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Morphological and Structural Properties of Silver Nanofilms Annealed by RTP in Different Atmospheres

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Abstract: This study aims at investigating the influence of gas atmospheres on the dewetting properties of DC sputtered and rapid thermally annealed silver (Ag) nanofilms. The annealing temperature ranged from 400℃ to 600℃ and the gases studied were argon (Ar) and nitrogen (N_2). Scanning electron microscope (SEM) and focused ion beam (FIB) were employed for morphological studies, while the X-ray diffraction (XRD) technique was applied in the structural analysis of the films. The SEM and top-view FIB-SEM images of Ag films annealed in both atmospheres were characterized by irregular shaped holes. At fixed temperature, the films annealed in the N_2 atmospheres gave higher hole density and larger hole sizes than the film annealed in the Ar atmosphere. Additionally, the hole density decreased with the annealing time. For films annealed in the N_2 atmosphere, isolated dewetted particles were only obtained at 600℃ substrate temperature. The XRD patterns of all the films were characterized by Ag metallic peaks. No significant difference was observed among the films' crystal structures. The annealing atmospheres mainly influences the morphologies of Ag nanofilms.

Keywords: Ag, Dewetting, Annealing Atmosphere, FIB

1. Introduction

Thin metal films tend to disintegrate into an array of particles upon annealing. The process is referred to as solid state dewetting and is driven by surface, interface and strain energy minimization [1]. In particular, the structural and morphological properties of thin metal films deposited on non-metal surfaces have drawn more interest due to their potential applications in numerous electronic, magnetic and optical devices [2].

Generally dewetting begins with the formation of holes reaching the substrate surface. The holes then grow and develop a thickened rim due to a local curvature gradient at their edges and as the rim thickens the net curvature is reduced and edge retraction slows down. Rims break down via a fingering or pinch-off instability that lead to formation of lines that subsequently decay into isolated islands through a Rayleigh-like instability [2]. Once the isolated solid metal particles are formed, their size, shape and spacing evolution depends on the annealing temperature, time and atmosphere [3]. The annealing atmospheres play a great role in their dewetting mechanisms. This is due to the fact that in the presence of adsorbates, different diffusion paths may change [4]. The adsorbates can change the surface energy and its anisotropy; the anisotropy can affect the dewetting process by causing the texture and grain boundary character distribution changes in polycrystalline thin films [4]. Despite of the potential role of annealing atmosphere in the dewetting process of thin films, there are only few studies documented on the subject.

Anna et al. [4] investigated on the influence of annealing atmosphere on the dewetting mechanisms of magnetron sputtered gold (Au) thin films on c-plane oriented sapphire substrates. The annealing atmospheres studied were air and forming gas. They found that Au films annealed in forming gas exhibit higher surface energy anisotropy than those annealed in air. It was also observed in their microscopic images that Au films annealed in air translated into a more branched, tortuous morphology of the holes, signifying lower degree of surface energy anisotropy.

Sharma et al. [5] investigated on the influence of annealing atmospheres on the morphologies of cathodic sputtered Ag thin films. They used quartz substrates and the annealing was done in vacuum, He, O_2 and Ar atmospheres using a large mobile furnace. In all annealing atmospheres, hillock formation took place and was explained on the basis of thermal stress relaxation by diffusion creep. The largest size of hillocks was recorded by the sample that was annealed in the O_2 atmosphere and was attributed to the enhanced surface self-diffusion of silver atoms, which tends to be enhanced up to a factor of 100 in the presence of oxygen. It was also reported that, with the exception of oxygen atmosphere, there were no holes even after 20 hours. The island formation took place by the holes joining together and ultimately leading to agglomeration. The reduction in the surface energy of the islands acted as a driving force for the surface diffusion of silver atoms during agglomeration. The maximum surface area of the substrate not covered with film was about 65 % after complete agglomeration and was observed for a film of thickness 50 nm annealed at 470℃ for 2 hours.

In another study [6], the thermally evaporated Ag films coated on quartz substrates were annealed in vacuum and air. The dewetted surface was covered by holes, whose density decreased with the increase in the film thickness. They also reported from their work that the hole formation in the Ag films annealed in air was faster than in those annealed in vacuum, the result that was attributed to the increased self-diffusion of Ag films due to the presence of oxygen in air.

In a recent study, Jongpil [7] thermally annealed e-beam evaporated Ag thin films on Si (100) substrate using a vacuum tube at 400℃ in the hydrogen and oxygen atmospheres. He investigated the dominant dewetting mechanism through evaluation of temporal changes in the spatial distribution of holes. His results showed stronger spatial correlation in samples with a greater number of holes. The observed trend was attributed to the formation site of new holes, which were spatially increasing due to the presence of other holes. Additionally, Ag films annealed in the O_2 atmosphere had a larger number density of holes than those annealed in the H_2.

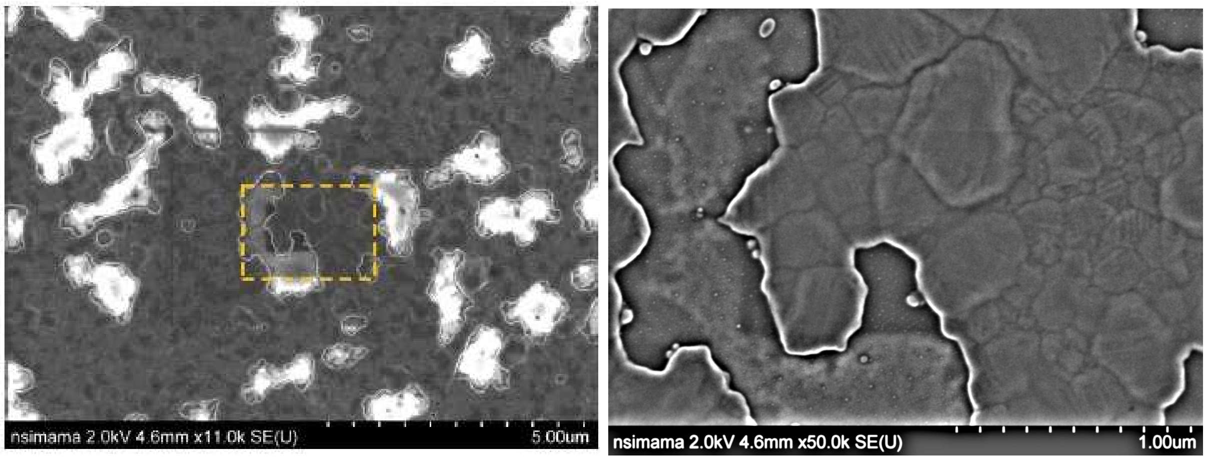
In this work we report on the influence of annealing atmospheres in the dewetting properties of Ag nanofilms prepared by DC magnetron sputtered technique. Two different atmospheres are considered, i.e. Ar and N_2. The sputtering technique has been chosen because of its simplicity and flexibility in the materials combination. The annealing was done using the rapid thermal process (RTP) at 400℃ for 30 minutes in both atmospheres and further at 500℃ and 600 ℃ in N_2 atmosphere. The RTP annealing is considered to be more effective than the tube furnace annealing since the sample is heated at a much faster rate. We show that Ag films annealed in different atmospheres result into different dewetting properties.

2. Experimental Details

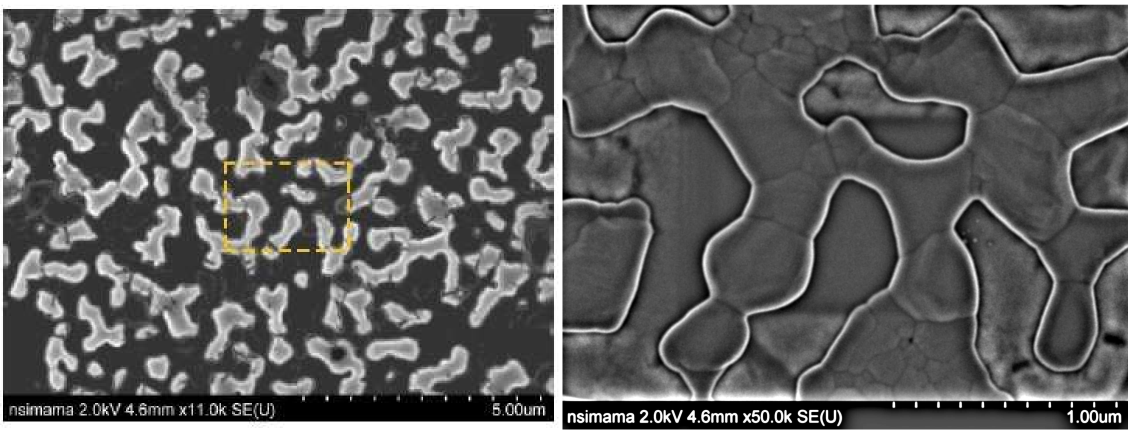
Ag films of 30 nm thickness each were deposited onto c-plane oriented sapphire ((0001) single crystal α-Al_2O_3) substrates at room temperature using *LA440S Von Ardenne Anlagentechnik GMBH* sputtering machine. Prior to deposition, the chamber was evacuated to a base pressure of 2 x 10^{-7} mbar. The DC power and argon flow rate were set at 200 W and 80 sccm respectively. The films were annealed using thermal process (*RTA, Jipelec Jetstar 100*) at 400℃ for 30 minutes in Ar and N_2 atmospheres. Then annealing in N_2 atmosphere was further done at 500 ℃ and 600 ℃ temperatures. While fixing the substrate temperature at 400℃, Ag films were annealed in the N_2 atmosphere for 10, 30 and 40 minutes. The details of the rapid thermal annealing process employed in the current work can be found elsewhere [8]. After annealing, the samples were cooled to room temperature in the furnace. The morphologies of films were investigated by high-resolution scanning electron microscopy (*SEM, Hitachi S-4800*). The machine is equipped with the energy dispersive (EDS) facility, which was used for elemental composition analysis of the films. The top view and cross-sectional FIB-SEM analysis of the samples was done by *Zeiss Auriga 60 DualBeam*. The electron and ion beam were employed to deposit carbon and Pt respectively to protect the thin film during FIB analysis. The particle distribution analysis of the annealed Ag nanofilms was done by using the online free software; ImageJ. The Grazing incidence X-ray diffraction (GIXRD) data were collected using *SIEMENS D 5000* theta-theta diffractometer machine with Cu Kα radiation of λ = 1.5405 nm.

3. Results and Discussion

3.1. SEM Results



(i)

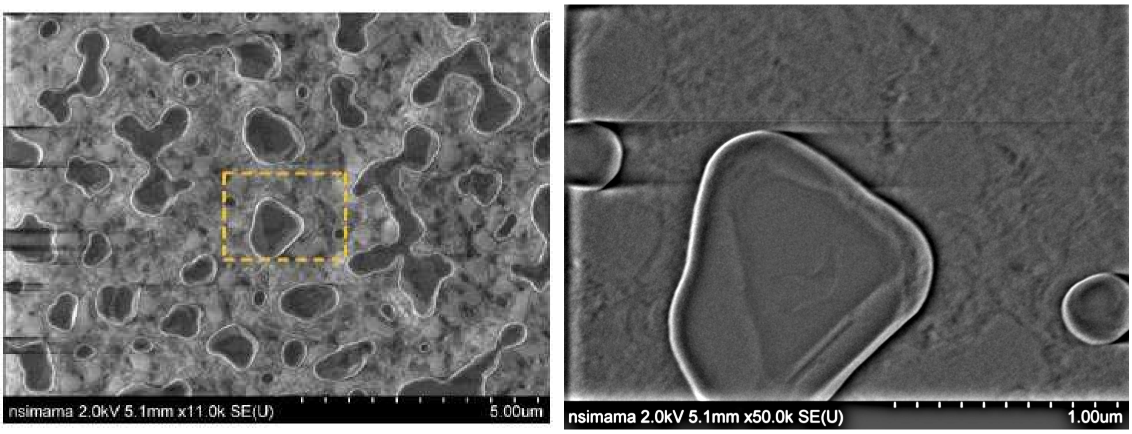


(ii)

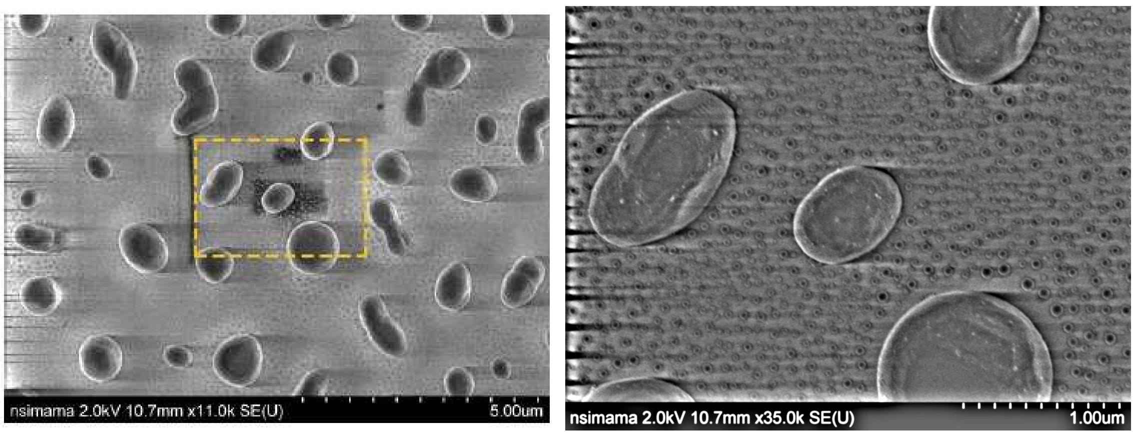
Figure 1. *SEM images for Ag nanofilms annealed at 400℃ for 30 minutes in (i) Ar and (ii) N_2 atmosphere. The higher magnification images represent the dotted lined-rectangles.*

Figure 1 shows the lower (5 µm x 5 µm) and higher (1 µm x 1 µm) magnification scale SEM images for the Ag films annealed in the Ar and N_2 atmospheres at 400℃ for 30 minutes. The surface images of samples annealed in both Ar and N_2 atmospheres (Fig. 1 (i) and (ii)) consists of irregular holes. The Ag film annealed in the N_2 atmosphere has higher hole density than the film annealed in the Ar atmosphere.

The SEM images for Ag films annealed in the N_2 atmosphere at temperatures higher than 400℃, i.e., 500 and 600℃ for 30 minutes are shown in Figure 2. The surface of the sample annealed at 500℃ (Fig. 2 (i)), has a combination of isolated particles and some which are connected by thin necks. Thin necks are signs of isolations/breaking upon further annealing process due to the Winterbottom effect. Despite the formation of isolated particles, the surface seems to be covered by undewetted Ag films at such a temperature.



(i)



(ii)

Figure 2. *SEM images for Ag nanofilms annealed at (i) 500℃ (ii) 600℃ for 30 minutes in the N_2 atmosphere.*

The surface of the sample annealed at 600℃ (Fig. 2 (ii)), has only isolated particles of spherical and elliptical shapes. At this temperature, almost the whole Ag layer seems to have undergone dewetting leaving only the substrate (sapphire). This is substantiated by the EDS spectra shown in Figure 3 in which, the spectrum for an isolated particle (Fig. 3 (i)) is dominated by Ag peak while that of the dewetted area (bare surface) is dominated by Al and O peaks. The observed carbon (C) is resulting from the contaminations during the annealing process.

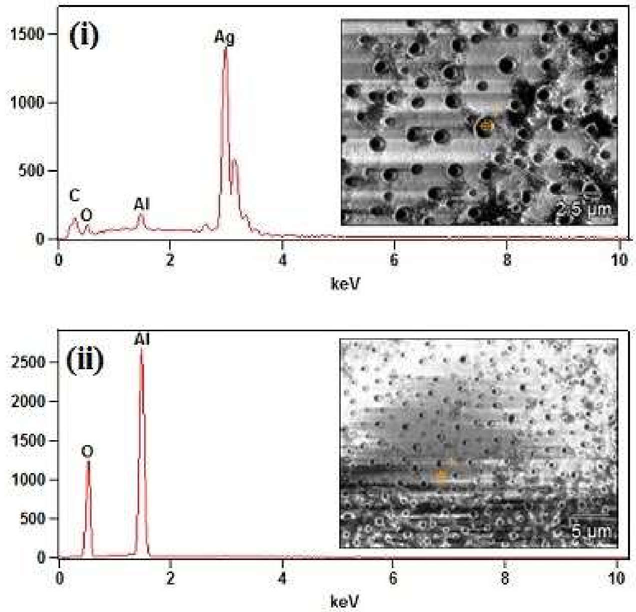


Figure 3. *The EDS elemental compositions for Ag film annealed at 600 ℃ in N_2 atmosphere for 30 minutes (i) on the particle and (ii) on the dewetted area. The symbol "⌗" indicates the analyzed area.*

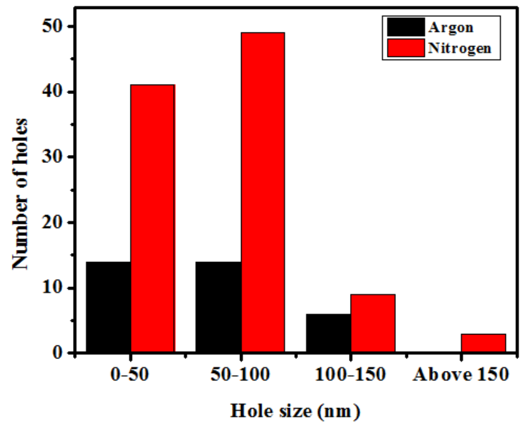
3.2. Holes Distribution Analysis

The results in this section are presented according to the following sequence: the hole size distribution is discussed before the analysis of the dewetted areas for different annealing atmospheres. This analysis excludes samples annealed at temperatures higher than 400℃.

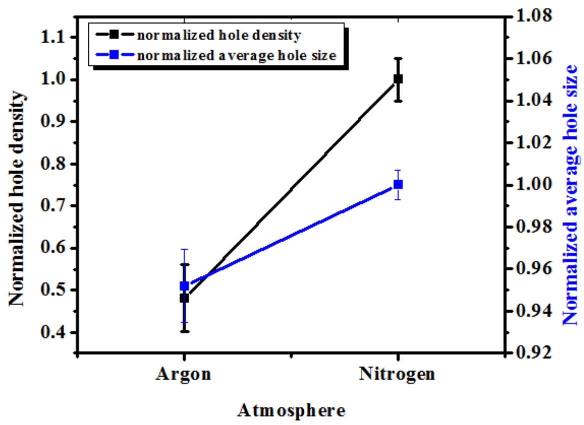
3.2.1. The Hole Sizes Distribution

The hole size distributions for annealed Ag films are shown in Figure 4 (i). Generally, the results show that Ag film annealed in the N_2 atmosphere records higher number of holes and bigger hole sizes than the film annealed in the Ar atmosphere. This implies faster dewetting of Ag films is obtained when the annealing is done in the N_2 atmosphere. It is worth noting that the majority of hole sizes for both films falls under the nano-range.

The variations of normalized average holes density and average hole size with the annealing atmospheres are shown in Figure 4(ii). The Ag films annealed in the N_2 atmosphere records superior normalized hole density and average hole size than the film annealed in the Ar atmosphere.



(i)



(ii)

Figure 4. *(i) The hole size distribution histogram for Ag films annealed in different atmospheres (ii) Variation of normalized hole density and normalized average hole size with the annealing atmospheres.*

3.2.2. The Dewetted Area

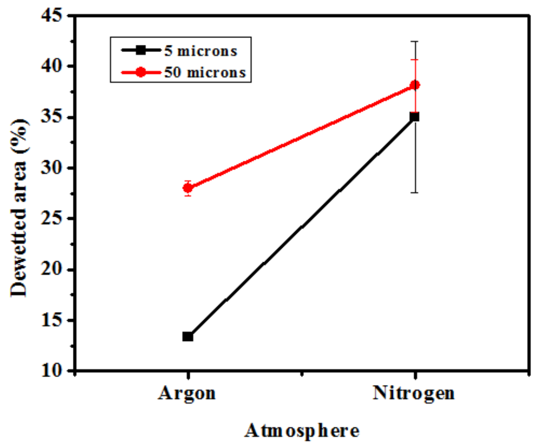


Figure 5. *Variation of dewetted areas with the annealing atmosphere; the 50 and 5 microns scale data from two different SEM image scales are compared.*

The analysis of dewetted areas for the samples was done by using both 5 microns and 50 microns scale SEM images to check the consistency of hole distribution data. The trend of percentage dewetted area for both magnification scales seem to be similar. Consistent with the results from Figure 4, the Ag film annealed in the N_2 atmosphere records higher dewetted area than the film annealed in the Ar atmosphere.

The diatomic molecule of N_2 is held tightly together by a strong triple bond between two nitrogen which requires a great amount of energy to break the bonds [9] minimizing the possibility of dissociation, which would have negatively influenced the diffusion process through attaching to the film surface. The same applies to the Ar atom, which is an inert gas. Therefore, the possible reason for slower and faster dewetting in the Ar and N_2 atmosphere respectively is to do with the atomic radii and masses of the two gases. The larger atomic radius (71 pm) and molecular mass (39.948 kg/mole) of Ar compared to those of N_2 (56 pm and 28.01 kg/mole) [10] might have interfered more with the free movement of Ag atoms in the surface diffusion process in the Ar atmosphere.

The changes of the dewetted areas, hole sizes and hole densities of the films with the annealing times for Ag nanofilms annealed at 400 ℃ in the N_2 atmosphere are summarized in Figure 6. The dewetted area and hole size increase with the increase in the annealing times due to the increase in the number of holes. On the other hand, holes tend to merge at higher annealing times leading to lower hole density.

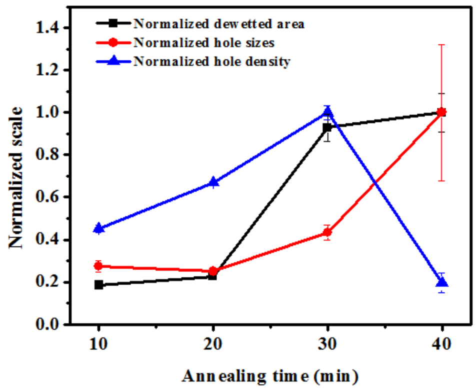
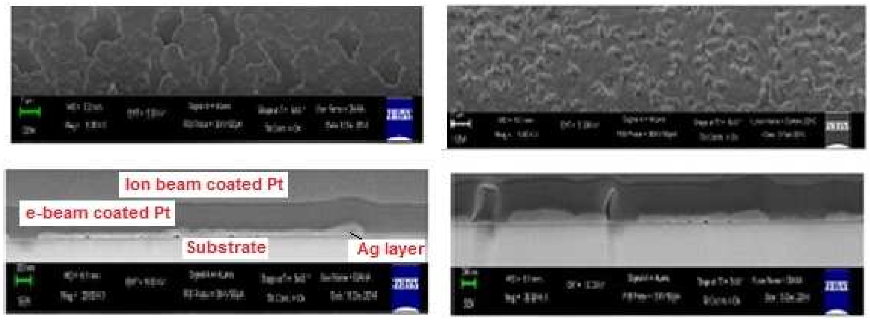


Figure 6. *The changes of dewetted areas, hole sizes and hole densities of Ag films with the annealing times; the temperature was fixed at 400°C.*

3.3. FIB-SEM Results

The top-view and cross sectional FIB-SEM images for Ag films annealed in the two atmospheres are shown in Figure 7. Comparing the top-view images one can notice that irregular shaped holes are observed on the surfaces of samples annealed in both Ar and N_2 atmospheres with the sample annealed in Ar having larger grains with well defined grain boundaries than the sample annealed in the N_2 atmosphere. The top-view FIB-SEM images are similar to those of the SEM images observed in Figure 1.



(i) (ii)

Figure 7. *Top view and cross-sectional view FIB-SEM images for Ag nanofilms annealed in (i) Ar and (ii) N_2 atmosphere.*

For the cross-sectional FIB-SEM images the arrangement of layers for each image is as labelled in Figure 7 (i). Both cross-sectional images have holes of varying sizes and spacing. The sample annealed in Ar atmosphere has the higher number of holes, which are uniformly spread across the Ag layer. Closely spaced holes are observed on the image of the sample annealed in N_2 atmosphere. The top-view FIB-SEM images look similar to SEM images from Figure 1.

3.4. XRD Results

The grazing incidence XRD patterns for the Ag samples annealed in different atmospheres are shown in Figure 8. There is no significance difference between the XRD patterns of the films, suggesting that the annealing atmospheres have no significant influence on the crystal structures of Ag films. Both samples are characterized by metallic Ag orientations, i.e. (111), (200), (220) and (311) [11].

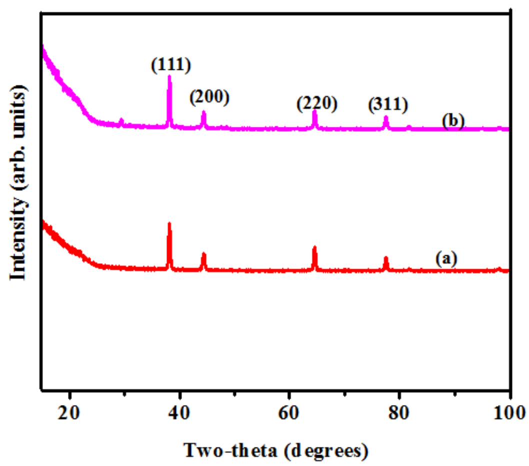


Figure 8. *GIXRD patterns for Ag nanofilms dewetted in different atmospheres; (a) Ar and (d) N_2.*

4. Conclusions

We have successfully investigated the influence of Ar and N_2 annealing atmospheres on the dewetting properties of magnetron sputtered Ag films coated on sapphire substrates. The annealing atmosphere influences the dewetting properties of Ag films. Ag films annealed in the N_2 atmosphere dewet faster than the film annealed in the Ar atmosphere. Holes tend to merge at higher annealing times leading to lower hole density. At higher annealing temperature (600℃) in the N_2 atmospheres isolated spherical and elliptical shaped particles were obtained. The top-view FIB-SEM images showed irregular shaped holes similar to the SEM images. The samples annealed in both atmospheres display similar XRD patterns, mainly from metallic Ag peaks.

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References

[1] Claudia Manuela Müller, Ralph Spolenak, (2010), Acta Materialia, 58, 6035-6045.

[2] F. Ruffino and M. G. Grimaidi, (2014), Vacuum, 99, 28-37.

[3] O. Malyi and E. Rabkin, (2012), Acta Materialia, 60, 261-268.

[4] Anna Kosinova, Oleg Covalenko, Leonid Klinger and Eugen Rabkin, (2015), Acta Materialia, 83, 91-101.

[5] S. K. Sharma and J. Spitz, (1980), Thin Solid Films, 65, 339-350.

[6] S. K. Sharma, S. V. M Rao and N. Kumar, (1986), Thin Solid Films, 142, L95- L98.

[7] Jongpil Ye, (2014), Appl. Phys. Express, 7, 085601.

[8] A. Herz, D. Wang, Th. Kups and P. Schaaf, J. Appl. Phys., (2014), 116, 044307.

[9] Satoko Kuwano-Nakatani, Takeshi Fujita, Kazuki Uchisawa, Daichi Umetsu, Yu Kase, Yusuke Kowata, Katsuhiko Chiba, Tomoharu Tokunaga, Shigeo Arai, Yuta Yamamoto, Nobuo Tanaka and Mingwei Chen, (2015), Materials Transactions, 56, No. 4, pp. 468-472.

[10] http://www.webelements.com/

[11] X. H Yang, H. T. Fu, K. Wong, X. C Jiang, A. B. Yu, (2013), Nanotechnology, 24, 415601 (10 pp).