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Young Modulus Measurement of Nanostructured Metallic Thin Films

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Abstract. We have uniformly coated cantilever of an Atomic Force Microscope (AFM) with metallic thin films. These films are deposited with a system of *Metal Plasma Immersion Ion Implantation and Deposition* (MePIIID). The metals used for deposition were gold, platinum and palladium. These films are nanostructured with thickness going from 18 up to 111 nm. We have determined the Young modulus of the metallic thin films (E_2). The E_2 values for gold, platinum and palladium are: 69,1 ± 2.6 GPa, 139.7 ± 2.7 GPa and 115.1 ± 2.1 GPa, that are about 12%, 12% and 7 % lower than the respective bulk elastic modulus.

Introduction

Nanostructured materials (ns-materials) have been largely studied due to their technological applications and academic interest [1-3]. These ns-materials may be defined as those material whose structural elements-clusters, crystallites or molecules, have dimensions D between 1 and 100 nm. They present considerable different electrical, optical, mechanical and magnetic properties, when compared with the corresponding bulk polycrystalline material.

Specifically the mechanical properties of nanostructured materials have presented remarkable experimental results [4-7], probably due to their typical small grain sizes (D < 100 nm), large fraction of interfaces (grain boundaries) and, frequently, porosity. Investigations, for instance, on the elastic properties of ns-Ag [6] showed that the Poisson's ratio, the shear and the Young modulus (E_2) are smaller than the bulk polycrystalline Ag values.

The discrepancies between the properties of the ns-materials and the corresponding bulk materials are not fully understood. These are essential aspects that still remain to be clarified, experimentally and theoretically, in the next thin films future. With this in mind, it was proposed recently [8] a new method to measure E_2. With this method [8], they have obtained E_2 = 616 GPa for diamond-like carbon (DLC) films. This result is in good agreement with E_2 = 580 GPa, found recently by Brillouin scattering [9]. Note that, this E_2 for the DLC films is about 40% smaller than the diamond bulk modulus, given by E_2 =1000 GPa. This DLC elastic constant softening is expected due to the amorphous character of this material, in contrast with the crystalline one of the diamond.

In this work, the same procedure developed by Salvadori *et al*. [8, 10, 11] was adopted to measure the Young modulus of metallic thin films. These films are deposited in AFM cantilevers with a system of *Metal Plasma Immersion Ion Implantation and Deposition* (MePIIID) [8, 12-14]. As will be shown, the films are nanostructured. The Au [10, 11], Pt [11] and Pd elastic modulus are determined by measuring the resonance frequencies of the cantilever before and after the film deposition. The resonance frequency of vibrating cantilever depends, 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 cantilever coated with several thicknesses of three metallic films [10, 11].

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.

Materials and Methods

Films Deposition and Resonance Frequency Measurements

The deposition of the films was carried out inside a vacuum chamber with a plasma gun and a particle filter. The plasma, formed of the cathode material, is produced by a discharge between cathode and anode. In this work we have used a Au, Pt and Pd cathodes. This plasma is guided to the substrate through a particle filter, eliminating macroparticles produced during the discharge. In the film depositions, the plasma gun was operated in a repetitively pulsed mode, with an arc current of 180 A, 5 ms for arc duration and at a rate of 1 pulse per second. The vacuum pressure during the depositions was about 3 x 10^{-6} Torr.

A uniform coating around the cantilever was important to prevent the cantilever bending [15]. So, to have a uniform coating, we used a rotating holder [8] located about 40 mm distant from the solenoid exit. 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 [8, 10, 11], were commercial ones microfabricated with silicon.

The thickness of the film was monitored using a small piece of silicon, which rotates coupled with the cantilever, with an ink mark. After the deposition, the ink was removed and the step was measured by contact AFM.

We first measured the resonance frequencies of the original cantilevers. Note that, we have used only one cantilever, for each metal, for all film thicknesses. These measurements have been done using a scanning probe microscope, NanoScope IIIA. This equipment allows measuring the resonance frequency as part of the oscillation mode procedure. Then, the thinner metallic films were deposited and the new resonance frequency was measured. Then, one more metallic deposition was carried out on the same cantilever and the new resonance frequency was measured. And so on up to get the thicker film.

Vibrating beam theory

According to the elasticity theory [16], the fundamental vibration frequency ν, of a clamped-free beam with density ρ_1 ,Young modulus E_1, length ℓ and cross section with area A, in the Rayleigh approximation, is given by

$$\nu^2 = \frac{12.36}{(2\pi)^2} \frac{E_1 I}{A \rho_1 \ell^4}, \qquad (1)$$

where, I is the second moment of area of the cross-section about the neutral axis through its centroid. For a beam with rectangular cross-section, with thickness t and width w, we have $I = w t^3/12$. In this case, Eq. 1 can be written as [16]:

$$\nu^2 = \frac{1.03}{(2\pi)^2} \frac{t^2}{\ell^4} \frac{E_1}{\rho_1}. \qquad (2)$$

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 >> δ, the resonance frequency of the coated beam will be given by [16]:

$$\nu_c^2 = \frac{12.36\, t^2}{(2\pi)^2\, \ell^4} \; \frac{E_1 w\, t/12 + E_2\, \delta\, (w/2 + t/6)}{\rho_1\, t\, w + 2\,\rho_2 \delta\, (w + t)}. \qquad (3)$$

In what follows, the original beam frequency ν (see Eq. 2) will be written as ν_u, to indicate "uncoated" beam frequency. From Eq. 2 and Eq. 3 we get the frequency ratio:

$$\frac{\nu_c^2}{\nu_u^2} = \frac{12\,\rho_1}{E_1} \; \frac{E_1 w\, t/12 + E_2\, \delta\, (w/2 + t/6)}{\rho_1\, t\, w + 2\,\rho_2 \delta\, (w + t)}. \qquad (4)$$

The elastic modulus E_2 of metallic films will be determined by fitting the theoretical frequency ratios, ν_c/ν_u, given by Eq. 4, with the experimentally measured frequency ratios.

Results

The measured resonance frequencies, thickness and morphologies of Au and Pt thin films are presented in our recent works [10, 11]. In this work we present only the palladium results and we discuss the results of the three metals.

In Figure 1 we have a scanning tunneling micrograph with the morphology of the thicker Pd films. The nanostructure of our films is clearly shown. Note that the scale, in the z direction, is 10 nm/division and, in the x and y directions, is 100 nm/division. So, the image is expanded in the z direction, emphasizing the grains profile. The roughness (rms) of this film is about 0.8 nm, what means that it is very smooth. As it can be seen, the average grain sizes $< D >$ in this micrograph is about 20 nm.

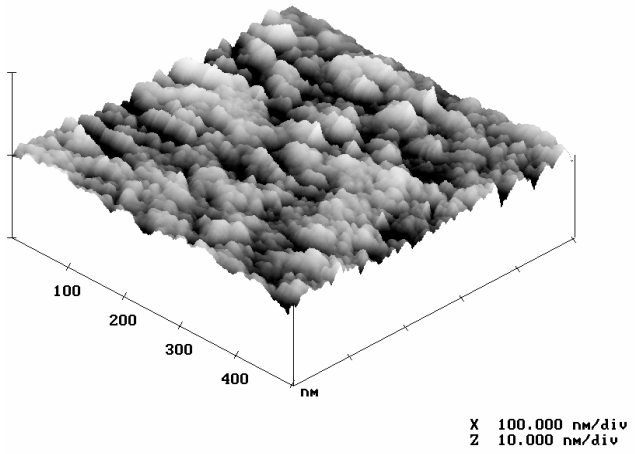

Fig. 1 Scanning tunneling micrograph with the morphology of the thicker Pd films.

In Table 1 are shown the cantilever uncoated frequency (ν_u), the films thicknesses δ and the corresponding measured coated cantilever frequencies (ν_c).

Frequency Uncoated ($\nu_u \pm 0.050$) [kHz]	Thickness of the Pd film δ [nm]	Frequency Coated ($\nu_c \pm 0.050$) [kHz]
317.293	20.86 ± 0.39	310.657
317.293	42.66 ± 0.49	306.675
317.293	62.52 ± 0.95	303.179
317.293	77.92 ± 0.99	300.287
317.293	94.3 ± 1.3	297.808
317.293	110.7 ± 1.7	295.257

Table 1. The films thicknesses, the frequencies of the uncoated and coated cantilever.

The cantilever used in our experiment had the following dimensions: w = 41.23 μm, ℓ = 135 μm and t = 4.23 μm. For the AFM silicon cantilever, the density is $\rho_1 = 2.33$ g/cm^3 and the elastic modulus is $E_1 = 162$ GPa [8]. The palladium films density, obtained by RBS (*Rutherford Back Scattering*) was found to be equal to the palladium bulk density $\rho_2 = 12.02$ g/cm^3. Taking into account these values we determined the elastic modulus E_2 of the Pd films by fitting the theoretical frequency ratios ν_c/ν_u, given by Eq. 4, with the experimental measured frequency ratios. Note that the E_2 obtained here is the elastic constant for Pd films with thickness between 20.9 and 111 nm. Increasing the film thickness, that is for δ larger that 110 nm, the elastic modulus tends to the bulk value.

Fig. 2 shows the ν_c/ν_u plot as a function of the palladium films thickness δ; the circles indicate the experimental data and the solid curve corresponds to the theoretical fitting. With the best fit we obtained $E_2 = 115.1 \pm 2.1$ GPa, about 7 % smaller than the bulk elastic modulus $E_2 = 124$ GPa.

The solid curve shows the theoretical fitting and the circles give the experimental data ($\delta = 0$ is taken only as a point of reference).

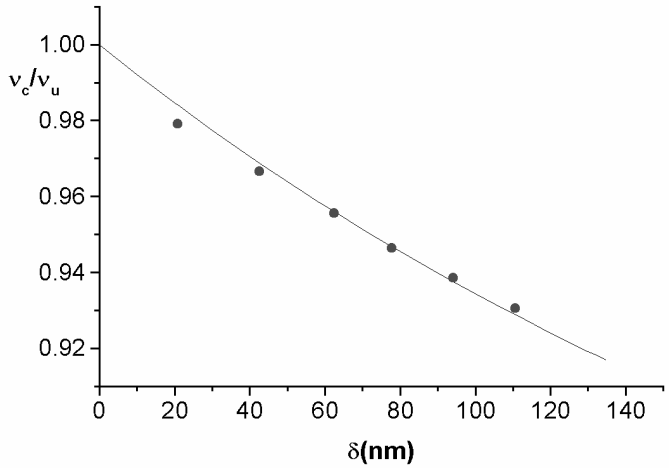

Fig. 2 - Plot of the frequency ratio, ν_c/ν_u, as a function of the palladium film thickness δ.

Summary and Discussions

In this work and recent works [10, 11] we used a successful method to uniformly coat an AFM cantilever with ns-palladium thin films. The resonance frequency of the cantilever, as is seen Fig. 2, decreased with the thickness δ of the Pd films, according to the predictions of the vibrating beam theory [16]. For Au, Pt and Pd films, the elastic modulus (E_2) were found to be 69,1 ± 2.6 GPa, 139.7 ± 2.7 GPa and 115.1 ± 2.1 GPa, that are about 12%, 12% and 7 % lower than the respective bulk elastic modulus.

As well known [1-7], the elastic constants of a material are directly related to its atomic bonds strength. Theoretical models show that the elastic moduli of nanocrystalline materials [1-4, 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 of the interfacial structure. It is expected that the interfacial structure, which is disordered, highly defected, produces an elastic softening [1-4, 17, 18]. According to computer simulations [17], interfacial effects between grains are responsible by an elastic moduli softening in ns-materials. This predicted softening effect is observed in our experimental results.

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