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Surface Morphology, Microstructure and Mechanical Properties of Thin Ag Films

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Abstract Thin Ag films deposited onto SiO_2/Si substrates by DC magnetron sputtering and thereafter annealed at temperatures 100-500°C are investigated by scanning tunneling and atomic force microscopy. It is shown that the film surface topography and microstructure are considerably changed as a result of annealing. To provide a quantitative estimation of the surface topography changes of Ag films the surface fractal dimension was calculated. Elasticity and hardness of the films are studied by a nanoindentation technique. The films are found to have value of elastic modulus close to that of bulk silver while their hardness and yield stress are essentially higher.

Keywords : Thin films, Silver, STM, Fractal dimension, Nanoindentation, Hardness, Yield stress

1. Introduction

Continuous increasing of the integration level and the on-chip packing density of very-large scale integration requires reliability growth and performance improvement of materials used for metallization. Although the primary functions of thin metal films are governed by their electrical properties, the mechanical reliability of metal interconnects is also of great importance, in particular, because of the heating and cooling cycles that are intrinsic to the fabrication and use of integrated circuits. The thermal-expansion difference between the substrates and interconnection materials leads to high mechanical stresses in thin-film structures[1-3]. Stress relaxation results in the plastic deformation of thin films followed by their fracture owing to voids formation or material extrusion.

Because of the small thickness and grain size of thin films as well as the effect of the substrate their mechanical characteristics considerably differ from those of bulk materials. Currently, nanoindentation methods are finding increasing use in the study of mechanical properties of thin films[1,4-7]. The technique provides the possibility to investigate the development of both elastic and plastic deformation into very small volumes.

In the present work we investigate the behavior of thin nanocrystalline Ag films in the course of thermal treatment. To reveal the cause of the plastic deformation and fracture of the films we focus on studying their mechanical properties by nanoindentation.

2. Experimental

Ag films were deposited onto SiO_2/Si substrates by DC magnetron sputtering. The preliminary cleaning of Si substrates involved washing in acetone and twice-distilled water and subsequent drying in isopropyl alcohol vapor. Next, a SiO_2 layer 200 nm thick was grown by thermal oxidation. An adhesive Cr layer 20 nm thick was deposited thereafter. Finally Ag films were sputtered at room temperature in vacuum at a base pressure 3×10^{-3} Torr. The films were 460 nm thick.

The surface topography of the films studied was examined using a scanning probe microscope working in two regimes: scanning tunneling microscope (STM) and atomic force microscope (AFM). The STM-images of the films were obtained in the constant current mode of operation. The tunneling tip was produced from Pt (99.99%) wire. The bias voltage between the tip and the sample was 300 mV and the tunnel current was 6 nA. AFM-measurements were performed with a silicon nitride tip (Park Scientific

Instruments) with a spring constant of 0.06 N/m. All the measurements were performed in air at room temperature and ambient pressure. Scan sizes ranged from 32.0 down to 1.0 μm square.

The thermal treatment of the films was performed in air at temperatures of 100-500°C. The annealing time was 1 hour. To estimate the morphological changes in the surface relief of thin films quantitatively, we calculated the fractal dimension D_f of the images. The fractal dimension was determined by surface triangulation [8].

Mechanical properties of the films were studied using NanoTest 600 nanoindenter with maximum imposed loads varied from 0.45 to 20 mN. Variations of the penetration depth as a function of applied load at the stages of loading and unloading were analyzed by the method developed by Oliver and Pharr[4].

3. Results and Discussion

3.1. Thermal treatment

Fig. 1 shows STM-and AFM-images of an Ag film before and after thermal treatment at different temperatures. Observed areas are 1.8×1.8 Fig. 1(a) and 8.0×8.0 μm^2 Fig. 1(b, c). The results are presented with different resolution to provide for clear understanding of the key features of the surface topography. The initial film surface is seen to be characterized by the fine-grained structure with grain size about 100 nm Fig. 1(a). Thermal treatment at a temperature of 100°C does not result in the marked changes in the film surface topography. After annealing at 200°C large structures with lateral dimensions of 2-3 μm are formed Fig. 1(b), which are not uniform and consist of smaller grains 300-400 nm in size. Thus, two processes are developed in the films: growth of grains and their agglomeration in large structures. The increase in the annealing temperature up to 400°C causes the film discontinuity owing to the formation of separate crystallites Fig. 1(c). Their average height is comparable with the film thickness. Further increasing of the annealing temperature results in the growth of the crystallite sizes, with their density being decreased.

The fractal analysis demonstrated a remarkable correlation between the fractal dimension and the observed changes in the film surface topography. The fractal dimension of the Ag film surface before annealing is constant for analyzed areas from 16 to 1 μm square and equal to about 2.50. Thermal treatment at 200°C only slightly decreases the value of D_f down to 2.47. On the contrary, annealing at 400°C leads to the sharp drop in the fractal dimension (D_f=2.18).

It may be concluded from the above-mentioned results that the different values of fractal dimension correspond to different scale levels of plastic deformation and fracture of thin films under annealing. The stage when fractal dimension is constant or slightly decreases corresponds to the grain growth and their coalescence. At this stage the film is continuous and homogeneous. The drop of the D_f relates to the formation of separate crystallites reflecting the stage of the thin film fracture.

The main reason of plastic deformation of Ag films under annealing is the difference in thermal expansion coefficient $\Delta\alpha$ of the film and substrate. Because the lateral dimension of the film during heating no longer match those of the substrate, biaxial stresses are imposed on the film to deform it so that it again fits

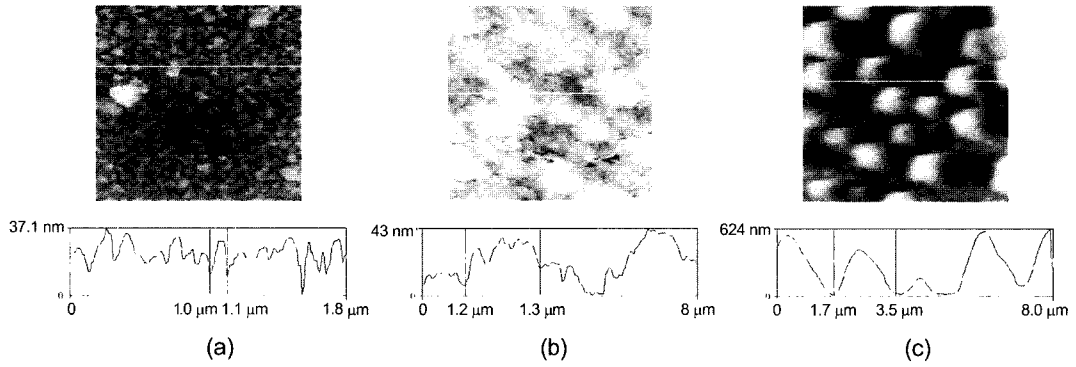

Fig. 1. STM- (a,b) and AFM-images (c) and profiles of an Ag film surface before (a) and after thermal treatment in air at temperatures of 200 (b) and 400°C (c). Observed areas are 1.8×1.8 (a) and 8.0×8.0 μm^2 (b,c).

the dimensions of the substrate. The value of the biaxial stresses can be conveniently calculated by multiplying the biaxial elastic modulus M of the film by $\Delta\alpha$. Since the coefficient of thermal expansion of silver (18.8×10^{-6} K^{-1}) is higher than that of silicon(3.0×10^{-6} K^{-1}), then $M_{Ag}\Delta\alpha_{Si\text{-}Ag}$=-2.0 MPa/K and compressive stresses will be developed into the film during heating up to annealing temperature. The value of these stresses may be as high as 350 MPa already at a temperature of 200°C and it may reach 750 MPa in the case of thermal treatment at 400°C.

Although these values far exceed the yield stress for bulk silver (30 MPa), thin films are known to have much higher strength than that for the same bulk materials. To estimate the real yield stress of the films studied we use some models considering the dislocation glide as a dominant relaxation mechanism during a thermal cycle. Following the model developed by Nix[1], the minimum biaxial stress needed to move the dislocation in a single-crystal thin film on a substrate, i.e. the minimum biaxial yield stress of a single crystal thin film on a substrate, may be written as

$$\sigma_y = 3.464\frac{b}{2\pi(1-\nu)s}\frac{\pi_f\pi_s}{\pi_f+\pi_s}In\left(\frac{\beta s}{b}\right) \quad (1)$$

where b is the Burgers vector, ν is Poissons ratio, s is the film thickness, μ_f and μ_s are the elastic shear moduli of the film and substrate, respectively, and β is constant. Notes, that this model neglects grain-size strengthening or other obstacles to dislocation motion.

In the case of nanocrystalline films the deformation propagates by means of formation of dislocation networks near grain boundaries. Stress fields induced by the dislocation networks initiate the nucleation and formation of dislocations in neighboring grains and, thereby, deformation propagates further. The possibility of dislocation nucleation, the length and density of dislocations greatly depend on the grain size d. It is, therefore, common to add a grain-size strengthening term, in the form of the Hall-Petch relation[1,2], to the yield-stress expression for fine-grained films:

$$\sigma = \sigma_0 + kd^{-1/2} \quad (3)$$

where σ_0 is expressed by Eq. (1), and k is the Hall-Petch coefficient.

Some authors[9,10] propose to use a dependence $\sigma_y \sim d^{-1}$ instead of the Hall-Petch relation $\sigma_y \sim d^{-1/2}$. So, in the model developed by Thompson[10] the room temperature yield stress is given by:

Table 1. Yield strength of Ag films

σ_y, MPa			
Experiment	Nix model	Nix+ Hall-Petchmodel	Thompson model
580	90	350	470

$$\sigma_y = 3.464\frac{b\mu_f}{4\pi}In\left(\frac{d}{b}\right)\left(\frac{2}{0.943d}+\frac{1}{s}\right), \quad (3)$$

which explicitly includes grain-size strengthening.

Values of σ_y for the Ag films obtained using Eqs. (1)-(3) and constants μ_{Ag}=27 GPa, μ_{Si}=66.5GPa, b= 2.89 Å, ν=0.37, β=2.6 and k_{Ag}=0.083 MN/m$^{3/2}$ are presented in Table 1. The difference between the values calculated by using different models is seen to be sufficiently high. However, even the highest value of yield stress calculated on a base of Thompson model is much lower than estimated thermal stress at a temperature of 400°C. In order to determine the experimental value of the yield stress of the films studied we investigated their mechanical properties by nanoindentation.

3.2. Nanoindentation

A typical load-displacement indentation curve obtained for Ag films under a peak load of 0.45 mN is shown in Fig. 2. During loading, both elastic and plastic deformation occur under the indenter as the contact area changes with increasing depth. The unloading part of the curve is dominated by elastic displacement. The two mechanical characteristics that can be measured using the nanoindentation technique are the hardness H and the elastic modulus E. The

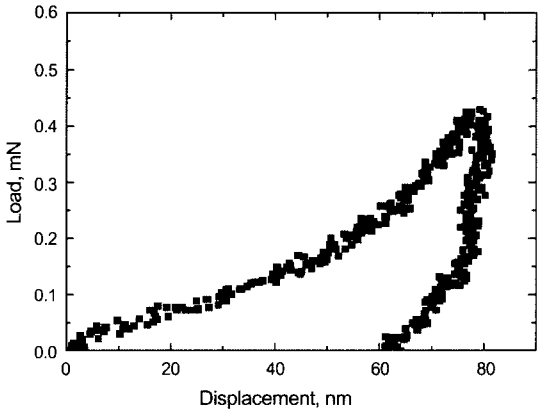

Fig. 2. Nanoindentation load vs. penetration depth curves for thin Ag films.

hardness is found by calculating the mean pressure under the indenter at the peak indentation load P_{max}:

$$H = \frac{P_{max}}{A} \tag{4}$$

where A is the contact area. According to the method proposed by Oliver and Pharr the contact area can be found from

$$A = 2.67h_c^2 + 1.646 \times 10^{-9} h_c, \tag{5}$$

where

$$h_c = h_{max} - 0.75P_{max}\left(\frac{dh}{dp}\right)_{p_{max}} \tag{6}$$

is the vertical distance along which contact is made (contact depth), h is the indenter displacement and h_{max} is the indentation depth at the peak load (see Fig. 3).

The elastic modulus of the material being studied can be measured from the slope of the unloading curve using the following equations:

$$E_r = \frac{\sqrt{\pi}}{2\sqrt{A}}\left(\frac{dh}{dp}\right)^{-1}_{p_{max}} \tag{7}$$

and

$$\frac{1}{E_r} = \frac{1-\nu^2}{E} + \frac{1-\nu_i^2}{E_i} \tag{8}$$

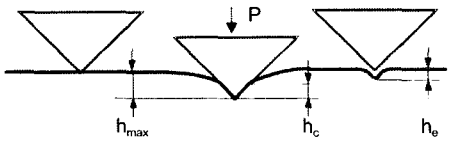

Fig. 3. A schematic representation of a section through a nanoindentation, h_e is the depth of residual impression.

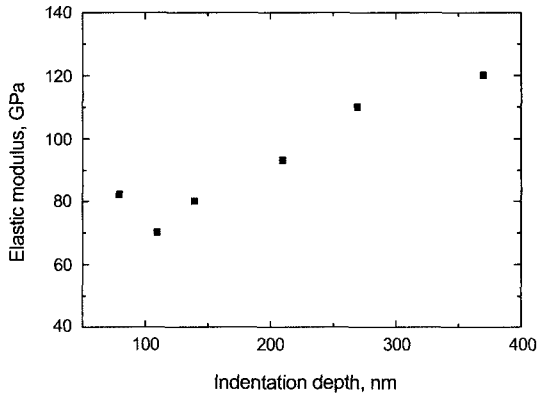

Fig. 4. Elastic modulus of thin Ag films as a function of indentation depth.

where E and ν are elastic modulus and Poissons ratio for the specimen and E_i and ν_i are the same parameters for the indenter.

When investigating thin films with nanoindenter, one of the most important parameters affecting the reliability of results obtained is the peak load. On the one hand, it should be sufficiently high to avoid the influence of oxide layer on the top of metal surface and the film surface roughness. On the other hand, the nanoindentation load should be sufficiently small to evade the effect of the substrate. The elastic modulus and the hardness of Ag films studied as a function of the indentation depth are presented in Figs. 4 and 5 respectively. The measured elastic modulus is seen to be about 80 GPa (that agrees with the elastic modulus of bulk silver) at indentation depths up to 140 nm (that corresponds to a peak load of 2 mN) and increases thereafter. This behavior can be explained by the influence of the silicon substrate, which elastic modulus (130 GPa) is higher than that of silver.

On the contrary, the measured hardness continuously increases with indentation depth (Fig. 5). This growth may be caused by several reasons. At first, it is well-known that very smooth specimens are required to obtain reliable contact stresses at small depths of indentation. Since the surfaces of the films studied are not perfectly smooth and have the developed surface topography, the actual contact area for a given indentation depth may be much less than predicted by the model, which assumes a flat surface. This can cause the apparent drop of the hardness below the actual value at small indentation depths. Secondly, for soft, strain-hardenable metals such as silver, the hardness is

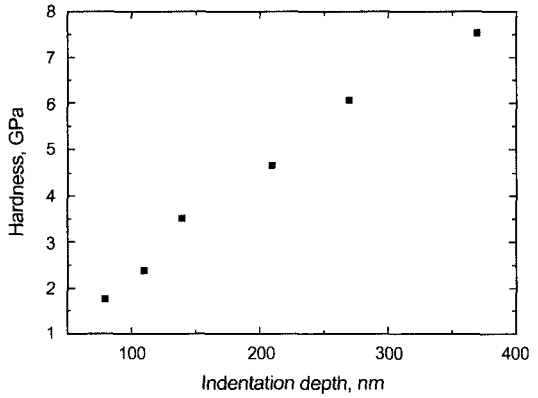

Fig. 5. Hardness of thin Ag films as a function of indentation depth.

known to depend strongly on the indentation depth[5]. This effect is explained by the formation of geometrically necessary dislocations. Thus, for such metals the indentation process itself can change the properties of the material being studied and, therefore, the results obtained. Finally, at sufficiently large indentation depths the hardness can be expected to approach the value for silicon substrate that is much harder than Ag films.

It is impossible to calculate a precise value of yield stress of the Ag films directly from the indentation curves. However, this quantity may be conveniently estimated using the Tabor relation[11] between Vickers hardness and yield stress $\sigma_y = H/3$. We used for the estimation the minimum experimental value of the hardness, since, on the one hand, in this case the indentation depth is already higher than the average surface roughness, and, on the other hand, the subsequent increase in the hardness testifies the beginning of strain hardening of the specimen, i.e. the beginning of its yielding. The obtained value for the yield stress of Ag films is 580 MPa. As expected, experimental estimations fall far from the value of yield stress calculated using the Nix model neglecting grain-size strengthening. On the contrary, this value is in reasonable agreement with yield stress calculated from the Thompson model.

It should be noted that the yield stress of thin films must decrease as the temperature increases[2]. Therefore, the yielding of the Ag films is observed already under annealing at 200°C, when predicted thermal stresses are 350 MPa, i.e. lower than estimated values of yield stress at room temperature. It is clearly understood that thermal treatment at a temperature of 400°C causing the stresses into the film as high as 750 MPa must result in its fracture.

4. Conclusions

Thin Ag films deposited onto SiO_2/Si substrates by DC magnetron sputtering were investigated. The films were found to be nanocrystalline with average grain size of 100 nm. Thermal treatment at temperatures 200-500°C results in considerable changes in the film surface topography and microstructure. Growth of grains and their agglomeration in large structures with lateral dimensions of 2-3 μm are observed under annealing at 200°C. Thermal treatment at 400°C leads to film discontinuity caused by the formation of separate crystallites.

Calculation of the fractal dimension of the thin films subjected to thermal treatment allowed us to characterize numerically changes in the surface topography at the stages of plastic deformation and fracture. The stage when fractal dimension is constant or slightly decreases corresponds to the growth and agglomeration of grains. The film fracture due to the formation of separate crystallites causes the D_f value to decrease.

The load vs. nanoindentation depth curves made it possible to investigate mechanical properties of the Ag films studied. It was concluded that as-deposited films have value of elastic modulus close to that of bulk silver while their hardness and yield stress are essentially higher. Values of elastic modulus and hardness was shown to depend strongly on the applied load. Comparison of experimental yield stress values of the films with calculated ones demonstrated that mechanical properties of nanocrystalline Ag films well agree with the Thompson model.

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