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Stress modification in gold metal thin films during thermal annealing

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Stress evolution during deposition of 50 nm Au thin films by thermal evaporation in a UHV system and then stress modification during thermal vacuum annealing have been performed. For stress measurement a substrate curvature approach has been applied. The changes in stress versus temperature linked to a modification of microstructure has been interpreted. To obtain any information about structural changes in the film X-ray diffraction measurements has been performed. We can conclude from the measurements that during the first cycle some irreversible structural modifications occur in a metal film.

Keywords: thin films, annealing, strain, stress.

1. Introduction

Extensive work has been done when studying the evolution of stress during annealing in Cu, Ag layers and for the most part in thin Al films deposited on Si substrates. We can correlate stresses present in films with deposition conditions, composition of the film or microstructure changes. The well known investigations were performed by Flinn and Gardner for pure and passivated Al films [1, 2]. The heating-cooling curves obtained by Flinn and Gardner did not reveal differences in successive thermal cycles and had close shape. Similar results for Al films were obtained by other authors [3–5], and also for Cu films [6–8]. We should mention that in most cases the film thickness was between 100 nm and 1.5 μm.

In this work, we report on stress evolution during deposition of 50 nm Au thin films by thermal evaporation in a UHV system and then stress modification during thermal vacuum annealing. Measurements were also made for 30 nm, 75 nm and 100 nm thick films [9]. The experiments were performed using the curvature measurement optical system [1].

2. Experimental

All thin films were deposited onto (001) oriented 100 μm thick silicon substrates by thermal evaporation in a UHV system at room temperature. The dimensions of the samples were 20 mm × 8 mm. Before deposition, the silicon substrates were washed for 15 min in acetone and ethanol in an ultrasonic bath. Then the substrates were dried in nitrogen gas.

For all deposition measurements, the base pressure in the deposition chamber was the same and equalled 1.8×10^{-9} hPa. The deposition rate was 7.2×10^{-3} nm/s while the pressure during deposition was about 6×10^{-8} hPa. To determine the evaporation rate during deposition a quartz thickness monitor was used.

During the annealing–cooling process the sample was positioned horizontally on a TECTRA® annealing table. To control the sample temperature a thermocouple was used. The measurements were performed during the thermal cycles of annealing from 35 °C up to 450 °C and cooled down to 35 °C at the rate of 10 °C/min. The base pressure in the annealing chamber was 2×10^{-7} hPa; during the experiment it was about 10^{-6} hPa.

For stress measurement a substrate curvature approach was applied. In this technique, stress is determined by measuring the change of substrate curvature induced by a deposited film. The scanning laser method described by FLINN *et al*. [1] was applied *in-situ* in both UHV and HV systems and yielded the evolution of stresses during deposition and annealing. Stress in both deposited and heated thin films is calculated by measuring the change in substrate curvature radius using Stoney's formula [10]. In the case of deposition, when the thickness changes during the film growth stress is commonly characterized by the force per unit width (F/w) versus thickness of the film. Of course, during annealing the shapes of the curves $\sigma(T)$ and $F/w(T)$ are identical. The values of F/w are the product of stress and film thickness. According to Stoney's formula F/w makes data independent of film thickness:

$$\frac{F}{w} = \sigma_f t_f = \frac{E_s}{1-\nu_s}\frac{t_s^2}{6t_f}\left(\frac{1}{R_f}-\frac{1}{R_s}\right) \tag{1}$$

where σ_f is the stress in thin films, E_s and ν_s are Young's modulus and Poisson's ratio for the substrate; t_f and t_s stand for the film and substrate thickness; R_s is the initial radius of the substrate before deposition, R_f is the radius of the substrate with a deposited film.

3. Results and discussion

The evolution of stress during evaporation of two samples of gold films at the rate 7.2×10^{-3} nm/s is shown in Fig. 1.

During the growth of Au thin films we have observed the so called compressive--tensile-compressive behavior. This type of stress evolution is characteristic of materials

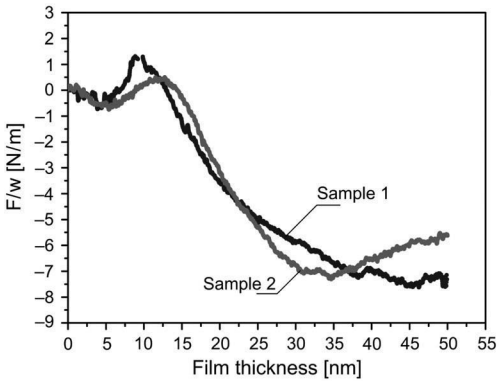

Fig. 1. Stress evolution during deposition of 50 nm gold films.

with low melting point [11] grown in Volmer–Weber growth mode [12, 13]. A low initial compressive stress for the thickness less than 7 nm was observed. For the thickness between 5 nm and 12 nm stress changed direction to tensile and upon further growth (above 10–12 nm) the change in compression direction was observed. For the second sample the above behavior occurred for less than 7 nm, 7–12 nm and above 12 nm, respectively.

Figures 2 and 3 show the evolution of force per unit width versus temperature for two samples deposited onto silicon substrate at room temperature. The first characteristic was plotted for two thermal cycles performed one by one. Upon the first annealing cycle, the films first deform elastically following the thermoelastic line in compression direction. At about 75 °C, the data deviate from this straight line indicating that a plastic deformation starts. The force per unit width in compressive direction reaches its extremum. Next, changes of the force per unit width indicate that stress tends to tension. Upon further annealing, the shape of the stress-temperature curve is determined by the strain rate of the plastic deformation processes [9]. Upon cooling the stress is tensile. In first stage of cooling, a short linear region with a slope about the same as that observed at the beginning of annealing appears. Further cooling changes the shape of the curve to nonlinear. This trend is continuing till the end of

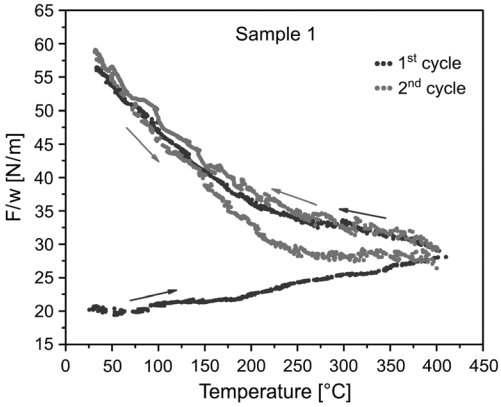

Fig. 2. Stress evolution for gold film deposited at the rate of 7.2×10^{-3} nm/s in two thermal cycles performed one by one.

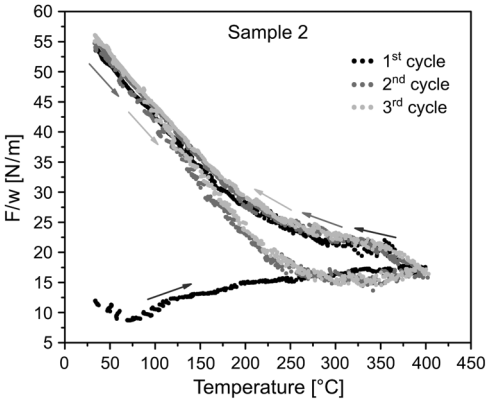

Fig. 3. Stress evolution for gold film deposited at the rate of 7.2×10^{-3} nm/s in three thermal cycles (the second and third cycles performed 3 days after the first one).

the first cycle. As we can see in Fig. 2, after the first annealing–cooling cycle had been completed, the values of the force per unit width for starting and ending points were not the same (the curve has an open shape). The force per unit width versus temperature for the second cycle gives the same values for starting and ending points. Therefore, we can call it a hysteresis loop. The second loop starts with a longer linear region (up to 200 °C) and higher slope and obviously does not superpose the loop of the first cycle. We can state that after the first cycle the layer becomes stable.

To prove our hypothesis the second 50 nm thick Au sample was prepared. For this sample, three characteristic thermal cycles were performed. The shape of the first heating-cooling curve was similar to the shape of that obtained for the first sample. The second and third loops measured 3 days after, performed one by one are identical to the second cycle curve of the first sample. We can suppose that such behaviour is linked to a modification of the sample microstructure.

A change in temperature ΔT produces stress in the film due to the difference in thermal expansion $\Delta\alpha$ between the film and its substrate. If the film does not deform plastically (the strain is pure elastic) the stress is equal to [1]:

$$\frac{\mathrm{d}\sigma}{\mathrm{d}T} = \Delta\alpha \frac{E}{1-\nu} \tag{2}$$

At high temperatures when plastic deformation plays a significant role the thermal stress is as follows:

$$\frac{\mathrm{d}\sigma}{\mathrm{d}T} = \frac{E}{1-\nu}\left(\Delta\alpha - \frac{1}{u}\frac{\mathrm{d}\varepsilon_p}{\mathrm{d}t}\right) \tag{3}$$

where u is the rate of the changes of temperature and $\mathrm{d}\varepsilon_p/\mathrm{d}t$ is the rate of plastic deformation mechanism. In paper [14], we have shown that in the first thermal cycle for metal films with the thickness below 100 nm a diffusional creep process plays a significant role in plastic deformation.

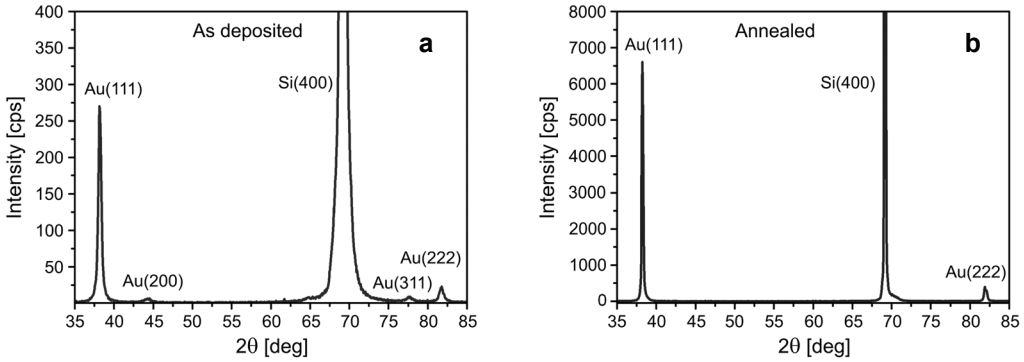

Fig. 4. X-ray θ–2θ scans for 50 nm Au film before (**a**) and after (**b**) annealing.

To obtain any information about structural changes in the film X-ray diffraction measurements were performed. θ–2θ scans before and after annealing are shown in Fig. 4. Before annealing diffracting peaks of (111), (200) and (311) planes were observed. After annealing only peaks corresponding to (111) planes are visible. Other peaks disappeared. Both the increase of (111) peak intensity and decrease of FWHM (full width at half maximum) are observed. The average grain size in the growth direction as deposited equals 22.5 nm while annealed one equals 47 nm. This indicates that the grain size in growth direction increases.

4. Conclusions

As we have shown, all the curves of first annealing–cooling cycle have open shape. The subsequent cycles become very similar to each other and are represented by a hysteresis loop. These examples show that the second, third and – we expect – next loops (even cycled after a few days) superimpose each other very well. We can treat the similarity of the hysteresis loops as a criterion of structural stability of the gold layer. We can conclude that during the first cycle some irreversible structural modifications occur in a metal film. Therefore, it seems very important to incorporate corresponding thermal treatment to any preparation procedure of thin film devices based on gold layers.

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