



Correlation between microstructure and salt-water durability of Ag thin films deposited by magnetron sputtering

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ABSTRACT

The effect of nitrogen addition to the sputter gas during Ag deposition on the salt-water durability of the Ag thin films was investigated. The Ag thin films deposited in sufficient nitrogen exhibited better salt-water durability and almost the same reflectance as the Ag thin films deposited in argon only. Additionally, it was found that the haze growth observed after soaking the thin films in salt water was prevented by using a ZnO under layer. From the microstructure analysis, it was found that the improvement in the salt-water durability was attributable to the small crystallite of the Ag and the strong adhesion between the substrate and each layer.

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1. Introduction

Ag thin films have high visible-light reflectance and high electrical conductivity; therefore, they have been widely used as optical reflectors [1–6] and electrodes [7,8]. Thin films deposited by gas phase methods generally exhibit good mechanical properties and strong adhesion between a substrate and a thin film; hence, these methods are usually used for the deposition of Ag thin films [1–7,9–12]. Various gas phase methods, such as sputtering [4–6,9,13], thermal evaporation [11] and electron-beam evaporation [7–10,12], and their applications to thin films have been reported. In particular, magnetron sputtering is the most promising technique for large-area coating because of its good uniformity.

Although Ag thin films exhibit excellent optical and electrical properties, their performance is easily reduced by several factors, such as moisture, heat and the presence of chlorine or sulphur [7–9,11,14]. Thus, it is necessary to improve the durability of Ag thin films. The doping of other metals into Ag thin films is an effective way to improve their durability [9,13,14]. The Ag alloy targets are often used for the fabrication of the durable Ag thin films in sputtering deposition; however, the Ag alloy target is expensive compared to the pure Ag target. In addition, the reflectance of the Ag alloy thin films is often lower than that of pure Ag thin films. For these reasons, an alternative method to improve the durability of Ag thin films without use of the Ag alloy target is desired. In this study, the effects of two methods that do not use the Ag alloy target on the salt-water durability of the Ag thin films were investigated; one is nitrogen addition to argon sputter gas during

Ag deposition; the other is a ZnO under layer. Additionally, the correlation between the microstructure and salt-water durability of the Ag thin films is discussed.

2. Experimental details

2.1. Deposition conditions

The Ag and ZnO/Ag thin films were deposited on 3-mm-thick soda–lime–silicate glass substrates, without heating, by magnetron sputtering. The deposition apparatus was equipped with a load-lock chamber system. The distance between the sputter target and substrate was maintained at 70 mm. The sputter deposition was performed in a multiple pass mode. The coating chamber was evacuated to a back pressure of less than 2×10^{-4} Pa. For the Ag single layer deposition, a mixture of argon and nitrogen was used as the process gas, and the total gas flow was maintained at 45 sccm. Each gas was introduced into the coating chamber through a mass flow controller. The total gas pressure was 0.30–0.34 Pa. The nitrogen gas flow ratio, defined as $[N_2]/(Ar + N_2)$, was set to 4, 20 or 60 vol.%. As a comparison, we also deposited the Ag thin film in pure argon, which is defined as a nitrogen gas flow ratio of 0 vol.%. Pure Ag was used as a sputter target. The dc power supplied to the Ag target was maintained at 0.52 W cm^{-2} . For the deposition of the ZnO/Ag layer, the ZnO thin films were deposited onto the glass substrates by reactive magnetron sputtering using oxygen and pure Zn as the process gas and sputter target, respectively. The total gas pressure was maintained at 0.34 Pa. The dc power supplied to the Zn target was maintained at 1.4 W cm^{-2} . Then, the Ag thin films were successively deposited on the ZnO under layer. The deposition conditions used to produce the Ag thin films corresponded to those used for the

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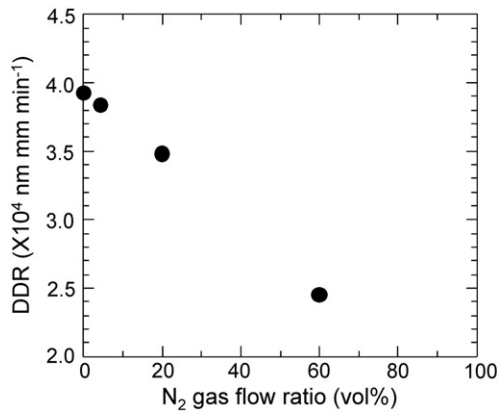


Fig. 1. DDR of Ag thin films as a function of the nitrogen gas flow ratio in the process gas.

Ag single layer. The Ag thin films with the thickness from 94 to 103 nm and the ZnO thin films with the thickness from 27 to 29 nm were obtained by adjusting the substrate conveyance speed. Additionally, the deposition rates of the Ag thin films were evaluated at each nitrogen gas flow ratio.

2.2. Evaluation

The front side reflectance of the Ag and ZnO/Ag thin films was measured with a spectrophotometer in the wavelength range from 300 to 2500 nm; furthermore, the visible-light reflectance (R_{vis}) was calculated on the basis of ISO 9050:2003(E). The sheet resistance of Ag and ZnO/Ag thin films was measured by four-point-probe system. In our previous experiments, the ZnO under layer did not exhibit electrical conductivity; therefore, the electrical conductivity of the Ag layer was calculated using the sheet resistance and the Ag thickness. The crystal structure of the thin films was evaluated by X-ray diffraction (XRD, RINT-Ultima III, Rigaku, using $\text{CuK}\alpha$ radiation) in the out-of-plane configuration, and the crystallite size of the Ag was determined from the peaks identified as the Ag(111) and Ag(200) crystal lattice planes using Scherrer's equation. The thickness of the Ag and ZnO thin films was determined by X-ray reflectometry. The surface morphology was observed with atomic force microscopy (AFM, SPM-9600, Shimadzu) in the contact mode using the silicon nitride cantilevers (OMCL-TR800PSA, Olympus). The surface roughness (R_a) was estimated by AFM analysis. The durability against salt water was evaluated by soaking the thin films in 5 wt.% salt water. Their appearance, reflectance, crystal structure and surface morphology were evaluated before and after the soak.

3. Results and discussion

Fig. 1 shows the deposition rate of the Ag thin films deposited with various nitrogen gas flow ratio. We used the moving substrate configuration; hence, the growth rate of the thin films is described as the dynamic deposition rate (DDR). The DDR is defined as the product of the substrate conveyance speed and the Ag layer thickness. It was found from Fig. 1 that the deposition rate of the Ag thin films simply decreased with increasing nitrogen gas flow ratio. Nitrogen ions exhibit low sputtering yield compared with argon ions; therefore, the Ag particles sputtered from the target decreased with nitrogen addition. Additionally, nitrogen ions show low secondary electron emission coefficient; hence, the electron concentration in the glow discharge decreased with increasing nitrogen gas flow ratio. The positive ion was produced by the collision of the process gas particles and the electrons, the positive ions which attack the target were decreased in the glow discharge with low electron concentration. It can be considered that the reasons of the deposition rate decrease were the increase of nitrogen ion with low sputtering yield and the decrease of positive ion which attacks the target.

The reflectance of the Ag and ZnO/Ag thin films is shown in Fig. 2. The reflectance of both Ag and ZnO/Ag thin films decreased with an increasing nitrogen gas flow ratio in the process gas; however, the difference in visible-light reflectance between the thin films deposited in the nitrogen gas flow ratio of 0 and 60 vol.% was very low and did not exceed 0.8%. Moreover, the reflectance of the Ag and ZnO/Ag thin films was almost equal, if they are compared using the same nitrogen gas flow ratio.

The conductivity of the Ag and ZnO/Ag thin films was plotted in Fig. 3. The conductivity of Ag decreased with increasing nitrogen gas flow ratio in both Ag and ZnO/Ag thin films. In addition, there was no big difference between the conductivity of Ag thin films and ZnO/Ag thin films when compared in same nitrogen gas flow ratio. The mechanism of the conductivity deterioration is discussed later on the basis of crystallite size analysis.

The appearances of the Ag and ZnO/Ag thin films that were soaked in salt water for 0.5, 1 and 3 h are listed in Table 1. Both the Ag and ZnO/Ag thin films deposited in a nitrogen gas flow ratio of at least 20 vol.% were not hazy, even after soaking for 1 h in salt water. In contrast, the Ag and ZnO/Ag thin films that were deposited in a nitrogen gas flow ratio of at most 4 vol.% became hazy after a 0.5-hour soak. In addition, the visible-light reflectance of the thin films before and after soaking for 1 h in salt water is shown in Table 2. When the Ag layer was deposited in a nitrogen gas flow ratio of at least 20 vol.%, the decrease in reflectance that resulted from soaking in salt water for both Ag and ZnO/Ag thin films was less than 3.5%. On the other hand, when the Ag layer was deposited in a nitrogen gas flow ratio of at most 4 vol.%, the reflectance decrease of the Ag thin films greater

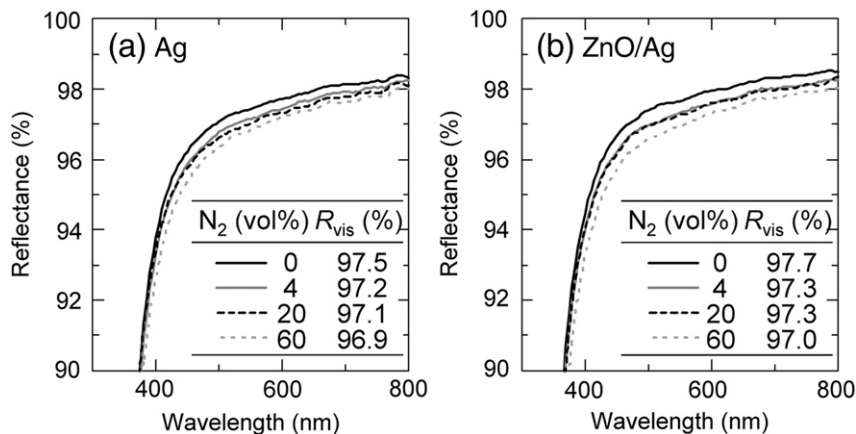


Fig. 2. Reflectance of (a) Ag and (b) ZnO/Ag thin films deposited in a mixture of argon and nitrogen during Ag deposition.

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