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Fracture toughness, hardness, and Young’s modulus of tantalum nanocrystalline films

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The fracture toughness, hardness, and Young’s modulus of tantalum thin films are investigated based on nanoindentation measurements. A lower estimate of the fracture toughness of a 100 nm tantalum film is 0.28 ± 0.07 MPa m1/2. The hardness increases when reducing the film thickness whereas Young’s modulus decreases slightly. More precisely, the hardness of the 100 nm thick film is four times higher than the bulk behavior. A simple theoretical model, based on the connection between Young’s modulus and melting temperature, predicts an inverse grain size variation in Young’s modulus confirmed by experiments. © 2010 American Institute of Physics.

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Despite the huge amount of literature dedicated to the size dependency of mechanical properties,1−3 the fracture behavior of nanocrystalline materials is still not well understood due to many factors influencing it.4,5 Moreover, the yield strength and hardness exhibit a Hall–Petch behavior or an inverse one depending on the nanograin size.6 Additionally, Young’s modulus varies also with size.7 A common point to all these size-dependent mechanical properties is the important role played in nanocrystalline materials by the large amount of grain boundaries which are places where interatomic bonds are weak compared to bulk.8 In the present study, elastic, plastic, and fracture properties of tantalum nanocrystalline films are investigated by nanoindentation as tantalum is used in many technological applications such as diffusion barrier in nano/microelectronics and wear protective coatings.9

Tantalum thin films were deposited on silicon substrate by e-beam evaporation.9,10 The curvature of the system was measured using a profilometer (DEKTAK 3030 from Veeco) in order to extract the residual stress. The films were characterized by a scanning electronic microscope (SEM, Ultra 55 from Zeiss), an atomic force microscope (AFM, Nanoscope IIIa from Veeco), and a nanoindenter (XP from MTS).

The hardness and Young’s modulus are extracted from the load-indentation depth data using the Oliver and Pharr method.11,12 The hardness is defined by \( H = P_{\text{max}} / A_p \), where \( P_{\text{max}} \) is the peak indentation load and \( A_p \) is the projected area of the hardness impression. Young’s modulus is defined by \( E=(1−\nu^2)(\sqrt{A_p}/\pi 2\beta S−(1−\nu^2)/E_i)^{-1} \), where \( \nu \) is the Poisson ratio and \( E_i \) and \( v_i \) are the same parameters for the indenter tip material. The stiffness, \( S \), is obtained from the tangent of the unloading part at the peak indentation load in the load-displacement curve. For a Berkovitch indenter (three sided pyramid), \( \beta = 1.034, A_p = 3\sqrt{3}h_f^2\tan^2 \theta \), where \( h_f \) is the final depth of the contact impression after unloading and \( \theta = 65.27^\circ \) is the face angle with respect to the central axis of the indenter.12 The usual indentation size effect (i.e., hardness increases with a decreasing indentation depth) is observed for indents with a depth to thickness ratio, \( \delta \), of up to −0.2.13 The substrate effect (i.e., hardness increases with an increasing indentation depth) occurs when \( \delta \) is above −0.75 (Ref. 14) for the elastic modulus mismatch in the present system. Therefore, the indentation depth range was chosen in such a way that \( H \) and \( E \) are almost constant with \( \delta \), i.e., between 50–70 nm for the 100 nm film and 60–90 nm for 200 nm film (inset of Fig. 1). For each film, 15 indentations were made and only the average value is indicated in Table I.

In polycrystalline materials, it is well known that the grain boundary strengthening is described by the Hall–Petch relation,15,16 i.e., the yield strength of the material increases when the grain size decreases as follows: \( \sigma_y(D) = \sigma_y^\infty + k_D D^{-1/2} \), where \( \sigma_y(D) \) is the size-dependent yield strength, \( \sigma_y^\infty \) is the bulk yield strength, \( k_D \) is the strengthening coefficient, and \( D \) is the grain size, measured on the AFM images.

![FIG. 1. (Color online) Hardness vs the inverse square root of the grain size. The linear and parabolic fits are indicated with solid and dashed lines, respectively. Inset: Hardness vs the indentation depth to thickness ratio for 100 and 200 nm films. The zones, where the indentation size effect and the substrate effect occur, are indicated.](http://apl.aip.org/resource/1/applab/v97/i14/p143115_1/pdf)
by the power spectral density.\textsuperscript{17} For nanocrystalline materials, an inverse relationship \( \rho_s = const. \cdot D^{-\lambda} \) can be justified as the size of dislocation source scales proportional to the grain size.\textsuperscript{18} Hardness follows also the Hall–Petch relation due to its proportionality to yield strength, \( H \sim 3 \rho_y \) for metals.\textsuperscript{19}

\[
H(D) = H_s + k_{H_s} D^{1/2},
\]

(1a)

\[
H(D) = H_s + k_{H_s} D^{1/2} + k_{H_s} D^{-1},
\]

(1b)

where \( H(D) \) is the size-dependent hardness of the material, \( H_s \) is the bulk hardness, \( k_{H_s} \) is the slope in the size-dependent hardness versus \( D^{-1/2} \) (Fig. 1); and \( k_{H_s} \) and \( k_{H_s} \) are the coefficients of a parabolic relationship between hardness and \( D^{-1/2} \). The resulting \( k_{H_s} \) and \( k_{H_s} \) values have been determined to be equal to \( 58 \pm 4 \) GPa nm\(^{1/2} \), \( 84 \pm 1 \) GPa nm\(^{1/2} \), and \( -170 \pm 1 \) GPa nm, respectively. The very high hardness of Ta nanocrystalline films has already been reported by Zhang \textit{et al.}\textsuperscript{20} for rf magnetron sputtered layers. They measured a hardness value equal to \( 11.6 \pm 0.4 \) GPa for films with an average grain size of 76.5 nm which is quite close to our value of 12.1 \pm 0.5 GPa for a 38 nm grain size, even though the deposition process is different. Zhang \textit{et al.}\textsuperscript{20} have announced that the highest hardness should be attained with a grain size equal to 35 nm which is close to the present data.

Different trends have been reported in the literature regarding the dependence of Young’s modulus with size.\textsuperscript{5,21} Ao \textit{et al.}\textsuperscript{7} have explained this behavior due to the competition between the surface bond shrinkage and melting temperature variation with size reduction. According to Gu \textit{et al.},\textsuperscript{22} the size-dependent Young’s modulus of the material, \( E(D) \), can be related to its Debye temperature \( \theta_{\text{Debye}} \), knowing the corresponding bulk quantities, \( E(D)/E_s = \left( \theta_{\text{Debye}}(D)/\theta_{\text{Debye}}(s) \right)^2 \). It has been shown previously\textsuperscript{23,24} that the size-dependent behavior of the Debye temperature and melting temperature are related and can be expressed by \( T_m(D)/T_m(s) = \left( \theta_{\text{Debye}}(D)/\theta_{\text{Debye}}(s) \right)^2 = 1 - \alpha_{\text{shape}}/D \), where \( T_m(D) \) is the melting temperature and \( \alpha_{\text{shape}} \) is the parameter quantifying the size effect on the material property, depending on the shape of the nanostructure. This parameter is defined as \( \alpha_{\text{shape}} = [D(\gamma_s - \gamma_d)\Delta H_m(s)]/A/V \), where \( A/V \) is the surface area over volume ratio, \( \Delta H_m(s) \) is the bulk melting enthalpy, and \( \gamma_s \) is the surface energy in the solid (liquid) phase. Therefore, the following size dependence of Young’s modulus is proposed as follows:

\[
E(D)/E_s = 1 - \alpha_{\text{shape}}/D.
\]

(2)

This relationship agrees with our experiments and literature data from Ref. 25 (Fig. 2). Zhang \textit{et al.}\textsuperscript{26} obtained 178 GPa for films with an average grain size equal to 76.5 nm while the present results give 176.1 \pm 3.6 GPa for a 38 nm grain size. Note that this apparent elastic softening could also be due to an increasing porosity in thinner films.\textsuperscript{25,26} The open porosity, \( p \), which refers to the fraction of total volume in which a fluid flow can effectively take place (i.e., it excludes closed pores) has been measured by AFM (Ref. 27) while the closed porosity could not be measured. As indicated by Table I, the open porosity increases with film thickness and thus cannot explain the decreasing behavior of Young’s modulus. Nevertheless, it can be shown theoretically that the closed porosity plays a role in the decreasing behavior of Young’s modulus as the grain boundary energy is lower than the surface energy \( \gamma_{gb} < \gamma_s \), therefore coalescence of nanograins reduces the value of \( \alpha_{\text{shape}} \) and then decreases the size effect on Young’s modulus.

\begin{table}
\centering
\begin{tabular}{|c|c|c|c|c|c|c|}
\hline
Thickness (nm) & \( \sigma \) (MPa) & rms (nm) & Grain size (nm) & \( E \) (GPa) & \( H \) (GPa) & \( p \) (\%)
\hline
100 & 641 \pm 156 & 1.1 & 38 \pm 1 & 176.1 \pm 3.6 & 12.11 \pm 0.46 & 10 \pm 2
\hline
200 & 351 \pm 104 & 1.8 & 47 \pm 1 & 175.0 \pm 3.4 & 11.59 \pm 0.42 & 12 \pm 2
\hline
400 & 159 \pm 21 & 13.4 & 47 \pm 1 & Not measurable & Not measurable & 21 \pm 2
\hline
600 & 88 \pm 23 & 31.6 & 36 \pm 1 & Not measurable & Not measurable & 83 \pm 8
\hline
Bulk & / & / & / & 185 \textsuperscript{a} & 2.94 \textsuperscript{a} & /
\hline
\end{tabular}
\caption{Properties of tantalum thin films measured by profilometry, microscopy, and nanoindentation.}
\end{table}
crack propagates if $G$ is higher than a critical value, $G_c$. The stress was evaluated through the measurement of the curvature of the film-substrate system, $\kappa$, by using Stoney’s equation,\textsuperscript{30} i.e., $\sigma = \kappa E_s t_s^2/[6(1-\nu_s)t]$, where $E_s$ and $\nu_s$ are Young’s modulus and Poisson ratio of the substrate, respectively, and $t_s$ is the thickness of the substrate. Stoney’s equation is still valid as long as the ratio $t/s$ is smaller or equal to 0.1.\textsuperscript{31} As shown in Table I, the residual stress state in the Ta films is tensile and decreases when the thickness increases, illustrating the existence of a relaxation process. For the 100 and 200 nm thick films, a lower limit on the critical energy release rate could be estimated as $G_c = 0.46 \pm 0.20 \text{ J/m}^2$ and $G_c = 0.28 \pm 0.19 \text{ J/m}^2$, respectively, using the measured residual stress $\sigma$. The stress intensity factor is related to the energy release rate by $K_{IC} = \sqrt{\pi G_c}$, assuming plane stress conditions.\textsuperscript{3} The corresponding lower bound for the stress intensity factor for the 100 and 200 nm thick films are $K_{IC} = 0.28 \pm 0.07 \text{ MPa m}^{1/2}$ and $K_{IC} = 0.22 \pm 0.06 \text{ MPa m}^{1/2}$, respectively. These values can be compared with $K_{IC} = 0.78 \text{ MPa m}^{1/2}$, the value announced by Gruber et al.\textsuperscript{32} for the bilayer system; Ta-19 nm-Cu-71 nm. They have shown that for a constant copper thickness, $K_{IC}$ decreases by increasing the thickness of the Ta film.

As a conclusion, a lower limit on the critical energy release rate for cracking has been determined for Ta nanocrystalline films. As expected, hardness follows the Hall–Petch relation for the investigated thickness range and an inverse grain size dependency of Young’s modulus is observed. A theoretical equation has been deduced from thermodynamics to evaluate the size-dependency of Young’s modulus and was found to be in agreement with experimental data.

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