_{eff} (nm)	78	55	42
λ_0 (nm)	∞	∞	∞
$\lambda_1 \text{ (nm)}$	92	50	28
$\lambda_2 \text{ (nm)}$	61	33	-
Weighting factor w	98.4% Pd, 1.6% Cr	97% Pd, 3% Cr	94% Pd, 6% Cr
f_{k0}	0.74	0.87	0.92
f_{k1}	0.13	0.065	0.08
f_{k2}	0.13	0.065	-

Table 5.3: Parameters used in the model.

is different for each film thickness (see table 5.3 for the numerical values). The effective grain size is computed using equation (5.4) and the TEM-measured grain sizes, giving $d_{eff} = 78$ nm for the 310 nm-thick film, $d_{eff} = 55$ nm for the 160 nm-thick film, and $d_{eff} = 42$ nm for the 80 nm-thick film. The twin spacing λ_i has been calculated by dividing the average grain height, presented in table 4.1, by the number of twins *i* in the grain.

Second, the material parameters found in the literature are exposed. An approximate value of the Peierls stress for Pd is taken from the empirical rule for FCC materials: $\sigma_{00} \approx 2.10^{-4} \mu$, giving $\sigma_{00} \approx 10$ MPa. The Taylor factor M is taken equal to 3 as is it generally considered for non-textured FCC materials (see section 1.2.1 (page 22) for more details about the Taylor factor), $\alpha = 0.8$ (this parameter is generally comprised between 0.5 and 1 [295]), $E_{Pd} = 120$ GPa, $\mu \approx 3/8 E_{Pd} \approx 45$ GPa, and b = 0.27 nm [23]. The value of E_{Pd} was confirmed by nanoindentation tests. Some nanoindentation results will be presented in the next chapter. The Young's modulus of Cr, E_{Cr} , is equal to 275 GPa [201].

Then, the third kind of parameters gathers the fixed parameters. As explained earlier, the strain hardening exponent n_i is taken very small for grains without twins, i.e. $n_0 = 0.03$, while, for twinned grains, it is fixed initially to a high value of 0.5. The strain hardening exponent for twinned grains is supposed to decrease linearly with plastic deformation: $n_i = 0.5 - \kappa \bar{\varepsilon}^{pl}$. This last parameter κ has been chosen by minimizing the error between experiments and numerical results (see further), with the constraint that n becomes equal to n_0 at large strains. As two grains are present over the film thickness, there are only two different K^p because there are only two different positions p, i.e. two different cases of confinement: the upper position where grains have one free surface and one grain boundary parallel to the surface, and the bottom position where grains have no free surface. The constant K^{bottom} should thus be higher than K^{upper} and the proportionality factor is chosen equal to 1.1. This proportionality factor is such that K^{bottom} is 10% higher than K^{upper} to the larger confinement. This factor is motivated from recent study based on a strain gradient plasticity analysis [297].

At the end, four parameters must be adjusted: K^{upper} , β_i , κ and ζ . The first one influences the level of initial yield stress while the three others impact the plastic part of the stress-strain curves. These parameters are supposed to be independent of the film thickness. The 310 nm-thick film is considered to identify these parameters. In order to reproduce the experimental yield stress of 450 MPa of this film, K^{upper} should be equal to 1.05. Then, β_i , κ and ζ have been selected to provide the best fit with the stress strain data, with a specific emphasis on capturing the strain hardening evolution. For a sake of simplicity, β_i is taken constant and independent of the number of twins in the grain. The identification gives $\beta = 1$ GPa, and $\kappa = 8$. The damage parameter D in Cr is chosen equal to 0 when no deformation is applied and linearly increases during deformation such that D = 1 when $\varepsilon = 0.06$, i.e. $\zeta = 16$.

Except for the parameters determined from TEM observations and which depend on the film thickness, all other parameters are kept constant for the different film thicknesses.

5.4.3 Parametric study and discussion

The results of figure 5.5 show that this simple model, based on a physical description of the main microstructure ingredients and mechanisms, i.e. the heterogeneity of the microstructure, the presence of a supplementary interface (the adhesive Cr layer) and the high strain hardening of the twinned grains, is able to reproduce, with a limited number of adjustable parameters, the hardening evolution and the thickness effect. The absence of crystallographic texture and the fact that we are always testing the samples in the same direction and using uniaxial tension justifies the use of isotropic plasticity as a first approximation. The yield stress level of each film thickness is well captured without injecting correction factors. However, the strain hardening capacity of the 80 nm-thick film is underestimated. Other choices for the homogenization and more physical hardening law could obviously improve the predictions. Note also that the experimental error is the largest for the thinnest film. The main ingredient missing in the present model concerns the rate sensitivity which probably plays a significant role if we refer to twinned nanocrystalline Cu [89]. Furthermore, the value of the parameter n_0 not available in the literature and/or not measurable independently, has been fixed quite arbitrarily.

Shishvan and Van der Giessen studied the size dependent yield strength of free-standing Cu thin films by using a discrete dislocation plasticity model with a focus on the importance of the distribution of the dislocation source



Figure 5.5: Comparison between the measured and predicted stress strain curves and strain hardening evolution for the 310, 160 and 80 nm-thick Pd films. The predictions are obtained using a simple empirical grain aggregate model involving the effect of the high strain hardening capacity of the nanotwinned grains and the heterogeneities in the microstructure. The symbols represent the experimental points.

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lengths [304]. Their results about the impact of the grain size/film thickness ratio on the yield stress (plotted in figure 15 in [304]) are in quantitative agreement with the strengths measured in this study when using the parameters for Pd. It provides some confirmation to the hypothesis that the early stages of plasticity is dictated by size depending nucleation of dislocations, through the term $M \alpha \mu b K^p \left(\frac{1}{d_{eff}}\right)$ in equation (5.3).

The origin of the strength increase with the reduction of the film thickness is due here both to differences in the effective grain size among the various film thicknesses, to the presence of twins which add a term in the first bracket of (5.3) and to the presence of the Cr layer. This layer is a barrier which prevents the escape of the dislocations through free surfaces and which is a known origin for the thickness dependence of the yield stress [279]. EFTEM analysis confirms that the Pd surface is not oxidized (the results are presented in section 4.4.2, page 86). Another interesting observation which can be made with the model is the increasing spread of the elastic-plastic transition when decreasing the film thickness: the entire film becomes plastic at a strain equal to 0.01, 0.019 and 0.022 for the 310, 160 and 80 nm-thick film, respectively. This means that thinner films are more heterogeneous than thicker films and that the relative contribution of kinematic hardening on the global strain hardening is increased. It is interesting to note that the experimental evolution of the incremental strain hardening coefficient presents two maxima, see figure 5.2(b). If one makes the hypothesis that the maxima are due to the addition of different hardening mechanisms taking place at different strain levels and that the first maximum is related to the kinematic hardening of the films (due to the elastoplastic transition), the end of the first maximum occurs at higher strain for thinner films. This is in good agreement with the numerically predicted longer elasto-plastic transition of the thinner film.

Now, starting from the identified set of parameters, some of them will be varied one by one in order to test their effect on the mechanical response and provide insights on possible improvements of the properties. Figure 5.6 shows the impact of twins on the global response of the 310 nm-thick Pd film. The quantity of twinned grains is such that there is the same number of grains containing one twin than grains containing two twins. The higher is the twin density, the higher is the strength of the Pd. The curve belonging to the 25% of twins corresponds to the experimental data. Assuming that the grain aggregate model is at least qualitatively correct, the potential strengthening effect of adding more twins is very large as observed already on Cu films [157]. Figure 5.7 presents the impact of the Cr layer on the stress-strain curve for the 310 nm-thick film². The thinner is the film, the more it will be influenced by

 $^{^{2}}$ It will be shown in section 6.5 that this predicted behaviour does not match with the experimentally observed effect of the Cr layer.



Figure 5.6: Numerical prediction of the influence of the twin density on the stress-strain curve of the 310 nm-thick Pd film. The strain hardening increases proportionally with the twin density.

the Cr layer because the Cr layer has a constant thickness equal to 5 nm.

The ductility can be estimated using Considère's criterion. Figure 5.8 presents the evolution of the ultimate strain and ultimate tensile stress when changing the grain size in the realistic range of 40 to 200 nm, and the twin density of the 310 nm-thick Pd film. The qualitative trend of the graph is the same for the two other thicknesses. Figure 5.8(a) shows the impact of the twin density (from 0% to 100% of twins) for different effective grain sizes. When no twins are present, the ultimate strain decreases when the grain size decreases and the ultimate tensile stress increases. When the grain size is sufficiently small (here, $d_{eff} < 60$ nm), adding twins has a positive impact on both the strength and the ductility up to a twin density of about 25% to 50%. If the twin density exceeds the optimum density, the ultimate tensile stress keeps increasing but at the expense of a moderate decrease of the ultimate tensile strain. When the effective grain size is larger than 80 nm, adding twins induces only an increase of the strength similar to a grain size reduction. Figure 5.8(b) shows the same results as figure 5.8(a) in a different way to highlight the effect of grain size when keeping the twin density constant. When no twins are present, the usual effect of a strengthening of the material at the expense of the ductility when reducing the grain size is observed. These results demonstrate the significant potential to harden the Pd films without losing the ductility if an increased volume fraction of twins can be generated with small grain sizes. One way to decrease the grain size d_{eff} is to break the columnar shape through depositing the films step by step in order to favour a more equiaxed shape. Note that no effect of the twin boundary spacing on a change of dislocation mechanism leading to an optimum twin spacing is taken into account in this work, see [57,289]. Finally, it is important to realize that the ductility is predicted here without accounting for possible imperfections and/or rate sensitivity [66] which could definitely



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Figure 5.7: Influence, predicted by the model, of the Cr adhesion layer on the stress-strain curve of the 310 nm-thick Pd film. The strain hardening capacity decreases when the Cr layer is removed. The decrease becomes more important when the film thickness decreases.

affect the predictions, though probably not the trends. The elimination of the extrinsic Cr layer can suppress one important source of imperfection.





Figure 5.8: Evolution of the Considère's criterion with respect to (a) the effective grain size and (b) the twin density. Below a grain size of about 60 nm, there is an optimal twin density regarding the ultimate strain. The twin density in (a) corresponds to the twin density presented in the legend of (b) and inversely for the effective grain size.

5.5 Conclusion

This study primarily aimed at elucidating the origin of the high strain hardening in Pd films. Experimentally, the uniaxial stress-strain response of three Pd films with different thickness (310 nm, 160 nm and 80 nm) has been extracted using internal stress actuated on-chip microtensile testing. A semi-analytical grain aggregate model has been developed, identified and validated. The ingredients explaining the high strain hardening observed in the Pd thin films are:

- 1. the presence of growth twins. The resulting microstructure is heterogeneous with a mixture of soft grains without twins and hard grains containing twins explaining the high initial strain hardening rate with very high levels of backstress,
- 2. the loss of coherency of the twin boundaries during deformation partly explains the evolution of the strain hardening exponent,
- 3. the presence of a Cr layer adds a degree of confinement on the grains next to it, artificially hardens the Pd films and probably decreases the ductility.

Besides the understanding of the high strain hardening capacity origin, the model was able to capture the thickness effect observed experimentally. However, the model underestimates the work hardening capacity of the thinnest films. At this point, it is not possible to determine if this underestimation comes from a change in the deformation mechanisms, from the homogenization procedures of other assumptions used in the model, or from experimental errors made during the measurement of the thinnest film. Additional experiments, based on films deposited under different conditions and possible heat treatments, have been performed in order to separate the grain size effect, the twin density effect and the confinement effect. Those results, presented in chapter 6, have been obtained much later and sometimes overturn hypotheses made in this chapter. Due to a lack of time, they have not been embedded into an improved model.

However, several improvements can be envisaged for the model:

- to include the grain size distribution. Indeed, it is expected from the literature that the narrower is the grain size distribution, the larger is the strength and strain hardening rate [150, 177];
- to take into account the TB thickness and spacing. The motivation for this improvement is similar to the one for the grain size distribution;
- to include a forest hardening term in the constitutive law. It will be shown in section 6.3 that dislocation storage occurs in Pd thin films and that hardening by dislocation interactions cannot be excluded;
- to use a visco-plastic law. In the results presented later in chapter 7, it is clear that nanocrystalline Pd is rate dependent and that visco-plastic effects are non-negligible;
- to include an imperfection analysis to take into account material and geometrical imperfections;
- to include an unloading step to investigate the possible presence of a Bauschinger effect. Indeed, the experimental results suggest that one could expect a Bauschinger effect, and a numerical validation of this effect could be interesting.
Chapter 6

Strength, strain hardening and ductility - Additional results

This chapter will enrich the results presented in the previous chapter. More tests and more experimental situations have been explored to reevaluate some assumptions and make clear some parameters of the model described in chapter 5.

First, the complete analysis of the thickness effect on the mechanical properties will be presented. This section will show all the mechanical curves generated during this thesis and obtained directly after the release step, thus before significant relaxation took place. Then, an extended analysis of the elasto-plastic transition by X-ray synchrotron diffraction, and of the deformation mechanisms observed using post-mortem TEM characterization will be presented. Also, the effect of the twin density will be studied using both the on-chip microtensile technique and nanoindentation. The results obtained from these two techniques will then be compared. After, attention will be paid to the effect of the adhesion layer. And, finally, the effect of grain size and the possible presence of a Bauschinger effect will be briefly discussed.

6.1 Thickness effect - All results

An important data set was produced during the thesis, involving different film thicknesses and deposition conditions. This section will focus on the thickness effect observed on films deposited on different adhesion layer (Ti or Cr), with different deposition rates (1 and 10 Å/s) and with different ageing times. The



Figure 6.1: Stress-strain curves of the complete data set involving films with different thicknesses, evaporation conditions, adhesion layers and ageing.

ageing time represents the waiting period between the film deposition and the film release. As the films contain a considerable amount of tensile internal stresses, relaxation of the as-deposited film could be expected. This could modify the initial microstructure of the films like, for instance, the dislocation density. The ageing effect will be addressed in more details in section 7.2.5 in the next chapter.

Figure 6.1 shows the stress-strain curves corresponding to the different films, while figure 6.2 presents the stress at 0.5% of strain as a function of the thickness of the films. These figures show a clear thickness effect. The effect of the twin density and of the adhesion layer will be discussed separately later in section 6.4 and 6.5. When Ti is used as the adhesion layer, a smaller thickness effect is observed. As it will be explained later (see section 6.5 page 145), the Ti is etched during the release of the microtensile stages, leaving a pure Pd film without any constrained surface, on the contrary to Cr. Unfortunately, it is impossible to dissociate (without using some advanced models) the effect of Cr on the stress-strain curves of the Pd films when Cr is used as the adhesion layer. It can thus be concluded that the presence of the Cr layer enhances the thickness effect, see figure 6.2. This increased strengthening effect when some free surfaces of the film are constrained, has already been observed in the literature on copper films [21], see figure 6.3.

The importance of the time between film deposition and release of the film is also illustrated in figure 6.2. In can be stated that when the film is released



Figure 6.2: Representation of the stress at 0.5% of strain as a function of the reciprocal of the thickness of the films. These results are extracted from the curves presented in figure 6.1.

a long time after deposition, the density of internal defects has decreased due to recovery under the influence of the internal stress. Note that the ageing effect seems to be extremely non-linear. Further discussion about relaxation and ageing of the samples will be presented in section 7.2.5.

Finally, the deposition rate does not seem to significantly affect the thickness effect. As said before, the deposition rate influences the twin density in the films. This will be discussed in section 6.4 hereafter.

The thickness effect has already been discussed in chapter 5. What is interesting here, is to confirm a systematic thickness effect despite the experimental errors made during the mechanical extraction of the stress and strain values.



Figure 6.3: Figure taken from [21] showing the effect of passivation on the yield stress. Note that the thickness of the films and the grain size are higher than for the Pd films tested here.

6.2 Synchrotron experiments - Evidence of the long elasto-plastic transition

A collaboration with the Paul Scherrer Institute in Switzerland and the group of Prof. Helena Van Swygenhoven has led to characterize deformed Pd films under tension by X-ray diffraction under a synchrotron monochromatic beam. As exposed before in chapter 5, there are clear but indirect experimental insights that the Pd films present a long elasto-plastic transition based on the high initial strain hardening rate as well as the modelling results. However, our experimental methods do not provide direct confirmation of the spread of the elasto-plastic regime. Therefore, X-ray diffraction was used to study the internal stress state of various Pd beams deformed at different levels of strain.

The microtensile stages fabrication has involved a back-etching step in order to create windows in the substrate under the Pd beams, see figure 3.3(b). The Pd film was 150 nm-thick and was deposited on Ti which has been etched away during the release process. The microtensile testing stages were released prior to the X-ray diffraction measurements. The strain level inside the Pd beams was ranging between 0.3% and 2.5%. The stress level has also been measured but the experimental error was high. Consequently, the microtensile stages series measured here present a much higher stress level than others coming from the same wafer. For this reason, the stress values will not be presented here, but one can expect a stress evolution close to what is shown in figure 6.1 for a 150 nm-thick film. Indeed, other series of stages coming from the same wafer were overlapping with the stress-strain curves of the 200 nm thick Pd film



Figure 6.4: Schematic view of the correlation between the deformation state of the sample and the diffraction results.

deposited on Ti. This discrepancy between different sets of structures extracted from the same wafer probably comes from spatial inhomogeneities during the back-etching step. Owing to the opened windows in the substrate, diffraction patterns were recorded in transmission. The X-ray beam had an energy of 14.93 keV and a size of about $2x1 \mu m$. Note that the width of the Pd beams was about 2 μm . At each beam, a CCD map with about 20 images was recorded. All the images were added together in order to obtain enough statistics. The patterns contained the (111), (200) and (220) rings. The intensity of the latter was too low and thus not included in the results.

Figure 6.4 schematically represents the effect of deformation on the diffraction results. Peak shift is mainly induced by the elastic part of the deformation. Note that plastic deformation may also lead to slight peak shift because of plastic anisotropy. The peak broadening is mostly caused by plastic deformation but elastic anisotropy can also contribute to this broadening.

The strain state of the samples has been measured using the microtensile stages. These values have been used to plot the diffraction results, see figure 6.5. Conventional one-dimensional diffraction spectra were obtained by azimutal integration of 5 degrees segments along the axial direction. The diffraction peaks are subsequently fitted by a Pearson VII function, yielding values for lattice strain, peak broadening and peak intensity for each Pd beam. More details about the analysis procedure of the diffraction results can be found in [305].

Figure 6.5(a) presents the evolution of the lattice strain as a function of the strain inside the Pd beams. The lattice strain for a given crystallographic direction hkl has been calculated as: $\varepsilon_{hkl} = -\cot(\theta_{hkl})\Delta\theta_{hkl}$ with θ_{hkl} and $\Delta\theta_{hkl}$ being respectively the peak position and the peak shift for the hkl diffraction peak. From figure 6.5(a), it can be concluded that the (200) oriented grains are more elastically deformed on average than the (111) oriented grains. It should be mentioned that the elastic anisotropy of Pd contributes to this effect as the (100) direction is a lot softer compared to the (111) direction, see section 4.1. This leads to strain gradients inside the film. Also, over the full range of



Figure 6.5: (a) Evolution of the lattice strain as a function of the average strain in the Pd beam; (b) Evolution of the full width at half maximum (FWHM) as a function of the strain inside the Pd beams. The strain state of the beams was measured by the microtensile testing technique.

the considered deformations here, the elasto-plastic regime is present. Even at 2.5% of strain, the totality of the grains is not plastically deforming. Indeed, if all grains were in a plastic regime, the lattice strain should have been almost constant (see figure 6.4)¹. But at the same time, almost none of the analysed Pd beams is deforming purely elastically, see figure 6.5(b) where a non-constant FWHM (full width at half maximum) evolution is found. Caution should be used when interpreting the FWHM evolution for strains below 1% due to the scatter on the data. As a matter of fact, one could claim that there are two regimes here: nearly constant FWHM below 1.2% and a clear increase above. This also agrees with the deviation from linearity of the lattice strain above $\sim 1.7\%$. The (111) peak does not exhibit such a deviation here but this behaviour is expected [306]. Note that the (111) FWHMs are smaller than the (200) data. This is expected because peak broadening from inhomogeneous strain is dependent on diffraction order [78].

It can be concluded that the synchrotron X-ray diffraction technique is a useful tool to analyse the deformation regime of the deformed Pd beams. Moreover, it confirms the expected presence of a long elasto-plastic transition of Pd under deformation.

 $^{^{1}}$ Of course, in a material presenting significant strain hardening, the elastic strain will increase even if the material is deforming plastically. However, the related increase of lattice strain will be much smaller than when the material is deforming elastically.

6.3 Deformation mechanisms

The Pd films studied during this thesis revealed a surprisingly large strain hardening capacity when considering the small ~ 25 nm grain size. This section will present the advanced TEM investigation performed to understand the plasticity mechanisms at the nanoscale. The results presented here have been published in [255] and are summarized in this section.

First, the grain size distribution and the texture have been characterized on cross-section and plan-view TEM samples prepared from 310 nm thick Pd beams either as-deposited or after 4% of deformation. The samples were cut by FIB within the homogeneous deformation region, i.e. away from the cracking region. Conventional BF and DF TEM and ACOMTEM were used to provide statistical measurements of the in-plane grain size and of the aspect ratio of the grains (grain height/in plane grain size). The related images are not shown here but can be found in [255]. Using BF and DF micrographs, the grain size distribution in the as-deposited film yields an average grain diameter of 25.6 ± 7.3 nm with an aspect ratio equal to ~7 . After deformation, the average grain diameter was measured as 22.0 ± 5.7 nm, with an aspect ratio around 6-8, meaning no change within the limits of precision of the measurements. In both cases, around 200 grains were included in the analysis. ACOMTEM was performed on plan-view FIB thinned samples coming from the same Pd film. The grain size distribution extracted by ACOMTEM is relatively narrow with an average grain size of 25.4 ± 1.1 nm in the as-deposited beams and 26.1 ± 1.2 nm in the 4% deformed beams, in very good agreement with the results extracted by conventional TEM observations, i.e. no grain growth during deformation. The investigation of the crystallographic texture before and after deformation reveals a low (101) fiber texture normal to the film surface. All these observations indicate that the deformation of the Pd films does not affect the grain size distribution as well as the crystallographic texture. Grain growth, grain boundary sliding and/or grain rotation can thus be excluded as possible mechanisms dominating the plastic deformation in the Pd films under investigation.

Second, the growth twins were characterized before and after deformation. As said before in chapter 5, most twins are not parallel to the surface of the film and their orientation changes randomly from one grain to another, confirming the absence of clear crystallographic texture. Also, the twins are initially perfectly coherent and are loosing coherency upon deformation. Careful analysis of BF and DF images does not reveal any significant change in the twin density after deformation, i.e. about 20% to 30% of the grains are estimated to contain 1 or 2 TBs before and after deformation. It can thus be postulated that no deformation twin appears during the loading of the Pd beams.



Figure 6.6: HRTEM images obtained in (a) as-deposited and (b,c) 4% deformed 310 nm thick Pd beams. Image (c) shows the loss of coherency of single TB. Note the strong inhomogeneous local strain fields in the lower grain in (b) due to the activation of slip systems under the applied stress in the deformed sample.

Third, the dislocation activity was evaluated by HRTEM before and after deformation. As the observations were made on FIB thinned samples, attention was paid to the distinction between lattice dislocations originating from the plastic deformation and possible point defect clusters induced by FIB such as Frank interstitial and/or vacancies loop [307].

Figure 6.6(a) taken from the as-deposited film presents a grain containing only one dislocation and some perfectly coherent TBs. After 4% of deformation, distortions associated to high inhomogeneous strain fields appear on the HR-TEM images, indicating the presence of several dislocations, see figure 6.6(b). This dislocation activity is responsible for the loss of coherency of the TBs. As coherent TBs are more thermally and mechanically stable compared to GBs, shearing along coherent TBs is extremely difficult. Interactions of gliding dislocations in the crystal lattice with the TBs must thus be invoked to explain the loss of coherency of the TBs. Other HRTEM analyses of Pd beams before and after the release step show similar results, confirming that the Pd films deform by the activation of slip systems inside the grains.

A careful investigation of individual dislocations lying at the twin/matrix interfaces has been carried out using HRTEM extending the analysis described in [8]. For this purpose Pd films subjected to moderate strain were selected, in order to avoid the large distortion of the atomic structure of the TB observed



Figure 6.7: *HRTEM image of a single TB in a Pd beam deformed at* 0.8%; 8 SPDs and only one Frank dislocation (FD) can be observed at the twin/matrix interface.

at large strains (see figure 6.6(c)). Figure 6.7 is a HRTEM micrograph of a single TB in a Pd beam subjected to 0.8% deformation. In this image, distinct atomic steps can be observed along the TB. These steps are due to the presence of several Shockley partial dislocations (SPDs) dragging large stacking faults in the twinning plane. The locations of the extra half planes related to these SPDs are indicated in figure 6.7. This figure also reveals strong local residual contrast related to one sessile dislocation located at the TB. The sessile dislocations have been identified as Frank dislocations (FD) (see [255] for more details). The two opposite GBs limiting the single TB are labelled *GB1* and *GB2*, and indicated by dashed lines in figure 6.7. Furthermore, eight SPDs can be identified along the TB, whereas only one Frank sessile dislocation is detected. Additional HRTEM observations confirmed that the number of SPDs in the twinning planes of moderately deformed grains is always larger than the number of Frank sessile dislocations.

As presented in chapter 1, GB-related mechanisms were first reported in the literature as the deformation mechanism of nanocrystalline systems. In the present case, GB migration can be excluded since no change of the grain size distribution was observed by conventional BF/DF measurements nor by using the more advanced ACOM-TEM technique on the deformed Pd samples. Moreover, in the work of Bachurin and Gumbsch [285], MD simulations revealed that GB migration is not predicted in nanocrystalline Pd subjected to tensile deformation even for smaller grain sizes (~10 nm). Also, GB sliding and/or grain rotation have been excluded as the ACOMTEM results show that the slight $\langle 101 \rangle$ texture present in the as-deposited Pd films remains nearly constant after deformation at 4% of total strain. Indeed, GB sliding and grain rotation generally leads to a randomization of the existing texture [308] which is not observed here. This means that at the resolution limit of the characterization methods used, no GBs mediated processes take place during the deformation



Figure 6.8: Schematic illustration of the two mechanisms expected to control the lattice dislocation/coherent TB interactions in nanocrystalline Pd films with coherent growth twins; (A) dissociation of the incident dislocation into a Frank sessile and a Shockley twinning partial dislocation; (B) slip transfer of the incident dislocation across the coherent TB, with the emission of a new SPD in the twinning plane.

of the present Pd films.

The average grain size observed in the present work (~ 25 nm) appears to be larger than the critical size usually required for the activation of dislocations through intra-grain sources. The plastic deformation of the films is thus controlled by the nucleation of dislocations at GBs and the glide of these dislocations, and their interactions with GBs and coherent TBs.

Two mechanisms have been proposed to explain the dislocation/coherent TB interactions in the nanocrystalline Pd films, see figure 6.8. The first scenario is labelled A on this figure. When a perfect dislocation in the matrix plane $(1\bar{1}\bar{1})$ with a Burgers vector b = a/2 [101] meets the $(1\bar{1}1)$ twinning plane, it can dissociate into a b = a/3 [111] Frank sessile dislocation and a new b = a/6 [121] SPD in the $(1\bar{1}1)$ twinning plane:

$$\frac{a}{2} [101]_{(1\bar{1}\bar{1}\bar{1})} \to \frac{a}{3} [1\bar{1}1]_{sessile} + \frac{a}{6} [121]_{(1\bar{1}1)}.$$
(6.1)

This dislocation/TB reaction has been proposed in the literature [161,309]. Ho-

wever, this dissociation reaction cannot explain the excess of SPDs compared to Frank sessile dislocations, as observed in the present work (figure 6.7). Indeed, from this reaction, for one incident extended dislocation, one Frank dislocation will be produced at the TB, with the emission of one SPD in the twinning plane. In this case, identical numbers of Shockley twinning dislocations and Frank dislocations should be found along a TB. Another dislocation/TB interaction mechanism involving the formation of new SPDs in the twinning plane but without any residual defect at the twin/matrix interface should thus be invoked in order to explain the excess of SPDs compared to Frank dislocations.

The second scenario, labelled B in figure 6.8, involves the complete transfer of an incoming extended dislocation across the TB, as proposed by [161]:

$$\frac{a}{2} [101]_{matrix} \to \frac{a}{2} [101]_{twin} + \frac{a}{6} [121]_{twinning \ plane} \,. \tag{6.2}$$

Two SPDs form a new extended dislocation gliding in the slip plane of the twin grain and a third one twinning partial which is left in the twinning plane. It thus explains the excess of SPDs compared to Frank dislocations observed. A similar combination of two mechanisms were already exposed in [74]. They reported the creation of FD at TB first, and at higher deformation, due to the TB bending and their coherency loss, TBs became dislocation sources.

To conclude, coherent TBs offer multiple barriers to dislocation motion as well as sources for dislocation storage and multiplication, via two major types of lattice dislocation/TB interactions: the creation of sessile Frank dislocations and the transmission of the lattice dislocations. All these mechanisms involve SPDs left along the twin boundary. The TBs progressively become incoherent and thus more resistant to dislocation penetration. These mechanisms provide a partial explanation for the elevated strain hardening capacity. Finally, forest hardening is also observed. Grains initially contain very few dislocations (see figure 4.8 page 91). As explained in more details later in section 7.1, the dislocation density increases also in grains without twins. The presence of dislocations prior to deformation offers pinning points to store more dislocations, leading to forest hardening.

6.4 Twin density effect

The best way to vary the twin density in the Pd films was to play on the deposition rate during the Pd evaporation. The effect of the deposition rate on the microstructure of as-deposited Pd films has been presented in section 4.4.4. The section is organized as follows. The overall results will be presented and

Chapter 6. Strength, strain hardening and ductility - Additional results

Deposition rate	1 Å/s	10 Å/s
σ_0 (MPa)		
0.2% offset strain criterion	450 ± 39	350 ± 30
Tangent modulus approach	500 ± 43	460 ± 38
σ_{int} estimated in Pd (MPa)	375 ± 20	470 ± 30
ε^f maximum (/)	0.04	0.07
Θ_0 (GPa)	~ 60	~ 90
Young's modulus (GPa)	112 ± 12	115 ± 12
Hardness (GPa)	5.06 ± 1.07	4.24 ± 0.77

Table 6.1: Summary of the properties obtained using on-chip microtensile testing on Pd films deposited at different rates. The hardness value is the averaged hardness measured between 25 and 50 nm of indentation depth.

then they will be discussed. The discussion will be divided into two subsections dealing first with the impact of the twin density on the yield stress, and second with its impact on the ductility and on the strain hardening. The properties of the films have been investigated using the microtensile on-chip testing method and nanoindentation to compare the obtained results.

Concerning the microtensile results, the 310 nm-thick Pd film deposited at 1 Å/s presented in section 5.3 will be compared to a 480 nm-thick Pd film deposited at 10 Å/s. Both films have been deposited on a thin Cr adhesion layer. Ideally the thickness of these two films should have been similar but the evaporation chamber was calibrated to deposit films at 1 Å/s, making the thickness control difficult at a different deposition rate. Of course a slight thickness effect should be expected on the results. However, this thickness effect is getting larger for films thinner than 300 nm, see figure 6.2. The experimental stress-strain curves in this section involve the smoothing procedure (see section 5.3.2) and are presented in figure 6.9. The information given by this figure is listed in table 6.1.

Nanoindentation tests have been performed on the three films deposited at 0.3, 1 and 5 Å/s presented in section 4.4.4, and from the film deposited at 10 Å/s tested here by the microtensile method. The nanoindentation results are presented in figure 6.10 while the values of the Young's modulus and of the hardness are listed in table 6.1 for the two films tested by the microtensile method and the nanoindentation. The indentation depth range considered was 25 to 50 nm². This is compatible with the thickness of the films (~250 nm for the 0.3, 1 and 5 Å/s films, and ~480 nm for the 10 Å/s film) [200]. The same results have been plotted as a function of the twin density in figure 6.11. As no TEM study was made on the film deposited at 10 Å/s, its TB density is

 $^{^{2}}$ This low indendation depth range can be questionable due to the possible important role of the indenter tip defects on the results at this depth scale. However, when considering deeper ranges, the same results are obtained qualitatively. One has to keep in mind that nanoindentation was only used in this work as a qualitative tool to improve the understanding of the results obtained using microtensile testing stages.



Figure 6.9: Mechanical behaviour of two different Pd films deposited on a Cr adhesion layer, with a thickness of 310 and 480 nm for the films deposited at 1 Å/s and 10 Å/s respectively. (a) Stress-strain curves. (b) Evolution of the incremental strain hardening exponent involving the Considère's criterion. (c) Evolution of the strain hardening rate.



Figure 6.10: Effect of the deposition rate, or equivalently, of the twin density on the Young's Modulus and the hardness, measured by nanoindentation. The indentation strain rate used was of 0.8 /sec.



Figure 6.11: (a) Evolution of the twin density as a function of the deposition rate. The red point has been extrapolated as no TEM study has explored the linked twin boundary density. (b) Presentation of the hardness as a function of the TB density.

unknown but can be extrapolated from figure 6.11(a) as equal to $13 \times 10^{21} \text{ m}^{-3}$.

6.4.1 Yield stress

A parallel between the yield stress σ_y found in tension and the hardness H found by nanoindentation can be made. The Tabor's law predicts that $\sigma_y \approx H/3$ for a material incapable of appreciable strain hardening [310]. Note that the proportionality factor has been found to vary with temperature and is lower than 3 at high temperature [311]. A reduced yield stress should thus correspond to a decrease of hardness. It is worth mentioning that here the Tabor's law is respected but that the proportionality coefficient is equal to ~12, which is much

higher than 3, like in the original law. However, the proportionality coefficient is strongly influenced by the indenter shape when the material is deforming in the elasto-plastic regime [100].

The yield stress of the film deposited at 10 Å/s is smaller than the yield stress of the film deposited at 1 Å/s, see table 6.1. As said before, it can be explained by the thickness difference between these two films. However, the hardness, which should not be influenced by the thickness effect³, also shows a decrease with the deposition rate. Even if a slight GB character evolution and a crystallographic texture change are observed when increasing the deposition rate, it can be concluded that an increased twin boundary density leads to a decrease of the yield stress and of the hardness.

The explanation of this decrease of the yield stress or equivalently of the hardness with the twin density is not obvious as several experimental papers in the literature reported the opposite, see e.g. [71, 73, 74, 81] and figure 1.15 (page 37). However, one should note that all these experimental studies focused on nanotwinned copper containing twins in all grains, with a grain size about hundred of nanometres. They all recognized twins as effective in strengthening, except under a very reduced twin spacing [157].

The microstructure of the Pd films tested in this work is not exactly comparable. Here, twins are not present in all grains and are randomly oriented. Also, as said in section 4.4.4, the $\langle 101 \rangle$ texture component of the films decreases when the deposition rate increases, leading to an increased twin density and a more heterogeneous microstructure. An heterogeneous microstructure is known to induce a long elasto-plastic transition, see chapter 5. If one considers that the film deposited at 10 Å/s presents a more pronounced elasto-plastic transition, this can explain why its observed yield stress is lower than for the film deposited at 1 Å/s. Indeed, the establishment of a proper definition of the yield stress quantity is not a simple question in heterogeneous materials. In [49], a similar observed decrease in the apparent yield stress is observed for an heterogeneous nc Al film as compared to an homogeneous nc Al film with the same grain size, see figure 6.12.

Moreover, the increased internal stress of the film deposited at 10 Å/s can promote early plasticity in the well oriented grains. Note that the internal stress of the film deposited at 10 Å/s is higher than the yield stress whatever the extraction method used. That can be explained with two different arguments. First, it can be due to experimental errors. Second, that can be explained by the higher heterogeneity which induces a long elasto-plastic transition. This

 $^{^{3}}$ In this work, the thicknesses of the films deposited at 1 Å/s and 10 Å/s were respectively equal to 250 and 480 nm. Considering the indentation depth range used, no substrate effect is expected. Hence, no thickness effect should be considered.



Figure 6.12: Effect of the heterogeneity on the yield stress of nc Al thin films. (a) Heterogeneous films, (b) homogeneous film. Figure taken from [49].

long transition can lead to measure a yield stress that does probably not correspond exactly to the level of stress at which the whole film behaves plastically. This second argument comes back to the difficulty to define the yield stress of materials presenting a long elasto-plastic transition.

6.4.2 Strain hardening and ductility

The strain hardening is also affected by the twin density. Figure 6.9 shows that a higher twin density leads to an improved strain hardening capacity in the early stages of plastic deformation. At large plastic deformations, the incremental strain hardening evolution of the two curves is similar even if the curve of the film deposited at 10 Å/s approaches closer the Considère's line. This is in good agreement with the increased ductility observed for the film deposited at the higher rate. However, to be statistically reliable, more than two data sets are required. Thus, only suggestions can be made to explain that trend, keeping in mind that this effect is not statistically confirmed.

Two suggestions can be put forward to interpret the increased ductility of the film deposited at 10 Å/s. The first explanation is related to the thickness difference of the two studied films. The higher thickness of the film deposited at 10 Å/s reduces the effect of imperfections on the ductility as compared to the film deposited at 1 Å/s. In [67], an imperfection analysis reveals that the thinnest is the film, the lower is its ductility due to an increased sensitivity to imperfections.

The second explanation is linked to the increased twin density. As exposed many times in the literature, the twin density positively affects the ductility while maintaining a high strength and a high strain hardening rate [73, 81, 157]. As a matter of fact, on the contrary to high angle boundaries like grain boundaries, twins possess a large capacity for dislocation storage. This allows

keeping a sufficiently high strain hardening capacity, hence a good ductility in terms of resistance to plastic localization [74]. As exposed in section 6.3, twins in the present Pd films can be viewed as a source and as a barrier for dislocations. When more twins are available, a higher number of dislocations can be nucleated. At the same time, the higher twin density provides a higher density of obstacles for dislocation motion and storage. These two ingredients can explain the difference between the curves presented in figure 6.9.

The initial strain hardening rate Θ_0 is also larger when the deposition rate is increased. As said before, the level of the initial strain hardening rate is an indication of the heterogeneity of the film microstructure. It is thus not surprising to observe a larger Θ_0 when the deposition rate increases as both the twin density and the dislocation density increase, leading to a high level of internal local stress inside the film. The higher heterogeneity in the film deposited at 10 Å/s observed through the the higher Θ_0 confirms the explanation given in the previous section about the effect of the twin density on the yield stress.

The last interesting point to consider is the evolution of the incremental strain hardening, see figure 6.9(b). For both curves, two maxima are observed. The first maximum, at the smaller plastic strain can be linked to the elasto-plastic transition of the films. As the film deposited at 10 Å/s is more heterogeneous, it can be expected to have a higher first maximum for this curve. When all grains behave plastically, this kinematic contribution to the strain hardening is progressively disappearing. Concerning the second maximum, one can view it as a sign of the progressive coherency lost of the twin boundaries. Twin boundaries constitute initially strong obstacles against the dislocation motion. After they interact with incoming dislocations, this blocking effect progressively loses its efficiency. Note that even if the TBs are initially less coherent when the deposition rate increases, it does not seem to degrade the strain hardening behaviour of Pd, as observed when comparing the incremental strain hardening of the two films here.

6.5 Adhesion layer effect

The adhesion layer effect has been studied in two different ways, see figure 6.13. First, the effect of the presence of an adhesion layer has been studied by changing the nature of this layer. And second, the effect of etching the adhesion layer before the release of the Pd samples has been investigated. These two options will be consecutively presented in the next two sections.



Figure 6.13: Schematic view of the two routes used to study the effect of the adhesion layer. The first option is to change the nature of the adhesion layer, (a) vs. (a'). The second one is to remove the Cr adhesion layer, (a) to (d).

6.5.1 Cr versus Ti adhesion layer

The two materials known to improve adhesion are titanium and chromium. The advantage of Cr is that it is resistant to hydrofluoric acid (HF) and thus totally compatible with the fabrication process of microtensile testing structures presented in section 3.3 (page 67). However, the related drawback is that Cr remains attached under the Pd beams during the tensile test and can thus affect the mechanical properties by acting like a so-called *passivation layer* confining one free surface of the film [21, 279].

Concerning the Ti adhesion layer, the main difficulty is its fast etching rate in HF. The thickness control of this layer is thus crucial. The only way to get rid of its weak HF resistance is to deposit a discontinuous layer of Ti. Doing that, the Pd deposited on top the Ti adhesion layer will protect and isolate the Ti island from the HF solution, see figure 6.13(a'). Beside this process constraint, the main advantage of using a discontinuous Ti adhesion layer is that the Ti lying under the Pd samples is etched during the release step. This ensure to analyse the properties of a pure Pd film without confining layers. The discontinuous Ti adhesion layer is however not as efficient as the Cr adhesion layer. Ti can not be used as an adhesion layer for films thicker than ~250 nm. Above that limit, the adhesion is not sufficient to perform a tensile test. Note that X-ray diffraction was performed to investigate the presence of intermetallics due to possible interactions between the Pd films and the adhesion layers (Ti or Cr) but no Pd-based compounds were found.

Pd films deposited at 1 Å/s on Cr and on Ti will be compared here. Due to the different nature of the adhesion layers, the films do not come from the same deposition batch. Indeed, in the deposition chamber used in this work, all the wafers from the same batch have to undergo exactly the same deposition stack, no wafer hiding is possible during the evaporation. This has lead us to develop an alternative to study the adhesion layer effect of films coming from the same



Figure 6.14: Mechanical behaviour of two Pd films deposited on different adhesion layers (Cr and Ti), with a thickness of 160 and 200 nm respectively. The two films have been deposited at 1 Å/s. (a) Stress-strain curves. (b) Evolution of the incremental strain hardening exponent involving the Considère's criterion. (c) Evolution of the strain hardening rate.

batch, as presented in the next section.

The smoothed mechanical curves are shown in figure 6.14. The resulting properties are listed in table 6.2. To compare films with a similar thickness, the film deposited on Cr addressed here is the 160 nm-thick already presented in section 5.3. The film deposited on Ti is 200 nm-thick.

It is interesting to mention that the yield stress is not significantly affected by the presence of a Cr layer at this thickness range. Different studies have observed a strengthening due to the presence of a passivation layer, either experimentally [21,210] or numerically [312]. Their mechanical explanation is that dislocation nucleation and glide are hindered by lattice distortions induced by the confining of the film [313]. This prevents the escape of the dislocations and creates dislocation pile-ups at the film interfaces.

Chapter 6. Strength, strain hardening and ductility - Additional results

Adhesion layer	Cr	Ti
σ_0 (MPa)		
0.2% offset strain criterion	690 ± 86	690 ± 65
Tangent modulus approach	690 ± 86	740 ± 71
σ_{int} estimated in Pd (MPa)	655 ± 30	500 ± 35
ε^f maximum (/)	0.052	> 0.1
$\Theta_0 (\text{GPa})$	~ 60	~ 100

Table 6.2: Summary of the properties extracted using on-chip microtensile testing on Pd films deposited on Cr and Ti.



Figure 6.15: Schematic view of the different surface contact between the grains and the passivation layer as a function of the grain shape and size.

However, Prokok and Espinosa demonstrated the opposite trend using a membrane deflection experiment [313]. This uniaxial tensile testing technique has been presented in section 2.3. They found a lower yield stress and a lower fracture strain when a passivation layer is present. Moreover, the reduction of yield stress is accentuated when the width of the membrane is increased from 2 µm to 20 µm. As the width of the sample used in this thesis was equal to 1 or 2 µm, the fact that there is no clear effect here of the passivation layer on the yield stress is in agreement with the observations of [313].

This contradiction between different studies can be related to the different loading configurations. In [21, 210], the bulge test technique was used while uniaxial tension was used in [313] and in this thesis. The divergence between the results using different loading configurations has been addressed in [313]: uniaxial tension leads to a limited confinement and a larger volume of deformed material as compared to the bulge test.

This contradiction can also be understood when comparing the grain size and shape. In all cited studies, the grains were bigger than here, their aspect ratio was smaller and the grain size distribution was larger. All these differences lead to a larger contact surface between the bottom (and/or) top of the grains and the passivation layer, see figure 6.15. The confining effect created by the passivation layer is reduced when the grains are more columnar: a smaller portion of the grain will interact with this layer.

The effect of a passivation layer on the hardening evolution has also been characterized, see figure 6.14 (b) and (c). Figure 6.14(b) shows that the Considère's criterion is fulfilled only for a pure Pd film without any confining layer. The fracture strain increases by a factor two when this layer is absent. The

presumably high tensile internal stress of the Cr layer can induce a premature fracture of the films due to the mismatch between its behaviour and the mechanical behaviour of the Pd. This argument has also been advanced in [313] to explain the reduced fracture strain when the film is passivated. This is a major observation as the motivation of this work is to understand which microstructural features can improve the ductility while keeping the very good strength of nanocrystalline thin films. Any process drawback is thus important to highlight.

The strain hardening capacity is lower when one side of the Pd film is covered by Cr, see figure 6.14(b). This is still in agreement with the results presented in [313] and with the lower ductility observed when the Cr layer is confining the Pd film. Also, the initial strain hardening rate is lower for the film deposited on Cr.

The incremental strain hardening evolution of the two films presents two maxima, as observed in the previous section. As for the films discussed in the previous section, the first maximum can be explained by the long elasto-plastic transition. Indeed, the film without any passivation layer shows a higher Θ_0 , which is a sign of a higher heterogeneity, leading to an increased apparent strain hardening. The second maximum is probably due to the presence of twins, as explained before.

The last observation is the increase of the internal stress when a passivation layer is confining the film, which was also observed in [313].

6.5.2 Selective etching of the Cr layer

The drawback of the option presented above is the impossibility to analyse the effect of a passivation layer on films coming from the same batch with exactly the same deposition conditions. The approach proposed here to circumvent this limitation is to release the sample selectively and by successive steps, see figure 6.13 (a) to (d). The first etching uses HF to only release the sample part of the microtensile structures, figure 6.13 (b). Then a selective Cr etchant (Cr etchant 1020AC from Transene Company, during 30 seconds at room temperature) is used to remove the Cr layer under the Pd beams, figure 6.13 (c). Finally, a second HF release is performed to fully release the microtensile stages, figure 6.13 (d). As the Cr etchant and the HF are in a liquid state, a super-critical drying is required after each etching step. This three-steps release is thus time consuming but allows the comparison of the same film with and without the Cr confining layer.

Two deposition batches of Pd films have been produced: a 400 nm-thick Pd



Figure 6.16: Schematic view of the two batches used to investigate the effect of a selective etching of the Cr passivation layer.

	Pd/Cr (K6)	Pd (K6)	Cr/Pd/Cr (K5)	Pd (K5)
σ_0 (MPa)				
0.2% offset strain criterion	400 ± 32	450 ± 44	400 ± 37	410 ± 38
Tangent modulus approach	474 ± 37	600 ± 58	500 ± 45	580 ± 54
σ_{int} estimated in Pd (MPa)	420 ± 30	420 ± 30	420 ± 30	420 ± 30
ε^f maximum (/)	0.032	0.027	>0.054	0.04
Θ_0 (GPa)	~ 60	~ 100	~ 60	~ 60

Table 6.3: Summary of the properties extracted using on-chip microtensile testing on the four different pieces of wafer deposited on Cr or covered on the two sides by Cr, with and without the Cr etching step.

film with one free surface and one surface constrained by the Cr adhesion layer, and another 400 nm-thick Pd film covered on both faces by Cr, see figure 6.16. Two different release conditions have been applied to each batch. One condition is the classical release. The second condition consists in the three-steps release. It provides thus four different samples to compare. The HF release steps of the four different samples were performed simultaneously to keep the best reproducibility. One key parameter for the mechanical analysis is the mismatch strain in the Pd film. As it is impossible to accurately determine the part of internal stress (or equivalently of mismatch strain) due to the Cr layer, the mismatch strain value used for the (Cr/)Pd/Cr film was also used for the Pd film with etched Cr.

The overall graphs containing the curves of the four configurations are presented in figure 6.17 and the numerical results are listed in table 6.3. The effect of etching the Cr layer on the ductility is contradicting what was expected from the results in the previous section. In figure 6.17(a), it is clear that the ductility is not improved when the Cr layer is etched. That remark is valid for the two batches. It is interesting to observe that the film presenting the highest fracture strain is the film with both sides covered by Cr, see table 6.3. Moreover, the fracture strain value of the Cr/Pd/Cr film is a lower bound of the true value as the last tensile structure (the mostly deformed structure on the piece of wafer) was not broken after the full release. The yield stress does not seem to be affected by the removal of the passivation layer.

The negligible effect of the removal of the Cr layer on the results was unexpected. X-ray photoelectron spectroscopy (XPS) was used to verify that the Pd film is recovering a free surface after the Cr etching step. Three samples were



Figure 6.17: Mechanical behaviour of two Pd films with one or two sides covered by Cr, and of their two corresponding etched configurations. The films have been deposited at 1 Å/s with a thickness of 400 nm. (a) Stressstrain curves. K5 and K6 are the name of the batches where the tensile stages come from. (b) Evolution of the incremental strain hardening exponent involving the Considère's criterion. (c) Evolution of the strain hardening rate.

analysed: a piece of the as-deposited Cr/Pd/Cr stack, a piece of Cr/Pd/Cr etched during 30 seconds in the Cr etchant, and a piece of Cr/Pd/Cr after 4 minutes in the Cr etchant.

On the as-deposited sample without etching, Cr and Pd were detected. Most of the Cr was oxidized and only a few percent of Pd was detected. XPS is a surface analysis method that provides information about the first ~ 10 nm of the surface. It is thus expected that only a small signal of Pd is detected due to the presence of the Cr layer.

After 30 seconds of etching, less than 1 at.% of Cr is found which means that the Cr etching was successful. However, in the mean time, the Pd that is now better detected is found in an oxidized state. Also, more than 4 at.% of cerium was observed. This comes from the etchant solution made of cerium ammonium nitrate (Ce(NH₄)₂(NO₃)₆). Almost the same chemical composition was found for the sample etched during 4 minutes. An analysis using variable angles between the X-ray beam and the sample was tried to evaluate the thickness of oxidized Pd. Unfortunately, due to an important carbon contamination on the surface of the film, the results do not give more information.

To summarize, the XPS study has shown that the Cr etching was successful but that at the same time, an oxide layer with cerium contamination was created on the Pd film surface. This oxide layer is somehow playing the same role as the Cr layer, which presumably explains why no effect on the mechanical properties was found after the Cr etching.

The only two curves that can thus be compared to study the effect of a passivation layer are the ones without the Cr etching step, with one or two passivated sides, see figure 6.18. Of course, here, the advantage of studying films coming from the same deposition batch is lost.

In this case, adding a supplementary confining layer helps to promote strain hardening and thus to rise the ductility. The results present the same increase of hardening when the confinement of the film is increased, in agreement with the results reported on electroplated Cu with micron-sized grains [21]. In figure 6.18, it is clear that the ductility is increased when the film is covered on both sides by a Cr layer. This is in accordance with the incremental strain hardening evolution of the two films. When the film is covered on both sides, it maintains a higher strain hardening capacity over the covered range of plastic deformation.

Adding a supplementary passivation layer improves thus the strain hardening by blocking the dislocations more efficiently inside the films. Another argument can be given: if the film is embedded between two passivation layers, the mismatch between the internal stress of the Cr and the Pd becomes symmetrical. This can attenuate the bending moment induced by the Cr layer when it



Figure 6.18: Mechanical behaviour of two Pd films with one or two sides covered by Cr. The films have been deposited at 1 Å/s with a thickness of 400 nm. (a) Stress-strain curves. (b) Evolution of the incremental strain hardening exponent involving the Considère's criterion. (c) Evolution of the strain hardening rate.

is present on one side of the Pd.

6.5.3 Concluding remarks

To conclude this section on the adhesion layer effect, an effect of the film thickness seems to interplay on the results. The films used to compare Ti vs. Cr layers were 200 nm thick. In that case, a beneficial effect of using a Ti adhesion layer which leads to analyse a pure Pd film without confinement is observed on the strain hardening and on the ductility. However, when comparing film with a thickness of 400 nm confined on one or two sides by Cr, it seems in that case advantageous in a ductility and hardening point of view to be covered on both sides by a passivation layer. If we come back to figure 6.2 presenting the stress at 0.5% of strain as a function of the reciprocal film thickness, one can assume that a critical thickness exists. Indeed, under around 160 nm it is beneficial to use Ti from the strength point of view. But over this limiting thickness, it is better to have confined surfaces in the films. The same trend seems to prevail for the ductility and the hardening of the Pd films.

Of course, one has to note that the adhesion between Cr and Pd is good enough to suppose that each film carry a portion of the applied load. No easy correction to subtract the effect of this Cr layer to the mechanical properties of Pd exists. A solution to overcome this difficulty should be to study the passivation effect by confining the film with purely linear elastic materials like SiO₂ or Si₃N₄.

Finally, no efficient experimental approach was found during this thesis to study the effect of a confining layer on the properties of films coming from the same deposition batch.

6.6 Grain size effect

In order to improve the mechanical properties of nanocrystalline materials and of thin films, huge effort has been undertaken by the scientific community to understand the grain size effect on the mechanical properties of nanocrystalline materials, see section 1.2.2. The easiest way to change the microstructure of a material is to perform thermal annealing to modify the grain size.

In the present thesis, two routes to change the grain size were tested. The first one consists in breaking the columnar shape of the grains. The second is based on a thermal heating of the samples to induce grain growth. None of them were successful in this work due to a mechanical weakness of the microtensile



Figure 6.19: Hardness evolution of a Pd film deposited at 1 Å/s upon annealing.

stages at the overlap between the Pd beams and the actuator beams. More details about these problems are presented in appendix B.

Nevertheless, nanoindentation measurements have been performed to investigate the effect of annealing on the hardness. As exposed in section 4.4.5, no grain growth appears during the annealing of a Pd film clamped to the substrate even at 500°C. Here, the annealing was performed at around 150-200°C. This low temperature will thus not cause grain growth but will probably remove some lattice defects such as vacancies or dislocations, as assumed in section 4.4.5. The hardness is found to decrease after annealing, see figure 6.19. In line with the high heterogeneity of the films, the annealing can reduce the internal stress gradients by providing a sufficient energy to relax them. This will reduce the heterogeneity of the films which in turn will lead to a reduced yield stress and thus a reduced hardness. It can thus be expected that the effect of annealing microtensile stages before deformation will lead to a decreased yield stress. If a lower heterogeneity is a correct explanation, it will lead to a reduced strain hardening capacity as the material would loose part of the kinematic hardening ability due to annealing. This will be detrimental regarding the ductility of the film.

6.7 Bauschinger effect

A close collaboration with the group of Prof. T. Saif from the University of Illinois at Urbana-Champaign has been established during this thesis. The scientific interest was to use the testing devices developed there (see section 2.3) to compare the results with those obtained using our microtensile onchip method, and to perform loading and unloading cycles to investigate the presence of a Bauschinger effect and of possible plastic strain recovery.

The results obtained during this collaboration were encouraging but not definitive. They are thus detailed in appendix C. These results suggest a possible presence of the Bauschinger effect as well as an important relaxation behaviour of the Pd films. But no plastic strain recovery is observed. Moreover, this study has revealed some weaknesses in the fabrication process of the Pd testing devices.

6.8 Conclusion

The additional results provided in this chapter have allowed eliminating and reevaluating some hypotheses made in chapter 5:

- 1. An isotropic contribution to the strain hardening has to be considered as a high dislocation activity has been detected upon deformation. The aggregate model presented in the previous chapter is thus missing a dislocation accumulation contribution term inside the description of the strength.
- 2. The Cr layer does not lead to the effect on hardening predicted in chapter 5. It has been demonstrated here that, only under a critical film thickness, the elimination of the Cr confining layer is beneficial to artificially increase the strengthening.
- 3. Pd seems to present significant relaxation as shown by the experiments done with Saif's devices. This point will be quantitatively studied in the next chapter. The model should thus include a viscous part in the constitutive equation.

The additional results have also strengthened previously made hypotheses. For instance, the long elasto-plastic transition has been confirmed experimentally by X-ray diffraction under a synchrotron beam, in good agreement with the results of the model of chapter 5. Synchrotron experiments should be used on the other Pd film configurations to confirm or to contradict the assumptions made in this chapter on the varying spread of the elasto-plastic transition with different experimental conditions, e.g. for films with different thicknesses, different deposition rates, or different confining states.

Chapter 7

Rate dependent plasticity

Nanocrystalline (nc) metals present excellent mechanical performances in terms of strength and fatigue resistance but often at the expense of a low ductility [39]. Furthermore, nc systems show moderate to high rate sensitivity at room temperature [314] which might help restoring the ductility but can lead to detrimental creep/relaxation effects in applications. Thin metallic films constitute ideal candidates for looking at the mechanics of nc systems as they can be easily produced with nanograined structures often involving only one grain over the thickness as well as sharp textures [10]. The small thickness allows for direct in-situ testing in transmission electron microscope (TEM) to characterize the deformation mechanisms [49, 246]. In addition to fundamental interest, thin nc metallic films represent essential constituents in microelectronics, MEMS, functional coatings or membrane applications.

The reliability of metallic microelectromechanical systems (MEMS) is an important issue. Indeed, a constant mechanical behaviour of all structural pieces and materials during the life time of MEMS is mandatory for their commercialization. One way to evaluate the reliability is to characterize the relaxation or creep behaviour of metallic thin films that are key components of MEMS. Moreover, creep is becoming more critical when considering miniaturized materials like nanocrystalline metallic films [315]. This chapter will present the relaxation behaviour and the strain rate sensitivity parameters of Pd thin films under different configurations, i.e. with various twin density, with or without passivation layers and annealing cycles. Finally, some results highlighting the importance of film ageing will be presented. Indeed, due to the relaxation already occurs before performing on-chip microtensile testing. Thus the relaxation

tion of free-standing Pd films and the relaxation of Pd films on a substrate will be presented here.

The experimental method used here to derive the strain rate sensitivity coefficient m and the activation volume V_{act} from the microtensile stages has been detailed in section 3.5. The theoretical framework used to derive the expression of the activation volume has been developed in section 1.2.1. Note that in this chapter and in section 8.4 of the next chapter, the term *activation volume* refers to the apparent activation volume as for microtensile testing stage relaxation, it is impossible to extract the evolution of the activation volume at constant microstructure. For instance, the dislocation density varies with the relaxed time. In parallel, nanoindentation was used to provide comparative results.

This chapter is divided into two sections. The first one presents the results obtained thanks to in-situ relaxation of very thin films, i.e. with a thickness lower than 100 nm. This small thickness ensures the electron transparency of the Pd film for TEM-based in-situ observations. The second section focuses on thicker films (from 200 to 450 nm) and on the effect of the microstructure on the relaxation parameters. The motivation to separate very thin films and thicker films is that it has been proven in the literature that the thickness of the films can affect the relaxation behaviour of thin films [98]. Effort has thus been made here to compare Pd films that are as similar as possible.

7.1 In-situ TEM relaxation of very thin films

This section presents the in-situ¹ study of the relaxation mechanisms in Pd films. The relaxation experiment is performed by using the microtensile testing method and by measuring deformation at different time intervals. Note that both stress and strain vary during the relaxation experiments. Activation volume and strain rate sensitivity are extracted following the methodology presented in section 3.5. After release and a first measurement, the specimens are transferred inside a TEM. Both in-situ HRTEM and automatic crystallographic orientation mapping in a TEM using the ASTAR system (ACOMTEM) methods were used to investigate the plasticity mechanisms. The results presented in this section have been submitted for publication.

¹The term *in-situ* has to be clarified in this work. Contrarily to what is usually found in the literature, here, due to the slow kinetics of the relaxation mechanism, the samples have been observed punctually day after day and not continuously. It means that between two successive observations, the sample is removed from the TEM. The Pd samples are thus not exposed during long period of time to the energetic electron beam. This remark is important as a long exposure of the samples under the electron beam can locally alter the material.

In-situ TEM relaxation of very thin films



Figure 7.1: Schematic view of the on-chip tensile testing method allowing in-situ TEM observation. Notches have been milled every two beams using FIB, as presented by the top view low magnification bright field TEM micrograph.

7.1.1 Sample presentation

In-situ study of the relaxation mechanisms in a 90 nm-thick Pd thin film has been performed using the microtensile on-chip technique, as exposed in section 3.1 page 62. Here, the Si wafer was selectively etched from the back face using deep reactive ion etching (DRIE) to open windows under the test structures. The windows enable direct in-plane TEM observation of the Pd specimens. The fabrication process used to prepare in-situ testing structures was presented in section 3.3. In addition to that process, one more step has been added after the back-etching and before the release step in order to create, using focused ion beam (FIB), notches in some Pd beams, see figure 7.1.

More specifically, notches have been milled every two Pd beams using focused ion beam of 30 kV/7pA. The goal was to concentrate the deformation in a small area to facilitate local HRTEM and ACOMTEM observations. The beams without notches, i.e. presenting a perfectly uniaxial state were used for the mechanical analysis. The stress and strain in the notched beams can be evaluated with respect to the geometrical dimensions of the notches and the evolution of these dimensions with deformation. Figure 7.1 shows a low magnification TEM image of a Pd beam with notches. Notches have a disc-shape and reduce the beam width by 40%. It is worth mentioning that, most of the in-situ HRTEM investigations (i.e. dislocation density and TBs thickness measurements) were performed very close to the edge of the notches. Indeed, because of the FIB milling, the thickness of these edges was smaller than in the rest of the Pd beam (~90 nm).

The microstructure and texture of the as-deposited Pd films deposited at 1 Å/s



Figure 7.2: (a) ACOMTEM orientation mapping of a plan-view FIB sample prepared from the as-deposited Pd thin film. The film has been thinned to ensure that there is only one grain through the thickness. (b) Inverse pole figure showing the [110] preferential orientation of the grains in the direction perpendicular to the film. (c) Inverse pole figure showing the random orientation of the grains in the direction parallel to the film, *i.e.*, in the tensile direction. (d) Grain size distribution of the as-deposited Pd film. (e) Bright field micrograph obtained on cross-sectional FIB sample of as-deposited Pd film with 2 or 3 grains over the thickness. (f) HRTEM image obtained in the as-deposited film showing a $\Sigma 3$ 60° {111} growth nanotwin with coherent TBs.

by e-beam evaporation were characterized using both cross-sectional and planview thin foils prepared by FIB, see figure 7.2. The structure is columnar with 2 or 3 grains over the thickness and with an in-plane grain diameter of ~30 nm. The dislocation density in the as-deposited film measured by HRTEM in four grains is $4\pm0.7 \ 10^{16} \text{m}^{-2}$. The microstructure involves $\Sigma 3 \ 60^{\circ} \ \{111\}$ coherent growth nanotwins in ~25% of the grains as reported earlier (13-15), see figure 7.2(f). A fibre texture is observed with the [110] direction oriented perpendicular to the film, with no in-plane preferential orientation.

7.1.2 Mechanical characterization

The stress and strain evolution during relaxation has been measured from straight beams under a purely uniaxial stress state, see figure 7.3. The fracture strain is about 3% and the yield stress $\sim 500\pm60$ MPa which is close to the internal stress value measured after deposition. The reproducibility of the measurements has been successfully verified by using different series of tensile stages coming from the same batch and measured each just after being released, see figure 7.4.

The experimental extraction of the strain rate sensitivity has been performed using two methods: a simple procedure needing some preliminary assumptions and a more complex one that has already been detailed in section 3.5 (page 74).

The first extraction procedure works as follows. After successive measurements of one specific structure inside a SEM, the evolution of displacements with time is obtained. A logarithmic function is selected to fit the evolution of displacements u versus the time t data. The fits are shown in figure 7.5 for the beams analysed here. A logarithmic variation of u with t gives a constant average activation volume independent of time when calculating the strain using the small displacement formula of strain, the plastic strain rate, the stress and taking the derivative. The small displacement assumption is valid up to $\sim 5\%$ of deformation which is higher than the strain level reached in this study.

Using this first extraction method, the activation volume, which is a direct signature of the dominating thermally-activated deformation mechanisms, has been obtained. The insert of figure 7.3 shows the variation of V_{act} as a function of the plastic prestrain. If the Taylor factor M is taken equal to $\sqrt{3}$ as proposed for face centred cubic (FCC) nanocrystalline materials [97], V_{act} is around 7 to 14 b³, and if M = 3 as for usual isotropic polycrystals [262], V_{act} falls between 12 and 24 b³, b being the Burgers vector of Pd. These values agree well with the values reported in the literature for nanotwinned Cu [89] and



Figure 7.3: Stress-strain curve of four Pd beams under uniaxial tension. The linear elastic regime has been measured by nanoindentation as equal to 120 GPa. The initial strain level ε_{pr} before relaxation has been indicated on the figure. The insert presents the mean activation volume evolution as a function of the initial plastic strain present in the different beams before relaxation. The activation volume decreases when the initial strain level increases.



Figure 7.4: Comparison of three different series of structures coming from the same batch. Each set has been measured directly after release.



Figure 7.5: Logarithmic fitting of the displacement vs. time data. The repeated wavy shape of the displacement curve for the different analysed beams comes from the systematic error made during the measurements. This error depends on the measurement day and not on the measured beam, and can be evaluated as equal to 20 nm.

nanocrystalline Ni [90]. These values are larger than when the deformation rate is dominated by diffusion or by dislocation nucleation events. The activation volume decreases with increasing plastic prestrain. This agrees with the idea that V_{act} is inversely proportional to the square root of the dislocation density (see later in this section), in agreement also with the results reported in [252]. This first identification method gives a value for V_{act} constant upon relaxation.

The second extraction procedure involves more sophisticated derivation procedures based on NURBS (non-uniform b-spline) or cubic splines to fit the uvs. t data, as explained in section 3.5. When this more sophisticated derivation procedure is used, V_{act} tends to increase by a factor 3 to 7 over 38 days of relaxation. The results are shown in figure 7.6. The results are scattered due to the effect of experimental errors. Nevertheless, the level of V_{act} does not change. The only new information is a moderate increase of V_{act} with relaxation. Note that all these measurements are performed on straight beams. The notches produced by FIB are only used for TEM analysis. But all test structures, with or without notches comes from the same wafer and are thus nominally the same.

7.1.3 In-situ TEM investigations

One set of specimens has been transferred in a TEM as quickly as possible after release and after a first measurement of the stress and the strain. The



Figure 7.6: (a) Activation volume evolution with respect to the amount of relaxed deformation obtained using the second extraction procedure involving splines to fit the u vs. t data. (b) Zoom on the small displacements part of (a).

first TEM observation has been performed 4 hours after the release and has led to a second dislocation density measurement (the first being made on the asdeposited specimen). The average dislocation density measured from different grains in a beam deformed up to 0.9% increases to $7\pm0.7 \times 10^{16}$ m⁻² which is almost 2 times larger than the initial density, see figure 7.7(a). Note that the scatter of dislocation density measured by HRTEM is caused by the local nature, i.e., individual nc grains, of HRTEM measurement. This dislocation density is more than one order of magnitude larger than the usually reported dislocation density of nc materials under deformation [316–318]. This increase in dislocation density is unusual in nc metals in which it is usually claimed that the small grain size prevents dislocation storage even tough some recent investigations also found significant dislocation accumulation in nc Ni [316, 318] and in nc Pt [317]. The presence of pre-existing dislocations and twins presumably favours additional storage (see further). As soon as one defect gets blocked in the grain, pinning mechanisms start acting, leading to dislocation accumulation. Only perfect dislocations were observed with no stacking faults or deformation twins appearing during deformation, in agreement with the high stacking fault energy (SFE) of Pd ($\gamma_{sf} \sim 180 \text{ mJ/m}^2$). For Pd, the critical grain size under which partial dislocations emission is favoured over full dislocations emission is around 13 nm [97]. Even if the partial dislocation is theoretically feasible in Pd, it has never been observed experimentally in the present Pd films.

During relaxation, the dislocation density decreases by a factor ~ 2 and reaches


Figure 7.7: (a) Average dislocation density (red solid squares) evolution of the Pd film versus time. The dislocation density in as-deposited Pd films is $4\pm0.7 \ 10^{16} \ m^{-2}$. On the graph, t=0 represents the dislocation density measured 4 hours after the release of the films. The dislocation density first increases when deformation is applied and then decreases upon relaxation. Numbers beside unfilled circles indicate the corresponding grain size (nm). (b) to (d) Filtered HRTEM images showing the continuous evolution of the dislocation positions with time. Note the formation and the destruction of Lomer-Cottrell dislocations indicated by L-C in (c). The perfect dislocations are indicated by "T" symbols.

a steady-state regime, see figure 7.7(a). In figures 7.7 (b) to (d), the inverse fast Fourier transforms (IFFT) images extracted from HRTEM images taken after different time intervals highlight the dislocation activity during relaxation. The images represent the evolution of exactly the same region over time. The positions of perfect dislocations lying in two different $\{111\}$ slip planes are continuously varying (figures 7.7 (b) to (d)). Some of these dislocations are shown by "T" symbols. Interestingly, Lomer-Cottrell dislocations have been detected. This kind of sessile dislocation is the most effective to induce hardening and is typical of FCC metals with medium to high SFE, like Pd [316]. More surprisingly, the Lomer-Cottrell locks, which constitute a strong obstacle for moving dislocations, disappear with time (figures 7.7 (b) to (d)). Recently, a similar formation and breaking of Lomer-Cottrell junctions has been observed in Pt thin films with 10 nm grain size [317]. Numerical simulations predict that a stress of \sim 750 MPa or equivalently a strain of 2% is needed to destroy the junction in Pd [319], i.e. in the range attained in our test specimens. Hence, despite the 30 nm grain size, dislocation based-mechanisms dictate the mechanical response of the Pd films.

Twins constitute strong barriers to dislocation motion. Initially, in the asdeposited film, most of the $\Sigma 3$ 60° {111} TBs are perfectly coherent, see figure 7.2(f). However, this coherency is lost during deformation due to the interaction of lattice deformation dislocations with the TBs [8,255]. The loss of coherency of these TBs keeps increasing upon relaxation as indicated by the progressive increase of the TB1 and TB2 thicknesses, see figure 7.8(d). This is due to the formation of residual interfacial defects at the TBs such as Frank sessile dislocations [8, 255] and/or the accumulation of lattice dislocations at these boundaries. Further HRTEM observations have confirmed the behaviour shown in 7.8(d) by following several twin boundaries. As the thickness of all TB follows the same trend, these additional curves are not presented here.

The term *TBs thickness* is defined here as the distance separating the two last non-distorted twinning planes delimiting the matrix and the twin. The positions of these planes are indicated by dashed white lines in the upper right insets of figure 7.8 (a) to (c), from which the inclined {111} planes indicated by white solid lines in the same insets start to deviate from their initial position. This is due to the accumulation of dislocations at the TBs, see section 6.3 for more details. Because the thickness may change along individual TBs, the measurements reported in figure 7.8(d) were always performed in the same region indicated by dashed lines in figure 7.8(a) and shown in the upper right insets of figure 7.8 (a) to (c). The calculated error for the TBs thickness ratio is ± 0.3 . Furthermore, in order to ensure HRTEM observation of TBs in as identical local orientation conditions as possible, the intensity symmetry of the FFT patterns were accurately compared (see the lower right insets of figure 7.8 (a) to (c)). The presence of twins clearly participates to the increased



Figure 7.8: (a) to (c) HRTEM images showing $\Sigma 3$ {111} TBs at t=0, 3 days and 36 days, respectively. Note the increase of the TBs thickness from (a) to (b) in the filtered images at the upper right insets of the micrographs. No significant change of the TBs thickness from (b) to (c) is observed. (d) Evolution of the TBs thickness ratio (T measured / T initial) of the TB1 and TB2 in (a). A plateau is reached after 10 days. More than two measurements have been performed, showing the same trend.



Figure 7.9: Grain size distribution of a Pd beam initially deform at 0.6%. No change of the grain size distribution is observed.

dislocation storage capacity of nanotwinned metals [113], as evidenced through the accumulation of dislocations at the TBs.

Another set of test structures was used for ACOMTEM measurements to provide statistical data on the grain size distribution variation upon relaxation, see figure 7.9. Note here that orientation indexation using ACOMTEM was impossible as the films contain more than one grain in the thickness and as the thickness of the Pd beams of the microtensile testing structures was not reduced by FIB. However, thanks to the columnar structure, the extraction of the grain size distribution evolution upon relaxation was possible. No evolution of grain size is observed, confirming the absence of grain boundary (GB) migration. No grain boundary sliding has been observed by conventional TEM analysis. Hence, there are strong evidences that no GB-based mechanisms contribute to relaxation. This also agrees with the fact that GB sliding entails a strain rate sensitivity exponent m of 0.5 or equivalently an activation volume of $\sim 1 \text{ b}^3$ [90] which is inconsistent with the values measured here. For the same reason, GB diffusion-mediated creep (Coble creep) is not a likely mechanism. Some studies postulate that Coble creep is the dominating mechanism in nc materials [44] but this is essentially for stress below the yield stress. Moreover, Coble creep and GB sliding are strongly influenced by the grain size and are not expected at a ~ 30 nm grain size [137, 320].

7.1.4 Discussion and conclusion

Based on the experimental evidence that dislocation based-mechanisms control the deformation during relaxation, several thermally activated mechanisms can be postulated: the time to nucleate new dislocations at GBs, the time to restore dislocations pinned by other dislocations and junctions, and the time to free dislocations from interactions with TBs. The activation volume related to the first mechanism is a few b^3 , while the activation volume for recovery is equal to ~14 b³ for a dislocation density of $7\pm0.7 \times 10^{16}$ m⁻² [82]. Those two values lie in the range of the experimental values found here. Depending on the identification method, V_{act} is found constant or to moderately increase upon relaxation, see figures 7.3 and 7.6 respectively. The increase of the activation volume can be quantitatively related to the decrease of the dislocation density with time using simple arguments as exposed in the next paragraph.

The activation volume for recovery, i.e. for relaxation mechanism based on the glide of dislocations, has been expressed by Argon [82] (see also equation (1.11) in chapter 1):

$$\Delta v^* = b\lambda \Delta y^*, \tag{7.1}$$

where Δv^* is the activation volume, b the Burgers vector, λ the distance between pinning points and Δy^* the activation distance, i.e. the distance over which a dislocation has to jump to overcome the energy barrier which retains it at its initial position. The distance between pinning points is related to the dislocation density ρ :

$$\lambda = \alpha \rho^{-1/2},\tag{7.2}$$

where α is a geometrical factor approximately equal to 1.

The HRTEM analysis has provided the variation of the dislocation density with relaxation time (figure 7.7(a)). By approximating the terms present in equations (7.1) and (7.2), we can obtain the range of the theoretical activation volumes related to the relaxation via dislocation glide:

$$\Delta y^* \approx b$$

$$\lambda = \left(7 \ 10^{16} \text{m}^{-2}\right)^{-1/2} \approx 4 \ 10^{-9} \text{m} \approx 14 \ b, \tag{7.3}$$

if we consider b = 0.275 nm for Pd [97]. This leads to:

$$\Delta v^* \approx 14b^3. \tag{7.4}$$

This theoretical value of the activation volume is in good agreement with the experimental value found here (see figures 7.3 and 7.6), indicating that recovery by dislocation depinning certainly contributes to setting the relaxation time. Additional effects probably contribute to the evolution of V_{act} such as the

loss of coherency of the TBs which can change the time of interaction of the dislocations meeting such TBs.

Another semi-quantitative model can also be proposed to explain the activation volume increase upon relaxation using the evolution of the dislocation density observed experimentally. The change of V_{act} with the plastic strain writes, based on equation (7.1),

$$\frac{\partial V_{act}}{\partial \varepsilon_p} = b\Delta y^* \frac{\partial \lambda}{\partial \varepsilon_p} = -b\Delta y^* \alpha \rho^{-3/2} \frac{\partial \rho}{\partial \varepsilon_p}.$$
(7.5)

The connection between the dislocation density and the plastic strain can be derived in the following way:

$$\frac{\partial \varepsilon_p}{\partial \rho} = \frac{\partial \varepsilon_p}{\partial n} \frac{\partial n}{\partial \rho},\tag{7.6}$$

where n is the average number of dislocations per grain. Each dislocation liberated during recovery leads to a shear strain increment equal to b/h where h is the film thickness and to an increment of the tensile strain equal to b/3hassuming a Taylor factor of 3. The dislocation density changes in the following way with a change of number of dislocations per grain:

$$\rho = n \frac{\gamma d}{\pi h d^2/4},\tag{7.7}$$

where d is the in-plane grain size and γd is the mean length of each dislocation segment. Based on equations (7.6) and (7.7), one thus gets

$$\frac{\partial \varepsilon_p}{\partial \rho} = -\frac{\pi}{12} \frac{bd}{\gamma},\tag{7.8}$$

hence,

$$\frac{\partial V_{act}}{\partial \varepsilon_p} = -\frac{6}{\pi} \alpha \gamma \frac{b}{d} \rho^{-3/2}.$$
(7.9)

Using $\alpha = 1$, $\gamma = 2$, d = 30 nm, $\rho = 7 \times 10^{16}$ m⁻² (for an initial plastic strain of 0.4%), equation (7.9) predicts an increase of V_{act} by ~ 1 b³ for a plastic strain relaxation of 0.01. This change of activation volume is smaller than the one measured experimentally. The present prediction assumes that all liberated

dislocations will effectively contribute to plastic deformation, but, in reality, only a fraction of them will contribute. The prediction of equation (7.9) should thus be corrected through dividing by this, unknown, fraction.

To conclude, the observation that dislocations control both deformation and relaxation of some nc materials even at 30 nm grain size opens new perspectives to improve the mechanical properties of nanostructured materials. The on-chip testing technique in combination with in-situ observation of the relaxation mechanisms during long periods of time yields data impossible to obtain using classical methods. This study further shows, for the first time, that $\Sigma 3$ {111} coherent TBs can be used as markers for the qualitative evaluation of the level of plastic deformation developed in individual nanograins during creep tests. The fast relaxation mechanisms observed in this study can be detrimental to the mechanical stability in applications involving Pd based nanobeams or membranes.

7.2 Ex-situ testing of thin films - Microstructure effects

The preparation of microtensile stages compatible with in-situ observation is laborious. To study more easily the mechanical stability of different Pd films with different specificities, classical microtensile stages without the back-etching step were used.

For all figures presented in this section, the activation volume has been normalized by the Taylor factor M. Indeed, as explained in section 1.2.1 and appendix A, the Taylor factor value is related to the deformation mechanism which is, in principle, not initially known and to other characteristics of the material.

Nanoindentation has been performed to compare the results obtained using the microtensile testing stages or to obtain results when microtensile testing stages were inoperable. A short remark about the comparison of these two techniques has to be presented here. The strain rate sensitivity exponent found using nanoindentation will always be smaller than the one obtained using on-chip microtensile testing stages. In fact, the different amount of tested material can lead to a different mechanical behaviour, as observed by Choi et al. for different nanoindenter tip shapes [100]. If the indenter tip shape can affect the measured strain rate sensitivity of materials, it is not surprising that it will also be affected when comparing nanoindentation results with purely uniaxial tensile results. Moreover, the initial loading rate using nanoindentation is lower than when using microtensile testing stages. As reported in [321], an increased loading rate leads to a higher rate sensitivity exponent.

The section is divided in five subsections. First, a reference experiment will be presented and will serve as a basis for further comparison. After, the twin density and the adhesion layer effect on the strain rate sensitivity will be presented. Then, the temperature effect will be discussed and finally, the ageing effect of the samples will be studied.

7.2.1 Reference relaxation experiment

The relaxation experiments performed on Pd films with different microstructures or configurations will be compared to one experiment made on a 400 nm-thick Pd film deposited at 1 Å/s by e-beam evaporation on a 5 nm-thick Cr adhesion layer. This is the reference film here. This film comes from the batch used to study the hydrogen effect on the mechanical properties, see chapter 8.

The activation volume and the strain rate sensitivity are linked and inversely proportional, see equations (3.12) and (3.13), page 75. The relaxation behaviour of the present film is shown in figure 7.10.

The normalized activation volume is found comprised between 3 and 12 b³ with a moderate increase upon the 25 days of relaxation. It can also be observed that the initial plastic strain level affects the evolution of the activation volume. When the initial plastic strain level is high, i.e. the dislocation density is high in the deformed Pd beam, the ability to creep with significant plastic strain, while keeping a small activation volume, increases. This can be related to the model exposed in section 7.1.4. Indeed, equation (7.9) presents that the evolution of the activation volume with the plastic strain is proportional to the dislocation density exponent (-3/2). It means that if the initial dislocation density is ten times lower in the beam subjected to the lower initial plastic strain than in the beam subjected to the higher initial plastic strain, the variation of its activation volume with the slopes observed for the different Pd beams at the initial stages of relaxation in figure 7.10.

As discussed in section 7.1, it is clear that the creep/relaxation in the Pd films studied here is dominated by dislocation-based mechanisms. It will thus not be discussed again here. However, it will be interesting to compare different experimental conditions and to see how it affects the strain rate sensitivity of Pd films.



Figure 7.10: Rate sensitivity of the 400-nm thick reference film deposited at 1 Å/s. The activation volume is presented both as a function of the relaxed plastic strain amount and of the time. The strain rate sensitivity exponent m is also shown with respect to the relaxation time. As mentioned before, V_{act} and m are inversely proportional.



Figure 7.11: Rate sensitivity of the 480-nm thick Pd film deposited at 10 Å/s. The activation volume is presented both as a function of the relaxed plastic strain amount and of the time. The initial plastic strain level is indicated in the legend. The strain rate sensitivity exponent m is also shown with respect to the relaxation time. As mentioned before, V_{act} and m are inversely proportional.

7.2.2 Twin density effect

The deposition rate of Pd affects the twin density of the as-deposited films and their mechanical behaviour, as presented in sections 4.4.4 and 6.4. Here, the effect of the twin density on the strain rate sensitivity of the Pd films has been characterized using microtensile stages and nanoindentation.

First, the microtensile testing method was used to deform and study the relaxation of a 480 nm-thick Pd film deposited at 10 Å/s on a 5 nm-thick Cr adhesion layer. This is the same film as the one presented in section 6.4. The results are shown in figure 7.11.



Figure 7.12: (a) Comparison of the kinetics of relaxation of two films containing different twin and dislocation densities. (b) Comparison of the initial activation volume evolution with respect to the initial plastic strain in the Pd beams for two Pd films deposited at different rates. The activation volume presented on the graph is the mean between the two first measurements of the activation volume of figure 7.11.

On this figure, the normalized activation volume increases with time from a few b^3 to more than 20 b^3 over 7 days while the strain rate sensitivity is decreasing from around 0.3 to 0.02. As in figure 7.10 for the film deposited at 1 Å/s, an effect of the initial plastic strain level is visible. But in the case of the film deposited at 10 Å/s, the increase of the activation volume with the time is faster than for the film deposited at 1 Å/s, see figure 7.12(a). Note that the initial activation volume evolution regarding the initial plastic strain is not affected by the twin density, see figure 7.12(b). The initial activation volume is the mean between the two first measurements of the activation volume. Figure 7.13 compares tensile structures initially deformed with the same amount of plastic strain before relaxation. For a same initial plastic strain level, the film deposited at 10 Å/s can relax a smaller amount of plastic strain before the activation volume increases sharply.

Nanoindentation was performed on the two Pd films deposited at 1 and 10 Å/s presented here and above, see figure 7.14. Attention was paid to indent the films as soon as possible after their deposition to avoid an ageing effect on the results. The strain rate sensitivity exponent is slightly increasing from 0.048 to 0.052 when the deposition rate increases from 1 to 10 Å/s. This is equivalent to a decrease of the activation volume with an increased deposition rate. This is in a certain manner coherent to the microtensile results obtained after a few days of relaxation, see figure 7.12(a). On this figure, when the relaxation time increases, the activation volume of the film deposited at 10 Å/s



Figure 7.13: Evolution of the activation volume for tensile structures deformed at the same initial plastic strain level (written in the legend) as a function of the relaxed plastic strain amount.

becomes higher than the activation volume of the reference film deposited at 1 Å/s. Note however that the two m extracted by nanoindentation are not significantly different. The discussion provided in this paragraph should thus been considered carefully.

As observed in section 4.4.4, the twin density and the dislocation density increase in the as-deposited films when the deposition rate increases. Once the film is deformed, a higher dislocation density is also expected in the film deposited at 10 Å/s. If a higher dislocation density is present, a higher driving force for relaxation is present, i.e. a higher driving force for the dislocations to escape. Moreover, it will be easier for a dislocation to be pinned as the material will contain more obstacles to dislocation motion. It can explain the faster increase of the activation volume as the dislocation density is expected to decrease faster.

Twins are known to affect the strain rate sensitivity of metals, as already exposed in section 1.2.2, page 29. In nanocrystalline materials, the activation volume for dislocation-mediated relaxation is reduced to the order of tenth of b^3 , since dislocation nucleation sources are changing from a typical Frank-Read source to GBs [90]. The plastic flow is thus accommodated by the interaction of dislocations with various boundaries. An analogy with the reduced grain dimension due to the presence of twins appears acceptable [100] and is in good agreement with the obtained results in this work even if here, the relaxation mechanism is mainly based on dislocation glide, see section 7.1.3.



Figure 7.14: Hardness evolution as a function of the indentation strain rate for a film deposited at (a) 1 Å/s and (b) 10 Å/s. The strain rate sensitivity exponent extracted from the slope of the linear fit is higher when the deposition rate is higher, or equivalently for a higher twin density.

7.2.3 Adhesion layer effect

As explained in the previous chapter, two routes have been used to assess the effect of the adhesion layer. First, results on a Pd film deposited on Ti will be presented. Then a short discussion concerning the comparison of the different configurations of a Pd film deposited on Cr or covered on both sides by Cr will be provided.

The time evolution of the stress-strain curve of the 200 nm-thick Pd film deposited on Ti and presented in section 6.5.1 has been recorded. This has provided the activation volume and the strain rate sensitivity exponent evolution, see figure 7.15. The film deposited on Ti presents a high ductility, as observed in section 6.5.1. The fracture strain was more than 10%. As described by the Hart's criterion and by Neale and Hutchinson (see section 1.2.1), a high rate sensitivity is a factor that can significantly increase the resistance to plastic localization. It is thus expected that the Pd film deposited on Ti showed a reduced activation volume as compared to the reference film that exhibits a lower ductility but a similar strain hardening behaviour.

The activation volume evolution of the reference film and of the film deposited on Ti are superposed in figure 7.16(a). First, one must note that the evolution of the activation volume has not been followed during the same duration. Nevertheless, it is obvious that the activation volume evolution does not show the same trend when the film is deposited on Ti. For instance, at the initial stages of relaxation, the activation volume of the film with two free surfaces is smaller for an identical initial plastic strain than for the film covered on one side by Cr, see figure 7.16(b). Note also that the thickness of the reference film was twice



Figure 7.15: Rate sensitivity of the 200-nm thick Pd film deposited at 1 Å/s on Ti. The activation volume is presented both as a function of the relaxed plastic strain amount and of the time. The initial plastic strain level is indicated in the legend. The strain rate sensitivity exponent m is also shown with respect to the relaxation time.



Figure 7.16: (a) Comparison of the kinetics of relaxation of two films constrained or not by a passivation layer during relaxation. (b) Comparison of the initial activation volume evolution with respect to the initial plastic strain in the Pd beams for two Pd films with different confinements. The activation volume presented on the graph is the mean between the first and the fourth measurements of the activation volume of figure 7.15.

the thickness of the present film deposited on Ti. The thickness effect on the strain rate sensitivity of thin films has not been studied in this thesis. In the literature, Hirakata et al. have found a marked thickness effect on the creep properties of Al thin films [98]. For film thickness around 100-200 nm, they observed a decreased creep rate compared to the creep rate of thicker films. For film thickness ranging between 200 and 400 nm, they observed a peak in the creep rate.

The film deposited on Ti is able to maintain a small activation volume longer than the film deposited on Cr. However, by considering two Pd beams initially deformed at the same plastic strain, the amount of relaxed plastic strain is smaller when the film was deposited on Ti, see figure 7.17. It means that the kinetics of the relaxation is different.

As the relaxation is dominated by the glide of dislocations, a scenario can be envisaged. Remember that the film deposited on Ti presents two free surfaces after release and that the dislocation glide is constrained due to, amongst others, the presence of a passivation layer [210]. It means that before relaxation, the film with one confined layer contains a greater amount of dislocations than the film with all free surfaces where dislocations were able to escape more easily from the film. The creation of pile-up is thus smaller for the film with two free surfaces. This influences the relaxation behaviour as the initial dislocation density is smaller, meaning that less vectors for relaxation are present in the film. It explains why a smaller amount of plastic deformation can be



Figure 7.17: Comparison of the activation volume evolution as a function of the relaxed plastic strain of Pd beams with similar initial plastic strain level before relaxation.

relaxed when no passivation layer is present. It also explains why the kinetics of relaxation is much slower for the unpassivated film. Indeed, the state of the film before relaxation is more stable, inducing a reduced activation energy for dislocation glide.

As the thickness of the film with two free surfaces is half the one of the constrained film, the argument that the dislocations are escaping more easily when no confining layer is present is still more prevalent. Actually, the dislocations located in the middle of the film thickness have much less distance to travel to reach the film surface. It can thus be expected that for thinner films, the image forces of dislocations due to the free surfaces are more intense which leads to a higher driving force for the dislocations to escape. This explanation can also justify the initially lower activation volume of the unpassivated film, see figure 7.16(b). A possible scenario is that the unpassivated film contains an initially lower dislocation density after deformation but that the dislocations can glide more easily during relaxation due to the lower thickness of this film and the presence of two free surfaces.

The second option tested to investigate the effect of a passivation layer on the mechanical properties was to remove selectively the Cr layer before the tensile test. As explained in section 6.5.2, the selective Cr etching oxidized the Pd surface. Hence, this method was useless to unlock the Pd surfaces from the Cr confining layer(s). Nevertheless, the relaxation of the four film configurations compared in section 6.5.2 has been recorded. No clear trend is manifesting on the results. The figures are thus presented in appendix D for the sake of brevity. What is clear is that the two films before the Cr etching present the

same behaviour as the reference film presented above. It is worth noting that the thickness of the two present films and of the reference film was similar (around 400 nm).

7.2.4 Temperature effect

To overcome the limitations of the microtensile testing method after annealing (see section 6.6), nanoindentation has been performed to study the effect of annealing on the strain rate sensitivity of Pd thin films. The indented film is the same as the one presented in the previous section, i.e. deposited at 10 Å/s. The Pd film has been tested as-deposited, and after an annealing at around 150-200°C. Unfortunately, the temperature has not been measured accurately due to experimental failure. From the in-situ measurement of the internal stress of a Pd film (deposited at 1 Å/s) during thermal annealing, it can be affirmed that the grain size is not affected by the temperature, see section 4.4.5. Even if the present film has been deposited at 10 Å/s, the expected behaviour should be similar. However, a temperature of 150-200°C will be sufficient to remove lattice defects and thus to alter the mechanical properties.

The results are shown in figure 7.18. A clear decrease of the strain rate sensitivity exponent appears after annealing. As dislocations are the vectors for plastic relaxation, a lower dislocation density due to annealing will results in a lower relaxation capacity. In a more general point of view, a decrease of the initial defect density will lead to an increase of the activation volume. This is valuable for the mechanical stability of the Pd films. But as advanced in the section 6.6 of chapter 6, this increased mechanical stability will happen at the expense of the strain hardening and thus of the ductility.

7.2.5 Ageing of the specimens

The internal stress of the Pd thin films studied in this thesis was not negligible. It has been observed that the mechanical properties of the films were dependent on the age of the sample, i.e. the elapsed time between the film deposition and the film testing. This has already been mentioned when presenting figure 6.1, page 130.

Different methods have been used to determine the ageing effect (at room temperature) on the mechanical properties of thin Pd films: the wafer curvature measurement technique, nanoindentation and the microtensile testing method. The wafer curvature measurements provided information about the internal stress evolution in the as-deposited films. Nanoindentation was used to support



Figure 7.18: Hardness evolution as a function of the indentation strain rate for a film deposited at 10 Å/s (a) as-deposited and (b)annealed at 150-200°C. The indentation depth range was comprised between 25 and 50 nm.



Figure 7.19: (a) Internal stress evolution as a function of time and of the deposition rate. Two different wafers were used for each condition. (b) Same results plotted using logarithmic axes.

the results obtained using microtensile stages. Indeed, nanoindentation is easy to perform, and very useful for repetitive measurements.

The internal stress evolution with ageing time has been measured successively using wafer curvature measurements. To strengthen the study, two films with two deposition conditions (1 and 10 Å/s) were analysed, see figure 7.19. When the deposition rate increases, the tensile internal stress level is systematically higher and the decrease of the internal stress level is faster than for low deposition rates. Different mechanisms can explain such a decrease: the elastic relaxation mechanisms or a plastic strain recovery due to a modification of the dislocation density in the films.

Some authors have proposed a simple methodology to extract the activation

energy and the athermal flow stress of creep in Al alloy thin films [322, 323]. Assuming that dislocation motion in the film is hindered by obstacles that can be overcome via thermal activation and an applied stress, the creep should be described by an equation of the type:

$$\dot{\gamma} = \dot{\gamma_0} \exp\left(-\frac{\Delta F}{kT} \left(1 - \frac{\sigma_s}{\tau}\right)\right),\tag{7.10}$$

where $\dot{\gamma}$ is the shear strain rate, $\dot{\gamma_0}$ a quasi-constant, ΔF the activation energy required for dislocation to overcome obstacles, σ_s the shear stress, τ the athermal flow stress, k the Boltzmann constant and T the temperature. This equation can be expressed in terms of the biaxial stress using the Von Mises equivalent stress and strain, see [322, 323]. By fitting the experimental relaxation data with this equation and using a nonlinear least squares fitting routine, they were able to extract the activation energy of the creep mechanisms in their films. Equation (7.10) should be valid in the present Pd films if the dominant relaxation mechanism is the glide of dislocations. Unfortunately here, this methodology cannot be applied as relaxation results were only produced at room temperature. Additional experiments at higher temperatures are thus required to allow the extraction of such information.

Nanoindentation was also repeated on these two different films following the same time intervals as the wafer curvature measurements. The hardness evolution is shown in figure 7.20. The hardness of the film deposited at 10 Å/s is smaller than for the film deposited at 1 Å/s. This effect has already been discussed in section 6.4.1. What is important here is the constancy of the hardness over time. As said in the previous paragraph, two mechanisms were proposed to explain the internal stress decrease with sample ageing. In view of the constant hardness, the discrimination of the plastic strain recovery mechanism should be obvious, and elastic relaxation should prevail during the ageing. Indeed, if the dislocation density was changing upon ageing, this should have a direct effect on the hardness.

To go further in the understanding, two years old microtensile testing stages have been released. Their stress-strain curve evolution was recorded, see figure 7.21. Note that the ageing time is higher here than for the films investigated by wafer curvature and nanoindentation measurements.

The activation volume is found to lie around 17 b^3/M and the strain rate sensitivity exponent is of the order of 0.018. Contrarily to what was reported before on 'fresh' films, these values do not seem to be affected nor by the initial strain level in the tensile structure nor by the time. Also, the activation volume is higher than for fresh samples and the strain rate sensitivity is one order of



Figure 7.20: Hardness evolution with time for the two films and using different indentation strain rate.



Figure 7.21: Rate sensitivity of a 310-nm thick Pd film deposited at 1 Å/s on Cr released two years after the film deposition. The activation volume is presented both as a function of the relaxed plastic strain amount and of the time. The initial plastic strain level is indicated in the legend. The strain rate sensitivity exponent m is also shown with respect to the relaxation time.



Figure 7.22: Comparison of the relaxation behaviour of two similar films after different ageing times.

magnitude smaller, compare figures 7.10 and 7.21. This important difference in the strain rate parameters of those two films with different ageing time should come from another relaxation mechanism than only elastic relaxation as proposed above regarding the constant hardness over around 100 days of relaxation.

To be coherent in terms of sample ageing, a new nanoindentation study was performed on a fresh film and on a 2 years old film. This time, an increase of the hardness with the ageing time is observed, see figure 7.23. This is in good agreement with the higher yield stress observed for an aged film as presented in figure 6.2 in the previous chapter. To be statistically relevant, this experiment has been repeated on other new and old films. It always shows the same behaviour. A long ageing thus leads to a decrease of the defect density (e.g. dislocations) which induces a higher yield stress and a higher hardness as dislocations have to be nucleated to activate plasticity. In 'fresh' samples, the dislocations present in the as-deposited state can directly participate to deformation.

From these nanoindentation data, the strain rate sensitivity coefficient of the films has been calculated, see figure 7.24. The strain rate sensitivity of the old film is one order of magnitude smaller than that of the fresh film, as expected regarding the microtensile stage results. The ageing effect appears extremely non linear, and both nanoindentation results and microtensile stage results (figure 6.2) agree on that point.

To conclude, it is clear that a long ageing time (at least one year) will affect the dislocation density of the films. At small ageing time, it is difficult to interpret



Figure 7.23: Hardness evolution as a function of the indentation strain rate for films with different ageing times.



Figure 7.24: Strain rate sensitivity exponent extracted from the slope of the linear fit on the hardness results as a function of the ageing time of Pd films deposited at 1 Å/s.

the results as it seems that only elastic relaxation occurs. Advanced microscopy may help to investigate the different relaxation or recovery mechanisms that occur in as-deposited films during ageing.

Note that annealing also results in a change of the mechanical behaviour and thus certainly of the film microstructure, see section 7.2.4. It is interesting to observe that a similar decrease of the strain rate sensitivity exponent is observed after 2 years ageing than after an annealing at 200°C. In both cases, plastic strain recovery is expected and this process is know to be thermally activated [79]. It should also be mentioned that in section 6.6, the hardness of the films was decreasing upon annealing while here, the hardness is increasing with ageing time. It can thus be concluded that the plastic strain recovery mechanism is not exactly similar in both cases.

To go deeper in the understanding, a microscopy analysis should be performed. For instance, there exists some silicon nitride grids on which it is possible to deposit thin films and to observe under plan-view TEM the ageing evolution. Indeed, the silicon nitride membrane is transparent to electrons and will play the same confining role as a classical substrate.

7.3 Conclusion

This chapter has provided understanding about the relaxation mechanisms of Pd thin films. In-situ HRTEM relaxation experiments have shown that dislocation-based relaxation mechanisms prevail in nc Pd thin films. Beside this fundamental observation, different film configurations were analysed. For instance, higher TBs and dislocation densities provide an improved mechanical stability as, after some days, the relaxation rate decreases importantly. Also, a film with two free surfaces will see his rate sensitivity to decrease faster due to the smaller initial dislocation density induced by the easy escape of the dislocation via the free surfaces. Finally, slight annealing or long ageing is beneficial from a mechanical stability point of view but provides indications that it will happen at the expense of the ductility.

The strain rate sensitivity exponent found using nanoindentation is always smaller than the one obtained using on-chip microtensile testing stages. This shows the importance to compare results by considering all the experimental conditions.

Chapter **8**

Hydriding effect on the mechanical properties of Pd thin films

Due to the continuous increase in energy consumption and the related field of new sustainable energy sources, hydrogen appears to be an attractive fuel candidate to replace conventional hydrocarbons. However, the hydrogen volatility is the main industrial limitation. Moreover, the reactivity of hydrogen in the air has to be considered for a safe use of this new fuel. To circumvent these obstacles, the scientific community has brought efforts to propose new routes for hydrogen storage and to develop efficient hydrogen sensors. Different materials have been proposed to address the challenges; palladium has been the most widely studied due to its important affinity and selectivity for hydrogen, even at room temperature, and due to the reversibility of its hydride formation [324].

The last chapter of this thesis is dedicated to the effect of hydrogen on the mechanical properties of Pd thin films. First, a short review of the Pd/H system will be provided. Then, the samples and the description of their hydriding will be presented. After, the effect of hydrogen on the properties measured immediately after the release, i.e. the strength, the ductility and the strain hardening, will be exposed and discussed. Finally, the effect of hydrogen on the relaxation of Pd thin films will be investigated.

8.1 Literature review - The Pd/H system

The hydriding of Pd is a two steps process involving a dissociative chemisorption on the surface, followed by a subsequent diffusion of the hydrogen atoms



Figure 8.1: Schematic illustration of the hydriding process at the atomic scale. Figure taken from [29].

into octahedral interstitial lattice sites of Pd, see figures 8.1 and 8.2(a). It is well known that the interstitial hydrogen atoms induce a volume expansion of the host material [325]. Palladium is able to increase more than 900 times its volume when absorbing hydrogen [326].

There exists two different solid-solutions of Pd hydride separated by a miscibility gap [324]. The first kind of hydride, called the α -phase is characterized by a low concentration of hydrogen in the Pd lattice and a lattice constant close to the palladium metal (3.89 Å for pure Pd versus 3.984 Å for an α -hydride with a H:Pd ratio of 0.008). The maximum atomic ratio H:Pd in the α -phase is equal to 0.008 at room temperature [324]. When the hydrogen content exceeds this limit, the lattice constant increases linearly with the hydrogen partial pressure until the β -phase appears. The minimum H:Pd ratio in the β -phase is equal to 0.6 at room temperature [327]. This corresponds to a lattice constant of 4.025Å [324]. The β -phase is characterized by a highly distorted lattice. The abrupt volume change associated to the phase transformation can induce microstructural changes like for instance dislocation nucleation. For coarse grained Pd, some authors reported that the dislocation density increases by three orders of magnitude after the $\alpha \rightarrow \beta$ hydride phase transformation [328]. The transition between the two phases is a function of the hydrogen partial pressure and of the temperature, see figure 8.2(b). Both phases present the same crystalline structure with the hydrogen atoms lying in the octahedral sites. This is a particularity of the Pd-H system.

The previous paragraph has addressed the solubility of H_2 in Pd as established for bulk Pd. It has been shown that in thin films and nanocrystalline Pd, the maximum H_2 solubility in the α -phase was increased up to 0.02 while the minimum H_2 solubility in the β -phase was decreased down to 0.43 [329]. This



Figure 8.2: (a) Schematic view of the octahedral sites in a Pd unit cell. On the image, each site is occupied and the H:Pd ratio is equal to 1. This stoichiometric composition has never been reached experimentally. Figure taken from [327]. (b) P-C-T diagram of the Pd-H system. Figure taken from [4].

observation has been associated to the increased density of grain boundaries due to the grain size reduction [330]. In fact, at low hydrogen concentrations, the low energy sites existing at grain boundaries are filled with hydrogen. But at higher hydrogen concentrations, only the grain interiors can host additional hydrogen atoms. This lowers the minimum solubility of the β -phase [329]. Hydrogen atoms can be trapped by lattice defects such as grain boundaries, dislocations and vacancies [331].

The use of palladium thin films is widespread for hydrogen storage [2], hydrogen sensing [3] and hydrogen purification and separation [4]. When a Pd film lying on a substrate is hydrided, the volume expansion is prohibited. This induces the apparition of compressive internal stress in the film, see figure 8.3. Different experimental techniques have been used to quantify the hydrogen concentration in palladium films, e.g. optical transmittance measurements [332] or wafer curvature measurements [3].

In this thesis, a method based on in-situ wafer curvature measurements was used to measure the internal stress evolution of the Pd films during hydriding cycles, see section 4.3. The level of stress during the hydriding is an indication of the plastic strain in the film. Indeed, if the yield stress of palladium is reached by the stress generated during hydriding, dislocations will nucleate and glide. As dislocations are preferential sites for hydrogen absorption due to their local tensile strain fields, it will affect the kinetics of the reversibility of the hydriding cycle as the desorption of hydrogen will be more difficult [329]. The maximum compressive stress undergone by a Pd film during hydriding is linked to the



Figure 8.3: Internal stress evolution of a Pd film containing 410 MPa of tensile internal stress in the as-deposited state. Figure taken from [29] with superimposed conditions of this study (the orange squares correspond to the different internal stress levels and hydrogen partial pressures studied in this chapter and experimentally measured in this work).

hydrogen partial pressure, see figure 8.3. The Pd film used to establish figure 8.3 was in tension after its deposition. It means that the hydriding has first released its internal stress. After, depending on the hydrogen partial pressure used during hydriding, the film has undergone compressive stress that can be extremely high and that can overcome the compressive yield stress of the film. In [37], the expected compressive yield stress for a Pd film prepared by inert gas condensation (IGC) is equal to around 1 GPa¹. In this work, the tensile yield stress is between 400-600 MPa depending the film thickness, which can be a good approximation of the compressive yield stress. The complete internal stress evolution of the film before, during and after hydriding will be presented in the next section.

Experimental evidence of the perfect reversibility of the hydriding reaction in Pd has been reported in [333]. This implies that no hydrogen atoms are found in the Pd film after the dehydriding process. Note that it does not mean that the Pd microstructure is identical than before the hydriding cycle. Indeed, the microstructure can involve new dislocations and modify local strain fields after hydriding. In this thesis, pure Pd films will be studied after hydriding cycles at room temperature. This information is important to keep in mind for two reasons. First, as hydriding is made at room temperature, the phase transition occurs for high hydrogen partial pressure, see figure 8.2(b) where a temperature

¹IGC is a preparation method that leaves some porosity inside materials. As pointed in sections 1.1.2 and 1.2, the porosity highly affects the mechanical properties of the material. The compressive yield stress of Pd given here has to be taken carefully. Indeed, the Pd films studied in this work do not present such a high porosity.

of around 300°C should be reached to avoid the phase transition. The phase transition leads to the creation of important strain in the material [4]. Second, this is a relevant information regarding the undesirable hydrogen embrittlement in metals which should not occur here if none of the hydrogen atoms remain in the Pd lattice. Alloying Pd with other metallic elements (e.g. Ag, Cu) prevents the phase transition and diminishes embrittlement problems, see [4, 334]. For instance, no effect of exposing Pd/Ag alloys to hydrogen was detected on the mechanical properties over a temperature range of 303-473°K [335]. The study of the alloying effect is out of the scope of this thesis.

Hydrogen embrittlement of metallic systems is a widespread phenomenon but the precise role of hydrogen in this mechanism is not well understood. Different mechanisms have thus been advanced, see [336] and [337] for a deeper review. It is accepted that microcrack tips constitute preferential sites for hydrogen absorption. Until a certain local hydrogen concentration at the crack tip, the precipitation of hydride becomes energetically favourable [338]. As the hydride phase is highly brittle (its fracture toughness is around 1 MPa \sqrt{m} [338]), a cleavage crack propagates and the scenario is repeated in front of the new crack. Another mechanism consists in considering that hydrogen atoms located around the crack tip prevent dislocation emission or absorption, which suppress crack-tip blunting and ductile fracture while promoting cleavage fracture [336]. Whatever the considered mechanism, the metallic material fractures through brittle mechanisms due to the presence of hydrogen atoms. This is an important issue for hydrogen-containing structures such as pipelines [339] but also for hydrogen sensors, membranes and storage applications.

An extensive study of the effect of the internal stress and microstructure on the hydriding and hydriding kinetics of Pd thin films can be found in the thesis of Renaud Delmelle [29]. The chapter here will focus on these effects from a mechanical point of view.

8.2 Sample presentation and hydrogen cycles

As Pd is a good candidate to understand and anticipate the effect of hydrogen on its mechanical properties and reliability, some microtensile stages where hydrided prior to deformation at different hydrogen partial pressures. Five hydrogen partial pressures (0, 5, 15, 30 and 80 mbar) were chosen to cover the different phases of hydrided Pd, see figure 8.3. A partial pressure of 5 mbar ensures to be located in the α -phase while 80 mbar ensures to be in the β -phase. The intermediate partial pressures generate a mixture of α - and β -phases with a dominance of the α -phase for 15 mbar of H₂ and a dominance of the β -phase for 30 mbar. The mechanical measurements using microtensile testing devices were carried out after the hydriding cycle. This means that no hydrogen atom should be present in the films during the mechanical testing as the hydriding process is reversible [333]. Only the Pd film is influenced by the hydriding cycle as hydrogen can induce a change of the defect density. The actuator film behaviour is unaffected by the hydriding. Indeed, Si_3N_4 is an enabling material against hydrogen diffusion due to its inert behaviour with respect to hydrogen [333].

The piece of wafer containing unreleased microtensile stages was hydrided simultaneously with a cantilever beam covered by an unpatterned Pd film coming from the same Pd deposition batch. The internal stress variation during hydriding has been followed in-situ on this beam thanks to the experimental set-up presented in section 4.3. The unpatterned Pd sample was also used to characterize the hydriding effect by nanoindentation. For each hydrogen partial pressure, a new piece of this wafer was used.

The film used to study the effect of hydrogen on the mechanical properties of Pd was deposited at 1 Å/s by e-beam evaporation on a 5 nm-thick Cr adhesion layer. The film thickness was 400 nm. The internal stress of this as-deposited film was 420 MPa in tension, in good agreement with the thickness effect presented in table 4.1.

During hydriding, the internal stress of Pd is varying due to the volume expansion created by the absorption of hydrogen atoms and due to the constraining substrate. Indeed, when the Pd is in contact with hydrogen, a Pd hydride is formed, creating compressive stress in the Pd film, see section 8.1. The internal stress evolution during an hydriding cycle is presented in figure 8.4. Hydrogen is injected into the chamber at time 0 on the graph. When the first stress equilibrium is reached, the hydrogen is pumped. Then a second stress equilibrium is attained under vacuum. Finally, the chamber is vented by injecting air and a last stress equilibrium is reached. Note that the sample hydrided at a partial pressure of 80 mbar has probably not reached its equilibrium before the end of the measurement due to a very slow dehydriding kinetics. As said before, the dislocations created due to the high compressive stresses delay the dehydriding reaction. When comparing it with the curve of the film hydrided at 30 mbar, one can suppose a final stress plateau at around 640 MPa. The numerical values of the different plateaus reached during the hydriding cycles are listed in table 8.1.

The knowledge of the stress level of the final plateau is important for the mechanical properties extraction as the internal stress of Pd is directly related to its mismatch strain which enters into the equations. Here, the mismatch strain of the actuator has been taken constant for the five hydrogen partial pressures. The mismatch strain of the Pd film has been calculated based on



Figure 8.4: Internal stress evolution of the Pd film during and after the hydriding cycle. Hydrogen has been injected into the chamber at t = 0 and was removed at the moment indicated by the blue squares. Air was injected into the chamber at the time indicated by the respective arrows.

	σ_{int} at the H ₂ plateau (MPa)	σ_{int} at the final plateau (MPa)
0 mbar	/	420
5 mbar	135	370
15 mbar	-105	405
30 mbar	-830	600
80 mbar	-880	640 (extrapolated)

Table 8.1: Summary of the different stress equilibriums reached by the Pd films for hydriding cycles performed at different hydrogen partial pressures.

the internal stress value of the final plateau which differs for each sample, see table 8.1.

8.3 Effect of hydrogen effect on the strength, the strain hardening and the ductility

The stress-strain curves, the evolution of the incremental strain hardening exponent and the evolution of the strain hardening rate are presented in figure 8.5. The numerical values of the different properties are listed in table 8.2. The subsections will successively discuss the effect of hydrogen on the yield stress, on the strain hardening and on the fracture strain.

8.3.1 Yield stress

An effect of the hydrogen partial pressure is observed on the yield stress, see table 8.2. When looking at the 0.2% criterion, the yield stress first decreases when the hydriding pressure increases from 0 to 5 mbar. Then, the yield stress begins to increase when increasing further the hydrogen partial pressure up to 80 mbar. When using the tangent modulus approach, this trend is not observed. But as discussed before in section 1.2.1, the definition of a valid criterion to quantify the yield stress is not obvious in materials presenting a long elasto-plastic transition. In each case, the yield stress is higher than the internal stress found after the hydriding cycle.

Figure 8.6 shows the link between the yield stress at 0.2% offset strain and the final internal stress in the film after hydriding. A linear relation links the final internal stress in the films and the related yield stress.

Nanoindentation was made in parallel with the microtensile testing method. Results are presented in figure 8.7. A small decrease of the hardness is observed.

	0 mbar	5 mbar	15 mbar	30 mbar	80 mbar
σ_0 (MPa)					
0.2% offset strain criterion	575 ± 49	500 ± 41	575 ± 49	700 ± 60	750 ± 63
Tangent modulus approach	772 ± 66	625 ± 52	700 ± 60	710 ± 61	700 ± 59
σ_{int} at final plateau (MPa)	420 ± 20	370 ± 30	405 ± 30	600 ± 40	640 ± 45
ε^f maximum (/)	0.081	0.0794	0.0704	0.0555	0.0357
$\Theta_0 (\text{GPa})$	~ 110	~ 80	~ 75	~ 75	~ 75

Table 8.2: Summary of the properties extracted using on-chip microtensile testing on the five different pieces of wafer hydrided at different hydrogen partial pressures.



Figure 8.5: Mechanical behaviour of one 400 nm-thick Pd film hydrided at different hydrogen partial pressures (0, 5, 15, 30 and 80 mbar). The films have been deposited at 1 Å/s on Cr. (a) Stress-strain curves. (b) Evolution of the incremental strain hardening exponent involving the Considère's criterion. (c) Evolution of the strain hardening rate.



Figure 8.6: Evolution of the yield stress defined at 0.2% of strain as a function of the internal stress in the Pd film after the hydriding cycle.



Figure 8.7: Effect of hydriding on the Young's modulus and hardness of Pd thin films. The indentation strain rate was 0.01 s^{-1} and the indentation depth range considered is between 25 and 50 nm.

The hardness and the yield stress are linked through the Tabor's law. The difficulty here is to choose the most correct criterion for the yield stress definition as it influences the yield stress evolution upon hydriding. Two scenarios will be thus considered for discussion. First, the nanoindentation results will be compared with the evolution of the yield stress defined at 0.2% offset strain. Then, the same nanoindentation results will be put in parallel with the yield stress evolution obtained using the tangent modulus approach.

First scenario: σ_y at 0.2% strain versus hardness

When comparing the hardness evolution with the yield stress at 0.2%, the results do not exactly present the same effect of the hydrogen partial pressure on the two linked properties, see figure 8.8.

As said before, two phases of palladium hydride exist. The α -phase, which appears at low hydrogen partial pressure, involves only a small level of compressive stress. The film hydrided at 5 mbar is lying in this α -phase regime during the hydriding cycle. An interesting point is that both the yield stress at 0.2% offset strain and the hardness present a slight decrease when the most part of palladium hydride created during hydriding is of an α -phase type, see figure 8.8. When increasing further the pH₂, an equilibrium of α and β -phase is created in Pd during hydriding, and the results of nanoindentation and microtensile testing start diverging.

If one assumes that the criterion at 0.2% of strain makes sense in the present work to define the yield stress, an interpretation of the observed evolution of σ_y can be advanced. When the Pd film is hydrided in the α -phase, Li and Chang reported that hydrogen atoms absorb at the low energy sites existing at grain boundaries [329]. The nanocrystalline Pd films studied here present a highly



Figure 8.8: Comparison of the evolution of the hardness and of the yield stress defined at 0.2% offset strain, as a function of the hydrogen partial pressure in contact with Pd during the hydriding cycle.

heterogeneous microstructure, see chapters 5 and 6. The hydriding in the α phase can thus be seen as a mean to relax the local strain gradients present in the film without the creation of any defects like for instance dislocations. If the hydrided film is less heterogeneous, its elasto-plastic transition will be smaller and its apparent yield stress will decrease.

By hydriding at higher hydrogen partial pressure, the $\alpha \rightarrow \beta$ phase transformation becomes important, generating dislocations due to the abrupt volume change [340, 341]. The nucleation and glide of these new dislocations promote the hardening in the β -phase regions [342]. This, in turn, leads to an increase of the yield stress, as observed in figure 8.6. The increase of the yield stress when the pH₂ increases is in good agreement with the literature [340]. However, the evolution of the hardness and of the yield stress are different. The different behaviours may be due to the different loading conditions between uniaxial tensile loading and nanoindentation where the film is deformed in compression with a complex configuration.

The yield stress and the hardness are thus affected by the extent to which the miscibility gap of the two hydride phases is traversed. Nevertheless, the hardness evolution is not in agreement with what is reported in the literature [340,342] but it will be discussed in the second scenario below.

Second scenario: σ_y extracted via the tangent modulus approach versus hardness

If one considers the tangent modulus approach as more appropriate to define the yield stress of Pd thin films after hydriding cycles, the comparison of these results with the hardness measured by nanoindentation gives a better similarity, see figure 8.9. However, as said before, a decrease of the yield stress (or



Figure 8.9: Comparison of the evolution the hardness and of the yield stress defined using the tangent modulus approach, with the amount of hydrogen in contact with Pd during the hydriding cycle.

respectively of the hardness) is not expected from what is reported in literature [340,342]. This discordance of the present results as compared to the literature has not yet been elucidated, especially since the decrease of the hardness upon hydriding as been systematically observed on our Pd samples [343,344].

At this point, the assumption made before that all hydrogen atoms escape from the Pd film upon dehydriding can be reevaluated. Indeed, Barnoush and Vehoff observed a reduced activation energy for the onset of plasticity during in-situ testing due to the dissolved hydrogen atoms [337]. In their study, 'in-situ testing' means that the mechanical test was performed on the material during its hydriding. It can thus be considered here that the reduction in yield stress and hardness after hydriding is caused by the presence of remaining hydrogen atoms in the Pd lattice. Cizek et al. have observed the presence of vacancylike open-volume defects in nc Pd deposited by sputtering [345]. This has been characterized by positron annihilation. The vacancy-like defects at GB act as trapping sites for hydrogen atoms. It will thus not be surprising to find such kind of defects in the Pd films of this work. These preferential trapping sites will probably affect the dehydriding process as it is favourable for the Pd host lattice to keep the hydrogen atoms in that sites.

The way to determine the more pertinent criterion to use for the definition of the yield stress remains however uncertain in this work but the tangent modulus approach provides a yield stress evolution in agreement with the nanoindentation results.
8.3.2 Strain hardening

The strain hardening capacity is also affected by hydriding. The two films containing a high concentration of β -phase during hydriding, i.e. 30 and 80 mbar, present a much smaller strain hardening exponent, see figure 8.5(b). This is related to the dislocation density increase during the $\alpha \rightarrow \beta$ phase transformation. As observed in [278], after hydriding at high pH₂, the dislocation density in Pd increases and the twin boundaries are loosing coherency. In chapter 5 and in section 6.3, it has been shown that the blocking effect against dislocation motion of the TBs is loosing its efficiency when loosing coherency. These observations confirm that the $\alpha \rightarrow \beta$ phase transformation leads to a decrease of the strain hardening capacity due to a loss of TB coherency during the hydriding.

Beside an increase of the dislocation density and a loss of the TB coherency, hydriding at pH_2 beyond the hydride phase transformation can lead to the emergence of a new crystallographic arrangement of the Pd atoms in specific regions [278]. These results were obtained by colleagues working on similar Pd films and can thus be considered as representative of the hydriding process of the present Pd films. More specifically, these authors observed a transformation from the FCC atomic arrangement to a 9R phase due to the dissociation of the $\Sigma 3$ {112} incoherent twin boundaries² into two phase boundaries bounding a 9R phase [278]. During hydriding, this dissociation appears energetically favourable. The fact that these 9R regions remain after hydriding is not obvious but has been attributed in [278] to the strong presence of newly nucleated dislocations which prevent the reverse phase transformation (9R \rightarrow FCC). The role of these remaining 9R regions in the Pd films on their mechanical response remains unclear.

Another interesting point concerns the shape of the incremental strain hardening curve, see figure 8.5(b). Only the curve extracted on an unhydrided sample presents two maxima. As detailed in section 6.4.2, the first maximum is expected to originates from the elasto-plastic transition while the second has been attributed to the interaction between twin boundaries and dislocations. When hydriding at 5 or 15 mbar, the elasto-plastic maximum is absent due to the hypothesis made previously that the film is more homogeneous once hydrided at small pH₂. But the incremental strain hardening of these two films is still high as the $\alpha \rightarrow \beta$ phase transformation has not yet occurred markedly, leaving the TBs almost perfectly coherent. This is not the same for the two films hydrided at higher pH₂ (30 and 80 mbar). Indeed for these films, in addition to present a reduced elasto-plastic transition, their TBs can be considered

 $^{^{2}}$ The presence of incoherent twin boundaries has been observed in the Pd films studied in this work. Incoherent twin boundaries are bounding the coherent twin boundaries that stop inside the grain, see section 4.4.2.

as incoherent due to the high amount of dislocation activity during the $\alpha \to \beta$ phase transformation.

Some authors reported a monotonic increase of the strain hardening capacity with the hydriding of Pd [340,342]. However, the palladium studied here presents a completely different microstructure with nanocrystalline grains and nanoscale twins. The plastic deformation mechanisms are thus incomparable.

The initial strain hardening rate is decreasing when the hydrogen partial pressure is increasing, see table 8.2. Most of the decrease occurs during the first stages of hydriding, i.e. in the α -phase. This indicates that the elasto-plastic transition of the hydrided films is reduced as compared to the unhydrided sample. This validates the advanced explanation concerning the observation of a decreased yield stress when hydriding at 5 mbar. Moreover, if one assume that most of the heterogeneity leading to a long elasto-plastic transition is due to the non-equilibrium grain boundaries and that hydriding can decrease this heterogeneity, it is logical to find this effect when hydriding in the α -phase. Indeed, hydrogen atoms absorb preferentially in grain boundaries when an α -Pd hydride is formed. By increasing the hydrogen partial pressure, some β -phase is created and hydrogen atoms then absorb in the grain interior but without affecting the heterogeneity of the palladium.

A reduced heterogeneity of the films will facilitate the definition of the yield stress. It is observed here that by increasing the hydrogen partial pressure, the difference between the yield stress defined using the 0.2% offset strain criteria and the yield stress defined using the tangent modulus approach is decreasing. It can thus be expected that the 0.2% offset strain criterion, which is usually problematic for materials presenting a long elasto-plastic transition, will become progressively more pertinent when the Pd films are exposed to a higher hydrogen partial pressure. In the previous section, the more correct definition of the yield stress should thus be given by the tangent modulus approach.

It is worth noting that only a few studies can be found in literature on the influence of hydriding on the hardening evolution of nanocrystalline materials, and more especially of nc Pd. Indeed, in most cases, indentation was used to investigate the hydrogen effect on the hardness. But indentation does not easily provide information about the strain hardening behaviour.

Finally, note that anisotropic hardening effect related to the fact that the phase transformation would take place along preferential crystallographic orientations can also contribute to locally change the Pd microstructure.



Figure 8.10: Evolution of the fracture strain with the hydrogen partial pressure as measured using the on-chip microtensile testing method.

8.3.3 Fracture strain

A marked decrease of the fracture strain is observed when increasing the hydrogen partial pressure, see figure 8.10 and table 8.2. The Considère's criterion is only fulfilled for the non-hydrided film. This is in agreement with the low strain hardening capacity of the films hydrided at high hydrogen partial pressures. The last point of the non-hydrided film in figure 8.5(b) is lying behind the Considère's line. This is not surprising as the Considère's criterion was established for materials presenting a strain rate sensitivity exponent m equal to 0, which is not the case for the Pd films studied here. It can also be due to the fact that the localization mechanism is different than the one envisaged by Considère.

On the contrary to the strain hardening evolution upon hydriding, the effect of hydrogen on the fracture strain has been widely studied due to the industrial interest to understand and to circumvent the problem of hydrogen embrittlement of metals.

The fracture strain evolution decreases slowly at low pH_2 and then more rapidly when the $\alpha \rightarrow \beta$ phase transition occurs importantly, see figure 8.10. As said before, this can be related to the segregation of hydrogen atoms in front of micro-crack tips during hydriding. The hydrogen atoms modify the fracture mode from ductile to brittle fracture in those regions, and increase the length of the micro-cracks. This is thus expected that once the hydrogen atoms left the Pd lattice, the films hydrided at high pH_2 exhibit a lower fracture strain as the micro-cracks content is more important and as the micro-cracks have been opened due to the hydrogen presence. This fracture strain reduction has been widely observed in literature, see e.g. [338, 339, 346, 347]. A proposed solution to limit this embrittlement due to hydriding is to alloy Pd with other metallic atoms like Ag or Cu [4,334]. Note that as exposed in the previous section, the presence of some 9R-phase regions after hydriding at high pH_2 can maybe help to explain the reduced fracture strain of hydrided Pd films.

8.4 Effect of hydrogen on the relaxation behaviour of Pd

The second part of the work on the hydrogen effect on the mechanical properties of Pd thin film focuses on the rate dependent properties. As presented in chapters 1 and 7, nanocrystalline and nanotwinned materials present an enhanced rate sensitivity as compared to their coarse grained counterparts. As hydrogen cycling induces the creation of defects in the Pd lattice, the scientific interest is obvious to study the impact of the pH_2 during hydriding cycles on the activation volume and on the strain rate sensitivity of the Pd films studied in this thesis. This section will thus broaden the results presented in chapter 7 where different film microstructures were investigated. Both nanoindentation and microtensile testing stages were used to assess the rate sensitivity of Pd thin films after different hydriding cycles.

The relaxation study has provided the evolution of the stress and strain state in different Pd beams with the time. For each hydrogen partial pressure, the evolution graph was recorded. For a sake of clarity, the raw results are shown in appendix E instead than here. From the stress-strain curves presented in figure E.1 in the appendix, the activation volume and the strain rate sensitivity exponent have been calculated. The results are shown in figures 8.11 to 8.15 for the different hydrogen partial pressures. Note that the figures for the nonhydrided film have already been presented in section 7.2 but are presented again is this section. Here, attention is paid to the activation volume. The same results can be represented in terms of the strain rate sensitivity. They are located in figure E.2 of appendix E.

When looking at the evolution of the activation volume versus the elapsed time, no clear effect of the plastic pre-deformation level is visible. To highlight this effect, one has to consider the same curves plotted versus the relaxed plastic strain amount, see figures 8.11 to 8.15. Whatever the hydriding cycle, it is clear that the most pre-deformed beams can sustain a lower activation volume over a spreader range of plastic deformation. As said before, the number of newly nucleated dislocations is proportional to the plastic strain amount during deformation. When several dislocations are present, an increased amount of relaxation can be brought by these dislocations. When only a small amount



Figure 8.11: Activation volume evolution as a function of time and of the relaxed plastic strain amount for a Pd film without hydriding cycle. The curves of different beams pre-deformed before relaxation at different level of plastic strain are superposed.



Figure 8.12: Activation volume evolution as a function of time and of the relaxed plastic strain amount for a Pd film hydrided at 5 mbar. The curves of different beams pre-deformed before relaxation at different level of plastic strain are superposed.



Figure 8.13: Activation volume evolution as a function of time and of the relaxed plastic strain amount for a Pd film hydrided at 15 mbar. The curves of different beams pre-deformed before relaxation at different level of plastic strain are superposed.



Figure 8.14: Activation volume evolution as a function of time and of the relaxed plastic strain amount for a Pd film hydrided at 30 mbar. The curves of different beams pre-deformed before relaxation at different level of plastic strain are superposed.



Figure 8.15: Activation volume evolution as a function of time and of the relaxed plastic strain amount for a Pd film hydrided at 80 mbar. The curves of different beams pre-deformed before relaxation at different level of plastic strain are superposed.

of dislocations are available for relaxation, the activation volume increased sharply and little amounts of plastic strain are relaxed. This observation is directly related to the experiments presented in section 7.1 where the dislocation density is decreasing upon relaxation, increasing the distance between pinning points of dislocations, and thus also the activation volume needed to impede the dislocations from the obstacles.

The best graphical representations to clearly interpret the hydrogen effect on the time dependent properties of Pd thin films are the activation volume area versus the elapsed time (see figure 8.16), and the activation volume versus the relaxed plastic strain amount for beams deformed at similar initial plastic strain (see figure 8.17).

Figure 8.16 collects the activation volume evolution areas for the different hydrogen partial pressures. Two information emerges from this graph. First, the vertical width of the activation volume measured soon after the deformation of the beams is decreasing when exposing the films to hydrogen. A smaller activation volume means that the material is more sensitive to relaxation. This can be related to the microstructure modifications during the hydriding.

The second information comes from the way the activation volume increases. When the hydrogen partial pressure increases, a higher dislocation density is present in the films before the release step, and by extension, one can assume that a higher dislocation density will also be present in the film after the deformation. It can be conclude from this graph that the higher is the initial dislocation density prior to relaxation, the faster is the increase of the activation volume. As a matter of fact, if the film contains a higher dislocation



Figure 8.16: Comparison of the activation volume evolution in different Pd films submitted to different hydriding cycles.

density, its microstructure is departing from the equilibrium which induces an accelerated kinetics for the dislocations to escape.

It can be noted that the initial plastic strain range of the samples hydrided at different partial pressures is almost similar except for the film hydrided at 80 mbar, see figures 8.11 to 8.15. Figure 8.17 compare the amount of relaxed plastic strain and the related activation volume evolution for Pd beams hydrided at different pH₂ but initially deformed with a similar level of plastic strain. At low pH₂, the beams relax a smaller amount of plastic strain before the sharp increase of the activation volume than the non-hydrided film. When the film has been hydrided at 30 and 80 mbar, the Pd beams can sustain a low activation volume over a spread range of relaxed plastic strain. But, as no plastic strain recovery seems to affect the microstructure of deformed Pd (see section 6.7), it should have been more pertinent to compare the films in terms of initial accumulated plastic strain to include both the plastic strain coming from the hydriding cycle and the plastic strain coming from the deformation of the Pd beams.

Nanoindentation at different strain rates was performed on the same samples hydrided at 0, 5 and 30 mbar to extract their strain rate sensitivity coefficient, see figure 8.18. The strain rate sensitivity exponent is equal to 0.048, 0.020 and 0.022 for the films hydrided at 0, 5 and 30 mbar respectively, see figure 8.19. These values are much lower than the values found using the microtensile testing stage, see figure E.2 in the appendix. This is not surprising as



Figure 8.17: Evolution of the activation volume as a function of the relaxed plastic strain for beams hydrided at different pH_2 and initially deformed at a plastic strain of around (a) 0.0012 and (b) 0.03.



Figure 8.18: Extraction of the strain rate sensitivity coefficient by nanoindentation. The strain rate sensitivity coefficient is equal to the slope of the plot on the graphs.

the two testing methods are different and does not impose the same loading configuration neither the same loading rate. Furthermore, it has been reported in the literature that the strain rate sensitivity is higher when the initial loading rate increases [321]. The initial loading rate is much higher for the on-chip microtensile method than for nanoindentation. Nevertheless, the evolution of m found by nanoindentation confirms the trend observed using the microtensile stages. As m and V_{act} are inversely proportional, an increased V_{act} upon hydriding is similar to a decreased m upon hydriding.



Figure 8.19: Influence of the hydriding cycle on the strain rate sensitivity measured by nanoindentation.

8.5 Conclusion

The effect of hydrogen on the mechanical properties is poorly documented in literature. The existing studies most often reported qualitative results and pained at interpreting it quantitatively. This is due to difficulties in exploring the plastic deformation mechanisms and interactions with hydrogen locally. Indeed, even environmental TEM is difficult to interpret due to the local heating induced by the electron beam and due to the high hydrogen fugacity.

Unfortunately, no microscopy analysis was made on the samples used for the hydrogen effect measurements in this work. Some useful observations could be made. For instance, the GB structure could be closely investigated and compared for different samples subjected to different hydrogen partial pressures, and submitted or not to the phase transformation. Also the dislocation density in the grain interior and the TB coherency should be an interesting information regarding the yield stress and the hardening evolution upon hydriding. A last point that should be investigated in more details is the link between the pH₂ and the presence of remaining 9R-phase in the hydrided Pd films and the role of this 9R-phase on the mechanical properties of Pd.

To summarize the results observed in this chapter, the hydriding of the sample prior to testing influences:

- negatively the yield stress if the tangent modulus approach is accepted at the best way to define the yield stress, but the inverse conclusion is observed when looking at the yield stress defined at 0.2% offset strain,
- negatively the strain hardening,
- negatively the fracture strain,
- positively the strain rate sensitivity and thus the mechanical stability.

This means that industrial systems dealing with hydrogen will benefit from an enhanced stability at the expense of the ductility. Some improvement routes have been proposed in the literature. For instance, alloying Pd with Ag leads to circumvent the degrading effect of hydrogen on the mechanical properties of the alloy [335].

Finally, one has to keep in mind that most studies do not systematically focus on the size effect related to hydriding although an effect of the grain boundary density has been established during hydriding. This requires a critical mind when comparing the results with the literature data.

_____ Part IV _____

Conclusion

The objective of this thesis was to study the deformation and the relaxation mechanisms of nanocrystalline Pd thin films and to link it with the microstructure of the films in order to be able to propose routes to improve the mechanical properties of such small scale materials. For that, on-chip microtensile testing stages were used to investigate the mechanical properties. Coupled microscopy studies have been performed to understand deeper the underlying mechanisms.

The state-of-the-art related to this work has been presented in chapters 1 and 2. The first chapter has reviewed the theory of thin films, the mechanical properties of nanocrystalline materials and their specific deformation mechanisms. The second chapter has provided an overview of the different testing methods available to characterize the mechanical properties of thin films.

Chapter 3 has presented in details the concept of the on-chip testing method used in this thesis. This method has proved to be useful to mechanically characterize free-standing thin films. Beside it, nanoindentation was also used as an alternative testing method in order to generate similar results for a sake of comparison. The very easy use of nanoindentation is a huge advantage of this technique. Moreover, it was compatible with the samples prepared for onchip testing and, thus, did not require additional time to prepare new samples for this supplementary testing method.

In addition to some basics about Pd, the experimental set-up used for the insitu monitoring of the internal stress evolution during hydriding and annealing cycles was briefly exposed in chapter 4. In this chapter, the as-deposited microstructure of Pd films deposited under various conditions and configurations was also characterized extensively by advanced microscopy methods. All the Pd films were deposited by e-beam evaporation. This deposition method induces a film microstructure presenting a columnar morphological texture with a grain diameter of ~ 30 nm. Around 25% of the nanograins contain coherent growth twins. A slight (101) fiber texture was observed and no clear dislocation activity was detected in the as-deposited state. Thanks to the high vacuum evaporation process, no impurities were found in the Pd films. Moreover, the intrinsic nature of Pd leads to the absence of an oxidized surface on the films. Increasing the deposition rate increases the twin density as well as the initial dislocation density. Annealing was performed to vary the grain size of the films, but no effective grain growth was observed in Pd films clamped to the Si substrate. Note that when using thin FIB thinned Pd samples, grain growth appears during heating due to the absence of the confining environment.

The thickness effect on the time independent mechanical properties has been studied and modelled using a semi-analytical grain aggregate model in chapter 5. Three ingredients explaining the high strain hardening observed have been envisaged: the presence of a long elasto-plastic transition, the loss of coherency of the twin boundaries and the presence of a confining layer under the Pd beams. These ingredients were integrated into the model which was able to capture the thickness effect observed experimentally.

To enrich the understanding and reevaluate some assumptions made to justify the results of chapter 5, new Pd films with different twin densities, with and without confining layer have been studied in chapter 6. Other parallel investigations were also performed to improve the understanding of the time independent results. First, it is observed that the thickness effect is systematically observed. Some X-ray diffraction experiments under a synchrotron beam have validated the assumption of a long elasto-plastic transition during the deformation of Pd. Then, intense dislocation activity after deformation was detected and the interaction mechanisms between dislocations and TBs have been understood using HRTEM analysis. An increased twin density yields to smaller yield stress and hardness, but leads to an increased strain hardening behaviour and consequently an improved ductility. It is thus favourable to increase the deposition rate for the improvement of the time independent results. The removal of the confining layer is also beneficial to increase the ductility. Similar effect is also observed when confining both sides of a thicker Pd film. No microtensile testing was feasible on annealed Pd films. The effect of the grain size was thus impossible to analyse. But an exploratory study by nanoindentation has indicated a smaller hardness after annealing at 200°C. Finally, reversible loadings were performed and established the absence of plastic strain recovery and the preliminary results show a small Bauschinger effect. To sum up, the best configuration to improve the strength-ductility-strain hardening of the Pd, is to deposit the film at high rate on Ti to avoid the presence of a confining layer. An annealing or a long ageing time are not valuable for these mechanical properties.

Then, the relaxation behaviour and the strain rate sensitivity of the Pd films were considered in chapter 7. In-situ HRTEM relaxation experiments using on-chip tensile stages have revealed that the relaxation was based on dislocation mechanisms, in agreement with the measured activation volume. Ex-situ studies were brought to look at the impact of different Pd configurations on the rate sensitivity. An increased twin density in addition to an increased dislocation density leads to an initially higher rate sensitivity as supported by nanoindentation. But after some days of relaxation, these increased densities lead to a faster increase of the activation volume with time which favours the mechanical stability over time. When the film presents only free surfaces, the kinetics for the dislocation-based mechanisms is highly delayed. Moreover, less dislocations are expected to be present and to contribute to relaxation which limits the amount of plastic strain that can be relaxed by the system. Then, annealing was observed as positive to reduce the rate sensitivity of the Pd films. The effect is similar on old samples after long ageing times. The ideal configuration for an optimal mechanical stability is to produce a Pd film deposited at high rate on Ti to avoid a confining layer and to add a small annealing at 200°C to recover the initial defects.

Finally, to come back to the initial motivation that has opened the study of Pd thin films, the effect of hydrogen on the mechanical properties has been investigated in chapter 8. Films exposed to five different hydrogen partial pressures were compared in order to cover the different Pd hydride phases before the mechanical tests. The higher the hydrogen partial pressure, the higher the yield stress but the lower the strain hardening capacity and the lower the ductility. However, the mechanical stability of the films increases with the hydrogen partial pressure. Hydriding is thus detrimental for the strain hardening and the ductility, but is interesting from a mechanical stability point of view.

This thesis concerns only the study of pure Pd films deposited by e-beam evaporation. This limits the possibilities to improve the properties. A perspective to increase the range of promising microstructures could be to alloy the films and to use other deposition techniques such as sputtering.

The use of adapted testing methods is also very important to investigate different properties. None of the existing techniques are ideal. However, a smart combination of them can circumvent their different limitations. In an ideal world, the best technique that can be conceived should be in-situ compatible with quantitative uniaxial loading of free-standing material while being processed easily with the co-fabrication of the sample.

To conclude, when working on nanoscale materials, it is important to stay as systematic as possible and to maintain the experimental conditions as similar as possible between samples. Indeed, too many factors can influence the results (e.g. the ageing time) and can confuse the interpretation of the results. Furthermore, this thesis highlights the importance to couple mechanical testing with microscopy to unravel the deformation mechanisms.

Appendix **A**

From single crystal plasticity to polycrystal formalism

This appendix aims at recalling some crystal plasticity notions and the formalism proposed in the literature to predict the behaviour of a polycrystal based on the single crystal plasticity theory. This section is inspired, among others, from [82]. The use of the crystal plasticity formalism was initially justified as, at room temperature, classical coarse grained metals predominantly deform by dislocation slip on specific crystallographic planes ({111} planes for FCC materials) and directions (<110> directions for FCC materials)¹. Their shear strength is thus determined by the resistance to dislocation motion.

In a single crystal, the plasticity theory is able to predict the onset of plastic deformation based on the shear stress resolved on the different slip systems of the crystal. If in one particular direction, the shear stress exceeds the critical resolved shear stress τ_c of a slip system, dislocations start gliding. In a more general point of view, the force that acts on the dislocation line is assumed to be the resolved shear stress. The components of the stress which are perpendicular to the slip plane do generally not contribute to the driving force for dislocation glide (except for instance in BCC crystals). This leads to the definition of the Schmidt factor m_s as:

$$\sigma_0 = \frac{\tau_c}{m_s},\tag{A.1}$$

where σ_0 is the tensile yield strength. For uniaxial tension, the value of m_s is

 $^{^{1}}$ The combination of one slip plane and one slip direction is defined as a *slip system*

comprised between 0 and around 0.5.

For polycrystals, different methods have been used to calculate the stress needed to deform plastically the grain aggregate. In a polycrystal, the yield stress is defined as the stress needed to activate slip in each grain simultaneously. Some methods are based on the same concept of τ_c but with the difference that the grains present different orientations with respect to the applied load. This means that the resolved shear stress in the most favourable slip planes varies from one grain to another. The Schmidt factor m_s is thus different in each grain.

A first model has been develop by Sachs (1928) [82]. The idea is to consider the tensile response of a polycrystal as the orientation average of the least tensile resistances of the individual grains deformed separately. If the tensile plastic resistance σ is equal to m_{Sachs} multiplied by the shear resistance of the slip τ , see equation (A.2), one obtains $m_{Sachs} = 2.238$ for FCC materials. This value is considered as a lower bound of the tensile plastic resistance as this approach does not satisfy local equilibrium and compatibility between grains;

$$\sigma_0 = m\tau. \tag{A.2}$$

Another model, which is widely used, has been proposed by Taylor (1938) [82]. He made the hypothesis that the strain rate in each grain is exactly equal to the macroscopic strain rate. This condition is satisfied only if slipping can occur simultaneously on five independent slip systems in each grain. This is a compatibility condition but the model still neglects the elastic part of the strains and the interactions between grains. Equation (A.2) presents the relationship between the shear stress and the global yield stress, with M (called m in equation (A.2)) being the Taylor factor. This factor is an average of the proportionality factor between the tensile stress and the shear stress of a single crystal for all possible grain orientations [348]. More specifically, the Taylor factor is obtained numerically and is found equal to 3.06 for FCC isotropic materials subjected to uniaxial tension and to 1.65 for pure shear deformation. This factor is thus highly dependent on the solicitation mode [349]. Also, this formalism can only be used for materials for which the deformation mechanism is governed by dislocation glide.

Besides the Sachs and Taylor theories developed from single crystal plasticity, Von Mises (1913) has proposed another theory by considering the polycrystal as a continuum media. He built a yield criterion valid for complex 3D loadings and proposed to express the mechanical behaviour of materials in terms of equivalent stress and strain to render the material equivalent stress-strain curve independent to the loading conditions. It is thus possible to obtain the equivalent stress for pure shear and the equivalent stress for uniaxial tension. In that case, the proportionality factor m as defined in equation (A.2) is equal to $\sqrt{3}$.

For nanocrystalline materials where dislocation glide is not obviously the main deformation mechanism, the value of m is still under debate; $m = \sqrt{3}$ is generally found in the literature according to the von Mises yield theory [97, 115, 321]. However, some authors still use m = 3 for nanocrystalline metals, e.g. [350].

Appendix **B**

On the impossibility to test Pd films with different grain sizes

As explained in the section 6.6 of chapter 6, two routes were tested to modify the grain size and grain shape of the Pd grains. None of them succeeds. The problems and limitations are exposed here under.

First, to avoid a columnar structure, the deposition was made in several steps of around 50 nm. Some groups applied this method successfully [25]. Unfortunately, in the case of the microtensile testing method used here, the deposition by steps was not adapted. The weak point of the microtensile structures is the overlap between the actuator and the sample, see figure B.1. This weakness is still more critical when the films are deposited conformally, like the Pd here to ensure the compatibility with the lift off patterning. Thus, by depositing discontinuously with steps smaller than the overlap to overcome, the fracture of the Pd beam occurs in that area without enabling any mechanical properties measurement.

The second route tested to change the grain size was to perform annealing cycles of the microtensile stages before the release. Again, all the Pd beams



Figure B.1: Schematic view of one microtensile structure with its overlap constituting a mechanical weak point.

were broken at the overlap during the release. The reason of this weakness is probably due to the migration of atoms from the highly stressed region of the overlap to more stable regions during the heating. The heating provides enough energy to the atoms for their migration. No results allowing the study of the grain size effect on the mechanical properties were thus produced here for nanocrystalline Pd. Nevertheless, the results shown in section 4.4.5 demonstrate that annealing cycles up to 500°C will not induce grain growth in thin films clamped to a substrate. This second route envisaged to modify the grain size will thus never succeed even if the fabrication process is modified to avoid the presence of a weak point in the structure. Appendix C

Bauschinger effect: a prospective experimental study

This section will present the results obtained in collaboration with the group of Prof. Saif in the University of Illinois at Urbana-Champaign.

The Pd film studied was 150 nm thick and was deposited at 1 Å/s on Cr. The different process steps have already been described elsewhere [217] but were slightly different for the present case as described in figure C.1.

Different specimens were loaded, see figure C.2. Unfortunately, only two gave exploitable results. Both devices involved a Pd beam with a width of 50 µm. The stress-strain curve obtained with the first tensile device is shown in figure C.3. The sample broke at very small strain and was only deformed elastically. The silicon frame stiffness of this device has been calibrated to give a direct access to the evolution of stress during the tensile test. The linear slope of the elastic regime is equal to 114.5 GPa, in good agreement with the expected Young's modulus of Pd. However, what is surprising here is the fact that the Pd beam did not enter in a plastic regime despite the high stress level. This lack of plastic deformation is not understood.

The second tested device provides more expected results. Figure C.4 presents the related stress-strain curve. The stress axis should be considered with caution as it is dependent of the silicon frame stiffness which was calibrated using the first device. This other device was coming from the same batch but some variations in the etching of Si can always occur during the deep RIE.

During the first loading cycle, it can be observed from figure C.4 that the Pd beam enters into a plastic regime when the stress is equal to \sim 550 MPa.



Figure C.1: Schematic fabrication process: (a) Photoresist coating of the front face of a double side polished 190 μ m-thick Si wafer, (b) lift-off photolithography, (c) Pd deposition, (d) Lift-off acetone and deposition of Al on the back face. The pattern of the Al is a mirror of the front face without the sample part. (e) Photolithography and patterning of the Al layer by wet etching, and (f) deep Si etching from the back face using ICP deep RIE.



Figure C.2: SEM images of the device used to characterize the mechanical properties of Pd thin films. On the left, the device before testing. On the right, the sample after fracture.



Figure C.3: Mechanical results of a 150 nm thick Pd film deposited on Cr obtained using the tensile method developed in Saif's group. Results of the first device.



Figure C.4: Mechanical results of a 150 nm thick Pd film deposited on Cr obtained using the tensile method developed in Saif's group. Results of the second device.

Taking into account the low accuracy on the present stress measurement, one can say that it is comparable to what was found using our on-chip microtensile technique.

After a first loading until 1% of deformation, the device was partially unloaded. As a matter of fact, a very small amount of stress (around 30 MPa) was maintained in the Pd beam (see the yellow circle in figure C.4). After two hours, the deformation level was two times smaller, indicating that relaxation took place (see the green arrow). By further unloading, the end of the cycle was obtained and the Pd beam relaxed to the origin of the stress strain curve. More specimen tests are needed but it seems that a small Bauschinger effect and a relaxation under zero stress are present.

The second loading was performed and involves only a linear elastic response, see figure C.4. Unfortunately, the sample broke at a deformation level close to the maximum deformation reached during the first cycle. Owing to the linear behaviour of the second loading, the related expected yield stress must be higher than the yield stress of the first loading. This indicates that no plastic strain recovery took place between the two loading cycles. Indeed, the behaviour is far from what is observed in [108].

The observed fracture strain is very small (about 1%) and hinders to observe clearly the presence of a Bauschinger effect. This fracture strain is such that only a small part of the grains is deforming plastically. Indeed, the fracture strain here is much lower than what was observed using the on-chip microtensile technique on films with similar thickness, see table 5.1 on page 113. Note that the strain here is expressed in percent. Two explanations can support this weak fracture strain. First, the geometry of the Pd beam highly differs from the geometry of the Pd beams used for the on-chip microtensile testing. The width of the devices here ($\sim 50 \ \mu m$) is much higher that the width of the UCL microtensile testing stages ($\sim 1-2 \ \mu m$). The second explanation is that during the fabrication of the device, the Pd film has been in contact with a plasma environment during the deep RIE (see figure C.1 (f)). When preparing our on-chip tests, the Pd film deposition constitutes the last step of the process. This means that the film can be considered as unaltered by the process, which is not true for the Saif's devices here.

TEM was performed on other devices prepared using the same process as the devices used to generate the curves in figure C.3 and C.4. Plan-view observation was made prior to deformation on the 150 nm thick Pd film. Thanks to the design of the tensile test, direct TEM observation was possible without any sample preparation. However, due to the high thickness of the present Pd film, quantitative measurements of the microstructural details (grain size, twin density, ...) were impossible to perform. Some porosity was found in the

Appendix C. Bauschinger effect: a prospective experimental study



Figure C.5: *TEM micrograph showing porosity inside the Pd film after the plasma etching steps.*

Pd films (see figure C.5), which has never been observed on films processed for our on-chip testing stages. Nanoindentation was made on films that have been in contact with plasma and on unaltered as-deposited films, see figure C.6. No effect of the plasma is visible on the Young's modulus value. However, nanoindentation results confirm an effect on the hardness of Pd which increases when the film has been subjected to the plasma. The plasma seems to cause a strengthening of the Pd film coupled with an increased brittleness. Note that the thickness of the compared films is different and than a slight substrate effect can be expected for the thinnest film, i.e. the plasma treated film. The plasma can induce the heating of the Pd film surface and change locally the internal stress of Pd [351]. This can in turn degrade the homogeneity of the film and lead to an early fracture of the film. Note that the effect of the plasma cannot be compared to the effect of an annealing here as, besides inducing local heating of the film, the plasma also creates porosity inside the Pd film.

To conclude, the experiments performed using the Saif's devices were encouraging but not definitive. These experiments are necessary to explore the mechanical response of the films during unloading as well as strain rate effects, which cannot be addressed using our on-chip tensile method. However, improvements about the fabrication process should be made to prepare specimens presenting a higher fracture strain. For instance, the use of a protecting layer under the Pd structures will protect the metal from the plasma etching steps. Finally, a larger fracture strain would ensure to deform the Pd film beyond the elasto-plastic transition, and will thus provide more reliable insight about the possible Bauschinger effect and the absence of plastic strain recovery.



Figure C.6: Nanoindentation, performed on samples before or after a plasma treatment, shows an increase of the hardness when Pd was in contact with a plasma.

 ${}_{\text{Appendix}} \, D$

Adhesion layer effect - Time dependent additional results



Figure D.1: Strain rate sensitivity parameters of a Pd film covered on both sides by a Cr confining layer. The activation volume is presented as a function of the plastic strain and of the time while the strain rate sensitivity exponent m is only plotted versus the elapsed time.



Figure D.2: Strain rate sensitivity parameters of a Pd film initially covered on both sides by a Cr confining layer after the three steps release. The activation volume is presented as a function of the plastic strain and of the time while the strain rate sensitivity exponent m is only plotted versus the elapsed time.



Figure D.3: Strain rate sensitivity parameters of a Pd film covered on one side by a Cr confining layer. The activation volume is presented as a function of the plastic strain and of the time while the strain rate sensitivity exponent m is only plotted versus the elapsed time.



Figure D.4: Strain rate sensitivity parameters of a Pd film initially covered on one side by a Cr confining layer after the three steps release. The activation volume is presented as a function of the plastic strain and of the time while the strain rate sensitivity exponent m is only plotted versus the elapsed time.

 ${}_{\text{Appendix}} \, E$

Hydrogen effect - Additional curves



Figure E.1: Stress-strain curve evolution of samples hydrided at different hydrogen partial pressures.


Figure E.2: Evolution of the strain rate sensitivity exponent of differently hydrided samples.

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