# Epitaxial and Island Growth of Ag /Si(001) by RF Magnetron Sputtering

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## I. INTRODUCTION

Considerable interest has been directed toward detailed understanding of metal-semiconductor systems with large lattice mismatch such as Al/Si and Ag/Si for both fundamental and practical reasons.[1] Epitaxial Ag films have been obtained mostly by evaporation techniques such as molecular beam epitaxy (MBE) where the energy of depositing particles is relatively low, about 0.1 ~ 0.3 eV.[2] In the sputtering process, however, most of the experimental results show a non-epitaxial growth of Ag. The purpose of this study is to explore the feasibility of growing epitaxial Ag films by controlling the energy of depositing particles in the sputtering process.

In this article, we present a synchrotron x-ray scattering study of microstructure of Ag/Si(001) together with a scanning electron microscopy (SEM) and an atomic force microscopy (AFM) study.

## II. EXPERIMENTAL DETAILS

Ag films were grown on Si(001) substrates using the radio frequency (RF) magnetron sputtering technique. The Ag target was 3 inches in diameter placed 9 cm away from the substrate. The substrate temperature was held at 300 °C during the entire growth process. The samples used in this study were prepared at relatively low RF powers of 0.22 watts (W)/cm$^2$ and 0.44 W/cm$^2$ to explore the possibility of epitaxial Ag film growth. The effect of post-annealing was studied by heating the fully grown samples to 500 °C for 3 h.

The x-ray scattering experiments were carried out at Beamline 3C2 at Pohang Light Source (PLS) in Pohang Accelerator Laboratory. The incident x-rays were focused both in vertical and horizontal directions by a focusing mirror. [Fig. 1(a)] A double bounce Si(111) monochromator was used to monochromatize x-rays to 7.73 keV (wavelength of 1.608 Å). A schematic illustration of the scattering geometry used in this experiment is shown in Fig. 1(b).

## III. MICROSTRUCTURE OF AS GROWN Ag FILMS ON Si(001)

### A. Epitaxial layer and 3d island formation under mild deposition : 0.22 W/cm$^2$

We first discuss the Ag films deposited at 0.22 W/cm$^2$, which was the lowest sputtering power involved in this study. Figure 2 shows the SEM and AFM micrographs of the Ag films with 200 Å (a, b) and 2000 Å thicknesses (c, d). The SEM pictures that illustrate a two dimensional plane view show that the 200 Å thick film was composed of very fine smooth grains, while the 2000 Å film was composed of well separated Ag islands. In the mean while, the AFM pictures show a surface topology which provides a depth profile as well as the plane-view information. The

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200 Å thick film was relatively smooth with a root-mean-squared (*rms*) surface roughness of 14 Å, while the 2000 Å thick film was composed of three dimensional, mountain-like islands with about 400 Å *rms* roughness. These micrographs illustrated that a fine-grained Ag layer formed initially and three dimensional Ag grains grew on top of the fine-grained layer as the growth proceeded.

To examine the detailed microstructures of the Ag films, we carried out a synchrotron x-ray scattering measurement on these samples. As shown in Fig. 3(a), the 200 Å thick Ag film showed a broad Ag (002) Bragg reflection and a small but relatively sharp (111) reflection. This indicates that the Ag grains were mostly oriented toward the <002> crystallographic direction. From the broadening of the powder scattering profile shown in Fig. 3, one may estimate the crystal domain size of the Ag film, $l$, as $l \sim \pi/\mathrm{HWHM}$. The crystal domain size of the (002) grains was about 40 Å, while that of the (111) grain was 100 Å.

As the film thickness was increased to 2000 Å, the intensity of Bragg reflections, especially the (111) reflection, increased as shown in Fig. 3(b). We attribute the growth of the (111) reflection to the formation of the large Ag islands, which were evident in the AFM and SEM pictures, on top of the (002) layers. The domain size of the (002)-grains, estimated from the width of the reflection, increased to 60 Å, while that of the (111)-grains increased to about 300 Å. The fact that the domain size of the (111) grains was close to the *rms* roughness of the Ag islands shown in the AFM picture, suggests that the Ag islands shown in the AFM picture were mostly single crystalline along the substrate normal direction. The powder diffraction profiles of the 200 Å, and the 2000 Å thick Ag films together with the AFM, SEM micrographs suggest that the fine-grained (002) film was nucleated initially, and it was followed by the growth of the three-dimensional Ag islands that are preferentially oriented towards the <111> direction.

Figures 4(a) and 4(b) show the scattering profile on the azimuthal circles obtained from 200 Å thick and 2000 Å thick films respectively. As indicated by the well defined peak on the azimuthal circle 1, the in-plane crystalline axis of the Ag(002) grains was distributed along the substrate crystalline axis direction with the HWHM of 1.7°. This indicated that the Ag(002) grains were grown epitaxially on the Si(001) substrate. The importance of this observation was the fact that by minimizing the sputtering power it was possible to grow an epitaxial Ag film using sputtering process that is much more viable economically than most MBE processes. From the relative directions of the film and the substrate crystalline axes, we concluded that the orientational relationship of the epitaxially grown Ag(002) grains was Ag(001) // Si(001), and Ag(111) // Si(111).

On the other hand, the in-plane crystalline axis direction of the (111)-grains was distributed isotropically around the azimuthal circle 2 as illustrated in Fig. 4(a) and 4(b). This illustrates that the (111) islands do not have epitaxial relation with the silicon substrate in both the samples 200 Å and 2000 Å. We conclude that the epitaxial growth of the (002) grains was followed by the growth of non-epitaxial 3d islands that had the <111> preferred growth direction.

## B. 3d island growth at a higher RF power of 0.44 W/cm$^2$

To understand the effect of the sputtering power, we have grown Ag films at a higher RF power of 0.44 W/cm$^2$. Figures 5(a) and 5(b) show the SEM and AFM micrographs of a 3000 Å thick Ag film grown at 0.44 W/cm$^2$ respectively. As is clear in the pictures, the Ag islands were larger than those grown under 0.22 W/cm$^2$ (see also Fig. 2), and packed more compactly. From the AFM picture, it was shown that the average size of the Ag islands was about 8000 Å in the film plane, and the *rms* roughness was about 500 Å. It is evident that larger islands occur by raising the sputtering power.

Figure 6(a) illustrates the powder diffraction profile obtained on this sample. Compared with the film grown at 0.22 W/cm$^2$ shown in Fig. 3, the (111) reflection became very intense and sharp. There was also a small (002) reflection. The crystal domain size deduced from the HWHM of the Ag(111) (the Ag(002)) reflections was 800 Å (300 Å). The powder scattering profile demonstrates that by raising the sputtering power, the growth of Ag islands preferably oriented toward the <111> crystalline axis was enhanced. As illustrated in Fig. 6(b), on the Ag film grown at 0.44 W/cm$^2$, the in-plane crystalline axis direction of both the (111) or the (002) grains was isotropically distributed around the azimuthal circle. This indicated that the (111) or the (002) grains were grown non-epitaxially at this power. It was noteworthy that even the (002)-grains, which were epitaxial at lower power deposition, were not epitaxial. We conclude that at 0.44 W/cm$^2$ RF power, the Ag films were nucleated in the form of non-epitaxial 3d islands from the very beginning of the growth. This comparative study of the film growth at different powers suggested that it was essential to minimize the sputtering power in obtaining the epitaxial Ag grains.

## IV. EFFECT OF POST ANNEALING AT 500 °C : ISLANDS CONGLOMERATION

Figure 7 shows the AFM and SEM micrographs of the 200Å (a, b) and 2000 Å thick (c,d) films after annealing them at 500℃ for 3 h. One may immediately notice that the size of the islands increased significantly in both films as compared with the pictures shown in Fig. 2. The AFM pictures showed that the *rms* roughness of the 200 Å thick film increased to about 50 Å, while that of the 2000 Å thick film increased to about 650Å. The drastic increase of the island size indicates that the Ag atoms were very mobile at the annealing temperature. The transformation of noble metal films into large islands by annealing has also been reported previously.[3,4]

The formation of large Ag islands suggests a vast rearrangement of the Ag atoms during the post-annealing. This would inevitably alter the microstructure of Ag films, especially the thin 200Å thick film. Figure 8(a) and 8(b) show the powder diffraction scan and the azimuthal scan (that shows in-plane distribution of crystalline axis direction) obtained on the annealed 200Å film respectively. We first observed that in the powder scattering profile, the peak intensities of the Ag(111) Bragg reflection were enhanced by the annealing, while the (002) reflection decreased. It is also noteworthy that the crystalline quality of Ag films was greatly enhanced by the annealing as is clearly shown by the decrease of the HWHM of the Bragg reflections. The out-of-plane domain sizes estimated from the HWHM significantly increased from 40 Å to 300 Å for the (002) grains and from 100 Å to 500 Å for the (111) grains

by the annealing. The fact that the crystal domain size in the film normal direction was greater than the original thickness of the film before annealing indicates that the Ag atoms moved drastically and recrystallized into three dimensional Ag islands. As shown in Fig. 8(b), the recrystallized Ag islands do not have any epitaxial relation with the substrate. As is clear from the azimuthal scattering profile and the broad rocking curves (data not shown), the recrystallized Ag islands were randomly oriented similar to complete powder crystalline Ag. We conclude that the 200 Å thick epitaxial Ag film was completely transformed into 3d Ag islands with random orientation by the annealing.

The effect of the annealing on the 2000 Å thick film was less severe. Figure 9(a) and 9(b) show the powder diffraction profile and the azimuthal scan obtained on the annealed 2000 Å film respectively. Different from the case of the 200 Å thick film, both the (111) and the (002) reflection increased in peak intensity and became sharper. The out-of-plane domain sizes estimated from the HWHM were 100 Å for the (002) grains and 800 Å for the (111) grains. The increase in the crystal domain sizes indicates that the crystalline quality was enhanced by the annealing. The diffraction profile along the azimuthal circle illustrated that the (002) grains were still epitaxial even with the enhanced intensity. The diffraction profiles together with the AFM picture indicate that the 3d islands grown in the late stage were transformed into bigger islands, while the epitaxial (002) grains grown in the early stage remained epitaxial in the process of the annealing. In fact, annealing improved the crystalline quality and epitaxiality of the early stage grown (002) grains, as is usually reported.[3,5,6]

## V. CONCLUDING REMARKS

In this work, we illustrated that it was feasible to grow heteroepitaxial Ag films on silicon substrates, by minimizing the sputtering power, in an RF magnetron sputtering process. This result is important because the commercially viable sputtering technique was used to grow epitaxial Ag films on Si substrates. By studying the effect of the sputtering power and the post-annealing, we have shown that the mobility of Ag atom was a key factor determining the morphology and the growth mode of the Ag film.

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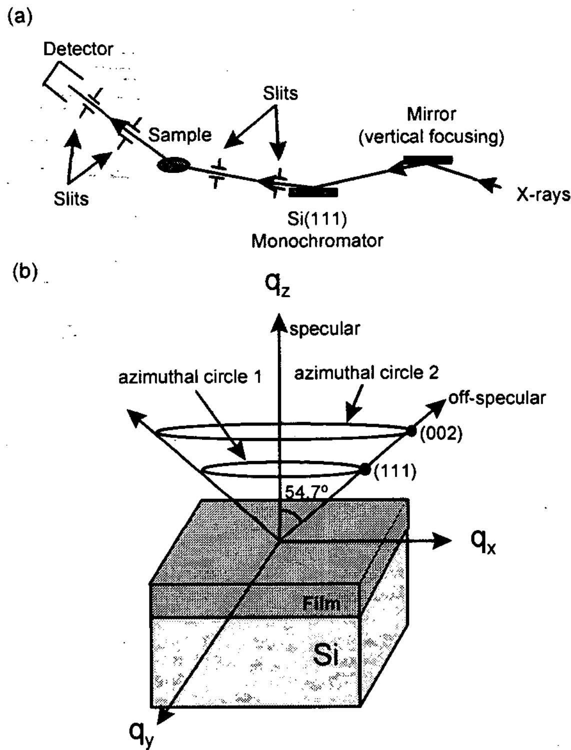


FIG. 1. (a) Schematic diagram of the x-ray scattering setup at 3C2, PLS. (b) The scattering geometry used in this experiment.
A conventional powder diffraction scan is obtained by measuring the scattering intensity along the specular *qz* direction. The nonspecular (111)-like or the (002)-like Bragg reflections are studied on the *off-specular* direction. The epitaxial relationship was studied by comparing the position of the non-specular reflections of the Ag film with that of the substrate on the azimuthal circles.

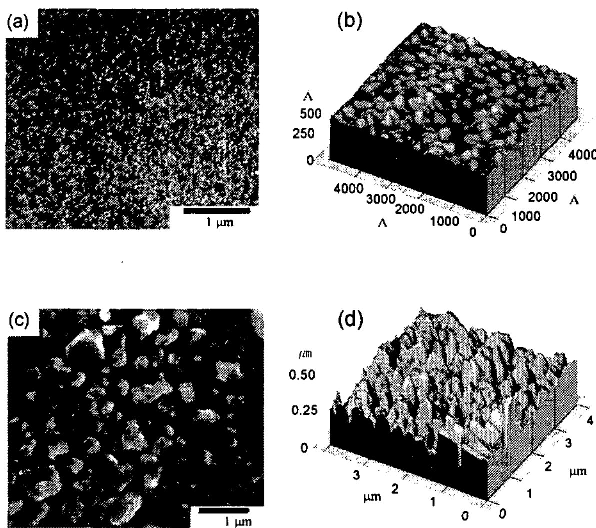


FIG. 2. SEM and AFM micrographs of the Ag films grown under the RF power of 0.22 watts/cm2 to 200 Å(a, b) and 2000 Å thicknesses (c, d). Note that the scales of the AFM pictures are different.

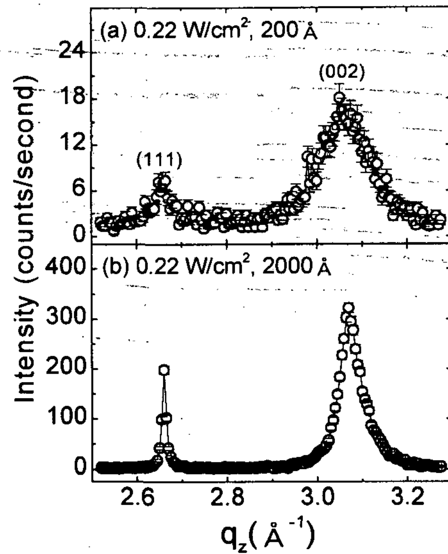


FIG. 3. Powder scans (scattering profiles along the substrate normal) of the Ag films grown under the RF power of 0.22 watts/cm2 to (a) 200 Å and (b) 2000 Å thicknesses.

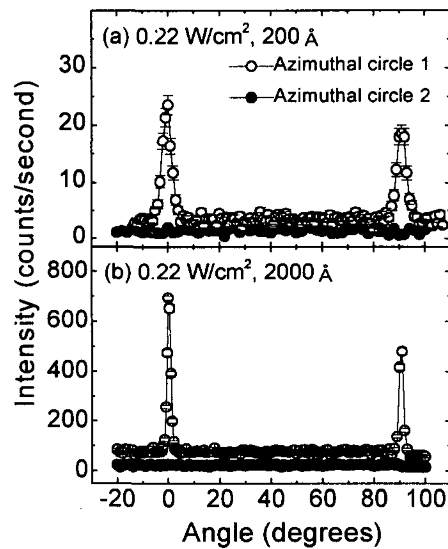


FIG. 4. The intensity profiles of the Ag(111) (azimuthal circle 1) and the Ag(002) (azimuthal circle 2) reflections for the Ag films grown under the RF power of 0.22 watts/cm2 to (a) 200 Å and (b) 2000 Å thicknesses. The sharp scattering features from the azimuthal circle 1 show that the Ag(002) grains were indeed grown epitaxially on the Si(001) substrate.

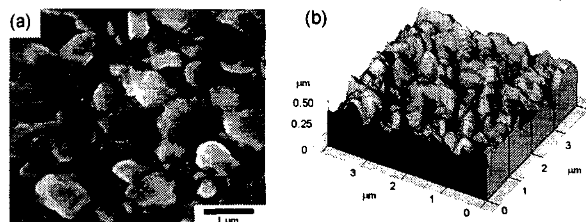


FIG. 5. (a) SEM, and (b) AFM micrographs of the 3000 Å thick Ag film grown under the RF power of 0.44 watts/cm2

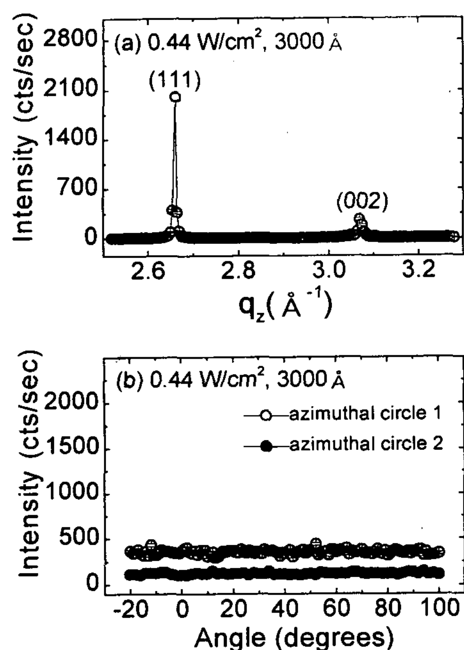


FIG. 6. (a) Powder diffraction profile, and (b) the intensity profiles of the Ag (111) (azimuthal circle 1) and the Ag (002) (azimuthal circle 2) reflections, for the Ag film grown under the RF power of 0.44 watts/cm2 to 3000 Å.

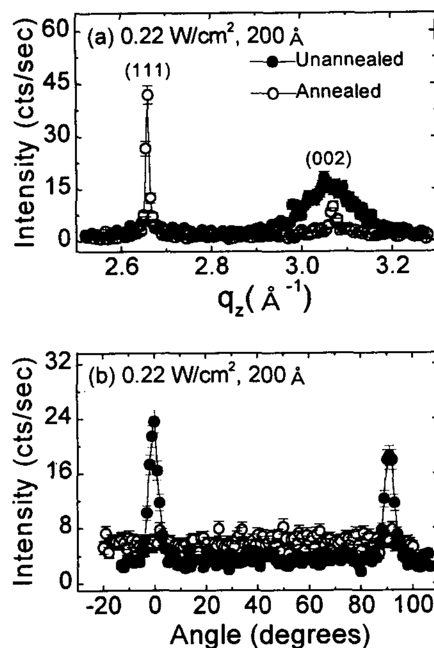


FIG. 8. (a) Powder diffraction profile, and (b) the intensity profile of the Ag(111) (azimuthal circle 1) reflection, for the Ag film grown under the RF power of 0.22 watts/cm2 to 200 Å, after annealing at 500 C for 3 h. The scattering profiles obtained on the unannealed sample were plotted as references.

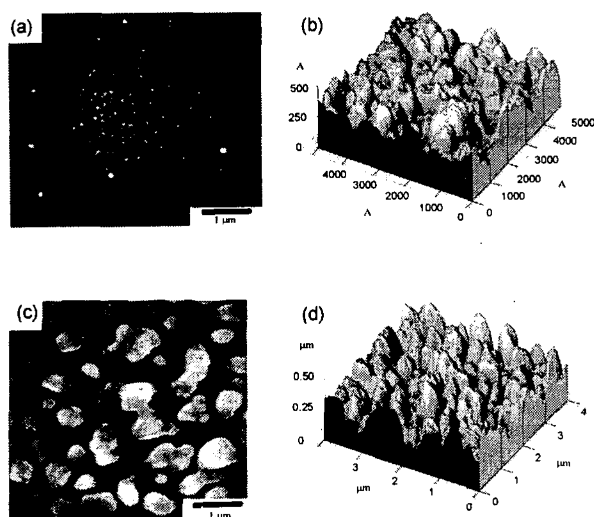


FIG. 7. SEM and AFM micrographs of the Ag films grown under the RF power of 0.22 watts/cm2 to 200 Å (a, b) and 2000 Å thicknesses (c, d), after annealing at 500 C for 3 h.

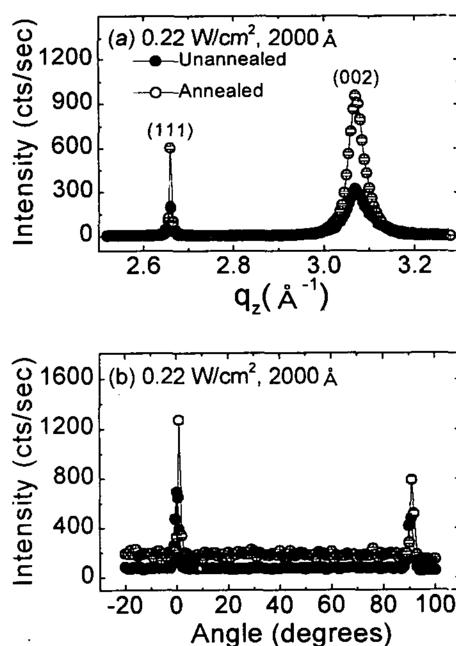


FIG. 9. (a) Powder diffraction profile, and (b) the intensity profile of the Ag(111) (azimuthal circle 1) reflection, for the Ag film grown under the RF power of 0.22 watts/cm2 to 2000 Å, after annealing at 500 C for 3 h. The scattering profiles obtained on the unannealed sample were plotted as references.