

## Thermally Stable Ag Thin Films Modified with Very Thin Al oxide layers

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Ag has long been of interest for use as a low-resistivity electrode material, but the problem of agglomeration caused by annealing must be resolved. One of the solutions is alloying Ag, but this often causes an increase in electrical resistivity. In this study, thermal stability of Ag thin films modified with thin Al oxide layers was investigated from the viewpoints of surface morphology and resistivity. It was found that agglomeration was suppressed in the multilayer films even after annealing at 600°C, similarly to Ag(Al) alloy films, which were investigated previously. As a result, it was suggested that the presence of the Al oxide layers at the film surface and interface played a major role in suppressing agglomeration in Ag(Al) films. Moreover, the resistivity of the multilayer film was 1.8  $\mu\Omega\text{cm}$ , which was much lower than that of alloy films. Consequently, to achieve both agglomeration suppression and low resistivity, the structural modification of the Ag films using Al oxide layers is more useful than alloying the films.

KEYWORDS: Ag thin film, electrode, agglomeration suppression, Al oxide layer, modification, resistivity,

### 1. Introduction

Low-resistivity metals have been used as electrode and metallization materials in various electronic devices, and the property requirements for the materials have become stricter with changes in device dimensions. Consequently, the main metallization materials in ultra large scale integrated (ULSI) Si devices changed from Al alloys to Cu a decade ago. Similarly, for gate electrodes in thin film transistors for liquid crystal displays (TFT-LCD), high-melting-point metals (such as Ta and Mo) were used initially and then replaced by Al (Al alloy), but lower-resistivity metals are now considered to be preferable. Since Ag has the lowest electrical resistivity among all metals, it is a candidate material for the uses described above.<sup>1-3)</sup> However, Ag films are less adhesive on substrates such as glass or SiO<sub>2</sub> and agglomerate easily with heat treatments. To resolve this drawback, many researchers have focused on the suppression of Ag agglomeration behavior, and one of the solutions is considered to be alloying Ag with other metals. An improvement due to the use of Ag(Al) films has recently been reported, as well as with other alloy films such as W and Ni.<sup>4-7)</sup> In our previous study, Ag(Al) films showed an excellent agglomeration suppression effect during annealing, and were found to form thin Al oxide layers at the film surface and the interface with the SiO<sub>2</sub> substrate, as determined by Auger depth profile analysis.<sup>5)</sup> It is considered that the Al oxide layer plays the role of a passivation and

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capping layer, which suppresses the migration of Ag atoms underneath, and leads to the suppression of Ag(Al) grain growth. In addition, we suggested that the thin Al oxide layer at the interface behaves as an adhesion layer, which lowers the interface energy with the substrate. A similar report has been published concerning the important role of Al oxide layers for thermal stability, which was achieved by introducing Ag(Al) alloy films as a reflector layer of GaN LED where Al oxide layers formed during annealing in air ambient.<sup>8)</sup> In general, alloying causes an increase in electrical resistivity owing to the impurity scattering effect, for example, the resistivity of Ag(Al) films with a high Al concentration cancels the low resistivity character of Ag itself.<sup>5)</sup> As a result, minimum usage of alloying elements is required to achieve low resistivity.

We prepared a multilayered structure of a pure Ag film sandwiched between very thin Al oxide layers at the film surface and the interface with the substrate. If this structure was thermally stable, homogeneous alloying would not be required. The surface morphology and electrical resistivity of the films after annealing were examined and compared with those of Ag(Al) alloy films to confirm whether thermal stability of the Ag(Al) alloy films arose only from the presence of the Al oxide layers at the surface and interface. In addition, Ag films with a very thin Al oxide layer at either the surface or the interface were prepared and their agglomeration behavior was compared to examine the mechanisms of agglomeration suppression.

## 2. Experimental Methods

The deposition of the Ag film and Al layers was carried out by vacuum evaporation with evaporation sources of Ag wire (99.99% purity) and Al wire (99.99% purity) after evacuation to below  $2.6 \times 10^{-4}$  Pa. A Si(001) wafer with a 100-nm-thick thermally grown SiO<sub>2</sub> layer was used as the substrate without heating during the deposition. The thickness of the deposited layer was controlled by a quartz crystal monitor (QCM) during the deposition and fixed to be 95 nm for the Ag film and 1 nm (nominal thickness) for the Al layer. The Al/Ag/Al multilayer structure and pure Ag as a reference were deposited. Annealing treatment at 500 or 600 °C was also carried out in a lamp-heating furnace under vacuum for 1 h after evacuation below  $1.0 \times 10^{-4}$  Pa. The thickness of the Ag films was confirmed to be 95 nm by multibeam interferometry. The crystal structure of the obtained films was investigated by X-ray diffraction (XRD) analysis using Cu K $\alpha$  radiation. The grain size in the direction of film depth was calculated using Scherrer's equation on the basis of the Ag(111) diffraction peaks. The surface morphology of the films was observed by scanning electron microscopy (SEM) and atomic force microscopy (AFM). Electrical resistivity was measured at room temperature using the four-point probe method.

## 3. Results and Discussion

### 3.1 Formation of Al oxide layer

After the film deposition, the samples were exposed to air before annealing. Therefore, a very thin Al oxide layer was considered to be formed by the natural oxidation of approximately 1-nm-thick

Al layer. To evaluate the thickness of the Al oxide layer formed, ellipsometry using a 633 nm laser beam at a  $70^\circ$  incident angle was carried out for the samples with Al layers on  $\text{SiO}_2$  and also on  $\text{Ag/SiO}_2$  before annealing. The results showed that the samples have an approximately 3-nm-thick Al oxide layer where a refractive index of 1.63 was assumed for Al oxide. This thickness coincides with the measured thickness of an Al oxide layer formed by natural oxidation.<sup>9)</sup> At the interface with the  $\text{SiO}_2$  substrate, natural oxidation of the Al film owing to air exposure is considered to be prevented by the Ag layer above. However, a thin Al oxide layer could be produced as a result of annealing, as shown in a previous work.<sup>5)</sup> This seems to be reasonable by comparison of the enthalpies of oxide formation. Namely, the  $\Delta H_0$  values of  $\text{Al}_2\text{O}_3$  and  $\text{SiO}_2$  are -1675.7 and -910.9 kJ/mol, respectively.<sup>10)</sup> In addition, taking into account that the  $\text{SiO}_2$  layer is amorphous, it is possible to form an (Al,Si) oxide layer, although this is not clarified yet. As a consequence, the exact structure of the present samples is considered to be Al oxide/Ag/Al oxide, but we refer to it as the Al/Ag/Al structure in this paper to avoid complexity.

### 3.2 Crystal orientation and grain size of the films

Figure 4 shows the XRD patterns of the Ag film and the Al/Ag/Al multilayer film before and after annealing. Both as-deposited films have a strong (111) preferential orientation. After annealing, the (111) peak intensity increased, particularly in the Ag film. It is reasonable to consider that the peak intensity of the closest packed plane is enhanced by annealing. The grain sizes estimated from the Ag(111) peak are about 65 nm for both as-deposited films, which are much larger than that of sputtered Ag films (about 25 nm) in our previous study. It is considered that these large grains of the films are caused by the high directionality of flying Ag atoms in the evaporation method. After annealing at  $600^\circ\text{C}$ , the grain size of both Ag and Al/Ag/Al films increased slightly to about 73 nm, which is a very small grain growth compared with that of sputtered films. The small grain growth implies little diffusion of atoms, and it appeared to be favorable from the point of view of agglomeration suppression.

### 3.3 Surface morphology and resistivity of modified films

Figure 4 shows representative SEM images of the Ag and Al/Ag/Al films before and after annealing at  $500^\circ\text{C}$  and  $600^\circ\text{C}$ . Both as-deposited films have very smooth surfaces, as shown in Figs. 2(a) and 2(d). After annealing at  $500^\circ\text{C}$ , void formation in the Ag film can be clearly observed, and the film is partly dewetted by further agglomeration after annealing at  $600^\circ\text{C}$ , as shown in Figs. 2(b) and 2(c). In contrast, the multilayer films modified with Al oxide layers show excellent morphology after annealing, although some small voids exist, as shown in Figs. 2(e) and 2(f). Thus, very thin Al oxide layers at the film surface and at the interface with the substrate are confirmed to be very useful for suppressing agglomeration in pure Ag thin films. Moreover, it can be concluded that this Al oxide layer significantly affects the thermal stability of Ag(Al) alloy films.

AFM observation of the films was also carried out. Figure 4 shows that the surface morphology

of the Al/Ag/Al film is very flat, even though the SEM observation showed partial void formation. The average rms value of Al/Ag/Al multilayer film after annealing at 600°C was as small as 2.5 nm, slightly increased from the rms of 1.5 nm of the as-deposited film. In our previous work,<sup>5)</sup> the rms of Ag(Al) film (Al: 4.3 at.%) annealed at 600°C was 2.2 nm, so a similar level of surface flatness was confirmed between the Al/Ag/Al multilayer film and the Ag(Al) alloy film.

Figure 4 shows the changes in the electrical resistivity of the films induced by annealing in a vacuum. For comparison, the resistivity of Ag(Al) alloy film is also shown in the figure. After annealing at 500 °C, the resistivity of both Ag and multilayer films decreases, then that of the Ag film increases after annealing at 600°C. This is caused by partial film dewetting, which reduces the conduction area for electrons. In contrast, the resistivity of the Al/Ag/Al multilayer film slightly reduced, mainly owing to the reduction in defect density in the film, and did not increase even after annealing at 600°C because void formation was negligible. In addition, the achieved resistivity is 1.8  $\mu\Omega$  cm, which is very close to that of bulk Ag (1.59  $\mu\Omega$  cm).<sup>11)</sup> In the structure, Al oxide layers should be highly resistive but very thin and the main part of the film should be pure Ag, in which no impurity scattering occurs. This structural feature could lead to a low resistivity. As a reason for the difference between the achieved resistivity and the bulk Ag resistivity, the effect of grainboundary scattering can be pointed out, because the grain size in the in-plane direction of Al/Ag/Al films is not increased by annealing, as determined by SEM observation. It is clearly demonstrated that the use of multilayer films resolves the problem of agglomeration in Ag films and also the problem of increased resistivity of alloy films.

### 3.4 Comparison of Al oxide layers at surface and interface

The multilayer consists of an Al oxide layer at the Ag film surface and another at the interface with the SiO<sub>2</sub> substrate. It is interesting to determine which Al oxide layer is more effective for suppressing agglomeration. We prepared structures of Al/Ag/SiO<sub>2</sub> and Ag/Al/SiO<sub>2</sub> and investigated their morphology after annealing. Figure 5 shows representative SEM images of the samples before and after annealing at 500 and 600 °C. The Ag/Al/SiO<sub>2</sub> films shows void formation, although it is more suppressed than in the pure Ag films, probably because of the improved adhesion to the substrate. However, the increase in in-plane grain size on the order of  $\mu\text{m}$  can be clearly observed in Figs. 5(b) and 5(c). This suggests that the grain growth due to the migration of Ag atoms cannot be prevented if the Ag film surface is bare. On the other hand, the increase in the grain size in the direction of film depth estimated by XRD analysis was in the same range as that in other film structures (less than 10 nm). In the Al/Ag/SiO<sub>2</sub> films, voids are observed after annealing at 600°C, but the surface appears to be much flatter than that of the Ag/Al/SiO<sub>2</sub> films. It is considered that the Al layer caused an improved adhesion of the Ag film to the SiO<sub>2</sub> substrate at the interface, and capping of Ag atoms to suppress migration at the film surface. From a comparison between Ag/Al/SiO<sub>2</sub> and Al/Ag/SiO<sub>2</sub> films, it is determined that an Al oxide layer at the film surface improves surface morphology, indicating that preventing surface migration of Ag atoms plays a more significant role in suppressing agglomeration.

#### **4. Conclusions**

We prepared structures of a pure Ag film with 3-nm-thick Al oxide layers at the film surface and the interface with the SiO<sub>2</sub> substrate. The multilayer film showed a very flat surface morphology even after annealing at 600 °C, similar to the Ag(Al) alloy films previously investigated. Consequently, it is found that the presence of the Al oxide layer mostly contributed to agglomeration suppression in Ag(Al) alloy films. In addition to its excellent agglomeration suppression behavior, the multilayer film showed a low resistivity that is close to that of bulk Ag, because the film consists mainly of pure Ag. Therefore, we determine that it is not necessary to alloy the entire Ag film to prevent agglomeration and that modifying the film structure provides sufficient agglomeration suppression and is also beneficial for achieving low resistivity.

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## Figure Captions

Figure 1. XRD patterns of Ag film and Al/Ag/Al multilayer film before and after annealing at 600°C. (a) Ag film annealed at 600°C, (b) Ag film as-deposited, (c) Al/Ag/Al film annealed at 600°C, and (d) Al/Ag/Al film as-deposited.

Figure 2. (color online) SEM images of Ag and Al/Ag/Al films before and after annealing. (a) Ag film as-deposited, (b) Ag film annealed at 500°C, (c) Ag film annealed at 600°C, (d) Al/Ag/Al film as-deposited, (e) Al/Ag/Al film annealed at 500°C, and (f) Al/Ag/Al film annealed at 600°C.

Figure 3. (color online) AFM image of Al/Ag/Al multilayer film after annealing at 600°C.

Figure 4. Resistivity changes of Ag and Al/Ag/Al films as a function of annealing temperature. Results of Ag(Al) film (Al: 4.3 at.%) are also shown.

Figure 5. (color online) SEM images of the films before and after annealing. (a) Ag/Al/SiO<sub>2</sub> film as-deposited, (b) Ag/Al/SiO<sub>2</sub> film annealed at 500°C, (c) Ag/Al/SiO<sub>2</sub> film annealed at 600°C, (d) Al/Ag/SiO<sub>2</sub> film as-deposited, (e) Al/Ag film annealed at 500°C, and (f) Al/Ag film annealed at 600°C.



