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逆向热蒸发制备望远镜主镜银反射膜

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摘 要:以自上向下热蒸发大型镀膜机为实验平台,开展了逆向蒸发制备大口径银反射镜研究.通过设计特殊蒸发舟及优化相关工艺参数,实现了金属银膜稳定、高速向下蒸发.根据逆向热蒸发工艺特点,选取熔点低、升华型材料 Cr 和 SiO 及特殊设计的蒸发舟,以 Cr 或 CrN_x 为粘结层,SiO_x 或 SiO_xN_y 为保护层,制备了三种具有四层结构的介质保护性银反射膜,并对所制备反射镜样品的反射率、断面形貌和环境稳定性进行了表征.实验结果表明:膜系结构为 3 nmCr/120 nmAg/0.6 nmCrN_x/150 nmSiO_xN_y 的银反射膜具有较好的环境稳定性和光谱特性;通过了 24 小时湿热实验(50℃/相对湿度 98%)和盐雾实验,在 400~1 800 nm 波段光谱范围内,银反射膜的平均反射率达到 97.8%.

关键词:薄膜;保护性银反射膜;向下热蒸发;SiO_xN_y 保护层;环境稳定性

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Protected-Silver Coating for Telescope Primary Mirrors Prepared by Downward Thermal Evaporation

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Abstract: By using a high-vacuum resistive heating evaporation coating machine with the materials evaporated downwards, the research of downward thermal evaporation for large-aperture optics was implemented. The silver coating was prepared at a high deposition rate by resistive heating tungsten filaments without splashing. The adhesion layer and protective layer were also thermally evaporated downwards with specially designed evaporation boats with Cr or CrN_x as the adhesion layer and SiO_x or SiO_xN_y as the protective layer. To evaluate the performance of the protected-silver coating, three kinds of protected-silver coatings were prepared and researched in details. The reflectance, cross-section morphology and environmental stability of the prepared coating samples were characterized. The results show that the coating with 3nmCr/120nmAg/0.6nmCrN_x/150nmSiO_xN_y structure has good performances on environmental stability and spectral characteristics. Especially, it has an average reflectance of 97.8% in the 400~1800 nm spectral range, and passed the tests of 24-hour humidity (50℃/98% RH) and salt folg.

Key words: Thin films; Protected-silver coating; Downward thermal evaporation; SiO_xN_y protective layer; Environmental stability

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0 Introduction

The coating of large-aperture primary mirrors is one of the key technologies for the high-performance telescope systems. In a conventional coating process of thermal evaporation, the primary mirror substrate, which is placed in the upper part of the vacuum chamber of a coating machine, faces downward for the deposition with the evaporation sources placed below the substrate. In this process, the primary mirror substrate has to be overturned firstly from the face up to the down for coating and then from the face down back to the up after the coating is finished. The safety and maintaining the surface figure of the primary mirror become a serious issue for mirrors with diameters in the meter level. As the primary mirror becoming larger and heavier, downward thermal evaporation or magnetron sputtering has been applied to coat primary mirrors such as Subaru, TAO and Gemini[1-2]. Up to now, downward thermal evaporation was only employed to prepare aluminum coatings for large-aperture primary mirrors[3].

Silver, which has the highest reflectance over the broadest spectral range of any metal materials and induces the least polarization effect into an optical system is therefore the choice for coating primary mirrors of large astronomical telescopes. However, an unprotected silver film quickly tarnishes or forms salts with halides in the presence of sulphides, chlorides, and oxides in the atmosphere[4-5]. To fabricate durable silver-based mirrors, the silver layer must be protected by barrier layers of transparent dielectric materials. And also, due to the poor adhesion of silver to common substrate materials and dielectric materials[6], additional protective and adhesive coating layers are needed, which may significantly affect the reflectance and environmental stability of the silver coating. Recently, dielectric coatings such as silicon nitride (Si_3N_4), hafnium oxide (HfO_2), tantalum oxide (Ta_2O_5) and yttrium oxide (Y_2O_3) were proposed to be used as the protection layers, while metal as well as metal nitride layers such as copper (Cu), chromium (Cr), nichrome (NiCr) or nichrome nitride ($NiCrN_x$)[7-10] are served as the adhesion layer. However, most of these dielectric materials are difficult to be thermally evaporated downwards, which makes a real challenge for the preparation of protected-silver mirrors with downward thermal evaporation.

In this paper, the preparation of protected-silver coating for meter-level primary mirror with downward thermal evaporation is studied in details. In the downward thermal evaporation process, it should pay more attentions to avoid mirror surface contamination by the dusts, flaking films deposited on surfaces and fixtures in the vacuum chamber, as well as the splashing during the coating process. The most important step is to eliminate the splashing by using specially designed evaporation boats and optimizing the process parameters. Three kinds of protected-silver coatings were prepared by downward thermal evaporation. The optical properties and cross-section morphology of these prepared coating samples were characterized by a Perkin Elmer Lambda 1 050 spectrophotometer and a Scanning Electron Microscope (SEM). The environmental stability was evaluated by the accelerated environmental tests, including humidity test and salt fog test. The optimal coating process will be found by comparing and analyzing the performances of these prepared samples.

1 Downward thermal evaporation

1.1 Coating machine configuration

A 3.2 m high-vacuum resistive heating evaporation coating machine is used to prepare the coating samples in the experiment. Fig. 1 shows the structure and size of the vacuum chamber of the coating machine. Resistive heating sources, which are placed on the top of the vacuum chamber, are used to evaporate downwards silver and dielectric materials for the reflective, adhesion, and protective layers, respectively. Six resistance evaporation sources placing on the same ring with 60-degree separation, which are controlled by six independent transformers, are used to evaporate the dielectric materials to form different combinations of dielectric materials for the protective layers. A 1.3 m high-vacuum coating machine is also used in the experiment.

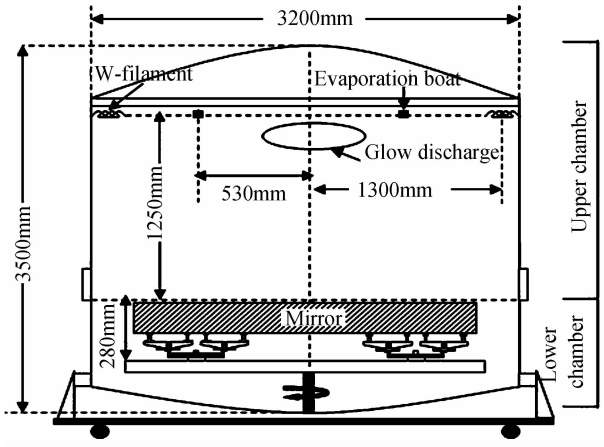

Fig. 1 Configuration and dimensions of the 3.2 m coating machine

1.2 Material selection

As the downward thermal evaporation is used for

preparing the coatings, the selection of appropriate materials for the protective and adhesion layers is of great importance. For safety of the primary mirror, no drops could be formed during the evaporating process. Therefore, only materials with sublimation property and low melting point can be used for the protective and adhesion layers. In these experiments, sublimation materials Cr and silicon monoxide (SiO) are selected as the evaporation materials.

2 Experimental details

2.1 Evaporation of the protected-silver coatings

Following the recipe of the durable protected-silver coating on Gemini 8 m primary mirrors[2, 11], a four-layer structure, which is shown in Fig. 2, is used to prepare the protected-silver coating.

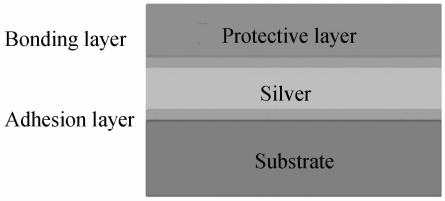

Fig. 2 Design of protected-silver coating

For preparing the protected-silver coating experimentally, the most important issue is to find the method how the silver evaporates downwards without spitting. The primary mirror would receive damages if the molten silver drops. Through enhancing a silver string and a chromium string together on a tungsten filament, sliver could be evaporated downwards at a high deposition rate by resistive heating tungsten filaments. Fig. 3(a) shows the sketch of tungsten filament, and Fig. 3(b) is a picture showing the silver evaporation source after coating. The Cr string remains on the tungsten filament after the coating process.

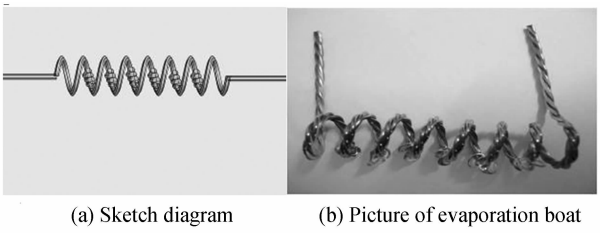

Fig. 3 Silver evaporation sources

Cr film is prepared by resistive heating tungsten rods electroplated with Cr. CrN_x film is prepared through filling N_2 into the vacuum chamber when heating tungsten rods. In the coating process, the base vacuum pressure is 4×10^{-4} Pa, and the deposition temperature is 100℃. The N_2 partial pressure is 9×10^{-3} Pa and the deposition rate is 0.02nm/s.

SiO_x and SiO_xN_y films are prepared by reactive evaporation of SiO in a controlled oxygen or nitrogen environment. Fig. 4(a) shows the SiO evaporation boat, and Fig. 4(b) is schematic diagram of work principle of the evaporation boat. SiO coating material is filled into the boat from the upside holes. When resistive heating, SiO transfers from solid to vapor and eventually moves downwards to the surface of the primary mirror for the film deposition.

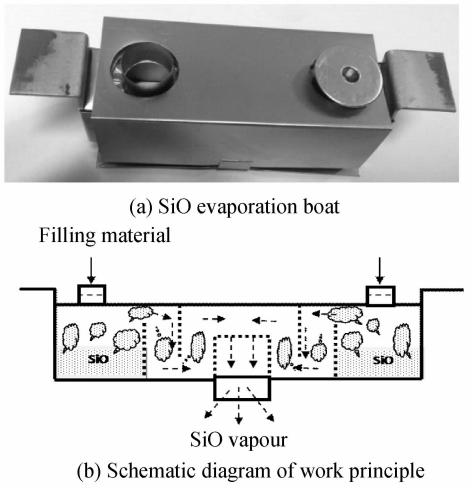

Fig. 4 The special designed SiO evaporation boat

Three kinds of protected-silver coating samples are prepared and tested. The prepared samples types are summarized in Table 1. The optical properties and environmental stability of these samples are analyzed and compared to optimize the coating process for preparing the protected-silver coating for large-aperture primary mirrors.

Table 1 Overview of prepared sample types

Sample No.	Layer thickness in/nm					
	Cr	Ag	Cr	CrN_x	SiO_x	SiO_xN_y
1#	3	120	0.3	-	150	-
2#	3	120	0.6	-	150	-
3#	3	120	-	0.6	-	150

2.2 Sample Characterization

Reflectance measurements of the three prepared samples are performed by a Perkin Elmer Lambda 1 050 spectrophotometer in the spectral region of 400～1 800 nm. A Hitachi Scanning Electron Microscope (SEM) is used to investigate the cross-sectional morphology of the samples.

According to GJB 2485-95[12], the durability of the prepared protected-silver samples is evaluated by accelerated environmental tests. Scotch tape test is used to evaluate the adhesion, and humidity test and salt fog test are performed to evaluate the environmental stability. The humidity test consists of a 24-hour exposure of the sample at 50℃ and 98% Relative Humidity (RH), and the salt fog test consists of spraying continuously the sample with 5% NaCl by weigh at 35℃ temperature for 24 hours. After the accelerated environmental tests, the surfaces of the

samples are cleaned by deionized water, and then the appearances and reflectance of samples are evaluated by naked eyes and Lambda 1050 spectrophotometer.

3 Results and Discussions

3.1 Optical properties

Fig. 5 shows the measured reflectance spectra of the prepared samples (Samples 1#, 2# and 3#) in the spectral range of 400nm to 1800nm. It is obvious that the reflectance of Sample 2# is lower than that of Sample 1#, indicating that 0.6nm-thickness Cr layer increases remarkably the absorption in the whole spectral region than 0.3nm-thickness Cr. On the other hand, the reflectance of Sample 3# in the short wavelength region is lower than that of the corresponding theoretical design because of insufficiently nitride SiO existed in SiO_xN_y layer.

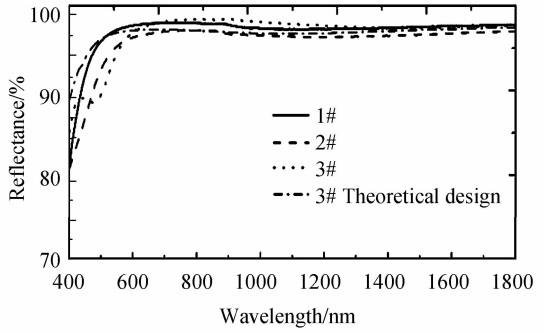

Fig. 5 Reflectance of samples 1#, 2#, 3# as-deposited and the theoretical design of sample 3# in the wavelength range of 400～1 800 nm

The average reflectance in the spectral range of 400nm to 1800nm of three protected-silver coating samples is listed in Table 2. Due to the additional 0.3 nm-thickness Cr layer as the bonding layer, the average reflectance of Sample 2# in the spectral range of 400nm to 1800nm drops 1.3% compared with Sample 1#. It is previously proved that a thicker Cr layer could produce a more durable protected-silver coating, but at the expense of a lower reflectance[13]. It is obvious that the metal bonding layer could decrease the reflectance, but it is of importance to the environmental stability of the protective-silver coating. We have attempted to use a dielectric layer to replace the metal layer as a bonding layer. It is found that the better optical performance is obtained by using Yb_2O_3 film as the bonding layer instead of metallic film, with some compromise of the corrosion resistance. Further investigation on Yb_2O_3 film is under way.

Table 2 The average reflectance of the three prepared samples

Sample No.	Recipe	Rav@ 400～1 800 nm
1#	Sub/3 nmCr/120 nmAg/ 0.3 nmCr/150 nmSiO_x	98.0%
2#	Sub/3 nmCr/120 nmAg/ 0.6 nmCr/150 nmSiO_x	96.7%
3#	Sub/3 nmCr/120 nmAg/ 0.6 nmCrN_x/150 nmSiO_xN_y	97.8%

3.2 Cross-section morphology

Cross-sectional SEM photographs of different samples deposited on silicon wafers with different recipes are shown in Fig. 6. From the thin film growth fundamentals[14], in a physical vapour deposition process the microstructure of the deposited thin films depends on surface diffusion. And the mobility of atoms on a surface will affect the surface diffusion. As a result, all prepared silver films deposited at a room temperature present a columnar microstructure. The chemistry of thin films is not the same as that of bulk materials. In bulk form, silver is relatively inert. But in thin film form, silver seems to participate in many different reactions in the presence of moisture[15]. So the protective layers on silver thin film should be dense enough.

From the cross-sectional SEM photograph of Sample 1#, 2# and 3#, it is obvious that no holes are observed inthe cross-section morphology of SiO_x and SiO_xN_y protected-silver layers which are prepared by reactive evaporation without ion assistance. The cross-sectional SEM photograph of Sample 3# shows that the bonding of Ag/SiO_xN_y is very strong and shows no delamination at all.

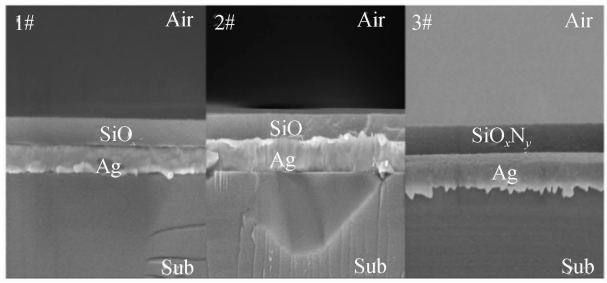

Fig. 6 Cross-sectional SEM photographs of the three protected-silver samples

3.3 Environmental durability

Durable protected-silver coating should be capable of enduring the mechanical test and corrosion resistance test, including humidity test and salt fog test.

3.3.1 *Mechanical test*

Adhesion test of the samples is performed before the accelerated environmental testing. Among all samples, no evidence of coating removal is observed when 3M-type scotch tape is pressed firmly against the film and quickly removed at a 90-degree angle to the coated surface. All the three samples have passed tape test.

3.3.2 *Corrosion resistance test*

It is well known that a tarnish film forms on

freshly deposited silver when exposed to atmosphere in the presence of moisture, sulphides and chlorides. The corrosion resistance of the silver-based film is evaluated by accelerated environmental test, including humidity test and salt fog test. All these protected-silver coating samples passed the humidity test with no significant reflectance loss, as shown in Fig. 7. This observation suggests that all the samples have excellent ability to resist water vapour diffusion. In the short wavelength region, it is found that the reflectance of Sample 3 # (3nmCr/120nmAg/0. 6nmCrN_x/150 nmSiO_xN_y) increases approximately 1% due to SiO_xN_y oxidation after 24 h humidity exposure. Before preparing the multilayer sample, the deposition rate and gas flow have been optimized. As no ion assistance is applied, and the mobility of atoms is low, so SiO could reactive with nitride completely. The nitridation of SiO_xN_y would be improved with high-energy ion bombardment during film growth.

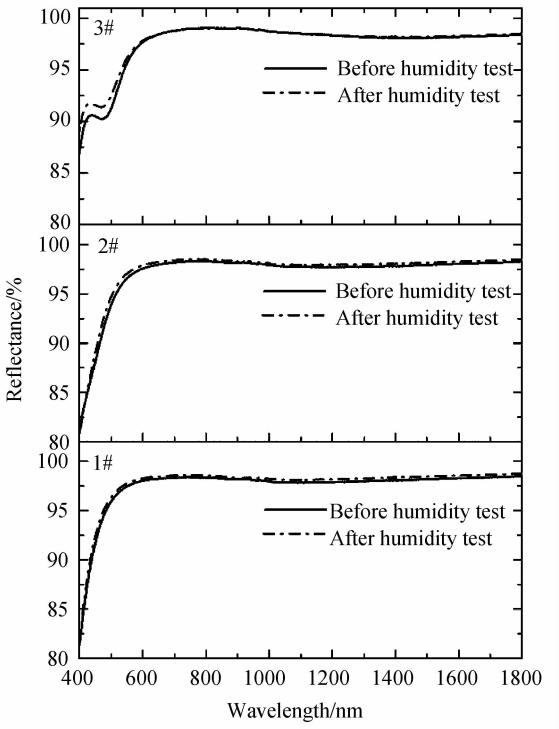

Fig. 7 Reflectance spectra of the three protected-silver coating before and after 24-h humidity test

The salt fog test is a much more severe test than the humidity test. According to GJB 2485-95[12], all samples are sprayed continuously with 5% NaCl by weigh at 35℃ temperature for 24 hours. Then the appearances of samples are checked by naked eyes under two 15W incandescent bulbs. The photographs of the three samples after 24-h salt fog test are shown in Fig. 8. Before taking photographs, the surfaces of all samples have been wiped with a cloth. Among all samples, Sample 3 # passes the salt fog test, whose appearance shows no blisters. However, there are many blisters on the appearances of Sample 1 # and Sample 2 #, and that some films of Sample 1 # and Sample 2 # have fallen off after wiping as shown in Fig. 8. On the other hand, the damage degree of Sample 1 # is worse than Sample 2 # after the salt fog test. According to the film growth fundamentals[14], without ion assistance, there exists columnar structure and voids in resistive heating evaporation films. The diameter of the chlorine ion is smaller than that of water moisture molecule, so the chlorine ion could penetrate through the protective layerand react with the silver.

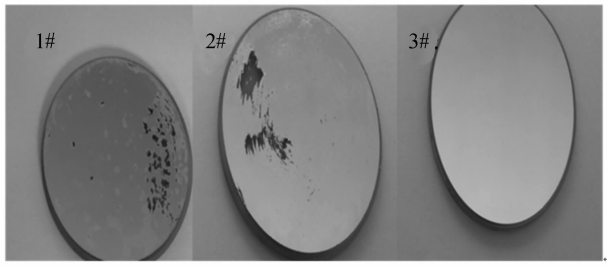

Fig. 8 Appearances of the samples after the salt fog test

The accelerated environmental test results show that only 0. 6 nmCrN_x/150 nm SiO_xN_y provides sufficient corrosion resistance against salt fog. The thicker Cr film as a bonding layer could not improve evidently the durability of the protected-silver coating, though at the expense of a lower reflectance. The mechanism behind the additional protection is intriguing[13]. The thin bonding layer CrN_x film serves as a seed layer for growing high quality silicon nitride film. CrN_x not only adheres well to SiO_xN_y, but also provides more nucleation sites for SiO_xN_y film growth. In the presence of more nucleation sites, complete coverage might be obtained rapidly, results in a much denser SiO_xN_y layer with minimum permeable voids. The results show that a thin Cr bonding layer only improves the adhesion between silver and the protective layer SiO_x, but does not change the morphology of SiO_x film.

The results presented above have demonstrated that durable protected-silver coating could be produced by downward thermal evaporation. Cr/Ag/CrN_x/SiO_xN_y structure shows a good corrosion resistance. A very thin CrN_x film plays a key role in protecting the silver film.

4 Conclusions

We have prepared the protected-silver coatings with downward thermal evaporation without ion assistance. By preparing the protected-silver coating with different adhesion and protective layers andcomparing their optical, mechanical, and environmental stability performance, reasonably good

coating process parameters are obtained. It was found that the coating with the structure of 0.3 nmCr/120 nmAg/0.6 nmCrN_x/150 nmSiO_xN_y shows an excellent corrosion resistance, which passes 24 hour humidity test and salt fog test, and has an average reflectance of 97.8% in the spectral range of 400 nm to 1 800 nm. The results have showed that 0.6 nm CrN_x interlayer played a crucial role in fabricating a dense SiO_xN_y protective overlayer by providing many nucleation sites. Further optimization of the coating process parameters of downward thermal evaporation is still under way.

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