

## Research Article

# Understanding the Preferred Crystal Orientation of Sputtered Silver in Ar/N<sub>2</sub> Atmosphere: A Microstructure Investigation

YuHao Hu,<sup>1</sup> Jiajun Zhu ,<sup>1,2</sup> Chao Zhang ,<sup>3</sup> Wulin Yang,<sup>1,2</sup> Licai Fu,<sup>1,2</sup> Deyi Li,<sup>1,2</sup> and Lingping Zhou<sup>1,2</sup>

<sup>1</sup>College of Materials Science and Engineering, Hunan University, Changsha 410082, China

<sup>2</sup>Hunan Province Key Laboratory for Spray Deposition Technology and Application, Hunan University, Changsha 410082, China

<sup>3</sup>Science and Technology on Power Sources Laboratory, Tianjin Institute of Power Sources, Tianjin 300384, China

Correspondence should be addressed to Jiajun Zhu; [jiajun@hnu.edu.cn](mailto:jiajun@hnu.edu.cn) and Chao Zhang; [zcmaster@163.com](mailto:zcmaster@163.com)

Received 9 May 2019; Accepted 9 July 2019; Published 6 November 2019

Academic Editor: Pramod Koshy

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Silver thin films were prepared by direct current (DC) magnetron sputtering technique in Ar/N<sub>2</sub> atmosphere with various N<sub>2</sub> volumetric ratios on Si substrates. Silver thin films prepared in pure Ar atmosphere show highly (111) preferred orientation. However, as the N<sub>2</sub> content increases, Ag (111) preferred orientation evolves into (100) preferred orientation gradually. When N<sub>2</sub> content is more than 12.5 vol.%, silver thin films exhibit highly (100) preferred orientation. Moreover, the average grain size decreases with increasing N<sub>2</sub> content. Silver thin films with low relative density are prepared at high N<sub>2</sub> content, which results in higher resistivity of films. By analyzing the resistivity and microstructures of silver thin films, the optimum range of N<sub>2</sub> content to get compact silver thin films is found to be not more than 33.3 vol.%. Finally, the mechanism of N<sub>2</sub> addition on microstructure evolution of silver thin films was proposed.

## 1. Introduction

Noble metal silver (Ag) has excellent characteristics, such as low electrical resistivity, high thermal conduction, high reflectivity in visible and infrared regions, and great weldable and antimicrobial properties [1–3]. Silver and corresponding composites are widely used in the fields of electronics, aerospace, medical instruments, etc. For example, Ag/GaN multilayer films are used as the conductor electrodes of light-emitting diodes (LEDs), the coatings of laser safety glasses, and display window materials which block microwave radiation [4, 5]. Ag/TiN or Ag/TaN multilayer films are potential materials to be used as interconnects on integrated circuits [6–8]. Beyond that, Ag/TiN multilayer films are also used in the photocatalytic field [9].

In the above applications, the silver thin films were generally prepared by physical vapor deposition (PVD) in Ar atmosphere while nitride thin films were prepared by PVD in Ar/N<sub>2</sub> atmosphere. During the preparation process of Ag/nitride multilayer films, the sputtering gas needed to be

changed; thus, the preparation process of Ag/nitride multilayer films was complicated. If the Ag/nitride multilayer films can be prepared in the same Ar/N<sub>2</sub> atmosphere, it will simplify the preparation process of Ag/nitride multilayer thin films. Therefore, it is necessary to study the influence of Ar/N<sub>2</sub> sputtering gas on microstructures of silver thin films.

Compared with Ar, N<sub>2</sub> exhibits higher chemical reactivity. It is difficult to obtain pure metal thin films in N<sub>2</sub> or Ar/N<sub>2</sub> atmospheres. Hence, N<sub>2</sub> is usually used to prepare nitride thin films via PVD (physical vapor deposition). Moreover, the influence of N<sub>2</sub> content in Ar/N<sub>2</sub> atmosphere on crystal orientation, grain size, and relative density of films is also demonstrated in previous research studies. In 2004, Kawamura et al. reported that the Ni thin films were prepared in low N<sub>2</sub> flow ratio; however, Ni<sub>3</sub>N phase was observed when the flow ratio of N<sub>2</sub> arrived to 12%. Furthermore, the crystal orientation of Ni thin films was changed from (111) to (100) due to the introduction of N<sub>2</sub> into the sputtering atmosphere [10]. Afterwards, they discovered that the intensity of (002) peak (C-axis orientation)

of Ru thin films decreased with the increasing N<sub>2</sub> sputtering gas proportion at a substrate temperature of 100°C, and the intensity of (002) peak of Ru thin films eventually disappeared when the N<sub>2</sub> content was 50% flow ratio. In addition, it was observed by Auger electron spectroscopy that the Ru film deposited at 50% N<sub>2</sub> content contained nitrogen [11]. Calinas et al. developed the formation of nanocrystalline copper thin films through controlled addition of nitrogen. According to their work, the average nitrogen content for the Cu-N thin films was found to be 1.5 at.%, 3.5 at.%, and 7 at.% for the samples with P<sub>N<sub>2</sub></sub>:P<sub>Ar</sub> ratios of 1:60, 1:30, and 1:2, respectively. And, the Cu<sub>3</sub>N phase was identified with the highest P<sub>N<sub>2</sub></sub>:P<sub>Ar</sub> ratio of 1:2. Moreover, when the nitrogen content in Cu thin films was low, the grain size of Cu thin films rapidly decreased with the increase of the nitrogen content [12]. Based on all above mentioned, the N<sub>2</sub> content has a significant influence on the microstructures and composition of metal thin films; however, the microstructures of silver thin films prepared at various N<sub>2</sub> contents in Ar/N<sub>2</sub> atmosphere are rarely reported. Thus, it is meaningful to research the effect of N<sub>2</sub> content in Ar/N<sub>2</sub> atmosphere on the microstructures of silver thin films and find a suitable range of N<sub>2</sub> content to prepare silver thin films.

In this paper, a series of samples were prepared by direct current (DC) magnetron sputtering in Ar/N<sub>2</sub> atmosphere with various N<sub>2</sub> contents (0 vol.%, 8 vol.%, 12.5 vol.%, 33.3 vol.%, 50 vol.%, 66.7 vol.%, and 100 vol.%) on Si substrates. Crystal orientation, texture coefficient, and grain size of silver thin films were characterized as a function of N<sub>2</sub> content. Furthermore, surface morphology, cross-sectional morphology, and electrical properties of silver thin films were investigated. In the end, the mechanism of microstructure evolution was also proposed.

## 2. Experimental

Silver thin films were prepared by direct current magnetron sputtering deposition system (MIS800). (100) single crystal silicon sheets were selected as the substrate material and cut into square-shaped of approximately 10 mm × 10 mm × 0.38 mm. These Si specimens were ultrasonically cleaned with acetone, ethanol, and deionized water in sequence before being dried. Prior to deposition, the base pressure was less than 4.0 × 10<sup>-4</sup> Pa. Then, the substrates were cleaned by Ar<sup>+</sup> beam bombardment with 600 V/50 mA lasting for 10 minutes to remove surface impurity. The substrate holder was then rotated to be perpendicular to the direction parallel with the Ag target (99.99% purity). During the deposition, the distance between Ag target and substrate was 70 mm. The working pressure was maintained at 1 Pa, and the power was 120 W. Finally, the films were deposited for 10 minutes at various N<sub>2</sub> contents in Ar/N<sub>2</sub> atmosphere. The samples numbered on the basis of N<sub>2</sub> content are shown in the Table 1.

The phase composition and crystallographic structure of silver thin films were analyzed by X-ray diffraction (XRD) measurement (MiniFlex made by Rigaku) with Cu K-α radiation source. Surface and cross-sectional morphologies of silver thin films were recorded by using a scanning electron microscope (SEM, Hitachi S-4800). The surface chemical compositions of the silver thin films were studied

by the K-ALPHA X-ray (Thermo Fisher Scientific) photoelectron spectroscopy (XPS) instrument. The sheet resistance of silver thin films on Si substrates was measured by a four-point probe (RTS-8). The resistivity was calculated according the following formula:

$$\rho = R_s d, \quad (1)$$

where  $d$  is the thickness of the film measured by SEM and  $R_s$  is the sheet resistance of the film.

## 3. Results and Discussion

**3.1. Crystal Orientation of Silver Thin Films.** Figure 1 shows X-ray diffraction patterns of silver thin films on Si substrates. The value of ordinate was set same in order to compare the Ag peak intensity of all samples easily. In Figure 1, high Ag (111) and (200) diffraction peaks are found clearly in all samples. The Si substrate peak is so high that Ag (220), (311), and (222) diffraction peaks could not be observed in almost all samples.

The phase of nitride is not detected by XRD, which is in accordance with the results of XPS spectra that are shown in Figure 2. Considering all the samples were exposed in air before XPS characterization, the sample was etched 5 minutes by Ar<sup>+</sup> (2 keV) to exclude the absorptions of C, N, and O elements from the air. As seen from the wide-scan spectra of S0, S33, and S100 in Figure 2(a), only Ag is observed. The high-resolution spectra of Ag 3d and the corresponding fitting curves are shown in Figure 2(b), the area ratio of the Ag 3d<sub>3/2</sub> and Ag 3d<sub>5/2</sub> peaks is about 2/3, and the binding energy of Ag 3d<sub>3/2</sub> and Ag 3d<sub>5/2</sub> is 374.4 eV and 368.4 eV, respectively, which agrees with the binding energy of metallic Ag [13, 14]. Based on the results of XRD and XPS, no nitride and oxide exist in the thin film, and pure silver thin films were obtained in pure N<sub>2</sub> atmosphere.

It is clear that the relative intensities of Ag (111) and (200) diffraction peaks are different for silver thin films prepared at different N<sub>2</sub> contents in Figure 1. Preferred orientation exists in all samples. In order to explain the degree of the silver thin films' preferred orientation, the texture coefficients of (111) plane and (100) plane ( $P_{(111)}$  and  $P_{(100)}$ ) were represented quantitatively by the Harris method in the following formula [15, 16]:

$$P_{(hkl)_i} = \frac{I_{(hkl)_i}}{I_{0(hkl)_i}} \left[ \frac{1}{n} \sum_{i=1}^n \frac{I_{(hkl)_i}}{I_{0(hkl)_i}} \right]^{-1}, \quad (2)$$

where  $I_{0(hkl)_i}$  is the standard intensity of the (hkl) plane for the  $i$ th peak from powder diffraction file (PDF) card,  $I_{(hkl)_i}$  is the detected intensity of the (hkl) plane for the  $i$ th peak, and  $n$  is the total number of diffraction peaks considered in the analysis. ICSD card no. 04-0783 of Ag was used in this calculation, and other peaks were so weak that only (111) and (200) peaks were considered. The values of  $P_{(111)}$  and  $P_{(100)}$  of silver thin films on Si substrates depending upon the N<sub>2</sub> content are shown in Figure 3 ( $P_{(111)} + P_{(100)} = 2$ ). The value of  $P_{(100)}$  suddenly increases when the N<sub>2</sub> content changes from 0 vol.% to 12.5 vol.% and slightly increases with the increasing N<sub>2</sub> content ranging from 12.5 vol.% to 33.3 vol.%. When N<sub>2</sub> content exceeds 33.3 vol.%,  $P_{(100)}$

TABLE 1: Ar/N<sub>2</sub> ratio and numbered messages.

N <sub>2</sub> content (volumetric ratio)	0%	8%	12.5%	33.3%	50%	66.7%	100%
Sample number	S0	S8	S12	S33	S50	S66	S100

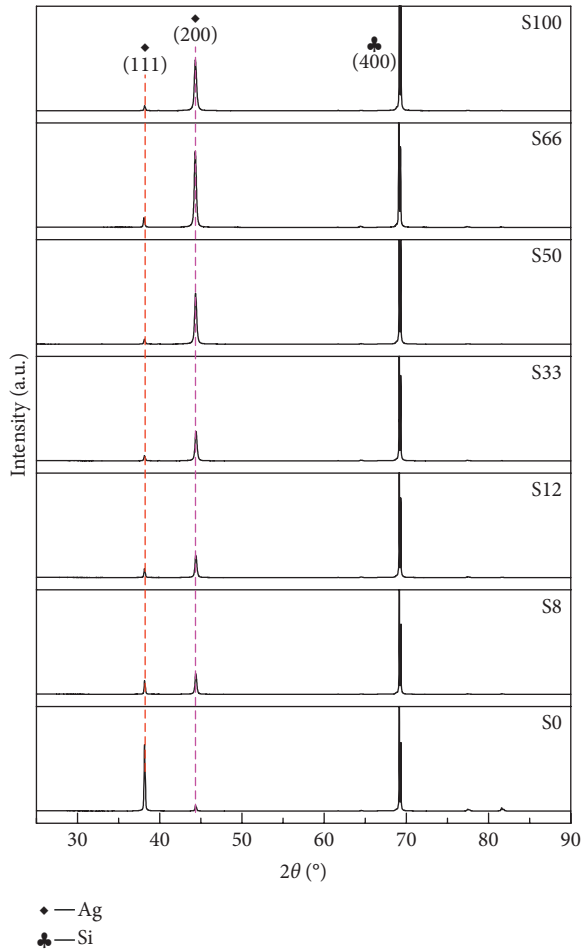


FIGURE 1: X-ray diffraction patterns (XRD) of silver thin films (S0, S8, S12, S33, S50, S66, and S100).

becomes stable. Overall, as the N<sub>2</sub> content increases, grains prefer to grow along (100) plane while (111) plane is restrained. Based on the above results, silver thin films with highly (111) preferred orientation were prepared in pure Ar atmosphere ( $P_{(111)} = 1.66 \gg 1$ ), and silver thin films with highly (100) preferred orientation were prepared at 12.5 vol.% N<sub>2</sub> content ( $P_{(100)} = 1.72 \gg 1$ ). Therefore, it is concluded that the preferred orientation of silver thin films can be adjusted successfully in Ar/N<sub>2</sub> atmosphere through controlling the N<sub>2</sub> content.

**3.2. Grain Size of Silver Thin Films.** The grain sizes of (111) plane ( $G_{(111)}$ ) and (200) plane ( $G_{(200)}$ ) were calculated based on the Scherrer formula:

$$G = \frac{k\lambda}{\beta \cos \theta} \quad (3)$$

where  $G$  is the grain size,  $k = 0.89$ ,  $\lambda = 0.154056$  nm,  $\beta$  is the full width at half maximum (FWHM) of the diffraction peak,

and  $\theta$  is the Bragg angle at corresponding diffraction peak. The instrument width was deducted by Si standard samples.  $\bar{G}$  represents the average grain size of silver thin films, which were estimated according to the following formula:

$$\bar{G} = \frac{G_{(111)}P_{(111)} + G_{(200)}P_{(100)}}{2} \quad (4)$$

Grain size of silver thin films is shown in Figure 4. It is obvious that  $G_{(111)}$  is bigger than  $G_{(200)}$  for all samples, and  $G_{(111)}$  decreases with increasing N<sub>2</sub> content. The average grain size  $\bar{G}$  decreases rapidly from 82 nm to 40 nm with the increasing N<sub>2</sub> content ranging from 0 vol.% to 12.5 vol.%, and then it decreases slightly. Finally,  $\bar{G}$  reduces to 31 nm when the N<sub>2</sub> content is 100%. The results of grain size suggest that grain growth was suppressed in N<sub>2</sub> atmosphere during the deposition.

**3.3. Surface and Cross-Sectional Morphologies of Silver Thin Films.** The SEM cross-sectional images of S0, S12, S33, S50, and S100 are shown in Figure 5. The cross-sectional structure of silver thin films is compact as shown in Figure 5(a). Denser structure is also observed in Figure 5(b). However, few holes are observed in S33 in Figure 5(c). Compared with S33, a large number of holes exist in S50 and S100 in Figures 5(d) and 5(e), and the mean diameter of holes in S50 and S100 is bigger than that in S33. The porous-style structure indicates the low relative density of films; thus, the relative densities of S50 and S100 are extremely worse than S33. In addition, the thickness of silver thin films decreases from 1.9  $\mu\text{m}$  to 1.6  $\mu\text{m}$  when the N<sub>2</sub> content ranged from 0 vol.% to 33.3 vol.%, which suggests that the deposition rate of silver thin films decreases with increasing N<sub>2</sub> content. However, the thickness of silver thin films prepared at 50 vol.% N<sub>2</sub> content is 1.8  $\mu\text{m}$ . Compared to S33, the increase of thickness in S50 may be caused by its loose structure. Although the structure in S100 is loose, the thickness of S100 reduces to 1.45  $\mu\text{m}$ , so a very low deposition rate existed in pure N<sub>2</sub> atmosphere. In summary, as N<sub>2</sub> content increases, the thickness of films decreases firstly, then increases, and decreases finally.

The SEM surface images of S0, S12, S33, S50, and S100 are shown in Figure 5. Clean and flat surface can be observed in S0, S12, and S33 in Figures 5(a1), 5(b1), and 5(c1). The average surface granule size of S0, S12, and S33 decreases in sequence. The relative flat surface in S50 is also observed in Figure 5(d1); however, many holes and a few big spherical crystalline granules are observed on the surface. In Figure 5(e1), spherical crystalline granules are dispersed on the surface, and a lot of holes and grooves exist. It is obvious that the surface of S100 is extremely sparser and rough. The morphology can indirectly reflect the relative density of films. According to the analysis of surface and cross-sectional morphologies, the relative density of films was evaluated. The sequence of films' relative density from high to

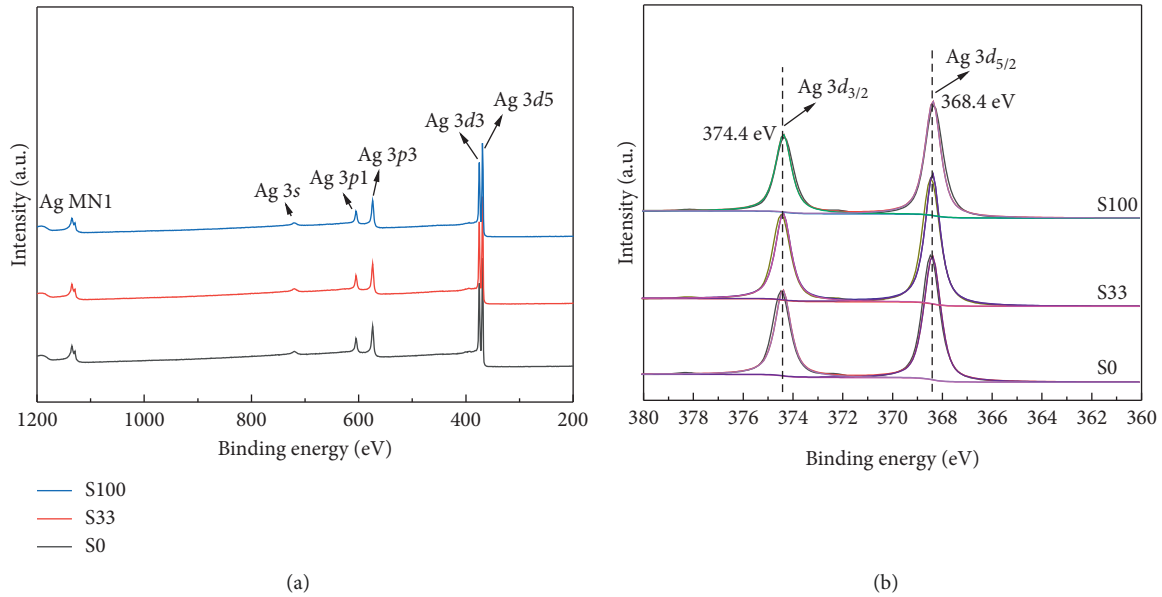


FIGURE 2: XPS spectra of S0, S33, and S100. (a) The wide-scan spectra of S100 sample. (b) Ag  $3d$  spectra.

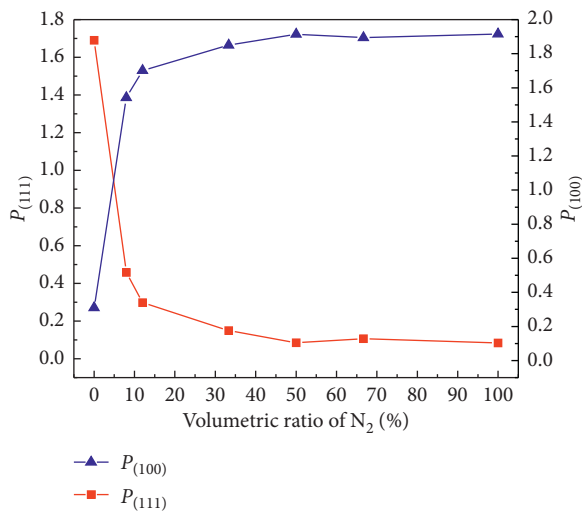


FIGURE 3:  $P_{(111)}$  and  $P_{(100)}$  of silver thin films on Si substrates as a function of the volumetric ratio of  $N_2$  content.

low is as follows: S0 and S12, S33, S50, and S100, which indicates that the high  $N_2$  content in Ar/ $N_2$  atmosphere resulted in the low relative density of films during the deposition. Therefore, to obtain a compact silver thin film through PVD process in Ar/ $N_2$  atmosphere, the  $N_2$  content does not exceed 33.3 vol.%.

**3.4. Resistivity of Silver Thin Films.** The resistivity of silver thin films is shown in Figure 6. It can be seen from the figure that the resistivity of silver thin films increased with increasing  $N_2$  content until the  $N_2$  content reached 66.7 vol.%, and then the resistivity of silver thin films stabilized with increasing  $N_2$  content. Generally, the resistivity of metal thin films is the collaborative results of surface scattering, defects and impurity scattering, and grain boundary scattering. When the

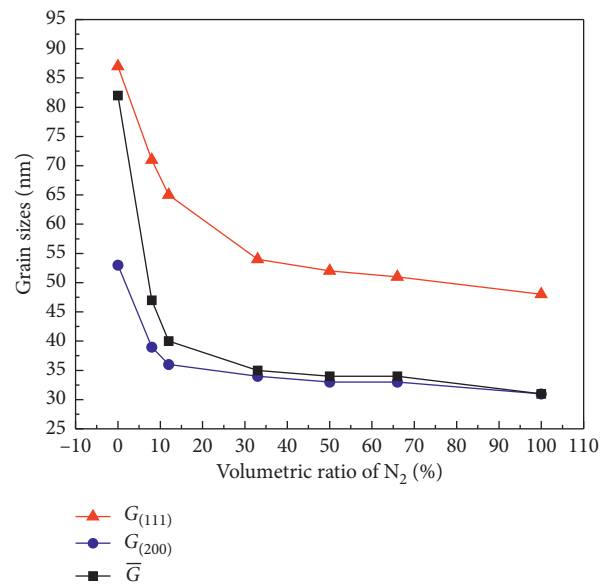


FIGURE 4: Grain size of silver thin films as a function of the volumetric ratio of  $N_2$  content.

thickness of metal thin films is comparable in magnitude with the electronic mean free path of bulk material, the resistivity of metal thin films increases as the thickness of films decreases due to the surface scattering, which has been demonstrated by the Fuchs-Sondheimer (FS) model [17, 18]. However, the thicknesses of silver thin films in this study ranges from 1.45  $\mu\text{m}$  to 1.9  $\mu\text{m}$ , and it is extremely higher than the mean free path of electron (52 nm) [19]. Thus, the effect of films thickness on the resistivity can be negligible.

The resistivity of silver thin films prepared in pure Ar atmosphere is close to the resistivity of bulk material (1.6  $\mu\Omega\cdot\text{cm}$ ). As the  $N_2$  content increases from 0 vol.% to 33.3 vol.%, the resistivity of silver thin films increases slightly,



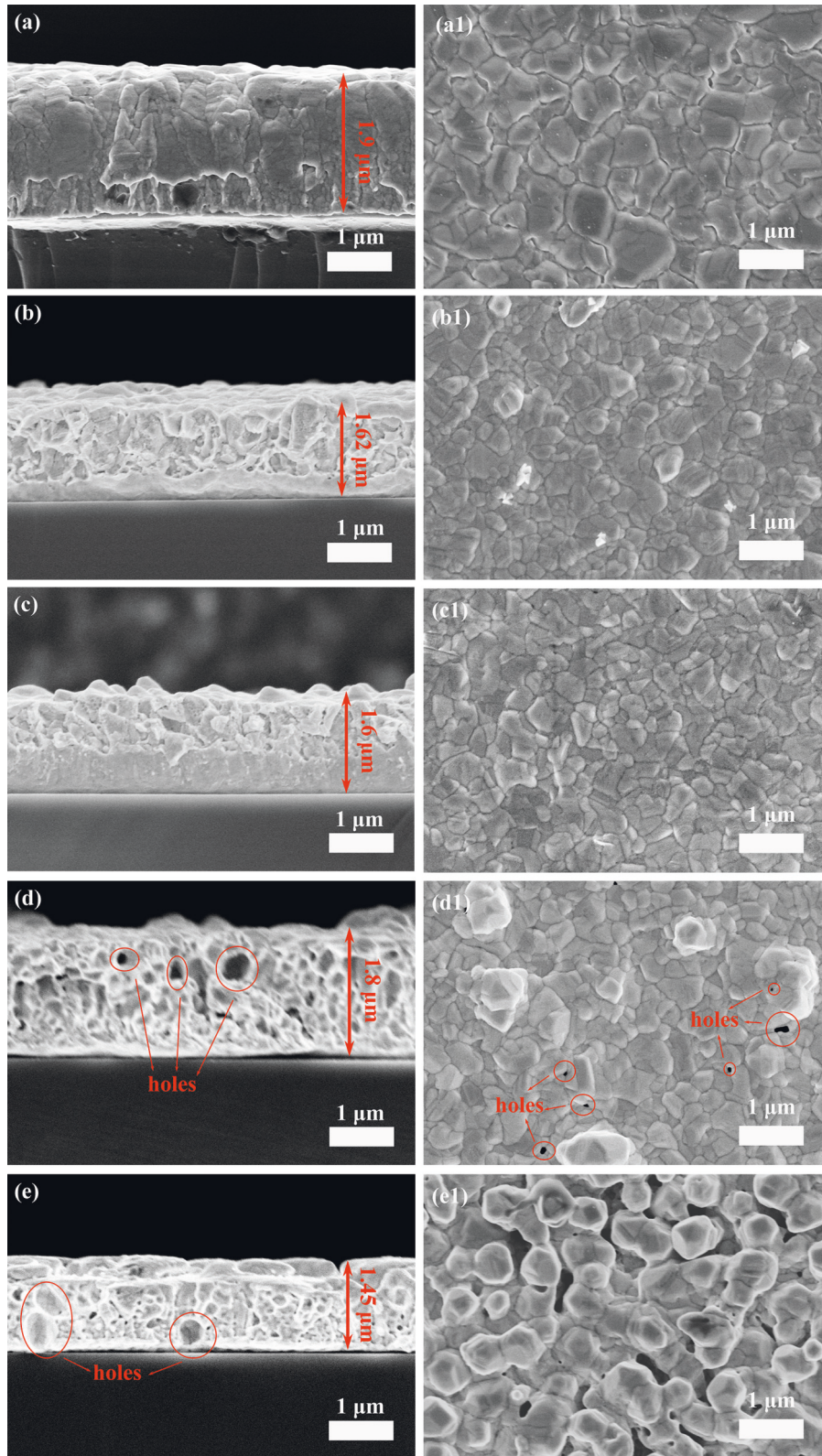


FIGURE 5: Surface and cross-sectional morphologies of S0, S12, S33, S50, and S100. (a), (b), (c), (d), and (e) show the cross-sectional morphologies of S0, S12, S33, S50, and S100, respectively. (a1), (b1), (c1), (d1), and (e1) show the surface morphologies of S0, S12, S33, S50, and S100, respectively.

while the average grain size of silver thin films decreases from 82 nm to 35 nm. The grain size is comparable with the mean free path of electron in our works. The famous

Mayadas and Shatzkes (MS) model explained the relation between grain boundary and resistivity, and the MS model is shown as follows:

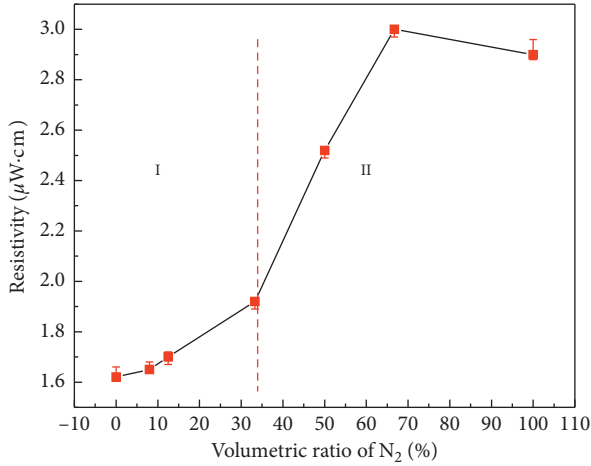


FIGURE 6: Resistivity of silver thin films as a function of the volumetric ratio of N<sub>2</sub> content.

$$\rho = \rho_0 \left[ 1 + \frac{3}{2} \times \frac{1}{G} \times \frac{R}{1-R} \right], \quad (5)$$

where  $G$  is the grain size,  $R$  is the grain boundary reflection coefficient,  $\rho_0$  is the bulk resistivity, and  $\rho$  is the measured resistivity. The amount of grain boundary per unit volume increases with the reduction of grain size. The grain boundary prevents the electron or phonon to transport, which leads to the increase of resistivity. Therefore, in phase I as shown in Figure 6, the main factor leading to the increasing resistivity of silver thin films is the grain boundary scattering. When the N<sub>2</sub> content exceeds 33.3 vol.%, the average grain size of silver thin films decreases from 40 nm to 31 nm slowly, so the resistivity caused by grain boundary scattering is close. When the N<sub>2</sub> content exceeds 33.3 vol.%, the relative density of films is low, and loose and porous structure can be observed from the surface and cross-sectional morphologies in Figure 5. The holes in films seriously hinder the transmission of electrons; thus, the defect scattering plays a major role in the dramatic increase in resistivity of films. In region II, the number of defects such as holes increases with increasing N<sub>2</sub> content; however, the number of defects no longer increases while the N<sub>2</sub> content arrived at 66.7 vol.%. Correspondingly, the resistivity of silver thin films increases rapidly, and then the resistivity of silver thin films stabilizes. As we all know, the quality of silver thin films can be estimated facily by the resistivity of silver thin film. When the N<sub>2</sub> content ranges from 0 vol.% to 33.3 vol.%, the grain boundary scattering is the main reason to lead to a small difference in resistivity, and the effect of defect scattering on resistivity is similar, so the relative density of silver thin films is close. When the N<sub>2</sub> content exceeds 33.3 vol.%, the higher resistivity indicates that silver thin films have a lower relative density.

**3.5. Mechanism of Microstructure Evolution.** The crystal orientation, grain size, morphology, and relative density of silver thin films changed with the increasing N<sub>2</sub> content. So, the N<sub>2</sub> content has a significant effect on the microstructures

of silver thin films. It can be speculated that the change in microstructures of silver thin films was related to the process of generation, transport, and deposition of sputtered particles. The schematic diagram of silver thin films' sputtering, transport, and deposition in pure Ar and pure N<sub>2</sub> atmospheres is described, respectively, in Figure 7.

During the complicated deposition process of silver thin films, the discharge is maintained by sputtering gas. In Ar/N<sub>2</sub> discharge, Ar<sup>+</sup> and N<sub>2</sub><sup>+</sup> are the main ions, and Ar atoms, N<sub>2</sub> molecules, and a small amount of N<sup>+</sup> ion also exist in the vacuum, which have been detected by plasma diagnostic techniques in some literatures [20–22]. There is no doubt that Ar<sup>+</sup> is the main ion in Ar discharge, and N<sub>2</sub><sup>+</sup> is the main ion in N<sub>2</sub> discharge. The electron density and ion density in Ar discharge are higher than those in N<sub>2</sub> discharge under other same parameters, which have been reported in literatures [20, 23]. A higher ionization rate of gas exists in Ar discharge compared with that in N<sub>2</sub> discharge, and a large quantity of sputtered Ar<sup>+</sup> result in high sputter yields in Ar discharge, so bigger and more Ag clusters exist in Ar discharge compared with those in N<sub>2</sub>. Moreover, another role of sputtering gas is to affect the energy distribution through the collision process with sputtered particles in the transport process of sputtered particles. Mean free path ( $\lambda$ ) was estimated according to the following formula:

$$\lambda = \frac{kT}{\sqrt{2}\pi d^2 P}, \quad (6)$$

where  $k$  is the Boltzmann constant,  $T$  is the absolute temperature (298 K is adopted here),  $d$  is the molecular diameter, and  $P$  is the working pressure (1 Pa). The molecular diameter of Ar (3.4 Å) is smaller than N<sub>2</sub> (3.64 Å); thus, the mean free path of N<sub>2</sub> ( $\lambda_{N_2}$  is about 7 mm) is lower than Ar ( $\lambda_{Ar}$  is about 8 mm). When sputtered particles are transported from target to substrates, the sputtered particles are disturbed due to the collision with sputtering gas molecules. The collision frequency between sputtered particles and sputtering gas molecules is more intense in N<sub>2</sub> sputtering gas due to the low mean free path. Compared with Ar discharge, the higher collision frequency in the transport process and lower sputter yields led to a lower deposition rate in N<sub>2</sub> discharge, which is directly reflected in the thickness of silver thin films. Moreover, the high collision frequency in N<sub>2</sub> discharge leads to severe energy loss during the transport process. So, Ag clusters have lower energy  $E_k$  in N<sub>2</sub> discharge than that in Ar discharge when they arrived to substrates.

The carrying energy of Ag clusters is the driving force for migration and diffusion, and Ag clusters have higher energy  $E_k$  in Ar discharge; therefore, the Ag clusters are able to move to the gap among the clusters due to higher migration and diffusion, which result in a close-packed growth model of Ag clusters during the deposition. The close-packed plane of FCC metal is (111) plane, and grain growth of (111) plane is promoted. Compared with Ar discharge, the Ag clusters in N<sub>2</sub> discharge have lower energy. Ag clusters with lower mobility and diffusion tend to hold the initial position after they deposit on the substrates, so a relative loose-packed growth model of Ag clusters exists in N<sub>2</sub> discharge, which is



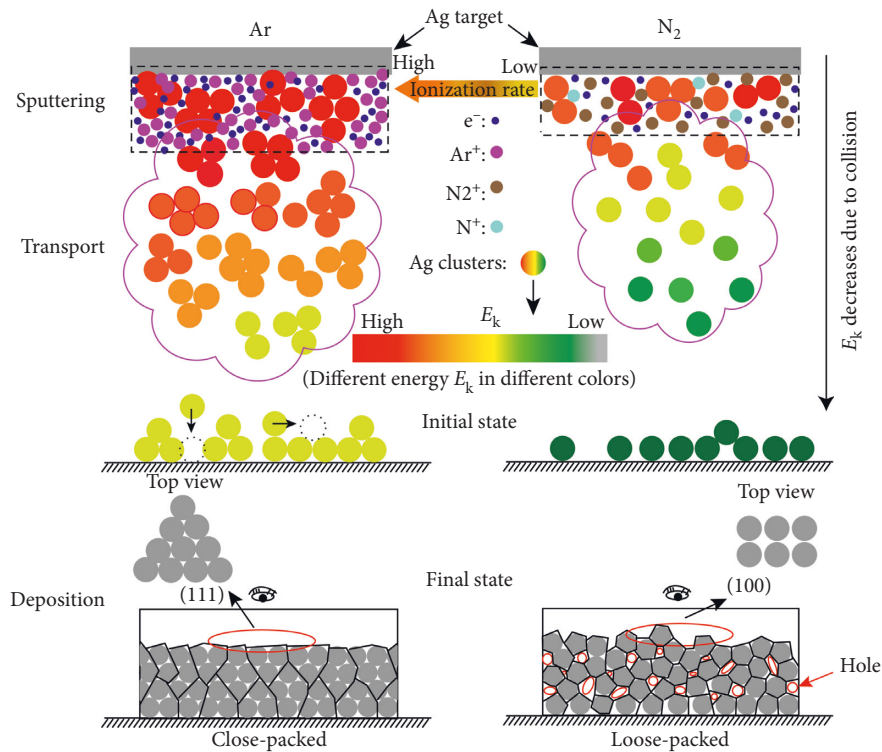


FIGURE 7: The sputtering deposition schematic diagram of silver thin films in pure Ar and pure  $N_2$  atmospheres.

proved by the cross-sectional morphology in Figure 5. Moreover, in Ar discharge, the high mobility and big size of Ag clusters lead to big initial grain size during the coalescence stage. During the grain growth, the lower mobility and diffusion leads to a higher nucleation rate in  $N_2$  discharge. Therefore, the initial and final grain size in Ar discharge is bigger than that in  $N_2$  discharge. In FCC metal, (111) plane has the lowest surface energy and (100) plane has the lowest strain energy [24]. The relative higher strain energy exists in silver thin films due to the fact that a lot of defects exist in loose-packed model of Ag clusters. Therefore, the competition between surface energy and strain energy is also responsible for the orientation evolution, which agreed with the mobility and diffusion results of Ag clusters. In conclusion, the  $N_2$  content has a significant influence on the microstructures of silver thin films, and the grain boundary scattering and defect scattering caused by the microstructures of films are mainly responsible for the change in electrical properties.

#### 4. Conclusions

The sputtering gas  $N_2$  content plays an important role on microstructures of silver thin films during the deposition. As the  $N_2$  content increases, Ag (111) preferred orientation is gradually evolved into (100) preferred orientation. When  $N_2$  is more than 12.5 vol.%, silver thin films have highly (100) preferred orientation. The average grain size decreases from 82 nm to 31 nm as the  $N_2$  content increases. Silver thin films exhibit low relative density when the  $N_2$  content exceeds 33.3 vol.%. The mobility, diffusion, and energy of Ag clusters are mainly responsible for changes in the microstructures of

silver thin films. The resistivity of silver thin films is altered with the changes of the microstructures in silver thin films. When the  $N_2$  content ranges from 0 vol.% to 33.3 vol.%, the resistivity of silver thin films increases slightly, which is mainly the result of the grain boundary scattering. The defects scattering is mainly responsible for high resistivity of films prepared at high  $N_2$  content. Based on the results of films' resistivity and microstructures, the optimum range of  $N_2$  content to get compact silver thin films is below 33.3 vol.%.

#### Data Availability

All data used to support the findings of this study are included within the article.

#### Conflicts of Interest

The authors declare that there are no conflicts of interest regarding the publication of this paper.

#### Acknowledgments

This study was financially supported by the Foundation of National Key Laboratory, P R China (6142808180102) and National Natural Science Foundation of China (grant no. 51401080).

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