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# Opto-electrical properties and internal stress in Al:ZnO thin films deposited by direct current reactive sputtering



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## ABSTRACT

In this work we study the effect of the oxygen concentration, deposition temperature, and post-deposition annealing on the optical and electrical properties of Al:ZnO thin films deposited by direct current (DC) reactive sputtering. The internal stress in the thin film is also monitored in-situ during growth with a multi-beam optical stress sensor. This latter technique allows to have an insight on the growth mechanisms. Coupled with an analysis of the discharge curve, the optical transparency, the electrical conductivity, and the chemical composition of the films as a function of the oxygen concentration and temperature during deposition, it allows to estimate what are the optimal deposition conditions to minimize the resistivity and maximize the transparency. The analysis of the internal stress is also of interest because it can be a source of premature fracture or delamination of thin films. The internal stress can also change the intrinsic properties of a thin film. The influence of the stress on the resistivity is therefore studied for samples deposited in the different sputtering regimes.

## 1. Introduction

Nowadays, transparent conductive oxides (TCO) are used on an industrial scale in several applications such as flat panel displays, glass coating and photovoltaics. [1] Indium-tin oxide (ITO) is still considered as the TCO with the best opto-electrical properties, but the cost and scarcity of indium will become problematic in the future. Aluminum-doped zinc oxide (AZO) is an interesting material for substitution of ITO because of the low cost of aluminum and zinc, and its non-toxicity. In addition, AZO is a material with a wide bandgap (3.3-3.8 eV) [2] allowing full transparency in the visible range, and a possible high doping inducing large charge carrier density and mobility, hence a resistivity around  $10^{-4} \Omega.cm[3]$ .

The difficulty for transparent electrodes is that two contradictory properties (electrical conductivity and optical transparency) must be combined. Indeed, in high bandgap materials, the electrical conductivity often comes from defects and impurities. These dopants often induce energy states that favor absorption, hence decrease the transparency. The free carriers in a material also limit the transparency because they favor reflection and absorption of light due to plasmons, at a frequency:[4]

$$\omega_P = \sqrt{\frac{ne^2}{m^* \varepsilon_r \varepsilon_0}} \tag{1}$$

To avoid having this plasmon frequency in the visible range, the charge carrier density must be kept under  $\sim 10^{21}$  cm<sup>-3</sup>. This corresponds approximately to the maximum possible doping in ITO and AZO. To increase the conductivity ( $\sigma = ne\mu$ ), the electronic mobility must therefore be maximized.

Metal thin films can also be used as transparent electrodes but their transparency is lower than in TCOs, because the minimum thickness needed to have continuous films already induces significant absorption. A promising material is therefore graphene because it combines a metallic behavior, high electronic mobility, and is thin enough to exhibit an excellent transmittance ( $\simeq 97.7\%$ ).[5] However, graphene production is still not mature enough contrary to AZO that is already used industrially.

To deposit AZO thin films, DC reactive sputtering has been chosen in this article because it has the advantage to be industrially scalable, and to allow low resistivity (on the order of  $10^{-4} \Omega$ .cm), high transparency ( > 95%), and low temperature deposition. Reactive sputtering is more difficult to control than non-reactive sputtering but is still interesting to deposit AZO thin films because it allows to finely tune the stoichiometry, which is of utmost importance for the opto-electronic

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**Fig. 1.** Description of the sputtering chamber. The samples are loaded in the deposition chamber through a load-lock. During deposition, the sample is rotated and can be heated with a radiative system. The chamber is also equipped with a Multi-beam Optical Stress Sensor (MOSS).

properties. Since sputtering is an out-of-equilibrium process, the kinetics of the reactions is very important and can be strongly influenced by temperature, which is also studied in this article. However, temperature can not always be controlled during deposition, therefore we also studied the impact of a post-deposition annealing and compared it with the effect of an in-situ heating during deposition.

In thin films technologies, internal stress can be problematic since it can cause premature fracture or delamination of layers. Controlling them is therefore important to ensure a good mechanical stability of samples. The evolution of stress is therefore studied in this article as a function of the oxygen concentration and temperature during deposition. Stress can also appear in applications such as flexible electronic. Therefore we measured the effect of an applied strain on the resistance of AZO thin films.

#### 2. Experimental method

AZO thin films were deposited by DC magnetron reactive sputtering in a chamber from AJA (description in Fig. 1), equipped with a turbomolecular pump with a maximum pumping speed of 315 l/s, calculated as the ratio between the gas flow and the pressure. The effective pumping speed can be decreased thanks to an automatic pressure control valve between the chamber and the pump. The base pressure in the chamber is around  $10^{-5}$  Pa before deposition, measured with a hotfilament ionization gauge. The gas flow of O2 and Ar are regulated by independent mass flow controllers. The pressure in the chamber during deposition is measured with a capacitance vacuum gauge and kept constant at  $2.7 \times 10^{-1}$  Pa. This type of gauge is used because it measures the pressure independently on the type of gas, which is interesting for reactive sputtering where different gases are used simultaneously, in variable proportions. To insure a good uniformity, the samples were rotated at 45 rpm and disposed at a relatively large sputtering distance (122 mm). AZO is deposited by sputtering of a two inch circular Zn<sub>98,68</sub>Al<sub>1.32</sub> target (99.99% purity) in a mixture of argon and oxygen, with a current fixed at 125 mA. The oxygen is introduced in the chamber through small holes at the level of the substrate and argon is introduced near the targets. The angle of incidence of the sputtering is approximately 40°. The chamber walls are grounded and the sample is kept at a floating potential. The temperature is changed by radiative heating and controlled with a thermocouple placed on the backside of the sample holder.

Internal stresses in thin films can be obtained from substrate curvature measurements, based on the well-known Stoney equation :

where  $Y_s = E/(1 - \nu)$  is the biaxial modulus of the substrate (182 GPa for silicon and 92 GPa for glass),  $h_s$  and  $h_f$  are the thickness of the substrate and the film, respectively, and h is the distance from the surface of the substrate.  $< \sigma_f >$  is the average stress in the thin film. Stoney formula is valid for thin films on thick substrates, and gives the stress in the thin film with no need to know its Young modulus.

The variation of curvature is measured in-situ, during the deposition, by an optical method. An array of  $3 \times 4$  parallel laser beams are sent and reflected on the sample front surface, and the reflection is captured by a CCD camera. To avoid noise from the plasma discharge, a band pass filter (660  $\pm$  4 nm) was mounted in front of the CCD camera. When the sample bends, the reflected beams are not parallel anymore and the distance between the spots in the camera changes and can be related to the variation of curvature. The position of the spots is defined as their geometric center (centroid), allowing to have a spatial resolution smaller than the size of one pixel. The variation in curvature is then used to calculate the stress in the thin film thanks to Stoney's formula. This technique is called Multi-beam Optical Stress Sensor (MOSS) and is described in Fig. 1.

Since the initial curvature of the substrate can vary locally, the curvature is always measured at the same position, at every rotation of the sample. The time resolution of this technique is about of 1.3 s (45 points per minute). The variation of curvature ( $\Delta \kappa$ ) of the sample is given by:

$$\Delta \kappa(t) = \frac{D(t) - D_0}{D_0} \cdot G,$$
(3)

where D(t) is the average distance between the centroids,  $D_0$  is the initial average distance between the centroids, and *G* is an optical parameter depending on the chamber geometry (0.68  $m^{-1}$  in our case). Because the lasers form a 2D mesh, the stress is measured in both inplane directions, with no visible difference, confirming that the deposition has a central symmetry.

From Eq. (2), when  $\langle \sigma_f \rangle \cdot h_f$  is plotted as a function of film thickness, its derivative is  $\sigma_{incr}$ , the instantaneous incremental stress in the film corresponding to the stress in the growing film and the relaxation of the stress in the whole film. Stress relaxation has been measured as being negligible in our experiments. Positive values of  $\langle \sigma_f \rangle \cdot h_f$  correspond to an average tensile stress. Curvature is measured as a function of time and needs to be converted as a function of film thickness to extract the incremental stress. The conversion of the time scale into a thickness scale is done assuming that the deposition rate is constant, as confirmed by a quartz-microbalance. The total thickness of the films is measured after the deposition by cross-sectional view in a Zeiss Ultra 55 field emission guns scanning electron microscope (FEG-SEM). The thickness (h<sub>f</sub>) and deposition rate (v<sub>dep</sub>) of the different samples are shown in Table 1.

Specular transmission (T) of the samples deposited on glass was measured with a spectrophotometer Specord 200 PLUS from Analytic Jena, for wavelengths between 300 and 1100 nm with a 1 nm resolution.

After deposition, X-ray diffraction (XRD) was performed to characterize the phase structure and orientation, with copper  $K_{\alpha}$  radiations in the  $\theta - 2\theta$  configuration.

Hall measurements were done to extract the charge carrier density and mobility, under a 0.55 T magnetic field (permanent magnet) in the van der Pauw geometry, with HMS-3000 from Microworld.

#### Table 1

Thickness  $(h_f)$  and deposition rate  $(v_{dep})$  of the samples deposited at room temperature and various oxygen concentrations (Top), and with 20% oxygen at various temperatures (Bottom).

$\begin{array}{c ccccccccccccccccccccccccccccccccccc$							
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	$O_2/(Ar+O_2)$ [%]	10	15	20	25	30	35
	h <sub>f</sub> [nm] v <sub>dep</sub> [nm/min] T [°C] h <sub>f</sub> [nm] v <sub>dep</sub> [nm/min]	343 22.1 20 328 10.1	347 19.7 60 334 9.0	337 15.7 100 325 8.1	333 9.3 140 328 7.1	339 6.9 180 355 5.2	384 6.0 220 355 4.4

Finally, chemical composition of the films was analyzed by inductively coupled plasma optical emission spectroscopy (ICP-OES) with a Varian 720ES, after being dissolved in an acidic solution, with an estimated error of 3%.

The parameters studied in this article are temperature and oxygen concentration, meaning that a series of samples was deposited at room temperature and various oxygen concentrations (AZO O) and a second series was deposited with 20% oxygen at various temperatures (AZO T). Each deposition was done on three types of samples at the same time:

- $2.5 \times 2.5 \text{ cm}^2$  squares of  $380 \,\mu\text{m}$  oxidized silicon substrates (300 nm SiO<sub>2</sub>) used for curvature measurements.
- $\bullet~1.25~\times~1.25~cm^2$  squares of 400  $\mu m$ -thick extra clear float glass used for optical transmission and Hall measurements.
- 1.25  $\times\,$  1.25  $cm^2$  squares of 380  $\mu m$  -thick silicon substrates used for SEM images and ICP-OES analysis.

Three samples have also been deposited at various oxygen concentrations on three inch oxidized silicon substrates. These substrates were bent during the resistance measurements to extract the piezoresistance coefficients.

## 3. Results and discussion

## 3.1. Reactive sputtering

In reactive sputtering of oxides the obtained results strongly depend on the regime (metallic, transition or oxidized) used during deposition. The type of regime depends on the competition between the oxidation of the target by the reactive gas and the ablation of the oxidized layer on top of the target by the plasma [6-8]. This competition is influenced by process parameters such as the partial pressures of oxygen and argon, and by the current applied on the target, but is also influenced by specifications of the chamber such as the dimensions of the target and the chamber, the disposition of gas injection, the pumping speed, etc. All these parameters are not always known and it is therefore of utmost importance to begin with the calibration of the target with a discharge curve (discharge voltage as a function of the applied current), to know the regime used for the depositions, and to be able to transpose the conclusions from one chamber to another one. Such a curve is presented in Fig. 2 for the Zn:Al target used here to deposit the AZO thin films, at 0.27 Pa, with a current of 125 mA. A first plateau is observed around 525 V between 0 and 10% oxygen, corresponding to the metallic mode where the target surface is metallic and the metal is oxidized on the surface of the sample. The increase of the observed deposition rate between 0 and 5% corresponds to the transition from the deposition of Zn:Al to AZO. A second plateau is observed at a voltage around 360 V, corresponding to the oxidized regime where the target is oxidized and an oxide is directly sputtered. The deposition rate decreases during this regime mainly because the argon is progressively replaced by oxygen that has a lower sputtering yield. Between these two regimes, the transition regime is observed with a monotonous decrease of the voltage and deposition rate. Contrary to what was observed for a pure Zn target in a previous publication [9], no peak in the voltage due to



**Fig. 2.** Discharge voltage and deposition rate measured in-situ with a microbalance, as a function of oxygen concentration in the plasma during sputtering, at 0.27 Pa, with a current of 125 mA.



**Fig. 3.** Discharge voltage (Top) and deposition rate measured in-situ (Bottom), as a function of the sputtering current, in the metallic regime (0% oxygen), transition regime (22.5%) and oxidized regime (66%). The total pressure is 0.27 Pa and the total flow  $(Ar + O_2)$  is 30 sccm.

adsorbed oxygen is observed in the beginning of the transition regime because the aluminum present in the Zn:Al target favors an oxidation of the surface instead of the adsorption of oxygen.

Fig. 3 is used as evidence to show the importance of the systematic use of the discharge curve to calibrate depositions by reactive sputtering instead of the sole process parameters. The black curve corresponds to the metallic regime (0% oxygen), the green curve corresponds to the oxidized regime (66% oxygen), and the red curve corresponds to an intermediate situation (22.5% oxygen). Depending on the current, pressure and other parameters of the sputtering chamber, this intermediate situation with a constant oxygen concentration can correspond to the metallic, transition or oxidized regime, leading to significantly different results. For this reason, all the depositions in this article have been performed at the same total pressure (0.27 Pa), same current (125 mA), and only the oxygen concentration or temperature have been changed.

## 3.2. Structural characterization and internal stress

The structural characterization of the thin films was done by SEM images of the cross-section and by XRD. The grain structure can be observed in Fig. 5, and XRD indicated that the structure of the AZO thin films was wurtzite with the *c*-axis oriented perpendicularly to the substrate (only the 0002 peak is visible). A small peak of metallic Zn



**Fig. 4.** XRD spectra of samples deposited at room temperature and various oxygen concentrations (Top), and at 20% oxygen and various temperatures (Bottom). The main peak of ZnO is (0002) at 34.5°. A small peak is also observable at 36.5° for the sample deposited at lowest oxygen concentration and is attributed to metallic Zn. The different spectra are shifted to increase the visibility. (For interpretation of the references to color in this figure, the reader is referred to the web version of this article.)



**Fig. 5.** SEM images of the cross section of different AZO samples, all at the same magnification. (Top) Deposited at room temperature at different oxygen concentrations. (Middle) Deposited at various temperatures, with 20% oxygen. (Bottom) Pieces of a sample deposited at room temperature, with 20% oxygen, and annealed for 15 min at different temperatures, under argon.

was also observed in the sample deposited with only 10% oxygen. No  $Al_2O_3$  peak was visible, indicating that if alumina is present, it is in an amorphous state. XRD spectra are shown in Fig. 4.

In general, if the sputtered atoms have a higher mobility they will induce larger grains than atoms sputtered with a low mobility because they will be able to diffuse at the surface during growth, allowing to decrease the concentration of defects and induce grain growth. Different parameters influence this atomic mobility on the surface of the sample during growth. First, temperature obviously increases the mobility of atoms since it increases their energy. It can indeed be observed in Fig. 5 that the grains are larger when the deposition temperature is increased. When a film is deposited at room temperature and annealed afterwards, a similar effect is observed at much higher temperature. A higher temperature is indeed necessary because in postdeposition annealing, the atoms are embedded in a 3D lattice, decreasing their mobility compared to atoms on a free surface. A second important parameter in reactive sputtering is that ZnO and Al<sub>2</sub>O<sub>3</sub> have a much higher melting point (1975 and 2054 °C, respectively) than Zn and Al (420 and 660 °C, respectively). This means that the homologous temperature  $(T/T_m)$ , hence mobility, of metallic atoms is much larger than for oxidized atoms. In the metallic regime, metallic atoms are deposited and oxidized on the surface of the sample. A higher oxygen concentration induces a faster oxidation of the atoms, hence a lower average mobility. In the oxidized regime, oxidized atoms are sputtered from the target and deposited on the surface of the sample, corresponding to a minimum mobility. It can be correlated to Fig. 5, where narrower grains are observed as the oxygen concentration is increased. At low oxygen concentrations, a nucleation layer can be distinguished, followed by columnar grains with a slightly increasing width as the film grows. In the oxidized regime, narrow columns are observed, without apparent grain growth over the whole thickness.

The monitoring of the internal stress during growth also allows to deduce information on the structure and growth mechanisms obtained in the thin films. The average stress achieved in AZO thin films deposited at room temperature and various oxygen concentrations, and with 20% oxygen and various temperatures is shown in Fig. 6. There are different possible origins of stress in thin films. The first are related to the growth of the grains. There is initially the creation of a nucleation layer, usually in compression due to surface tension. Then, there is coalescence and the grains attract each other, inducing tensile stress (zipping effect). Finally there is a partially epitaxial growth that propagates the tensile stress as the film grows. This propagation of tensile stress along the thickness of the film can be limited by atoms that diffuse at the grain boundaries (adatoms). Superimposed on these effects, peening can induce compressive stress due to the impact of the energetic particles. At high oxygen concentration, the incorporation of interstitial oxygen could be a source of compressive stress as well. At low oxygen concentrations, the presence of interstitial zinc could also induce compression. In a previous article about intrinsic ZnO [9], we observed tensile stresses in the transition regime (up to 340 MPa), and compressive stresses in the oxidized regime (down to -1.14 GPa) with a steep transition between those two regimes. Additionally to these tensile and compressive regimes, a lower absolute value of the stress was observed when the oxygen concentration was decreased. This was attributed to an increased mobility of atoms when there is less oxygen, allowing a limitation of the sources of stress. In this article we observe a similar trend for the metallic and transition regime: a slight tensile stress that increases up to a few hundreds MPa (520 MPa) when the oxygen concentration is increased in the transition regime. In the oxidized regime however, only a slight decrease of the tensile stress is observed, instead of a strong compression. We attribute this to the presence of substitutional aluminum, and probably nanoscopic alumina clusters, that induce tensile stress and compensate the peening effect. At high oxygen concentration, there are also probably amorphous grain boundaries. As the film grows, this amorphous part decreases and is replaced by denser, crystalline grains, as it is suggested by the stress



**Fig. 6.** (Top) Average stress in AZO thin films, as a function of oxygen concentration in the plasma. (Bottom) Average stress in the AZO thin films, as a function of the deposition temperature. The stress is shown at the end of deposition (before cooling, at  $T_{dep}$ ), and after cooling, at room temperature.



Fig. 7. Evolution of the product Stress  $\times$  Thickness as a function of the deposited thickness, for different oxygen concentrations (Top), and different deposition temperatures (Bottom). For the samples heated during deposition, the cooling down has been recorded to have the average stress at room-temperature.



**Fig. 8.** Charge carrier density and mobility (Top), and resistivity (Bottom) of AZO thin films as a function of oxygen concentration. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

gradient observed in Fig. 7 for the sample deposited with 50% oxygen. This induces a reduction of the free spaces and induces tensile stress [10] that also compensates the peening effect.

For the samples deposited at various temperatures with 20% oxygen, a transition from tensile to compressive stress is observed as temperature is increased. This can be explained by an increased incorporation of adatoms at the grain boundaries or even in the bulk of the grains as the temperature increases [11,12]. Due to the difference of thermal expansion coefficients between the AZO thin films and the silicon substrate, an additional thermal stress is observed after cooling down the sample (Fig. 6. Because the thermal expansion coefficient of AZO is lower than for Si, the cooling down induces tensile stress.

#### 3.3. Electrical properties

When reactive sputtering is performed in the metallic regime, the deposited thin film is not completely oxidized. As previously stated some metallic Zn clusters have been observed by XRD on the sample deposited with only 10% oxygen. These clusters act as dopants, leading to a high free electron density as shown in Fig. 8. These metallic defects however act as strong diffusion centers and limit the electronic mobility. When the oxygen concentration is increased these metallic defects decrease drastically (increase of the mobility), and the Al atoms still act as dopants (high electronic density). The high electronic density also allows an efficient screening of the defects, increasing furthermore the mobility. When the oxygen concentration is increased up to the oxidized regime, part of the aluminum forms Al<sub>2</sub>O<sub>3</sub> clusters instead of being in substitution in the Zn lattice [13]. In this configuration the aluminum does not act as a dopant (decrease of electronic density) but as a diffusion center, and the decreased electronic density leads to a poor screening of the defects (decrease of the electronic mobility). To obtain the highest conductivity, it is therefore important to work in the middle of the transition regime, where there is a minimum amount of metallic clusters and alumina, leading to a maximum charge carrier density and mobility, and thus a minimum resistivity.

When the deposition is done at room temperature, the sputtered atoms have a low mobility and the aluminum can not always be placed in substitution. In this situation the aluminum atoms do not always act as dopants. When the deposition is done at higher temperature, the dopants are activated and take part to the conduction as it can be seen



Fig. 9. Resistivity (Top), and charge carrier density and mobility (Bottom) of AZO thin films deposited on glass as a function of deposition temperature.



Fig. 10. ICP-OES analysis of the AZO samples for different deposition temperatures (at 20% oxygen), and different oxygen concentrations (at room temperature).

in Fig. 9. A doping of 1.32% (as in the Zn:Al target used here) leads to  $\sim 5.5 \times 10^{20}$  Al/cm<sup>-3</sup> similar to the maximum carrier density observed at 180 °C. This increase of the charge carrier density is also accompanied by a decrease of defects, leading to an increased mobility, and a decreased resistivity. However, thermal activation is not the only cause of the increased charge carrier density. When the temperature is increased, Zn has a tendency to re-evaporate more than Al, leading to an Al-enrichment at higher temperatures as shown in Fig. 10. This enrichment combined to a high temperature ( > 200°C) leads to the formation of alumina that decreases the charge carrier density and mobility, hence increase the resistivity. Heating at moderate temperature during deposition is therefore interesting to enhance the electrical properties. However it is not always technically possible and a post-deposition annealing can therefore be considered to replace the in-situ heating.

To investigate this, we annealed the samples deposited at different oxygen concentrations at various temperatures under argon atmosphere. The annealings have been done successively at increasing temperatures (from 100 to 700 °C, with steps of 100 °C) on the same piece of sample, for 15 minutes. Between each annealing, the resistivity, charge carrier density and mobility, and the optical transmission have been measured. As can be seen in Fig. 11, a post-deposition annealing at moderate temperature increases the electronic



**Fig. 11.** Charge carrier mobility (Top) and density (Middle), and resistivity (Bottom) of AZO samples deposited at various oxygen concentrations and annealed at various temperatures. The error bars represent the standard deviation of the measurements.

mobility and density, in a similar way as it was observed for an in-situ heating during deposition. When the annealing is done at high temperature however (  $> 400^{\circ}C$ ), the electronic density and mobility drop drastically and the resistivity increases by more than two orders of magnitude. We attribute this variation in the electrical properties to a temperature where the aluminum atoms form alumina clusters instead of acting as dopants, similarly to what was observed in the high temperature deposition. It can be seen in Fig. 11 that this transition occurs at the same temperature (300-400 °C) for all the samples, except the ones deposited with only 10 and 15% oxygen. This is not due to a variation in the thermodynamic equilibrium, but in the kinetics of the annealing. Indeed, these two samples contain a high amount of metallic elements so that 15 min was not enough to reach the thermodynamic equilibrium.

In applications where AZO is used as a passive and conductive element, it is preferable that its electrical conductivity does not vary much with strain, to ensure a stability of the devices. The variation in resistance of thin films deposited with 10% (metallic regime), 17.5% (transition regime), and 30% (oxidized regime) oxygen has been measured. The measurement of the resistance was performed on a substrate that was bent, as shown in Fig. 12. The gauge factor for piezoresistance is defined as  $\Delta R/R_0/\varepsilon$ , with  $\Delta R$  the variation of resistance,  $R_0$  the initial resistance and  $\varepsilon$  the applied strain. Typical values for metals are comprised between 2 and 3, mainly due to the geometric variation [14–16]. Here we observe gauge factors of -1.6, -1.3 and -4.2 for the samples deposited with 10%, 17.5% and 30% oxygen. It means that for samples deposited in the metallic and transition regimes, the absolute value of the gauge factor can be lower for AZO than for metals, inducing a slightly better electrical stability.



**Fig. 12.** (Top) Setup used to bend the silicon substrates, to apply uniaxial strain on the AZO thin films. (Bottom) Relative variation of resistance as a function of the applied strain, for AZO thin films deposited at various oxygen concentrations.

#### 3.4. Optical properties

The optical properties are intimately related to the electronic properties and the transmission spectra (Fig. 13) strongly depend on the charge carrier density, and on the defects that influenced the electronic mobility. In general the defects act as absorption centers hence decrease the transmission. This is dominant in the visible spectra of the samples deposited with lower oxygen concentrations, and to a smaller extent also for the samples deposited at low temperature, that exhibited a lower electronic mobility. At higher oxygen concentrations (oxidized regime), the formation of alumina clusters does not limit the transmission since alumina is a large bandgap material.

When the charge carrier density is increased to a point where a semi-conductor is degenerate (which is always the case for the samples in this article), the fundamental absorption of light is not defined by the electronic bandgap, but by the optical bandgap (difference between the Fermi level and the top of the valance band). An increased carrier density corresponds to an increased Fermi level, and an increased optical bandgap (Burstein-Moss effect [17]). It was shown previously that the charge carrier density decreases monotonously when the oxygen concentration is increased. It can be seen in Fig. 13 (Top) that the transition from absorbent to transparent shifts to higher wavelengths (lower energies) when the oxygen concentration is increased, because it corresponds to a decrease of the charge carrier density, hence of the optical bandgap. The sample deposited with only 10% oxygen does not have a clear transition between absorbent and transparent because, due to the metallic clusters, it does not have a semi-conductor behavior. Another consequence of a high free charge carrier density is an increased reflectance in the infra-red (IR) range. It is verified here since the transmission in the IR decreases at low oxygen concentrations and high temperature deposition, corresponding to the conditions with the higher charge carrier densities.

When the sample deposited with 20% oxygen was annealed up to 300 °C, the metallic defects disappeared, increasing the transmission in the visible range. The thermal activation of the dopants increased the charge carrier density, hence the near-UV transmission. When the sample was annealed at 400 °C, the appearance of alumina clusters inactivated the dopants and decreased the charge carrier density,



**Fig. 13.** Transmission spectra of AZO samples deposited at room temperature for different oxygen concentrations (Top), deposited at room temperature with 20% oxygen and annealed under Ar for 15 min at different temperatures (Middle), and deposited at 20% oxygen and different temperatures (Bottom).

increasing the transmission in the visible (less absorbing defects) and in the IR range (lower reflection by free carriers), but reducing the optical bandgap.

With the transmission and reflection spectra it is possible to extract the absorption coefficient of the layer  $\alpha$ :

$$\alpha(\lambda) = \frac{1}{h_f} \left[ \frac{(1-R)^2}{2T} + \sqrt{\frac{(1-R)^4}{4T^2} + R^2} \right]$$
(4)

where  $h_f$  is the thickness of the film, and R and T are the reflectance and transmittance of the sample respectively. Here we could not measure the reflection so we assumed that the reflection was small (R < 0.1) and that the absorption coefficient can be approximated by:

$$\alpha(\lambda) = \frac{1}{h_f} \ln\left(\frac{1}{T}\right)$$
(5)

This approximation is valid for most samples, except for the sample deposited with low oxygen (10%). With the absorbance it is possible to make a Tauc's plot, and extract the optical bandgap. The results are presented in Fig. 14. If we extrapolate the intrinsic bandgap at n = 0,



Fig. 14. (Top) Bandgap as a function of deposition temperature (at 20% oxygen) and oxygen concentration (at room temperature). (Bottom) Evolution of the optical bandgap with charge carrier density. The bandgap of the sample deposited at 10% oxygen is not represented because its quasi-metalic behaviour makes it invalid.

we obtain a value of 3.28 eV, consistent with what was observed in our previous publication (see Ref. [9]).

If we assume that the conduction band is parabolic, the difference between the optical and electrical bandgaps ( $E_{o,g}$  and  $E_{e,g}$ ) is given by:

$$\Delta E_g = E_{o,g} - E_{e,g} = \frac{\hbar^2}{2m^*} (3\pi^2)^{2/3} n^{2/3}$$
(6)

With a linear fit of the optical bandgap as a function of  $n^{2/3}$  (see Fig. 14) it is therefore possible to obtain an effective mass of  $0.49m_e$ , with  $m_e$  the electron rest mass, consistent with what is being reported in the literature.[18–21]

#### 4. Conclusions

In this article we analyzed the effect of oxygen concentration and temperature (in-situ and post-deposition) on the electrical and optical properties of Al-doped ZnO. The internal stress was also measured insitu thanks to a Multi-beam Optical Stress Sensor (MOSS), giving some insights on the possible growth mechanisms, and the resulting defects that appear during reactive sputtering. The importance of the discharge curve in reactive sputtering was also stressed out to allow comparison of results obtained in different sputtering equipments.

It was proven that the optimum oxygen concentration for transparent electrodes is around the middle of the transition regime (here, around 20% oxygen). Indeed, the metallic regime and the beginning of the transition regime lead to the formation of metallic clusters that reduce the electronic mobility (hence the conductivity), and increase the optical absorption. In the oxidized regime and end of the transition regime, a second electrically insulating phase appears and makes the dopants inactive. This does not lower the optical transmission but results in a drastic decrease of the electronic mobility and density. The middle of the transition regime is therefore an optimum, providing a low concentration of metallic defects and alumina clusters, resulting in a low resistivity while still maintaining a high optical transmission.

The influence of temperature was also investigated, and it was shown that a moderate heating was highly beneficial because it increases both the charge carrier density and mobility, as well as the optical transmission. The optimum temperature depends if it is an insitu heating or a post-deposition annealing. However, when the temperature is too high, it favors the appearance of alumina clusters that increase the electrical resistivity. An annealing at 300 °C was observed as the best temperature to lower the resistivity and significantly increase the optical transmission, while an annealing at 400 °C increases the resistivity by two orders of magnitude. Heating during deposition allows to use a lower temperature (180 °C) to obtain the optimum properties as compared to a post-deposition annealing, but decreases the deposition rate by a factor of 2 due to re-evaporation.

Samples deposited at room temperature always exhibited tensile stress, from 70 to 510 MPa when going from the metallic regime to the beginning of the oxidized regime. Heating during deposition induced a reduced tensile stress or even a slightly compressive stress, which could be beneficial for the mechanical behavior of the thin film, since fracture often occurs due to the tensile stress.

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