

Improvement in salt-water durability of Ag thin films deposited by magnetron sputtering using argon and nitrogen mixed gas

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ABSTRACT

Ag thin films were deposited by magnetron sputtering in a mixture of argon and nitrogen. The salt-water durability and reflectance of Ag thin films were investigated as a function of nitrogen gas flow ratio during sputter deposition. The reflectance of as-deposited Ag thin films decreased with increasing nitrogen gas flow ratio; however, the difference in visible-light reflectance between the Ag thin films deposited with and without nitrogen was less than 1%. The reflectance of Ag thin films that were deposited using pure argon significantly decreased after the films were soaked in salt water. In contrast, the salt-water durability of Ag thin films was improved when the nitrogen gas flow ratio was increased. X-ray diffraction and atomic force microscopy analyses revealed that the Ag thin films deposited in sufficient nitrogen exhibited smooth surfaces and small crystallite sizes. Hence, the agglomeration of Ag thin films was suppressed; as a consequence, the reflectance of Ag thin films deposited in nitrogen did not decrease to the same extent, despite being soaked in salt water.

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1. Introduction

Ag thin films have been widely used as optical reflectors [1–6] and electrodes [7,8] because of their high visible-light reflectance and high conductivity. The Ag thin films have been deposited using gas-phase methods [1–7,9–12], liquid-phase methods [13], and electroplating [14]. For gas-phase preparations, various methods, such as sputtering [4–6,9,15], thermal evaporation [11], and electron beam evaporation [7,10,12], have been reported. Such methods are known to have several advantages, such as the hardness of the resulting films and good adhesion between the thin film and substrate. In the case of a front-surface mirror application, gas-phase methods are frequently used because high reflectance and good mechanical properties are required. Additionally, among the gas-phase methods, magnetron sputtering is probably the most promising technique for obtaining uniform coatings in large areas of more than 1 m².

Front-surface mirrors are composed of several layers, including an intermediate layer between the substrate and reflection layers, a reflection layer, an optical-interference layer to enhance the reflection, and an overcoat layer [1,3,6]. The Ag thin film is

a candidate for the reflection layer for this application. However, Ag thin films deteriorate easily because of many factors, including heat, moisture, and the presence of chlorine or sulfur [7,9,11,16]. Therefore, techniques to improve the durability of Ag thin films are necessary. The doping of other metals into Ag thin films has been reported as an effective way to improve their durability [9,15,16]. However, the Ag alloy target is more expensive, and the reflectance of Ag alloy thin films is often less than that of pure Ag. Therefore, another method to improve the durability of Ag thin films without using an Ag alloy target is desired. In this study, Ag thin films were deposited using a pure Ag metal target in a mixture of argon and nitrogen. The effects of nitrogen gas addition on the salt-water durability of Ag thin films were investigated, and the correlation between the durability and microstructure of Ag thin films is discussed.

2. Experimental

The Ag thin films were deposited on 3-mm-thick soda-lime-silicate glass substrates without heating substrates by magnetron sputtering. The deposition apparatus was equipped with a load-lock chamber system. The distance between the sputter target and the substrate was maintained at 70 mm; the sputter deposition was performed in multipass mode; the substrate can pass through

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the sputter target front and be moved in one direction as well as the opposite direction. The coating chamber was evacuated to a back-pressure of less than 2×10^{-4} Pa. A mixture of argon and nitrogen was used as the process gas, and each gas was introduced to the coating chamber through a mass flow controller; the total gas pressure was kept at 0.3 Pa. The total gas flow was maintained at 45 sccm. 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 argon only, 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} . The thickness of the Ag thin films was adjusted to about 100 nm by changing the substrate conveyance speed.

The reflectance of the Ag thin films was measured with a spectrophotometer in a wavelength range of 300–2500 nm; furthermore, the visible-light reflectance (R_{vis}) was calculated on the basis of ISO 9050:2003(E). The crystal structure of the thin films was evaluated by X-ray diffraction (XRD); moreover, the crystallite size was calculated from the peaks identified as the Ag(111) and Ag(200) crystal lattice planes using Scherrer's equation. The surface morphology was observed with atomic force microscopy (AFM). Surface roughness (R_a) was estimated through the AFM analysis. The durability against salt water was evaluated by soaking the Ag thin films in 5 wt% salt water. After the films were soaked, their appearance, reflectance, crystal structure, and surface morphology were evaluated.

3. Results and discussion

The reflectance of the Ag thin films is shown in Fig. 1. Although the reflectance decreased with increasing nitrogen gas flow ratio in the process gas, the difference in visible-light reflectance between the Ag thin films deposited in nitrogen gas flow ratios of 0 and 60 vol% was only 0.6%.

The appearances of the Ag thin films after soaking in salt water are arranged in Table 1. The Ag thin films deposited in a nitrogen gas flow ratio below 4 vol% became significantly hazy because of significant white turbidity, and then exfoliated further with increased soaking time. Alternatively, when the Ag thin films were deposited in a nitrogen gas flow ratio of no less than 20 vol%, their defects were not confirmed, even though they were soaked for 1 h. Additionally, the Ag thin films became a little hazy after soaking for 3 h. The Ag thin films deposited in nitrogen gas flow ratios of no less than 20 vol% exhibit sufficient reflectance and better salt-water durability.

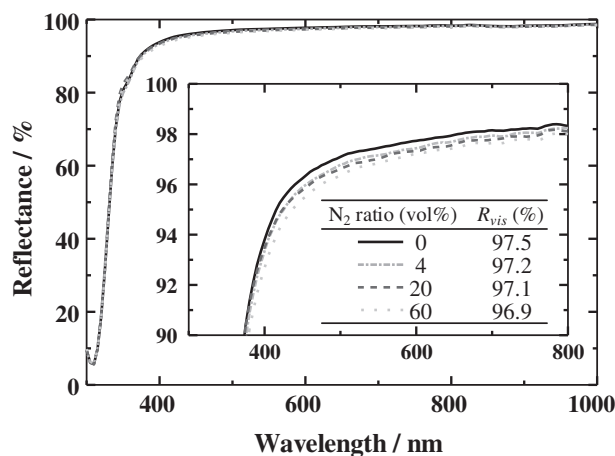


Fig. 1. Reflectance of Ag thin films deposited in a mixture of argon and nitrogen.

Table 1
Appearances of Ag thin films after soaking in salt water.

N ₂ ratio (vol%)	Soaking time (h)		
	0.5	1	3
0	White turbidity	White turbidity	Exfoliation
4	White turbidity	White turbidity	Exfoliation
20	No change	No change	White turbidity
60	No change	No change	White turbidity

Fig. 2 shows the reflectance of the Ag thin films that were soaked in salt water for 1 h. For comparison, the reflectance of the as-deposited Ag thin film is also shown in Fig. 2. As a general trend, the reflectance of the Ag thin films soaked in salt water decreased compared with that of the as-deposited Ag thin film. In particular, the reflectance of the Ag thin films drastically decreased over all wavelengths after being soaked in salt water when they were deposited in nitrogen gas flow ratios below 4 vol%. Additionally, as evidenced in Fig. 2, the visible-light reflectance of the Ag thin film deposited without nitrogen was greater than that of the Ag thin film deposited in a nitrogen gas flow ratio of 4 vol%. This might be because of poor uniformity of the Ag thin films that exhibit significant white turbidity. In contrast, the reflectance of the Ag thin films deposited in nitrogen gas flow ratios of no less than 20 vol% decreased after they were soaked in salt water. However, it is obvious that the degree of the reflectance decrease was quite small compared to the case of the Ag thin films deposited in nitrogen gas flow ratios of 0 and 4 vol%.

The AFM images of the Ag thin films taken before and after soaking for 1 h in salt water are shown in Figs. 3 and 4, respectively. Based on the image in Fig. 3, the grain size and surface roughness decreased with increasing nitrogen gas flow ratio. The decrease in grain size can be explained as the result of nitrogen gas preventing the preferential crystal growth of the Ag thin films, which is also mentioned later, in accordance with the XRD analysis. Additionally, it can be seen as a general trend in Figs. 3 and 4 that the grain size and surface roughness of all Ag thin films increased after soaking and this increase in the grain size was probably caused by the agglomeration of the Ag thin films. However, the grain size and surface roughness did not increase as much in the case of the Ag thin films deposited in nitrogen gas flow ratios of at least 20 vol%. This fact indicates that the surface morphology of the soaked Ag thin films can be influenced that of the as-deposited Ag thin films. If the surface of the Ag thin films is considerably rough, the reflectance can decrease due to light scattering. Therefore, it was

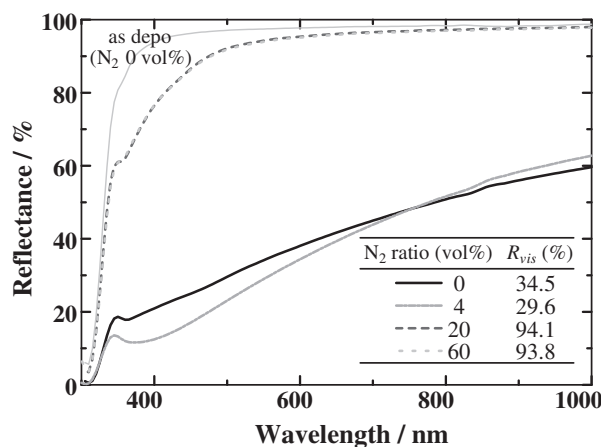


Fig. 2. Reflectance of Ag thin films after soaking for 1 h in salt water.

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