The Effects of Crystallization on Mechanical Mechanism and Residual Stress of Sputtered Ag Thin Films

F. Y. Hung1,* T. S. Lui1, Z. S. Hu2, S. J. Chang2, L. H. Chen1 and K. J. Chen3

1Department of Materials Science and Engineering, Center for Micro/Nano Science and Engineering, National Cheng Kung University, Tainan 701, Taiwan, R. O. China
2Institute of Microelectronics & Department of Electrical Engineering, National Cheng Kung University, Tainan 701, Taiwan, R. O. China
3The Instrument Center, National Cheng Kung University, Tainan 701, Taiwan, R. O. China

Silver film is widely used in optoelectronic and semiconductor industries, but its stress problem has not been verified. Sputtered Ag films of different thicknesses were used to investigate the effect of the crystallization on their solidification residual stress and electrical properties. From XRD data (2θ > 90°), an increase the thickness of the Ag film from 30 to 400 nm, not only raised the index of crystallization, but also obtained a lower resistivity. However, the peak (331) had a dissolution tendency due to the residual stress. The grain size of Ag films with greater thickness had grown because of the longer sputtering duration. Due to variations in the crystallized texture, the 30 and 110 nm films showed no sign of elasticity under nano-indentation testing. Under low-energy XRD (30 kV-20 µA), the 30 nm film not only had more residual stress, but also formed a new plane of diffraction at 104.2° of 2θ. After an electrical current induced crystallization (EIC) test, the resistivity and residual stress of Ag film were improved. [doi:10.2320/matertrans.M2012199]

1. Introduction

In the semiconductor and optical industries, thin metallic Ag film is a promising candidate as an interconnect material because of its low electrical resistivity and optical characteristics.1,2) Certain properties of silver film have been studied, such as optical properties, surface roughness3) and structure.4–7) However, the crystallization mechanisms have still not been examined. For applied science, the Ag thin film needs higher crystallization and conductivity, however its lower nano-scale thickness reduces the reliability of conductivity, and even its structural characteristics.8) In addition, the structure of thin film is closely related to the residual stress. So, the crystallization mechanism of nano-scale thin film is very important.

Many nano-indentation studies9) have discussed the hardness and the fracture characteristics of thin films under normal force conditions. However, the residual stress effects of nano-scale thin film have been largely ignored.10,11) Thin film XRD of high degree-low-energy and interrupted indentation can be used to analyze the solidification residual stress on nano-scale sputtered film.12) In addition, electrical current testing is a low temperature process carried out in atmosphere.13) Its mechanism is an electrical current induced crystallization (EIC).14,15) Thus, this paper not only investigates the crystallographic texture of nano Ag thin film (30–400 nm), but also discusses the solidification residual stress before and after EIC testing, as well as the near surface hardness and conductivity so as to further understand the potential for use as a thin film material.

2. Experimental Procedure

The deposition of Ag film on the quartz glass was carried out by RF sputtering with a 3 inch Ag target. The system was evacuated to below 0.23 Pa and the reactive gas was introduced with the flow rate controlled at 20 sccm. The gas pressure was fixed at 199.5 Pa during the sputtering process. The RF power was set at 80 W, and the distance from the target to the sample surface was fixed at 3 inches. A quartz glass was used as the substrate without heating during the whole deposition process and three thicknesses of thin films (30, 110 and 400 nm) were selected to study the relevant properties.

The crystalline behavior of the films was analyzed using X-ray diffraction (XRD) with Cu-Kα radiation. The grain size was calculated using Scherrer’s equation on the basis of Ag (111) diffraction peak.10) The surface morphology of the Ag films was observed using a scanning electron microscope (SEM). In addition, electrical resistivity was measured at room temperature using the four-point probe measurement.

The mechanical properties of the films were studied using the nano-indentation technique (MTS Nano Indenter G200). Notably, fatigue loading was used and increased twofold after unloading every time on the same notch. The residual stress measured by a nano-indentor was also compared to the data from high angle (2θ > 90°)-low energy (30 kV-20 µA) thin film XRD spectra. Before and after the electrical current testing (3.75 V, 0.68 A, 10 min, in atmosphere), we analyzed the crystalline structure, residual stress and resistivity of the Ag thin film.13–15) The 2-prob of current tester can parallel to symmetry mobile (advance and retreat) and the effective area is enough to perform the current testing. In addition, multipurpose X-ray thin film diffractometer (Rigaku ATX-E; D/MAX2500) was used to measure the stress value.17,18)

3. Results and Discussion

3.1 Crystallization mechanism

Figure 1 shows SEM images of three Ag films (30, 110

*Corresponding author, E-mail: fyhung@mail.ncku.edu.tw
and 400 nm) with different thickness. According to observations, the grain size of the matrix increased with increasing the thickness of Ag films (Table 1). In addition, the sputtering rates of the films are shown in Fig. 1(d) and it is clear that the films had a neat surface.

We used the Scherrer Formula and SEM images to calculate the grain size. The grain sizes of the Ag films were calculated according to the Scherrer Formula: 
\[ D = \frac{0.89 \beta}{\cos \theta} \]
where \( \lambda \) is the X-ray wavelength (\( \lambda = 0.154 \text{ nm} \)), \( \beta \) is the full width at half maximum (FWHM) of the (111) reflection as a function of \( 2\theta \), \( \theta \) is the angle of incidence of the X-radiation measured for the sample surface and \( \theta \) is the Bragg angle. The interplanar spacing \( d \) can be evaluated from the relation: 
\[ 2d \sin \theta = \lambda \text{CuK}\alpha \].

We divided the Ag films into three thicknesses (film I: 400 nm, film II: 110 nm and film III: 30 nm, Table 1).

The XRD spectra are shown in Fig. 2. The results are compared between the structure of the Ag films versus film thickness. It can be seen that the crystalline quality and texture of all films are very similar, and the 30 nm thin film possessed a certain degree of crystallization. In addition, all FCC-Ag grains and five diffraction peaks occur in the spectra, which we shall call the (111), (200), (220), (311) and (222) peaks. The (111) Ag peak is the most intense, which implies that the preferential orientation of the Ag grains was along the crystalline direction (111). As mentioned previously, when the film thickness increases and the grain size increases in turn, then we can see bigger grains on the surface and a stronger intensity in these XRD spectra. Notably, the evidence demonstrates that the grain size and the film residual stress are influenced by the film thickness (thick film had larger grain size and lower residual stress, due to the deposited heating).

From XRD peaks from 20 to 90°, we assumed the relative index of crystalline (IOC) of 400 nm Ag film to be 100% (IOC is a comparison value), then we could obtain the IOC of...
other films as 65% (110 nm) and 48% (30 nm) as shown in Fig. 3 (the electrical resistivity was also shown here). We can see the electrical resistivity of the films decreased with increasing thickness. The electrical properties improved following the increased thickness arising from a longer sputtering duration. Different grain size or crystalline will induce different thin film residual stress, so we carried out a nano-indentation experiment to study the effect of residual stress.

3.2 Nano fatigue strain–stress

Figures 4–6 demonstrate the 3-step and 5-step fatigue loading curve of Ag film of three different thicknesses. According to previous paper,22) the moving distance of dislocation was closely related to the depth of indention. So, the fatigue test of nano indention not only contained the effect of work-hardness, but also measured the residual stress. We individually increased the load gradually, followed by unloading three times in the same round on the surface of 400 nm film (Fig. 4(a)). Using a 3-step fatigue loading test, the L–D (load vs. displacement) curve of the nano-indentation is shown in Fig. 4(b). It is clear that the effect of working-hardness would vary according to the film depth (displacement). This means the structures at different depth-layers will be different. In the past, many studies9) applied the load continually to investigate the indentation properties. However this cannot completely reveal the deformation behavior of elasticity-plastic. Notably, 3-step fatigue loading can be used to estimate the indentation behavior of thin film in many applications. In Fig. 4(b), the displacement in region II is obviously narrower than that of region I, so the relationship between the stress–strain and the structure of the thin film is worth investigating.

Because the total displacement of region I and region II was ~110 nm, we intentionally fabricated 110 nm Ag thin film and carried out the nano-indentation experiment using 3-step fatigue (Fig. 5(a)), as shown in Fig. 5(b). We found that the displacement of region A was nearly equal to that of region B, and both were different from Fig. 4(b). In Fig. 4(b), the displacement of region III is greater than that of region II. In addition, the slope of the loading process in region C (Fig. 5(b)) is linear which suggests that the surface roughness of the sample was affected less than that of region I (Fig. 4(b)). The unloading curves of Fig. 5(b) were almost vertical to the X-axis and that of Fig. 4(b) was not present at all. This must be one reason why decreasing the Ag film thickness (from 400 nm to 110 nm) decreased the recovery effect (the elastic deformation) after nano-indentation. Notably, the phenomenon still occurred in the 30 nm Ag film (Fig. 6).

For 30 nm film, the 5-step fatigue loading test was selected to avoid the effects of surface structure. In Fig. 6, the width of displacement of region A is equal to that of region B. There are two reasons for this behavior. The first reason is that the working-hardness phenomenon wasn’t obvious in the layer of 10 nm deep and the loading was less than 2 µN. Regardless of nano-indentation conditions and the thickness of the Ag films, the loading forces of the 10 nm deep layer near surface (Figs. 4–6) were compared, and these forces (110 nm and 400 nm) were greater than 5 µN (30 nm ~2 µN, 110 nm ~5 µN, 400 nm ~5 µN). This is the main reason that the loading rate of nano-indentation is different. For the first step of Figs. 4–6, the depth of their indentation are below 20%. In order to identify the mechanical effect on the thin layer near the surface of film, the nano-indentation was only used at a depth of 10 nm in the 400 nm film and the 30 nm film with an identical load increase rate.

Relevant reports23,24) show that the residual stress makes a contribution to nano-indentation for thin films of thickness...
more than 200 nm. When the thickness of the film is very thin (<~100 nm), the effect of the substrate on nano-indentation will be enhanced. As for solidification stress, the present study used high angle (2θ ≥ 90°) XRD to analyze the stress data of Fig. 7 (30 and 400 nm). In Fig. 7, the peaks of the 400 nm film are stronger and narrower revealing that the crystalline is better. The sample (30 nm film) had a weak (331) peak due to the high energy XRD. Additionally, the (331) peak of the 30 nm film has a tendency toward dissolution, so the effect of the residual stress is substantial in the 30 nm film.

3.3 Thin film residual stress and nano-indentation

This study avoided the effect of quartz glass and compared the 30 nm film with the 400 nm film using a low-energy XRD (30 kV-20 µA). Figure 8(a) shows that the 30 nm film has a new plane of diffraction at 104.2° of 2θ. Notably, the 400 nm film does not exhibit the same peak in Fig. 8(b). According to studies, the strained peak of 104.2° is neither Ag nor AgO. When annealing at 250°C for 10 min was performed on the 30 nm film, the peak at 104.2° disappeared. Thus, we confirmed that the high-angle peak was a compressible plane of residual stress that was induced during solidification. In fact, the 110 nm film also exhibited the same tendency. To understand the both effects of annealed and forced air, the annealing was performed on the 110 nm film (250°C for 1hr in vacuum and cooling to room temperature) to release the stress, fusing will occur on the film surface (Fig. 9(a)). Figure 9(b) shows the compression fracture characteristics of 110 nm film after forced air (10⁻²). Increasing film thickness, this phenomenon would gradually show down. In addition, the residual stress values of 30 and 110 nm Ag films were detected using Multipurpose X-ray Thin Film Diffractometer (Table 2). It is clear that the compressive stress increased with decreasing film thickness and the strain fractured the film (Fig. 9(b)).
other words, Ag thin film ($\leq 110$ nm) is more susceptible to thin film residual stress. The residual stress of as-deposited thin films was able to affect the nano-indentation. In addition, we can be fairly certain that the dislocations moved easily when the crystallization of Ag film was raised.  

3.4 Current induced crystallization (EIC) and physical properties of Ag thin film

To achieve crystallization of Ag thin film on the glass substrate, an electrical current was applied (a probe: DC $3.75$ V, $0.68$ A) for $10$ min at room temperature (Fig. $10$).$^{13,28,29}$ After this, the $30$ nm Ag film possessed the current induced crystallization (EIC). A comparison of crystallization, residual stress and resistivity between the as-sputtered and electrical current treatment is shown in Table $3$. This table also indicates that the electrical current mechanism (electrical current changes the structure of matrix) is not only induced by the thermal effect. So, it is safe to say that the electrical current method increased crystallization and reduced resistivity and residual stress at lower temperature.

With regards to the mechanism of crystallization, the structural characteristics can be explained by Fig. $11$. When the film thickness was less than $110$ nm, both the compressible lattice and amorphous structure had not only accumulated residual stress, but the relative index of crystalline (IOC) was also affected. Conversely, when the film thickness was increased, nano fatigue strain–stress of thin film became closely related to elasticity and dislocation climb.

4. Conclusions

The crystallization of Ag thin film was closely related to the electrical resistivity and the nano-indentation data. Nano-
indentation was carried out using the fatigue method and XRD, and the residual stress of the sputtered Ag film increased with decreasing the thickness of thin film. When the film thickness was ≤110 nm, the deformation behavior of elasticity and the recovery effect decreased. Notably, the solidification stress increased with decreasing the relative index of crystalline (IOC). After EIC, index of crystalline (IOC), residual stress and electrical resistance of Ag film were improved.

### Acknowledgements

The authors are grateful to The Instrument Center of National Cheng Kung University, the Center for Micro/Nano Science and Technology (D101-2700) and NSC 101-2221-E-006-114; NSC 100-2622-E-006-030-CC for the financial support.

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