PHYSICAL REVIEW B **67**, 153404 (2003)

Measurement of the elastic modulus of nanostructured gold and platinum thin films

M. C. Salvadori,[1] I. G. Brown,[2] A. R. Vaz,[1] L. L. Melo,[1] and M. Cattani[1]
[1]*Institute of Physics, University of São Paulo, Caixa Postal 66318, CEP: 05315-970, São Paulo, São Paulo, Brazil*
[2]*Lawrence Berkeley National Laboratory, 1 Cyclotron Road, Berkeley, California 94720*

(Received 30 September 2002; published 25 April 2003)

Cantilevers of atomic force microscope (AFM) have been uniformly coated with gold and platinum thin films. These films are nanostructured with thickness between 18 and 73 nm. Measuring the resonance frequencies of the cantilevers, before and after the Pt and Au coatings, and using the vibrating beam theory we determined the elastic moduli E_2 of the films. We have obtained $E_2 = 69.1 \pm 2.6$ GPa for gold and $E_2 = 139.7 \pm 2.7$ GPa for platinum, that are about 12% lower than the respective bulk elastic moduli.

DOI: 10.1103/PhysRevB.67.153404 PACS number(s): 68.55.−a, 68.60.Bs

Over the past decade there was an explosion in both academic and industrial interest in nanostructured materials (ns materials).[1–3] These materials may be defined as those materials whose structural element clusters, crystallites, or molecules have dimensions D in the 1 to 100 nm range. This is due to the remarkable variations in fundamental electrical, optical, mechanical,[4,5] and magnetic properties. So, such materials have been developed and have attracted great interest due to both scientific and technological significance in recent years.

Nanostructured materials have manifested some novel or superior mechanical properties,[6–8] probably due to their grain sizes (typically $D < 100$ nm) and large fraction of interfaces (grain boundaries). Investigations, for instance, on the elastic properties of ns-Ag (Ref. 6) showed that the Poisson's ratio, the shear and the Young's modulus (E_2) are smaller than the corresponding bulk polycrystalline Ag values. According to these analysis[6] and recent works,[1–9] the relations between grain sizes, grain boundaries, and porosity, with the sound and mechanical properties of ns materials, are not fully understood. These are essential aspects that still remain to be clarified, experimentally and theoretically, in the future. With this in mind, a method was recently proposed[10] to measure E_2 for thin films. This procedure was adopted because the determined values by nanoindentation, which is the classical method to measure E_2, in thin films, is affected by the substrate. With this technique Salvadori *et al.*[10] have obtained $E_2 = 616$ GPa for diamondlike films (DLC's). This result is in good agreement with $E_2 = 580$ GPa found recently by Brillouin scattering.[11] Note that this E_2 for the elastic constant of DLC films is about 40% smaller than the diamond bulk modulus, given by $E_2 = 1000$ GPa. This elastic constant softening is expected due to the amorphous structure of the DLC, in contrast with the crystalline one of the diamond.[1–9]

In this work, the same procedure adopted in the precedent work[10] will be used to measure the Young modulus of gold and platinum thin films. These films are deposited in AFM cantilevers with a system of metal plasma immersion ion implantation and deposition (MePIIID).[10,12–14] As will be shown, the films are nanostructured. The Au and Pt elastic moduli are determined by measuring the resonance frequencies of the cantilevers. The resonance frequencies of vibrating cantilevers depend not only on the properties of the original cantilevers, but also on the coating properties: elastic modulus, density, and thickness of the films. We have carried out a systematic investigation of vibrating cantilevers coated with several thicknesses of Au and Pt films. The elastic modulus determination is performed using the vibrating beam theory and taking into account the measured resonance frequencies of the coated and uncoated cantilevers.

The deposition of the Au and Pt films was carried out inside a vacuum chamber with a plasma gun and a particle filter (MePIIID).[10,12–14] The gun cathodes were made from Au and Pt, which were the material sources for the films deposition. The plasma of the cathode material is produced by a discharge between cathode and anode. This plasma is guided to the substrate through the particle filter, eliminating macroparticles produced during the discharge. The parameters used for the gold and platinum thin films deposition were 180 A for the arc current, 5 ms for arc duration, and 1 Hz for the pulse frequency.

A uniform coating around the cantilevers was important to prevent the cantilevers from bending.[15] To have a uniform coating around the cantilever, we used a rotating holder.[10] The rotation axis was in the direction of the cantilever length. The holder rotation frequency was between 1 and 2.5 rpm, which means that in each complete turn the plasma gun has been shot between 24 and 60 times, covering the cantilever uniformly around the direction perpendicular to the rotation axis. The AFM cantilevers used in this work, and in the precedent one,[10] were commercial ones microfabricated with silicon.

In our technique, for the E_2 determination, the thickness of the film is the more sensitive parameter, so we have used a very precise method to measure it. A small piece of silicon, with an ink mark, was placed close to the cantilever, rotating coupled with it.[10] After the deposition, the ink was removed and the step obtained was measured with an atomic force microscope. We have measured about ten different regions of the silicon piece. Then an average value and its error were calculated for each sample.

We first measured the resonance frequencies of the original cantilevers. Note that we have used only one cantilever for each metal (Pt and Au). These measurements have been done using a NanoScope IIIA microscope in AFM tapping mode. This equipment allows us to measure the resonance frequency as a part of the oscillation mode procedure. Then

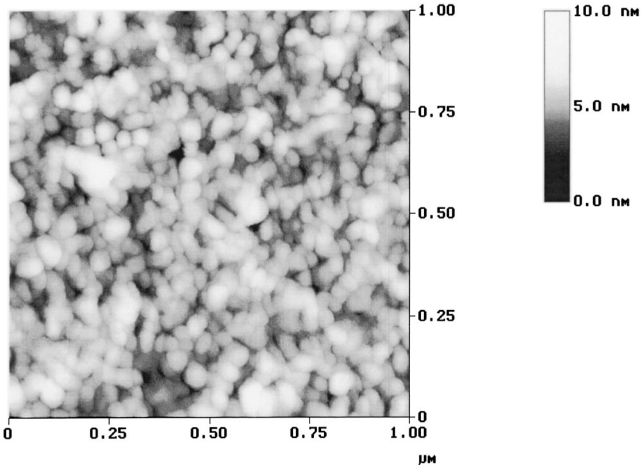

FIG. 1. Scanning tunneling micrograph with a typical morphology of our Au films.

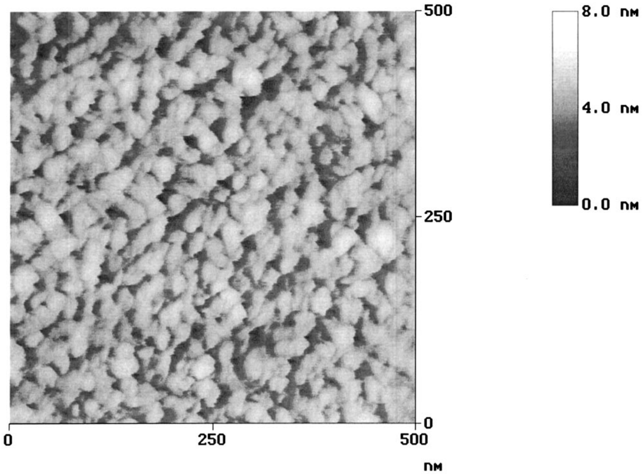

FIG. 2. Scanning tunneling micrograph with a typical morphology of our Pt films.

the thinner film was deposited and the new resonance frequency was measured. Then one more deposition was carried out on the same cantilever and the new resonance frequency was measured and so on, until obtaining the thicker film.

According to the elasticity theory,[10,16] the fundamental vibration frequency ν, in the Rayleigh approximation, of a clamped-free beam with length ℓ and rectangular cross section, with thickness t and width w, is given by

$$\nu^2 = \frac{1.03}{(2\pi)^2}\frac{t^2}{\ell^4}\frac{E_1}{\rho_1}, \tag{1}$$

where E_1 and ρ_1 are, respectively, the Young modulus and the density of the beam.

Let us assume now that this beam is coated with a different material, with density ρ_2 and elastic modulus E_2. For a thin and uniform coating, with thickness δ, where thin means $w, t \gg \delta$, the resonance frequency of the coated beam will be given by[16]

$$\nu_c^2 = \frac{12.36t^2}{(2\pi)^2\ell^4}\,\frac{E_1(wt/12) + E_2\delta[(w+2\delta)(1/2+\delta/t+\delta^2/2t^2)+t/6]}{\rho_1 tw + 2\rho_2\delta(w+t+2\delta)}, \tag{2}$$

where higher order terms in δ/w and δ/t are now taken into account, improving Eq. (2) of our preceding work.[10]

In what follows, the original beam frequency ν [see Eq. (1)] will be written as ν_u, to indicate "uncoated" beam frequency. From Eqs. (1) and (2) we get the frequency ratio

$$\frac{\nu_c^2}{\nu_u^2} = \frac{\rho_1 wt + 12(E_2/E_1)\delta[(w+2\delta)(1/2+\delta/t+\delta^2/2t^2)+t/6]}{\rho_1 tw + 2\rho_2\delta(w+t+2\delta)}. \tag{3}$$

The elastic modulus E_2 of gold and platinum films will be determined by fitting the theoretical frequency ratios ν_c/ν_u given by Eq. (3), with the experimentally measured frequency ratios.

In Figs. 1 and 2 we have scanning tunneling micrographs presenting the typical morphologies of our Au and Pt films. These pictures show clearly the nanostructured character of the films.

In Table I are given the film thicknesses δ and the corresponding measured frequencies of the uncoated and coated cantilevers. The dimensions of the cantilever used in the Au coating set are $w = 39.38\ \mu$m, $\ell = 136.9\ \mu$m, and $t = 4.23\ \mu$m. The cantilever used in the Pt coating set, has $w = 41.23\ \mu$m, $\ell = 138.8\ \mu$m, and $t = 4.41\ \mu$m.

The grain sizes, for Au and Pt, increase with the film thickness. The average grain size $\langle D\rangle$ goes from 10 to 40 nm for gold films, and from 20 to 35 nm for platinum films.

For the AFM silicon cantilevers, the density is $\rho_1 = 2.33$ g/cm^3 and the elastic modulus is $E_1 = 162$ GPa.[10] The gold and platinum films densities ρ_2, obtained by Rutherford back scattering (RBS) were found to be equal to the bulk values, for both cases, with an error around 2%. In this way, taking into account the bulk densities $\rho_2^{\mathrm{Au}} = 19.32$ g/cm^3 and $\rho_2^{\mathrm{Pt}} = 21.44$ g/cm^3, we determined the elastic modulus E_2 of the Au and Pt films by fitting the theoretical frequency ratios ν_c/ν_u, given by Eq. (3), with the experimental measured frequency ratios. Note that the E_2 obtained here are the elastic constants for Au and Pt films with thickness between 18 and 73 nm.

Figures 3 and 4 show the ν_c/ν_u plot as a function of the

TABLE I. The film thicknesses δ and uncoated (ν_u) and coated (ν_c) resonance frequencies of the cantilevers.

Cantilevers Coated with Au			Cantilevers Coated with Pt		
Uncoated frequency ($\nu_u \pm 0.050$) kHz	Film thickness δ (nm)	Coated frequency ($\nu_c \pm 0.050$) kHz	Uncoated frequency ($\nu_u \pm 0.050$) kHz	Film thickness δ (nm)	Coated frequency ($\nu_c \pm 0.050$) kHz
308.745	18.78 ± 0.40	300.849	309.924	21.67 ± 0.53	302.267
308.745	28.55 ± 0.25	294.537	309.924	31.33 ± 0.87	296.623
308.745	39.68 ± 0.32	288.672	309.924	39.6 ± 1.2	291.300
308.745	54.19 ± 0.51	283.135	309.924	57.9 ± 1.1	286.614
308.745	61.62 ± 0.40	277.756	309.924	61.2 ± 1.0	282.013
			309.924	72.9 ± 1.1	277.837

film thickness δ, for Au and Pt, respectively. The circles indicate the experimental data. The solid curves correspond to the theoretical fitting (the $\delta = 0$ is taken only as a point of reference). With the best fit we obtained $E_2 = 69.1 \pm 2.6$ GPa for the gold films and $E_2 = 139.7 \pm 2.7$ GPa for the platinum films.

The resonance frequencies of the cantilever, as seen in Figs. 3 and 4, decreased with the thickness δ of the Au and Pt films, according to the predictions of the vibrating beam theory.[16] For Au films, the elastic modulus was found to be $E_2 = 69.1 \pm 2.6$ GPa, about 12% smaller than the bulk elastic modulus $E_2 = 78.9$ GPa. For the Pt films $E_2 = 139.7 \pm 2.7$ GPa, also about 12% smaller than the Pt bulk modulus $E_2 = 158$ GPa. As is well known,[1–3,6–9] the elastic constants of a material are directly related to its atomic bonds strength. Theoretical models show that the elastic moduli of nanocrystalline materials[1–3,6,17] are essentially due to the grain sizes D and the grain boundaries structures. The interfacial adhesive energy between grains and, consequently, the interfacial strain, depends critically on the interfacial structure. It is expected that the interfacial structure, which is disordered and highly defected, produces an elastic softening.[1–3,6,17,18] According to computer simulations,[17] interfacial effects between grains are responsible for elastic moduli softening in ns materials. This predicted softening effect is observed in our experimental results. In order to get an estimate of the elastic softening of the interfacial structure, let us propose a simple model. First, let us assume that it is composed of almost cubic crystalline grains, with dimensions D, and the grain boundaries are formed by disordered and highly defected structures with thickness d.[17] Second, the Young modulus of the interfacial material would be given by E_i and of the grains would be the bulk modulus E_b. Third, d being a small fraction of D will obey the relation $d/D = x$, where $1 \gg x \neq 0$. With these assumptions and knowing that $E_i/E_b = (\Delta D/D)/(\Delta d/d)$, we can easily show that E_2 of the ns material can be written as

$$E_2 \approx \frac{(1+x)}{(x/E_i + 1/E_b)}. \tag{4}$$

According to Eq. (4), if there is no interfacial structure, that is, $x = 0$, we have $E_2 = E_b$. Now, let us use Eq. (4) to estimate E_i for our Au films. So, taking $E_b = 79$ GPa, $E_2 = 69$ GPa, and assuming that $x = 0.2$, which is a reasonable

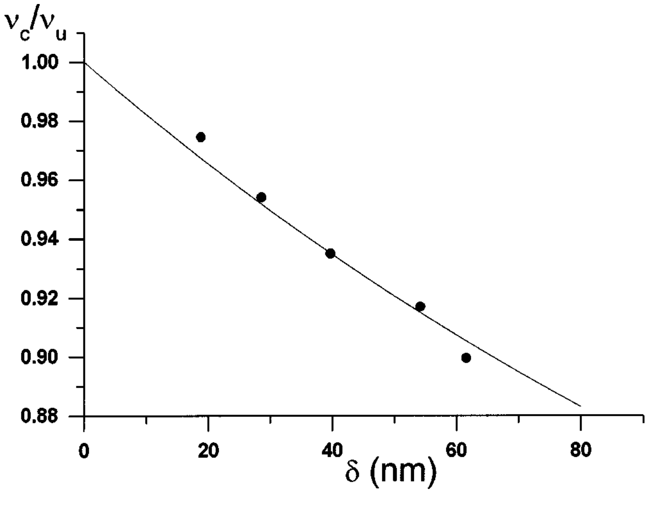

FIG. 3. Plot of the frequency ratio ν_c/ν_u as a function of the gold film thickness δ. The circles give the experimental data and the solid curve shows the theoretical fitting.

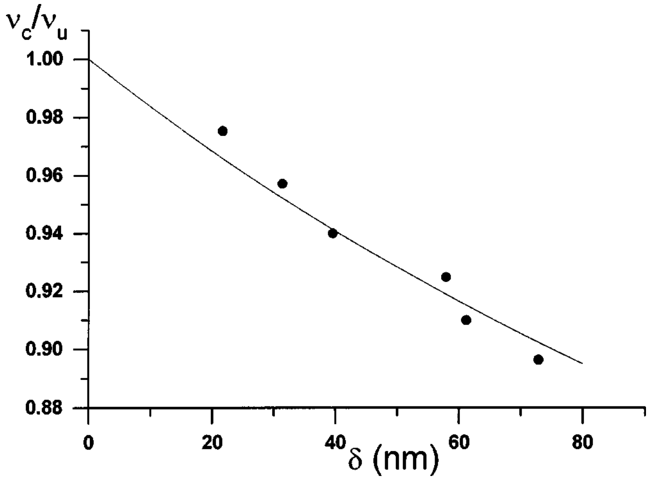

FIG. 4. Plot of the frequency ratio ν_c/ν_u as a function of the platinum film thickness δ. The circles give the experimental data and the solid curve shows the theoretical fitting.

value for this parameter,[17] we obtain $E_i \approx 44$ GPa. Thus, the interfacial structure of our Au films would have an elastic constant similar, for instance, to the Mg bulk modulus. However, in order to get a clear understanding and a precise quantitative estimate of this softening, more detailed experimental and theoretical analysis of the interfacial structures and their effects will be necessary.

This work was supported by the FAPESP (Fundação de Amparo *à* Pesquisa do Estado de São Paulo) and by the CNPq (Conselho Nacional de Desenvolvimento Científico e Tecnológico). The authors are grateful to the ''Laboratório de Análise de Materiais por Feixes Iônicos'' (LAMFI) of the Institute of Physics of the University of São Paulo, for the RBS analysis.

---

[1] P. Moriarty, Rep. Prog. Phys. **64**, 297 (2001).
[2] N. Cowlam, Solid State Phenom. **56**, 145 (1997).
[3] H. Gleiter, Acta Mater. **48**, 1 (2000).
[4] A. R. Layson, J. W. Evans, and P. A. Thiel, Phys. Rev. **65**, 193409 (2002).
[5] C. Mathioudakis, P. C. Kelires, Y. Panagiotatos, P. Patsalas, C. Charitidis, and S. Logothetidis, Phys. Rev. B **65**, 205203 (2002).
[6] X. Y. Qin, X. R. Xang, G. S. Cheng, and L. D. Zhang, Nanostruct. Mater. **10**, 661 (1998).
[7] J. Karch, R. Birringer, and H. Gleiter, Nature (London) **330**, 556 (1987).
[8] G. W. Nieman, J. R. Weertman, and R. W. Siegel, Scr. Metall. Mater. **24**, 145 (1990).
[9] L. H. Liang, J. C. Li, and Q. Jiang, Solid State Commun. **121**, 453 (2002).
[10] M. C. Salvadori, M. C. Fritz, C. Carraro, R. Maboudian, O. R. Monteiro, and I. G. Brown, Diamond Relat. Mater. **10**, 2190 (2001).
[11] O. R. Monteiro, I. G. Brown, R. Sooryakumur, and M. Chirita, in Materials Modification and Synthesis by Ion Beam Processing, edited by Dale E. Alexander *et al.*, Mater. Res. Soc. Symp. Proc. No. **438** (Materials Research Society, Warrendale, PA, 1997), p. 599.
[12] A. Anders, Surf. Coat. Technol. **93**, 158 (1997).
[13] O. R. Monteiro, Nucl. Instrum. Methods Phys. Res. B **148**, 12 (1999).
[14] I. G. Brown, A. Anders, M. R. Dickinson, R. A. MacGill, and O. R. Monteiro, Surf. Coat. Technol. **112**, 271 (1999).
[15] P. Lemoine, J. F. Zhao, A. Bell, P. Maguire, and J. McLaughlin, Diamond Relat. Mater. **10**, 94 (2001).
[16] R. E. D. Bishop and D. C. Johnson, *The Mechanics of Vibration* (Cambridge University Press, Cambridge, 1960).
[17] J. Wang, D. Wolf, and S. R. Phillpot, Philos. Mag. A **73**, 517 (1996).
[18] B. M. Clemens and G. L. Eesley, Phys. Rev. Lett. **61**, 2356 (1988).