Thermally stable very thin Ag films for electrodes

M. Kawamura,[a] D. Fukuda, Y. Inami, Y. Abe, and K. Sasaki
Department of Materials Science and Engineering, Kitami Institute of Technology, Kitami, Koen-cho 165, Hokkaido 090-8507, Japan

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Low-resistivity metals such as Cu and Ag have been investigated for substitution of Al alloy films in the electrodes of thin film transistor used in active matrix liquid crystal displays. Though Ag has the drawback of agglomerating easily during heat treatment, improved thermal stability by modification of the Ag film into an Al/Ag/Al structure has been confirmed. In this paper, the surface morphology and electrical resistivity of this structure with various Ag layer thicknesses (from 95 to 50 nm) are investigated. The Al/Ag/Al structure showed excellent stability after annealing at 600 °C in vacuum, even with reduced thickness. The resistivity of the Al/Ag(95 nm)/Al film and of the Al/Ag(50 nm)/Al film after annealing were 1.8 and 2.4 $\mu\Omega$ cm, respectively. For comparison, properties of Ag films with the same thickness were investigated, but these films became discontinuous after annealing due to agglomeration. Modified Ag films maintained excellent properties after annealing, even when the Ag layer thickness was reduced.
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I. INTRODUCTION

Low-resistivity metals have been used as electrode and metallization materials in various electronic devices, but the required properties of the materials have become severe with the change in device dimension. For gate, source, and drain electrodes in thin film transistors used for active matrix liquid crystal displays (TFT-LCD), refractory metals such as Ta and Mo were replaced by Al (Al alloy) to lower the resistivity. However, this improvement is insufficient to allow any further increase of screen size, leaving Cu and Ag as the only remaining candidates to substitute.[1,2] Since Ag has the lowest electrical resistivity of all metals, it is a very important candidate for the electrodes in TFT-LCD, as well as the metallization material in ultra large scale integration. However, Ag films are less adhesive on substrates such as glass or SiO_2 and agglomerate easily during heat treatment. To resolve this drawback, many reports have focused on the suppression of this agglomeration behavior, and one proposed solution is to alloy Ag with other metals.[3–7] However, it is well known that alloying sometimes causes an increase in electrical resistivity due to an impurity scattering effect.

Recently, we have investigated a multilayer structure of 95-nm-thick Ag film modified with very thin Al oxide layers at the surface and interface with the substrate. It was found that the modified Ag film ("Al/Ag/Al film" for short) was thermally stable and achieved a lower resistivity than Ag(Al) alloy films.[8] Generally, Ag film tends to agglomerate at lower heating temperature, especially in thinner films.[9] For future applications, stable films of decreased thickness will be required. In this paper, we investigate the thermal stability, morphology, and electrical resistivity of modified Ag films as thin as 50 nm after annealing. The results are compared with those of Ag films of the same thickness.

[a]Electronic mail: kawamumd@mail.kitami-it.ac.jp

II. EXPERIMENTAL PROCEDURE

The preparation of modified Ag films has been described in detail elsewhere.[8] The deposition of Ag 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 2.6×10^{-4} Pa. A (001)Si wafer with a 100-nm-thick, thermally grown SiO_2 layer was used as the substrate without heating during deposition. The thickness of the deposition layer was controlled by quartz crystal monitor during deposition and fixed to 1 nm for Al films and varied from 95 to 50 nm for Ag films. In our previous study, it was confirmed that the top Al layer transforms into 3-nm-thick Al oxide layer by natural oxidation. On the other hand, the bottom Al layer was considered to become oxide by thermal reaction with SiO_2 substrate.[8] Annealing treatment from 300 to 600 °C was also carried out in a lamp-heating furnace under vacuum for 1 h after evacuation below 1.0×10^{-4} Pa.

The surface morphology of the films was observed using a scanning electron microscope (SEM) and an atomic force microscope (AFM). Electrical resistivity was measured at room temperature using the four-point probe method.

III. RESULTS AND DISCUSSION

A. Morphological change of the films by annealing

First, Ag and Al/Ag/Al films with a 95-nm-thick Ag layer were compared. Figure 1 shows representative SEM micrographs of the Ag films and Al/Ag/Al films before and after annealing at 400, 500, and 600 °C. Both as-deposited films had very smooth surfaces. Void formation was confirmed after annealing at 400 °C in both films, as was Ag film agglomeration at 500 °C. Finally, the Ag film was partly dewetted by agglomeration after annealing at 600 °C. On the contrary, the Al/Ag/Al films showed flat surface morphology after annealing at 600 °C though some small voids were

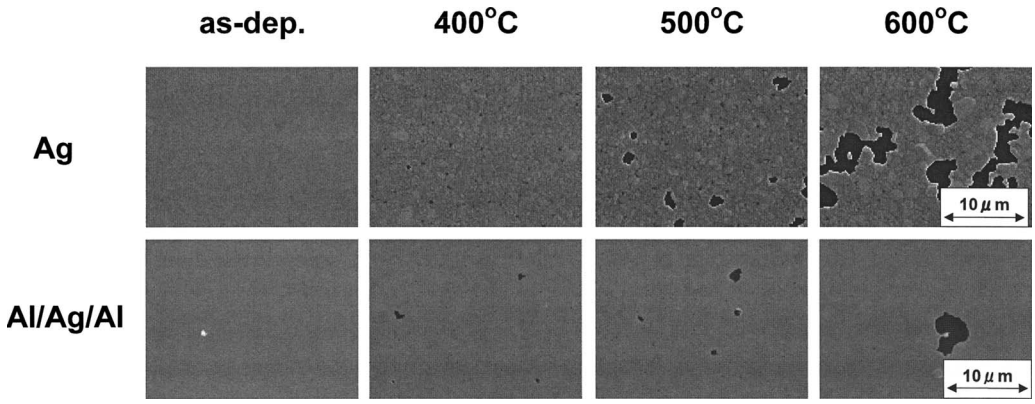

FIG. 1. SEM images of Ag and modified Ag films before and after annealing. The thickness of Ag film and layer is fixed to 95 nm.

evident. This was because the Al/Ag/Al films have a very thin Al oxide layer at the film surface and at the interface with the substrate, which functioned as a capping layer to suppress surface migration of Ag atoms and an adhesion layer to lower interface energy, respectively.[8]

Next, Ag films with reduced thicknesses (80 and 60 nm) were prepared. The surface morphology of the Ag films before and after annealing is summarized in Fig. 2. As reported previously,[9] it is clear that thinner films agglomerated at lower annealing temperatures. For example, an 80-nm-thick film became discontinuous at 600 °C, as did a 60-nm-thick film at 400 °C. On the contrary, Al/Ag/Al films showed excellent thermal stability. The results of SEM observation of the Al/Ag/Al films, including results for an additional 50-nm-thick Ag layer, are shown in Fig. 3. There were small voids in each annealed film, and the void size is increased after annealing at a higher temperature. However, the film surface, except where there were voids, appeared very flat even after annealing. This is remarkably different from Ag films after annealing. The roughness was further investigated in detail by AFM, and rms roughness of the surfaces annealed at 600 °C was in the range from 1.1 to 1.5 nm among these films. Therefore, surface morphology of Al/Ag/Al films with reduced Ag thickness as low as 50 nm was found to be very flat with the exception of void formation.

In the modified structure, an approximately 3-nm-thick Al oxide layer forms at the surface and interface with SiO_2 substrate.[8] These oxide layers work to suppress migration of Ag atoms and improve adhesion in cases where Ag thickness is reduced. It is considered likely that migration of Ag atoms easily leads to voiding in thinner films. Consequently, the roles of the Al oxide layer become more significant in thinner films, and it was found that the difference between Ag films with and without these very thin Al oxide layers expanded as film thickness was reduced.

B. Electrical resistivity of the films

Figure 4 shows the resistivity of as-deposited Ag and Al/Ag/Al films as a function of Ag layer thickness. The resistivity of both films with the same Ag layer thickness is nearly identical. The very thin Al oxide layers probably do not affect the film resistivity because the current flows into an Ag layer with much higher conductivity. In addition, in the as-deposited state, no roughening at Ag/Al oxide interfaces due to intermixing reaction occurs, so the surface scattering conditions for conduction electrons should be the same for both Ag and Al/Ag/Al films with reduced Ag thickness. Indeed, the resistivity of both films slightly in-

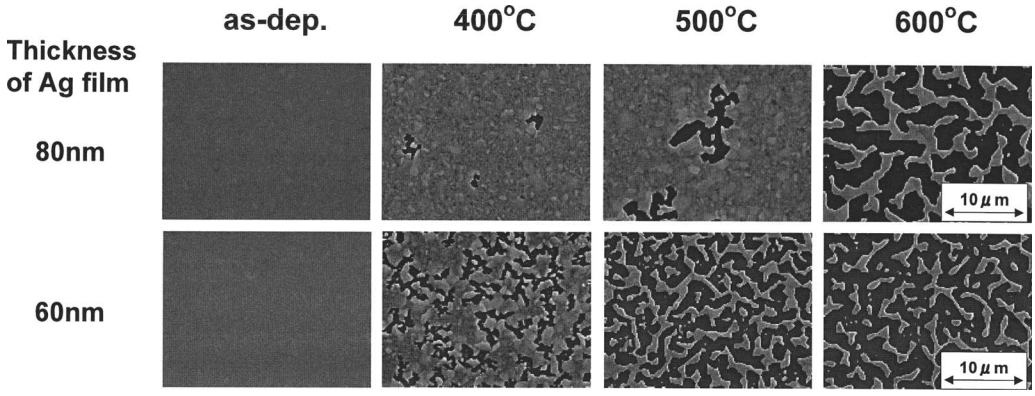

FIG. 2. SEM images of Ag films (60 and 80 nm thick) before and after annealing.

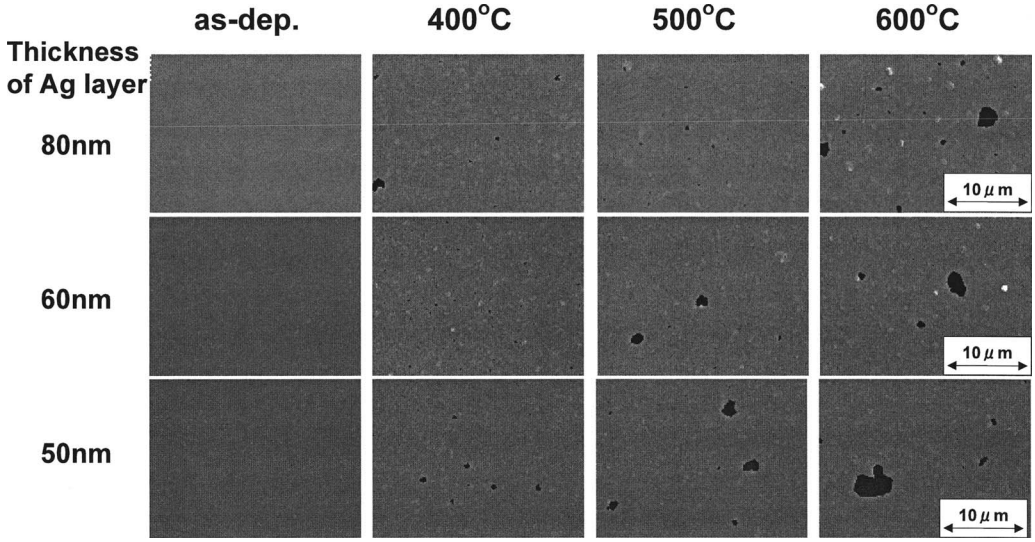

FIG. 3. SEM images of modified Ag films (50, 60, and 80 nm thick) before and after annealing.

creased with decreasing Ag thickness. This is because the thickness is close to the mean free path of electron in bulk Ag [52.3 nm (Ref. 10)].

Resistivity of the agglomerated Ag films increased remarkably, and could not be measured by the present method. This occurred in both a 60-nm-thick film annealed at 400 °C, and an 80-nm-thick film annealed at 500 °C. However, modified Ag films with high stability maintained low resistivity, as shown in Fig. 5. After annealing, resistivity of all films became slightly lower than that of the as-deposited state. This is probably due to reduced defect concentration of the films. The resistivity of the thickest (95 nm) film was 1.8 $\mu\Omega$ cm, very close to 1.59 $\mu\Omega$ cm of bulk Ag,[11] and that of the thinnest (50 nm) film was found to be 2.4 $\mu\Omega$ cm, slightly increased but still a low resistivity. In the structure, Al oxide which should be highly resistive is very thin and the main part of the film is pure Ag. This feature could lead to a low resistivity.

Consequently, we find that modified Ag films with reduced Ag thickness have very high stability, in terms of both morphological and electrical properties.

IV. CONCLUSION

High stability of modified Ag thin films during thermal treatment was confirmed for films with thickness down to 50 nm. It was found that the difference in thermal stability between Ag films and modified Ag films expands at reduced Ag thickness. As a result, the role of the 3-nm-thick Al oxide layer was found to be significant. The excellent morphological stability and low resistivity of the modified Ag films are expected to be very advantageous for future use.

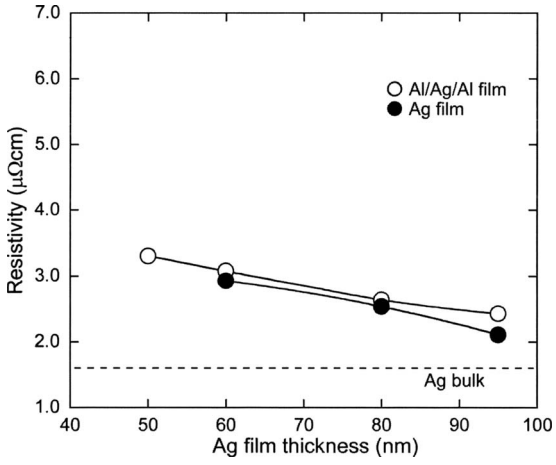

FIG. 4. Resistivity of as-deposited Ag and modified Ag films as a function of Ag layer thickness.

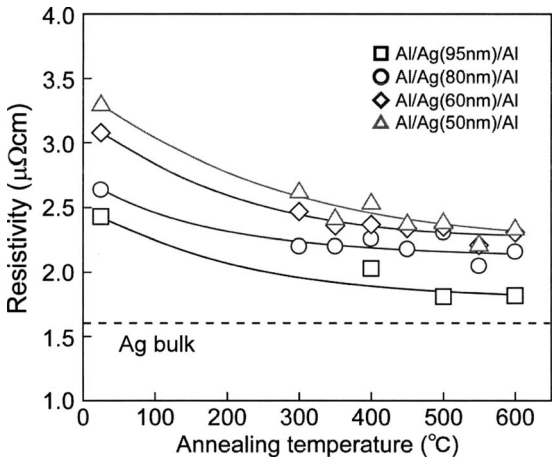

FIG. 5. Resistivity of modified Ag films with various Ag layer thickness as a function of annealing temperature.

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[1]C. O. Jeong *et al.*, J. Electron. Mater. **31**, 610 (2002).
[2]J. Koike, K. Neishi, J. Iijima, and Y. Sutou, Proceedings of the International Display Workshop IDW'07, 2007 (ITE, Tokyo, 2007), Vol. 3, p. 2037.
[3]T. L. Alford, D. Adams, T. Laursen, and B. M. Ullrich, Appl. Phys. Lett. **68**, 3251 (1996).
[4]H. C. Kim and T. L. Alford, J. Appl. Phys. **94**, 5393 (2003).
[5]K. Sugawara, M. Kawamura, Y. Abe, and K. Sasaki, Microelectron. Eng. **84**, 2476 (2007).
[6]E. E. Glickman, V. Bogush, A. Inberg, Y. Shacham-Diamand, and N. Croitoru, Microelectron. Eng. **70**, 495 (2003).
[7]M. Kawamura, M. Yamaguchi, Y. Abe, and K. Sasaki, Microelectron. Eng. **82**, 277 (2005).
[8]M. Kawamura, Y. Inami, Y. Abe, and K. Sasaki, Jpn. J. Appl. Phys., Part 1 **47**, 917 (2008).
[9]H. C. Kim, T. L. Alford, and D. R. Allee, Appl. Phys. Lett. **81**, 4287 (2002).
[10]K. L. Chopra, *Thin Film Phenomena* (McGraw Hill, New York, 1969), p. 369.
[11]D. Lide, *CRC Handbook of Chemistry and Physics*, 84th ed. (CRC, Boca Raton, FL, 2003), Vol. 2, pp. 12–45.