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The thermal stability of silver-based high reflectance coatings

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ABSTRACT

Silver-based highly-reflective coatings are widely used in the manufacture of optical instruments. However, it is still difficult to achieve both high reflectivity and long-term stability of the protected silver-based mirrors simultaneously. Here the thermal stability of silver-based high reflectance coatings is investigated both theoretically and experimentally. Silver-based mirrors are annealed at different temperatures, and then are characterized by X-ray diffraction and UV-VIS spectrophotometer. The microstructure of Ag-Cu alloy film is affected by the annealing temperature, which leads to the decreasing of reflectance of the alloy film with the increasing of annealing temperature obviously.

1. Introduction

Silver-based high reflectance coatings are widely used in astronomical telescopes, space sensors and optoelectronic devices owing to their low emissivity and high reflectivity from 400 nm to the infrared wavelength [1–3]. Silver is soft and has poor environmental resistance, its optical performance losses when silver-based reflectors are exposed to the atmosphere over time [4,5]. Protective and adhesive layers, such as SiNx, NiCrNx, and Cu, are often added to overcome its major deficiency when silver-based reflectors are fabricated. However, the protective layer can only slow the corrosion process [6,7]. Therefore electrochemical impedance spectroscopy and manual corrosion methods are used to study the mechanism of silver corrosion in order to get long-term durability of Ag mirrors under harsh environments. It shows that S and Cl are the activators of silver corrosion, while particles and permeable defects can damage the protective layers [8,9]. Corrosion damage of protected silver-based mirrors and the resulting reduction of reflectivity have been studied intensively.

The working environment has great influence on silver-based optoelectronic devices, especially for space-based applications, which has received considerable attention in recent years [10–11]. James et al. describe the influence of simulated space environment full of ultraviolet light and low-energy electron radiation on the optical property of dielectric multilayer composed of Nb_2O_5 and SiO_2 [12]. When copper was introduced as interlayer bounding to silver, the durability can be improved [6]. Such mirrors can be widely used in many special cases if this kind of coatings has long-term stable reflectivity, for silver and copper being deposited easily using thermal evaporation method. However, the thermal stability and optical properties of silver-based mirrors have not been systematically studied [13–15]. In this paper, we investigate the influence of annealing temperature on the reflectivity of silver-based mirrors owing to grain-boundary diffusion of silver and copper.

2. Sample preparation

In order to get the significant reflective performance, the parameters of silver-based mirror, such as the thicknesses of silver, copper and dielectric (Ta_2O_5/SiO_2) layers, should be optimized at first. The prepared structure S_0 is shown in Table 1. Samples S_1, S_2 and S_3 are used to study the variation of the reflectance with different thickness of M, where M is the alloy of Ag-12.5 at.% Cu.

Copper and silver are deposited using thermal evaporation method, and the deposition pressure is lower than 2.5×10^{-4} Pa. Dielectric layers are added on the top of silver layer to boost the reflectivity and to protect silver against the environment corrosion. Ta_2O_5 and SiO_2 layers are deposited by ion-assisted electron-beam evaporation method in an oxygen atmosphere with growth rate of 2.0 Å/s and 4.0 Å/s, respectively. In order to improve the density of the dielectric coatings, Mark II HO ion source is used to bombard thin films during their growing process. The anode voltage and current are in the range of 180 V–280 V and 5 A–10 A, respectively. Pure oxygen (99.99%) is introduced into the chamber during dielectric layers deposition and the working pressure is automatically controlled. Layer thickness is monitored by thin film deposition controller (IC6). Substrate material is BK7. Relevant deposition parameters are summarized in Table 2. In order to compare, we use the samples from the same batch to study. After deposition, the

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Table 1
Structure of silver-based mirrors studied in the paper.

Name of the mirror	Layers	Thickness of Ag (nm)	Thickness of M (nm)
S_0	$Sub/Cr/Cu/Ag/SiO_2/Ta_2O_5$	180	–
S_1	$Sub/Cr/M/Ag/SiO_2/Ta_2O_5$	50	150
S_2	$Sub/Cr/M/Ag/SiO_2/Ta_2O_5$	40	160
S_3	$Sub/Cr/M/Ag/SiO_2/Ta_2O_5$	30	170

samples are annealed at 100 °C, 150 °C and 200 °C for 1 h under atmosphere circumstance, respectively.

3. Results and discussion

3.1. Structure analysis

Rigaku Ultima IV X-ray diffraction (XRD) was used to determine the phase composition, grain size and lattice parameters of the samples before and after being annealed. The scanning angle was from 15° to 80°, with the step of 0.02°. Fig. 1 shows the XRD patterns of deposited silver-based reflector (sample S_0) and that of annealed samples at 100 °C, 150 °C and 200 °C, respectively. There are two main peaks at 37° and 44°, corresponding to (111) and (200) plane of face-centered cubic (fcc) Ag phase, respectively. It is shown that the intensity of peak around 37° increases with the annealing temperature from 100 °C to 150 °C, while the intensity decreases when annealing temperature achieves to 200 °C. The shape of diffraction peak around the (111) is slightly non-symmetrical, one of the possible reasons is that silver deposited by thermal evaporation method may contain more than two kinds of lattice parameter for fcc structure. Compared to PDF card, the two kinds of Ag phase corresponding to PDF-658428 and PDF-652871 are the most possible ones in the fcc silver thin film. These may be caused by the deposition parameters such as deposition rate, pressure and etc.

The structure parameters are listed in Table 3. The grain size is calculated using Debye-Scherrer's formula [16],

$$D = \frac{K\lambda_{CuK\alpha}}{L_{2\theta}\cos\theta} \quad (1)$$

where D is the crystal size, $\lambda_{CuK\alpha}$ is the X-ray wavelength, $L_{2\theta}$ is the full width at half maximum, θ is the Bragg diffraction angle and $K = 0.89$ is a constant.

In Table 3, it can be seen that the peak of Bragg diffraction moves to higher degree under higher annealing temperature. The peak of (111) plane moves from 37.945° to 37.999° and that of (200) plane moves from 44.153° to 44.282°. The lattice parameter is 4.1037 Å without anneal, and decreases to 4.098 Å after being annealed at 200 °C. It has been reported that such phenomena is caused by the increasing of the copper addition in metal silver [17] during anneal. With the increase of the anneal temperature, boundary diffusion of copper through silver film is strengthened. Accordingly, the doping of copper in silver increases and the average lattice parameters of the fcc Ag phase structure decrease owing to copper possessing a smaller lattice constant than silver, which is in excellent agreement with other experimental results [18,19]. When this kind of mirror is used at ambient temperature higher than 100 °C, the boundary diffusion of copper through silver film will occur.

The grain sizes of deposited and annealed samples are also shown in Table 3, which increases from 36.23 nm without annealing to 44.95 nm after being annealed at 150 °C, while decreased to 42.89 nm after being annealed at 200 °C. The reason may be the relief of intrinsic stress of the deposited films by the annealing effect. With the increasing content of copper after being annealed at 200 °C, the lattice of Ag-Cu alloy is squeezed, which reduces the grain size.

Table 2
Deposition parameters of Ta_2O_5/SiO_2.

Material	Ion source		Temperature	Pressure
	Anode voltage	Anode current		
Ta_2O_5	280 V	9 mA	100 °C	1.6×10^{-2} Pa
SiO_2	250 V	9 mA	100 °C	1.4×10^{-2} Pa

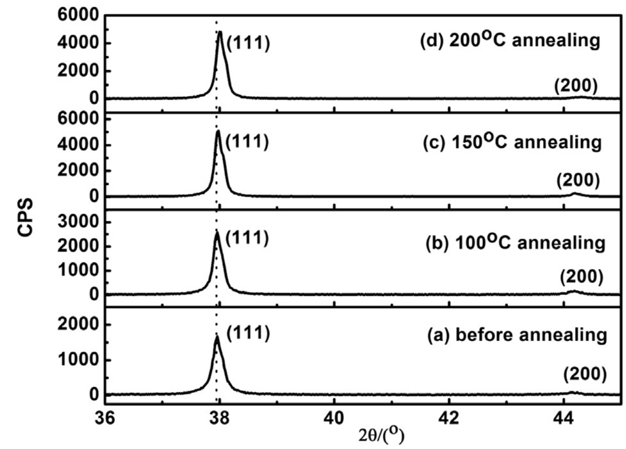

Fig. 1. The XRD patterns of S_0 being annealed at different temperature.

3.2. Optical property

To estimate the thermal stability of silver-based mirror, the reflectance spectra of the samples were measured using UV-VIS spectrophotometer (Lambda 950) in the wavelength range of 400 nm–800 nm at 8° incident angle. The results were shown in Fig. 2. It can be seen that the reflectivity decreases obviously in the wavelength range about 400 nm–500 nm with the increase of the annealing temperature, especially for the sample annealed at 200 °C in Fig.2(c). It is shown that when copper is chosen as interlayer to prevent silver-based mirror to be tarnished, the optical property will degenerate in short wavelength range as it works at ambient temperature higher than 100 °C shown in Fig.2(a)–(c).

3.3. First principle calculations

The XRD measurement results show that the compositions of Ag-Cu alloy films are different for different annealing temperatures. We calculate the refractive index and extinction coefficient for Ag-12.5 at.% Cu alloy using the first principle method [20]. The results are shown in Fig. 3.

The calculations were performed by the ultra-soft pseudopotential approach based on the density-functional theory. In the linear response range, the dielectric function $\varepsilon(\omega) = \varepsilon_1(\omega) \pm i\varepsilon_2(\omega)$ is dominated by

Table 3
Structure parameters of S_0 before and after being annealed.

Annealing temperature	2θ(°)		Lattice parameters(Å)	Grain size(nm)
	(111)	(200)		
RT	37.945	44.153	4.1037	36.23
100 °C	37.950	44.157	4.1032	40.61
150 °C	37.968	44.191	4.1013	44.95
200 °C	37.999	44.282	4.0980	42.89