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Study on texture evolution and properties of silver thin films prepared by sputtering deposition

Yeon Sik Jung*

R&D Center, Samsung Corning, 644, Jinpyoung-dong, Gumi, Kyoung-buk 730-725, South Korea

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Abstract

By observing XRD profiles, the evolution of the crystallographic orientation of silver thin films was monitored. Sputtering process conditions such as working pressure, deposition power and substrate temperature significantly influenced the relative fraction of the grains with (1 1 1) orientation (lowest energy plane in FCC structure). Sputtering conditions for higher adatom mobility such as moderate range of sputtering pressure (0.14–0.71 Pa) and higher deposition power resulted in more (1 1 1)-preferred orientation. The Ag thin films deposited under those conditions showed lower resistivity, higher film density, and optical reflectance. These phenomena were explained from the change of adatom mobility with varied process parameters. Higher adatom mobility could be obtained under moderate range of sputtering pressure and higher sputtering power. Higher adatom mobility promoted the growth of (1 1 1)-oriented grains at the expense of other grains, and resulted in higher film density and improved electrical and optical film properties.
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1. Introduction

It is a well-known fact that polycrystalline thin films generally have crystallographic texture [1]. There also have been some reports about out-of-plane texture of silver thin films [2,3]. From a viewpoint of thermodynamics, the preferred orientations of thin films are known to be the perpendicular directions to the planes of lowest surface energy [1], which correspond to the most densely packed planes for metallic materials [4]. Accordingly, metallic thin films of FCC structure such as Ag, Cu, and Al show (1 1 1)-preferred orientation [3], and (1 1 1) planes have the highest packing density. However, not every grain is oriented to (1 1 1) direction since there is another factor influencing the preferred orientation of thin films. It is the initial orientations that nuclei have at early growth stage. The initial orientations of nuclei are governed by the adsorption energy of adatoms to substrate and bonding energy between adatoms. In general, island type growth mode (Volmer–Weber growth mode) is classified into two types according to wettability on substrates [5]. Wetting mode nuclei have smaller contact angles and preferential orientations. On the contrary, nuclei of non-wetting mode usually orient randomly. If secondary nucleation does not take place during film growth, the texture of thin films at a certain thickness

* Tel.: +82-54-470-7494; fax: +82-54-470-7814.
E-mail address: ysjung@bomun.kaist.ac.kr (Y.S. Jung).

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would be determined by the evolution speed of film texture from initially formed nuclei. Adatom mobility and shadowing effect are known to be the main factors governing the speed of the evolution [6]. It has been reported that ion beams can be used to modify thin film texture [7–9]. Some researchers reported the change of texture by ion beam, and insisted that different re-sputtering rate causes different texture [7,9]. Chiu and Barber proposed that ion flux and ion energy control the texture formation of Ag thin films in ionized magnetron sputtering deposition technique [2]. Moreover, they explained that ion bombardment increases adatom mobility and promotes the growth of lower-energy planes. Previously, it was suggested that the preferred orientation of thin films is controlled by the competition between the surface energy and the strain energy [10]. However, results that are more recent show that the strain energy might not be the main cause for determining preferred orientation [11,12].

In this study, the sputtering parameters of DC magnetron sputtering were varied to observe the change of Ag thin film texture. On the basis of the results, the influences of these parameters on the adatom mobility and the texture formation mechanism of Ag thin films were discussed. Moreover, the variations in the electrical, optical and mechanical properties were investigated, which were found to be closely related with the change of film texture.

2. Experiment

The thin films of Ag were sputter-deposited using a silver target in an in-line magnetron sputter-deposition system equipped with DC power suppliers. The chamber, which was equipped with a load-lock system and diffusion pumps, had a base pressure of 6×10^{-4} Pa. The target (128 mm × 450 mm) used was a pure Ag (99.99%). The sputtering was carried out in pure Ar gas with varying sputtering parameters such as sputtering pressure (0.05–2.8 Pa), power (0.5–5.0 kW) and deposition temperature (RT, 250 °C). The films were deposited on non-alkali glasses (Corning 1737), which were placed 50 mm apart and parallel from the target surface, after the target was pre-sputtered for 3 min. The thickness of the silver film was 60 nm–1 μm.

X-ray diffraction (XRD) studies on the films were carried out in a Philips PW1710 diffractometer using Cu Kα radiation. Film density was measure by X-ray reflectometry (D8DISCOVER, Bruker) technique. Sheet resistance was measured using four-point probe method. The stress in the films was measured by the substrate curvature method. The indices of refraction as well as the extinction coefficients of the films were determined by using a spectroscopic ellipsometer (VASE, J.A. Woollam Co. Inc.). Optical calculations were carried out using a simulation software (The Essential Macleod, Thin Film Center Inc.).

3. Results and discussions

3.1. Evolution of texture

Fig. 1(a) and (b) exhibit the change of the XRD profiles of Ag thin film samples and the relative portion of (1 1 1) peak intensity $(I(1\,1\,1)/(I_{(1\,1\,1)} + I_{(2\,0\,0)}))$ depending upon film thickness. The sputtering pressure

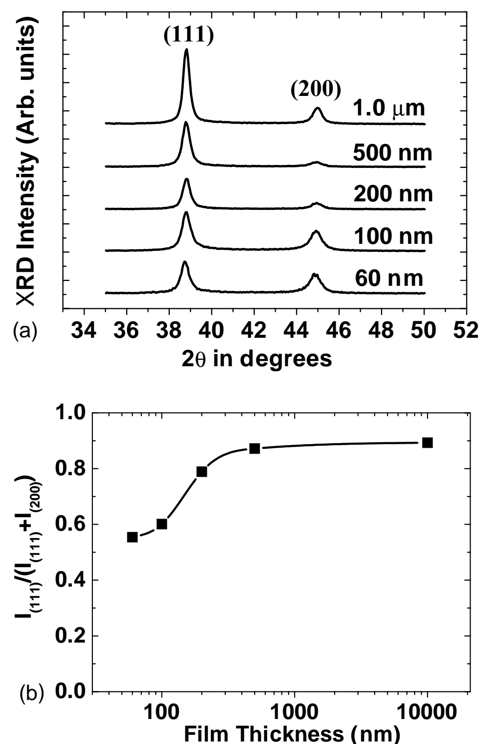

Fig. 1. (a) Evolution of XRD profiles depending upon Ag film thickness and (b) change of $(I_{(1\,1\,1)}/(I_{(1\,1\,1)} + I_{(2\,0\,0)}))$.

and power was 0.14 Pa and 3 kW, respectively. The intensity of each peak was calculated by fitting and integrating a Gaussian function. As previously mentioned, the XRD profiles of Ag thin film samples showed strong (1 1 1)-preferred orientation. No other peaks were observed in the range of $2\theta = 10-70^{\circ}$. As the thickness increased, the relative portion of (1 1 1) intensity increased. This confirms that the grains of Ag thin films evolve to (1 1 1) direction with increasing thickness and that (1 1 1) planes have the lowest surface energy. For very thin Ag thin films, (2 0 0) peak also had strong intensity, as compared with (1 1 1) peak. This means that the nucleation of Ag thin films on glass substrates is a type of non-wetting mode from the fact that the nuclei have mixed orientations. The observed peak intensity of (2 0 0) plane was observed even for very thick samples because the diffracted X-ray beam was from almost entire depth of the samples.

The change of the relative portion of (1 1 1) intensity ($I_{(1\,1\,1)}/(I_{(1\,1\,1)} + I_{(2\,0\,0)})$) depending upon sputtering pressure are shown in Fig. 2(a). One series of deposition was performed with equal sputtering power (3 kW), and another one was done with equal deposition rate by adjusting power to avoid the effect of different deposition rate. The samples were deposited without heating the substrates. The thickness of the films was about 300 nm. When the sputtering power was fixed, the dynamic deposition rate ranged from about 400–450 nm $\times$ m/min in the pressure range. The deposition rate increased until 1 Pa, and decreased as pressure above 1 Pa. Thus, for the series of samples with equal deposition rate, higher sputtering power (3.2–3.3 kW) was needed for low and high pressure conditions. At the lowest pressure (0.05 Pa) and the highest pressure (2.8 Pa), the intensities of XRD peaks were considerably low. That means relatively much lower crystallinity of the samples. Fig. 2(a) shows that the relative portion of (1 1 1) orientation was highest in the moderate range of sputtering pressure (0.14–0.71 Pa). The similarity of two graphs indicates that different texture at the lowest pressure (0.05 Pa) and the highest pressure (2.8 Pa) does not originate from different deposition rate.

The diffusivity of adatoms on the surface can be expressed in the following equation:

$$D_s = \frac{1}{2} a_0^2 v \exp\left(-\frac{E_s}{kT}\right) \quad (1)$$

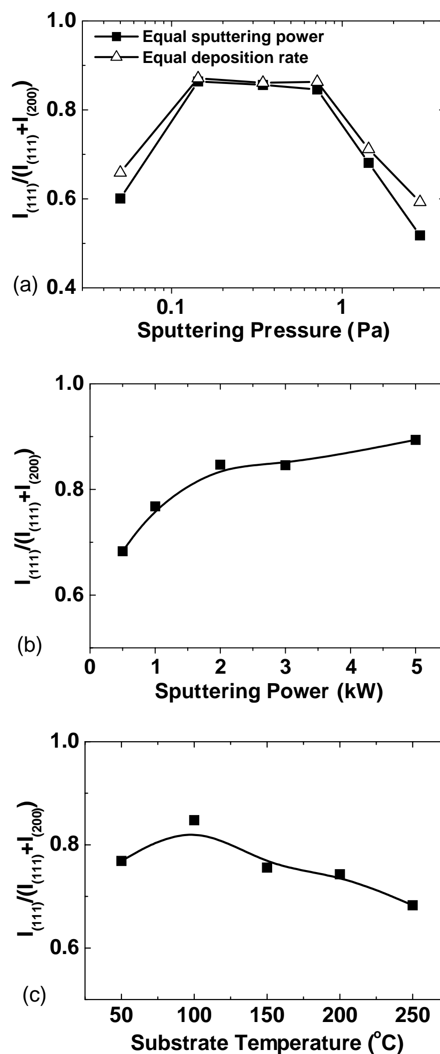

Fig. 2. Change of ($I_{(1\,1\,1)}/(I_{(1\,1\,1)} + I_{(2\,0\,0)})$) depending upon (a) sputtering pressure; (b) power; and (c) temperature.

where a_0 is atomic dimension, v the vibrational frequency of adatoms, and E_s the activation energy for surface diffusion. Adatom mobility would be proportional to that value [13].

The main factors that influence the energy (kT) of adatoms are substrate temperature, Ar^+ ion bombardment energy, and the kinetic energy of adatoms just before arriving on the surface. If the average mobility of adatoms is higher, then they can move more actively on the film surface. Also the possibility that the adatoms can be bound at lower-energy sites would

be higher. If adatoms arrive with sufficient adatom mobility on the region near a boundary of grains of different orientations, they can travel on larger area of surface than the adatoms of lower mobility. Accordingly, those adatoms can have higher possibility to move from the grains of higher surface energy to the grains of lower surface energy. As a result, under the process conditions for higher adatom mobility, the texture of Ag thin films could be evolved faster to the plane of lower surface energy. Chiu and Barber proposed that the product of ion flux and the incident energy represents the resultant energy per deposited silver atom [2]. In that point of view, they attributed the increased (1 1 1) peak intensity to higher ion bombardment effect at lower sputtering pressure. However, in this study, it was found that the (1 1 1) peak intensity decreased again when sputtering pressure decreased below 0.1 Pa. This may be due to very low ion flux in spite of higher ion energy at very low pressure. Its XRD peak intensity was very low compared with that of other conditions, which means bad crystallinity. At higher pressure (over 1.4 Pa), the ion flux seems to be higher but Ar^+ ion energy is very low due to frequent collision of ions with other gas molecules or ions, and thus the supplied energy by ions becomes very low. The kinetic energy of sputtered atoms would be very low due to similar reasons.

Fig. 2(b) presents the relative portion of (1 1 1) intensity $(I_{(111)}/(I_{(111)} + I_{(200)}))$ depending upon sputtering power. The samples were deposited under the pressure of 0.14 Pa without heating the substrates. The thickness of the samples was about 300 nm. The dynamic deposition rate ranged from about 70–750 nm × m/min when the sputtering power increased from 0.5 to 5 kW. As the sputtering power increased, the (1 1 1) peak intensity became stronger. At lower sputtering power, the ion density is expected to be relatively lower. When the power increased from 0.5 to 5 kW, the discharge current increased from 1.56 to 12.26 A. The discharge voltage increased from 317 to 406 V by increasing the power 10 times. This may cause relatively lower effect than current, however, the magnitude of electric field, which accelerates ions, would be smaller at lower sputtering power, and thus the ions have smaller kinetic energy. Within the range of our experiment, the adatom mobility seems to be enhanced with increasing sputtering power. On the other hand, the capture length (the maximum distance at which a flux atom can attach to an atom on the surface) would decrease as sputtering power since the adatoms are more likely to be buried by incident atom flux at higher power conditions. If the movement of an adatom is assumed to follow random-walk model, the average distance that it can move in a time t is $\sqrt{2D_s t}$. If the deposition rate increased, the time t, which adatoms can move within, becomes smaller, and consequently the chance that the adatom can find the lowest energy site may be reduced. Thus, relative portion of (1 1 1) peak may decrease as power if it was possible to increase the power more than the limitation of this research.

Fig. 2(c) shows that the change of the relative portion of (1 1 1) intensity $(I_{(111)}/(I_{(111)} + I_{(200)}))$ depending upon substrate temperature. The films were deposited under the pressure of 0.14 Pa and at the power of 3 kW. The portion of (1 1 1) grain was highest at the temperature of 100 °C, and decreased again over 100 °C. Although the adatom mobility increased continuously, the texture was not steadily developed to (1 1 1) direction.

Based on our results and previous reports of other researchers, the scheme of Ag film texture change can be summarized as follows. At the initial stage of film growth, the nuclei have mixed orientation. After forming a continuous film, the grains of (1 1 1) plane, which have lower surface energy, occupy more area of film surface. The rate of this evolution would be determined by adatom mobility and shadowing effect [6]. Sputtering parameters control the adatom mobility and shadowing effect. In other words, with the process conditions for higher adatom mobility and lower shadowing effect, the development of (1 1 1)-oriented grains would be promoted.

Meanwhile, there have been some reports that (1 1 1)-preferred orientation became stronger, as ion energy increased [2,8]. However, when the ion energy increased more than a limit, (2 0 0) texture became stronger [2,8]. They proposed a selection mechanism of texture development, and suggested that the (2 0 0)-oriented grains have the highest chance of surviving under re-sputtering condition since the (2 0 0) planes have the lowest sputtering yield. However, in this study, ion energy could not be considerably changed by raising substrate temperature, as a result, the increase of (2 2 2) peak portion at higher deposition

temperatures would not be related with re-sputtering yield. The structure zone model proposed by J. A. Thornton show that thin films deposited at high temperatures have zone 3 structures rather than zone 2 or zone T structures [14]. The films deposited under zone 2 or zone T contain columnar structures, and consequently they have preferred orientation. However, zone 3 structures have much more randomly oriented grains by secondary nucleation and recrystallization. The increase of (2 2 2) peak portion seems to be from higher portion of zone 3 structures at higher deposition temperatures.

3.2. Properties of silver thin films

Figs. 3(a) and (b) show the change of film stress and density as functions of pressure and sputtering power, respectively. The samples were deposited without heating, and the thickness was about 300 nm. The film density was higher in the moderate range of sputtering pressure of our experiment. As previously mentioned, the portion of (1 1 1) peak was also highest in that range. Consequently, higher film density is attributed to higher adatom mobility. At higher pressures, the silver film density decreased significantly, and residual stress was converted from compressive to tensile stress due to reduced Ar^{+} ion peening effect. Higher sputtering power resulted in higher film density and compressive stress, as shown in Fig. 6(b). Those results are also consistent with the change of adatom mobility, as explained in previous section.

These variations of films density as functions of sputtering parameters were in accordance with the change in specific resistivity, as shown in Fig. 4(a) and (b). Moderate range of sputtering pressure and high sputtering power led to the lowest resistivity of silver films. However, lower impurity content in the films deposited with higher sputtering power may also contribute to lower resistivity.

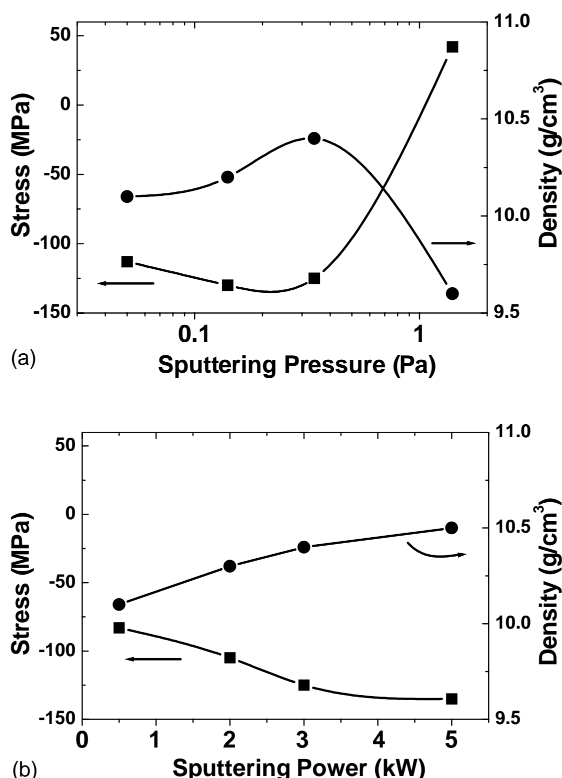

Fig. 3. Variations of films stress and density depending upon (a) sputtering pressure and (b) power.

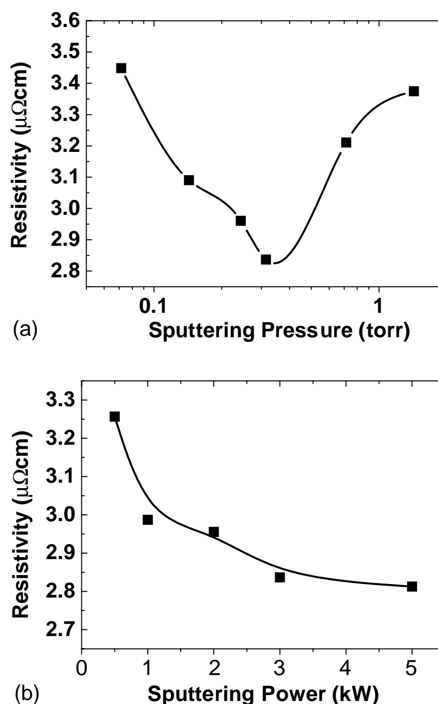

Fig. 4. Variations of specific resistivity depending upon (a) sputtering pressure and (b) power.

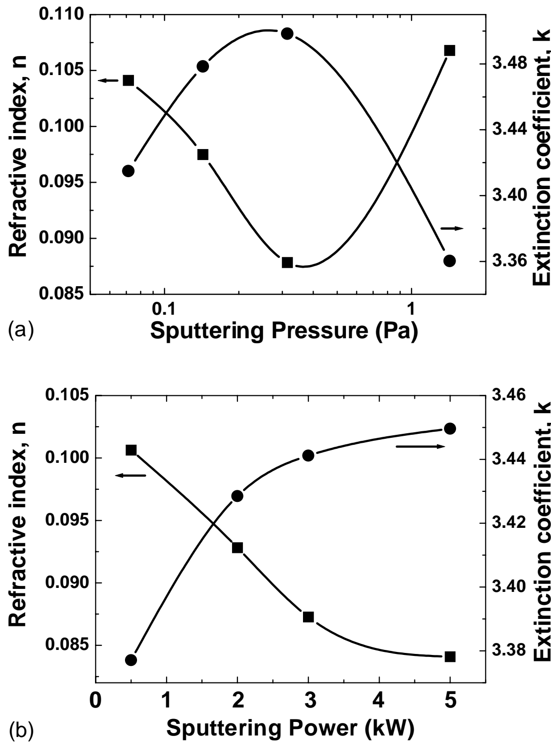

Fig. 5. Variations of optical constants n and k depending upon (a) sputtering pressure and (b) power.

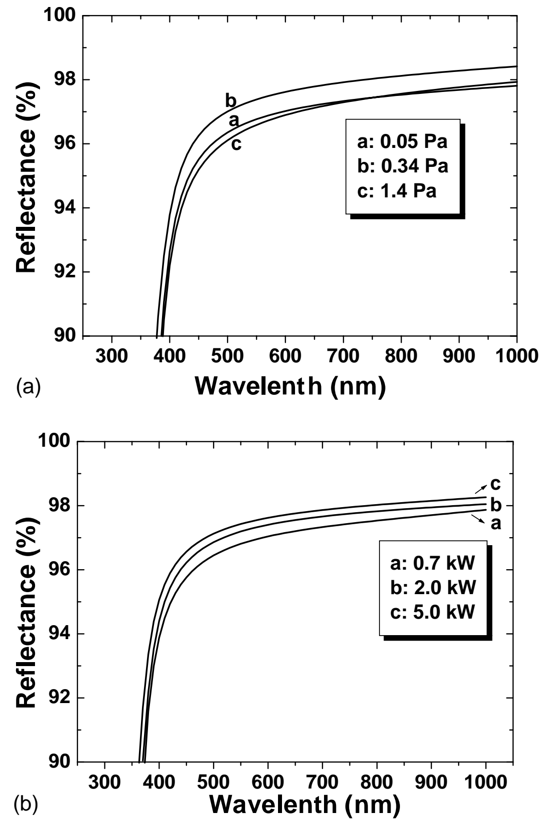

Fig. 6. Variations of optical reflectance depending upon (a) sputtering pressure and (b) power

Fig. 5(a) and (b) present the optical constants, n and k values at the wavelength of 550 nm as functions of sputtering pressure and power, respectively. Spectroscopic ellipsometry measurements were performed applying a model combining Drude and Lorentz terms. For the deposition conditions where n value was higher, k value was lower. If the relationship between optical constants and film packing density follow linear law of mixing [13], then the refractive index of film n_f equals $n_b + (1 - P)n_v$. (n_f, n_b, and n_v are the refractive indices of film, bulk, and void, respectively. P is film packing density.). The extinction coefficient, k would also follow similar law. The n and k values of void are close to 1 and 0, respectively, so if the packing density P of Ag film decreased, the complex optical constants would approach to $1 - 0i$. Thus, n value would increase (become closer to 1), and k value would decrease (become closer to 0) under the conditions for lower Ag film density. With the optical constants measured in the spectral range of 350–1000 nm, specular reflectance curves were calculated. As shown in Fig. 6(a) and (b), denser film showed better reflectance, which means lower optical loss.

4. Conclusions

The crystallographic orientation of Ag thin films deposited by DC magnetron sputtering technique was evolved to the grains of (1 1 1) planes, which have the lowest surface energy. In the moderate range of sputtering pressure (0.14–0.71 Pa), the fraction of (1 1 1) grains as well as the film density and optical reflectance were higher, which may be due to better adatom mobility induced by more effective ion bombardment during deposition. By similar mechanism, higher sputtering power in our experimental range was found to be helpful for higher fraction of (1 1 1) grains, higher film density and optical reflectance. Specific

resistivity was also lowest for the Ag films deposited under those conditions.

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