Surface & Coatings Technology 324 (2017) 175–181

Contents lists available at ScienceDirect

Surface & Coatings Technology

journal homepage: www.elsevier.com/locate/surfcoat

SiN_x thickness dependence of spectral properties and durability of protected-silver mirrors

Xu Xu [a,b], Wenyan He [a,b], Changjun Wang [a], Ming Wei [a], Bincheng Li [a,c,*]

[a] Institute of Optics and Electronics, Chinese Academy of Sciences, Chengdu 610209, China
[b] Graduate School of the Chinese Academy of Sciences, Beijing 100039, China
[c] School of Optoelectronic Information, University of Electronic Science and Technology of China, Chengdu 610054, China

ARTICLE INFO

Article history:
Received 2 January 2017
Revised 25 May 2017
Accepted in revised form 26 May 2017
Available online 27 May 2017

Keywords:
Spectral properties
Durability
Protected-silver mirrors
SiN_x protective coatings

ABSTRACT

Both long-term environmental durability and high broadband reflectance of protected-silver mirrors are of great importance to the developments of optical instruments for a variety of applications under harsh environments. In this paper, the dependences of spectral properties and environmental durability of protected-silver mirrors with a $Sub/NiCrN_x/Ag/NiCrN_x/SiN_x/Air$ structure on thickness of SiN_x protective layer were investigated in details. The reflectance, transmittance, total scattering loss measurements and scanning electron microscope (SEM) imaging were employed to characterize the spectral properties and surface morphology, and accelerated environmental tests, including humidity test and salt fog test, were applied to investigate the environmental durability. Five magnetron-sputtering prepared protected-silver mirrors with SiN_x layer thicknesses between 8 nm to 16 nm were tested. The results showed that both optical and corrosion-resistant properties of protected-silver mirrors were SiN_x thickness dependent and the optimum SiN_x thickness should be approximately 14 nm for $Sub/NiCrN_x/Ag/NiCrN_x/SiN_x/Air$ protected-silver mirrors to have both reasonably high reflectance in the visible spectral range and high corrosion resistance for long lifetime applications in harsh environments.

1. Introduction

Durable broadband highly-reflective metal mirrors have long been a goal for many optical applications such as large astronomical telescopes, large-scale high-power laser systems and space-based optics [1–3]. Silver possesses the highest reflectance, lowest emissivity, and lowest polarization splitting of all metals, making it the choice of reflective coating material for the most demanding applications in visible and infrared spectral ranges. The theoretical reflectance of silver is 97.9% at 500 nm and better than 99% at far-infrared wavelength region [4]. However, an unprotected silver film tarnishes quickly or forms salts with halides in the presence of sulfur compounds, chlorine and ozone in the atmosphere [5–7]. To fabricate durable protected-silver mirrors, the silver layer must be protected by transparent dielectric materials. In addition, due to the poor adhesion of silver to common substrate materials and dielectric materials, additional adhesive layers between silver and substrate/protective layer are needed. Unfortunately, these protection and adhesion layers often reduce excellent initial optical performance of silver film, while improving the silver mirror durability. Hence, a better understanding of the corrosion resistance of the protected-silver mirrors and finding a balance between optical properties and environmental durability is of great importance to preparing high-performance protected-silver mirrors for applications in harsh environments.

Various schemes have been developed in the past to prepare durable silver mirrors. In early 1970s, Hass et al. [8] applied refractory metal-oxides as protective layers for silver film to improve the durability. Protected-silver mirrors with a $Sub/Al_2O_3/Ag/Al_2O_3/SiO_x/Air$ structure had less than ten months of lifetime when exposed to the atmospheric environment [1]. Until 1985, Song et al. [1] replaced the Al_2O_3 layer with a copper (Cu) layer to act as the under-layer between silver and substrate, the lifetime of the protected-silver mirrors were somewhat prolonged. In the 1990s, researchers [9] from Lawrence Livermore National Laboratory (LLNL) developed a protective-silver mirror with a structure of $Sub/NiCrN_x/Ag/NiCrN_x/SiN_x/Air$. It was successfully applied to coat the Gemini telescopes [10,11]. Still, more improvements in environmental durability is needed for protected-silver coatings to meet the requirements of about 10 years operation before recoating is necessary [12]. Although it was demonstrated that a SiN_x protective layer combined with an extremely thin $NiCrN_x$ interlayer provided excellent corrosion protection for silver [12,13], and also Fuqua et al. [14] and Chu et al. [15] have proven that an ultrathin $NiCrN_x$ interlayer played a crucial role in the durability of the Gemini-style reflective coating, a better understanding of the corrosion resistance mechanism of Gemini-style reflective coating under harsh environments is still needed. Recently,

* Corresponding author at: School of Optoelectronic Information, University of Electtronic Science and Technology of China, Chengdu 610054, China.
E-mail address: bcli@uestc.edu.cn (B. Li).

http://dx.doi.org/10.1016/j.surfcoat.2017.05.078

Schwinde et al. [16] reported a particle-induced damage mechanism for silver corrosion, and believed that the deposition of impervious protective layers is necessary but often not sufficient for long-term environmental stability. More in-depth investigation on the corrosion resistance of protected-silver mirrors is certainly needed for the preparation of more durable silver mirrors.

On the other hand, silicon nitride (SiN_x) is a dense refractory ceramic material with high refractive index, high electrical resistivity, resistances to sodium ions and moisture permeation, as well as high thermal stability [17,18]. It has been used as protective coatings in various applications [19,20]. It is certainly an excellent material as the protective layer to enhance the environmental durability of the Gemini-style protected-silver coatings. However, SiN_x film is also absorptive in the short-wavelength region [21], which reduces the initial reflectance of silver in the visible spectral range when used as protective overcoats.

Apparently, an optimization of the SiN_x overcoat is required to balance the spectral reflectance properties and environmental durability of SiN_x protected silver mirrors, which is still missing in literature. In this paper, by analyzing the influence of humidity test and salt fog test on the spectral properties and surface morphology of magnetron-sputtering prepared protected-silver mirrors with a Sub/$NiCrN_x$/Ag/$NiCrN_x$/SiN_x/Air structure with SiN_x layer thicknesses between 8 nm to 16 nm, the SiN_x layer thickness is optimized for both high reflectance in the visible spectral range and high corrosion resistance for long life-time applications in harsh environments. In addition, the corrosion-resistant mechanisms of protected-silver mirrors were discussed.

2. Experiment

Five protected-silver mirror samples with the structure of Sub/$NiCrN_x$/Ag/$NiCrN_x$/SiN_x/Air were prepared by a magnetron sputtering coating machine (Helios 400, Leybold Optics, Germany) equipped with a middle frequency (MF) source power and a direct current (DC) source power. The thicknesses of the SiN_x protective overcoats of the five samples were 8 nm, 10 nm, 12 nm, 14 nm, and 16 nm, respectively. For sample preparation, routinely polished and manually cleaned BK7 plates were used as the substrates. The base pressure of the vacuum chamber was evacuated to lower than 2.0×10^{-4} Pa. MF source power was used for reactive deposition of the nitride layers, and DC source power was used for deposition of silver film. The deposition parameters were given in Table 1. The source power and deposition rates were optimized per previous experiments. Deposition rates were calibrated from thicker films by using an Alpha-step Surface Profiler and a J. A. Woollam variable angle spectroscopic ellipsometer (VASE). Layer thickness was controlled via the deposition time.

Specular reflectance spectra of the prepared samples was measured at 8° angle of incidence in the wavelength range of 400 nm to 1800 nm, using a Perkin-Elmer Lambda 1050 spectrophotometer equipped with a specular reflectance accessory. The nominal reflectance measurement uncertainty was $\pm 0.3\%$. Total scattering loss at 632.8 nm was measured by a total scattering instrument (Laser Zentrum Hannover, Germany). The reported value was the average of the scattering losses measured at the central area (12 mm diameter) of the sample. The nominal repeatability error was $\pm 5\%$. Surface morphology was characterized by a Hitachi SU8000 SEM. In order to evaluate the pinhole density and durability of the prepared protected-silver mirror samples, a transmittance measurement setup was built with a He—Ne laser (632.8 nm) of beam diameter of approximately 1 mm. The measured transmittance was the power ratio of the directly transmitted beam to the input beam. The measurement uncertainty was comparable to that of a spectrophotometer. For each sample, the reported transmittance was the average of five measurements at different areas of the sample. In our study, two groups of prepared protected-silver mirror samples were exposed to accelerated degradation tests, one group was for humidity test (under 50 °C temperature and 98% relative humidity) and the other was for salt fog test (under 5% NaCl by weight and 35 °C temperature). The total duration of the accelerated degradation tests of these samples was 360 h. Every 24 h, the accelerated degradation tests were halted and the samples exposed to humidity and salt fog were subsequently rinsed with de-ionized water and blown dry with nitrogen. Then the reflectance spectra and transmittance of the samples were measured. After 360-hour accelerated degradation tests, the surface morphology of the samples was characterized and the total scattering loss was measured, respectively.

Table 1
Deposition parameters for preparation of the protected-silver mirrors.

Compound	Target	Power (W)	Thickness (nm)	Rate (nm/s)
$NiCrN_x$	80Ni-20Cr	125	6	0.005
Ag	Silver	2500	120	0.86
$NiCrN_x$	80Ni-20Cr	125	0.3	0.005
SiN_x	Silicon	500	8–16	0.014

3. Results and discussion

3.1. Optical properties

Fig. 1 shows the measured reflectance spectra of the as-deposited protected-silver mirror samples with various SiN_x thicknesses in the spectral range of 400 nm to 1800 nm. Obviously, the reflectance spectra of the protected-silver mirrors were SiN_x thickness dependent, and at the short-wavelength end of the visible spectral range, especially from 400 nm to 500 nm, the reflectance decreased rapidly with the increasing SiN_x thickness. For wavelength 1000 nm to 1800 nm, the reflectance became approximately SiN_x thickness independent. The reflectance at 400 nm, 550 nm, and the average reflectance (R_{av}) in the short-wavelength region of 400 nm to 500 nm and in the NIR wavelength region of 1000 nm to 1800 nm were listed in Table 2. It shows that per 2 nm-thick SiN_x layer the reflectance of the protective silver mirror reduced by approximately 2.4% at 400 nm and 0.4% at 550 nm. The reduction of the measured reflectance is due to the absorption behavior and interference effects of the SiN_x protective layer. Clearly, to obtain high reflectance at the short-wavelength end of the visible spectral range, a thinner SiN_x layer is preferable. On the other hand, the thickness of the SiN_x protective layer is also of great importance to the environmental durability of the Gemini-style protected-silver mirrors, as to be discussed in the next sub-section.

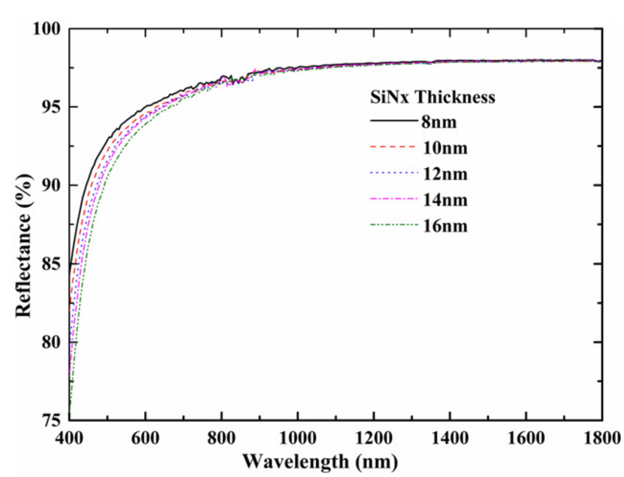

Fig. 1. Reflectance spectra of protected-silver mirrors with different SiN_x thicknesses.