Metal nanolayer deposited highly stable Ag thin films and their optical properties

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Abstract. We have reported that deposition of several-nm-thick Al surface layer on Ag thin films improved thermal stability remarkably. In the present study, we investigated the influence of the deposition of Al nanolayer on the reflectance of the Al/Ag multilayer. 100-nm-thick Ag film and 1–5-nm-thick Al surface layer were deposited successively by vacuum evaporation, and their optical properties were measured. The reflectance of the samples on which a 1- or 3-nm-thick Al layer was deposited on the Ag film was almost the same as that of the Ag single-layer film. However, the samples on which a 5-nm-thick Al layer was deposited on the Ag film showed decreased reflectance. It was considered that the deposited Al nanolayer was fully oxidized in the former samples, but metallic Al and oxidized Al coexisted in the latter sample, which coincided with the simulated reflectance data. As a result, we revealed that thermally stable Ag films formed by 1- or 3-nm-thick Al nanolayer deposition have also high optical reflectance.

1. Introduction

Silver (Ag) is known for its excellent electrical and optical properties, such as the lowest electrical resistivity, highest optical reflectance, and lowest emissivity. However, a drawback is that Ag thin films agglomerate readily under heat treatment because of low adhesion to glass (oxide) substrates and Ag atoms migrate easily as shown in Fig. 1a. This leads to the deterioration of film properties, namely, an increase in electrical resistivity and decrease in reflectance. Alloying Ag films with other metals is well known as a useful way to suppress agglomeration [1, 2], but it also influences the physical properties of Ag films and causes the increase of electrical resistivity.

We reported thermally stable Ag thin films (Fig. 1b) sandwiched between surface and interface nanolayers of metals such as Al, Ti and so on [3-6]. We also found the features required for the nanolayer materials, namely, high cohesive energy or high free energy of oxide formation and low solid solubility in Ag [5, 6]. It is well known that Al is readily oxidized by exposure to air. Approximately 2.5-nm-thick porous oxide layer on Al nanoparticles was confirmed by high-resolution transmission electron microscopy [7]. We confirmed that a 1-nm-thick Al layer (nominal thickness) was oxidized to form an approximately 3-nm-thick Al oxide layer by ellipsometry [3]. Therefore, the current method is simple and facile method to form very thin metal oxide layer on Ag thin film, making use of feature of Al. In a sense, this is favourable way to form oxide nanolayers because a method such as reactive sputtering often damages the underlying metal layer.

In the present study, we investigate optical properties of the Al nanolayer deposited Ag films. It is known that Al film have lower reflectance than Ag film, except in the ultraviolet region. Even if the Al layer is several nanometers thick, it might influence the reflectance. By contrast, if the surface layer is
Al oxide, it may be optically transparent owing to its wide energy band gap about 8.4 eV [8]. Therefore, it is worthwhile to investigate the optical properties of highly stable Ag thin films fabricated by the simple deposition of Al and Ag thin films. Influence of thick (>100 nm) protective coatings has been reported [9, 10]. But our current purpose is to clarify the influence of deposited several-nanometer-thick Al surface layer on the multilayer.

Figure 1. 3D AFM images of samples after annealing at 600°C for 1h in vacuum. a) 100-nm-thick Ag single film (scanning area: 15×15μm²), b) 100-nm-thick Ag film sandwiched between 1-nm-thick Al nanolayers (scanning area: 10×10μm²)

2. Experimental procedure
We prepared multilayers consisting of an Al nanolayer (1-, 3-, 5-nm-thick) and 100-nm-thick Ag thin films on glass substrates (Corning EAGLE XG). The multilayers were deposited by means of vacuum evaporation of Ag wire (99.99%) and Al wire (99.99%) successively without breaking vacuum after evacuated below 4.0 × 10⁻⁴ Pa. The deposition rates of Ag and Al were about 0.4 nm/s and 0.05 nm/s, respectively. Here, only the surface nanolayer was deposited for the current purpose. The electrical resistivity of the prepared films was measured using the four-point-probe method. The surface morphology was observed using an atomic force microscope (AFM). The optical reflectance spectra were measured by a spectrophotometer equipped either with an absolute reflectance measurement unit or an integrated sphere at wavelengths ranging from 200 to 2000 nm at a scanning rate of 20 nm/min. We compared the experimental results with simulation results obtained using Fresnel equations for multilayers [11].

3. Results and discussion
The resistivity of the obtained Ag single films was 2.5 μΩcm, which is almost the same as the value obtained in our previous study [3].

AFM measurements revealed that the surfaces of all films were very smooth. 2D images of the samples are shown in Fig. 2. The root mean square (RMS) roughness of the Ag single layer was 2.2 nm and that of the Al/Ag films was 1.2 nm. These changes suggest the film surface became smoother upon Al deposition. However, even though the RMS value of 2.2 nm is extremely small compared to the wavelength of light, it is believed to be adequately smooth to achieve high reflectance.

The absolute specular reflectance spectra of the Ag single layer and the Al/Ag multilayers at an incidence angle of 5° are shown in Fig. 3. Inset is enlarged view of the 300–700 nm region of these spectra. The reflectance spectrum of the Ag single layer is close to other high-quality films formed by vacuum evaporation and sputtering [10, 12]. In terms of the influence of the deposition of Al nanolayer on Ag films, we found that the spectra of Al/Ag multilayers, where Al thickness is 1 or 3 nm are similar to that of the Ag single layer. The deposition of the 1- or 3-nm-thick Al layer did not affect the
reflectance because the layer was oxidized immediately after it was removed from the deposition chamber. The reflectance of the films obtained herein is higher than that the values reported in the literature for thicker (100-nm-thick) Al$_2$O$_3$ layer [10] or SiN layer [13] deposited on an Ag film. However, the multilayer sample in which 5-nm-thick Al was deposited shows remarkably lower reflectance. It is considered that the deposited 5-nm-thick Al layer remained partly in the metallic state, which has a larger extinction coefficient than that of Ag. Therefore, it led to a noticeable decrease in reflectance. The total reflectance of the films measured using an integrated sphere was slightly (about 2%) higher than the specular reflectance spectra. This suggests that the films show negligible level of diffuse reflectance.

Figure 2. 2D AFM images (1×1 μm$^2$) of the samples: a) Ag single film, b) Al(1nm)/Ag film, c) Al(3nm)/Ag film, d) Al(5nm)/Ag film.

Figure 3. Absolute specular reflectance spectra of Ag film and 1–5 nm thick Al surface layer deposited Ag films. Inset: enlarged view of the 300–700 nm region.

Then, we compared the measured specular reflectance spectra and the simulated spectra, which were based on the complex-matrix form of the Fresnel equations [11], where optical constants were referred to from separate articles [14, 15]. As models for the simulation, Al metal (M), Al oxide (O), and Al oxide/Al metal (O+M) layers were assumed on Ag film as shown in Fig. 4 (a). For Al(1 nm)/Ag multilayers, a model in which the surface is 1-nm-thick Al metal does not fit well, but better coincidence is obtained by assuming a surface comprising 3-nm-thick Al oxide because of oxidation of the Al layer (Fig. 4(b)). Similarly, for Al (3 nm)/Ag multilayers, simulation using the model in which the surface layer is not 3-nm-thick Al metal but 4-nm-thick Al oxide leads to better coincidence, as shown in Fig. 4(c). Here, the thickness of the Al oxide layer was varied from 3 nm to 5 nm, and the best match was obtained for the 4-nm-thick layer. By contrast, neither the metal layer nor the oxide layer fits the measured result for the Al (5nm)/Ag multilayer, as shown in Fig. 4(d). However, the best match was
obtained for a model with a surface layer consisting of 4-nm-thick oxide and 1-nm-thick Al layer, though slight difference remained. These results also support the assertion that the decrease in reflectance is caused by the metallic Al in the surface layer.

Figure 4. Comparison of measured reflectance spectra and simulated spectra of Al surface layer deposited Ag films: a) simulation models for the surface layer on Ag films, b) the spectrum of 1-nm-thick Al deposited Ag film, simulation spectra of 1-nm-thick Al layer on Ag film (M) and 3-nm-thick Al oxide layer on Ag film (O), the spectrum of 3-nm-thick Al deposited Ag film, simulation spectra of 3-nm-thick Al layer on Ag film (M) and 4-nm-thick Al oxide layer on Ag film (O), d) the spectrum of 5-nm-thick Al deposited Ag film, simulation spectra of 5-nm-thick Al layer on Ag film (M) and 5-nm-thick Al oxide layer on Ag film (O), and 4-nm-thick oxide and 1-nm-thick Al layer on Ag film (O+M).

4. Conclusions
In conclusion, we investigated the influence of Al surface nanolayer deposition on 100-nm-thick Ag thin films. The deposition of an Al layer measuring up to 3 nm in thickness leads to the preservation of high reflectance, in addition to imparting high thermal stability and low electrical resistivity, which has been already confirmed. The multilayer is prepared by simple metal layer deposition by means of the vacuum evaporation method, accompanied with natural oxidation of the surface Al nanolayer, which also helps avoid any possible damage while depositing the metal oxide layer on Ag films.

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