Young Modulus Measurement of Nanostructured Palladium Thin Films
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Abstract

We have uniformly coated cantilever of an Atomic Force Microscope (AFM) with palladium thin films. These films are nanostructured with thickness going from 20.9 up to 111 nm. The resonance frequencies of this cantilever have been measured, before and after the Pd coatings. Taking into account these frequencies and the vibrating beam theory, we determined the Young modulus of the Pd films, obtaining $E_2 = 115.1 \pm 2.1$ GPa, that is about 7 % lower than the respective bulk elastic modulus.

Keyword: thin films, Young modulus, nanostructures

1. Introduction

Nanostructured materials (ns-materials) have been largely studied due to their technological applications and academic interest. 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 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 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 a new method to measure $E_2$. With this method, 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. 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. was adopted to measure the Young modulus of palladium thin films. These films are deposited in AFM cantilevers with a system of “metal plasma immersion ion implantation and deposition” (MePIIID). As will be shown, the films are nanostructured. The Pd elastic modulus is 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 Pd 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.

2. Materials and Methods

2.1. Films Deposition and Resonance Frequency Measurements

The technique used in this work to deposit palladium thin films was “metal plasma immersion ion implantation and deposition” (MePIIID). 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 Pd cathode. 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.

An uniform coating around the cantilever was important to prevent the cantilever bending.
So, to have a uniform coating, we used a rotating holder 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, 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 all film thicknesses. These measurements have been done using a NanoScope IIIA microscope in AFM tapping mode. This equipment allows measuring the resonance frequency as part of the oscillation mode procedure. Then, the thinner palladium film was deposited and the new resonance frequency was measured. Then, one more palladium deposition was carried out on the same cantilever and the new resonance frequency was measured. And so on up to get the thicker film.

2.2. Vibrating beam theory

According to the elasticity theory, the fundamental vibration frequency \( \nu \) of a clamped-free beam with density \( \rho_1 \), Young modulus \( E_1 \), length \( \ell \) and cross section with area \( A \), in the Rayleigh approximation, is given by

\[
\nu^2 = \frac{12.36}{(2\pi)^2} \frac{E_1 I}{A \rho_1 \ell^4},
\]

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:

\[
\nu^2 = \frac{1.03}{(2\pi)^2} \frac{t^3 E_1}{\ell^4 \rho_1}.
\]

Let us assume now, that this beam is coated with a different material, with density \( \rho_2 \) and elastic modulus \( E_2 \). For a thin and uniform coating, with thickness \( \delta \), where thin means \( w, t >> \delta \), the resonance frequency of the coated beam will be given by:

\[

\nu^2 = \frac{12.36 t^2}{(2\pi)^2} \frac{E_2 w t^2}{\ell^4} + \frac{E_1}{\rho_1 t} w + 2 \rho_2 \delta (w + t) \quad \text{(3)}.

\]

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

\[

\frac{\nu^2}{\nu^2_u} = \frac{12 \rho_1}{E_1} \frac{E_2 w t^2}{\ell^4} + \frac{E_1}{\rho_1 t} w + 2 \rho_2 \delta (w + t) \quad \text{(4)}.

\]

The elastic modulus \( E_2 \) of palladium films will be determined by fitting the theoretical frequency ratios, \( \nu^2/\nu^2_u \), given by Eq. (4), with the experimentally measured frequency ratios.

3. Results

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.

![Figure 1. Scanning tunneling micrograph with the morphology of the thicker Pd films.](image-url)
The cantilever used in our experiment had the following dimensions: \( w = 41.23 \, \mu \text{m}, \ell = 135 \, \mu \text{m} \) and \( t = 4.23 \, \mu \text{m} \). For the AFM silicon cantilever, the density is \( \rho_1 = 2.33 \, \text{g/cm}^3 \) and the elastic modulus is \( E_1 = 162 \, \text{GPa} \). The palladium films density, obtained by RBS (Rutherford Back Scattering) was found to be equal to the palladium bulk density \( \rho_2 = 12.02 \, \text{g/cm}^3 \). Taking into account these values we determined the elastic modulus \( E_2 \) of the Pd films by fitting the theoretical frequency ratios \( v_c/v_o \), 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 \( \delta \) larger than 110 nm, the elastic modulus tends to the bulk value.

Figure 2 shows the \( v_c/v_o \) plot as a function of the palladium films thickness \( \delta \); the circles indicate the experimental data and the solid curve corresponds to the theoretical fitting. With the best fit we obtained \( E_2 = 115.1 \pm 2.1 \, \text{GPa} \), about 7% smaller than the bulk elastic modulus \( E_2 = 124 \, \text{GPa} \).

### 4. Summary and Discussions

In this work we used a successful method to uniformly coat an AFM cantilever with npalladium thin films. The resonance frequency of the cantilever, as is seen Figure 2, decreased with the thickness \( \delta \) of the Pd films, according to the predictions of the vibrating beam theory. For these films, the elastic modulus was found to be \( E_2 = 115.1 \pm 2.1 \, \text{GPa} \). It is about 7% smaller than the bulk elastic modulus \( E_2 = 124 \, \text{GPa} \). As well known, the elastic constants of a material are directly related to its atomic bonds strength. Theoretical models show that the elastic moduli of nanocrystalline materials 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. According to computer simulations, 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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