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Preparation of novel SiO_2 protected Ag thin films with high reflectivity by magnetron sputtering for solar front reflectors

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ABSTRACT

The Essential Macleod Program (EMP) has been used to successfully assist in the design of a SiO_2 protected Ag thin film. The film is applied through magnetron sputtering onto a glass substrate for use in a solar front reflector. In the following experiments, Ag films were first deposited on glass substrates using direct current (DC) magnetron sputtering, and then SiO_2 films were deposited as a protective layer onto the surface of the Ag films using radio frequency (RF) magnetron sputtering. The reflectivity of the obtained samples was calculated and tested under light wavelengths ranging from 250 to 2500 nm with films of Ag and SiO_2 of different thicknesses. The solar reflectivity (SR) and the light reflectivity (LR) of the 130 nm Ag film and the 320 nm SiO_2 film were found to be up to 96.66% and 98.84%, respectively, which is almost identical to the calculated results based on the designed model. Additionally, the deposited films exhibited high anti-corrosion properties in harsh abrasion and aging resistance tests. More importantly, the films were proven capable of operating in high-temperature systems by testing under different annealing temperatures. The high performance of the films was attributed primarily to the SiO_2 layer, which served as a good means of protection without experiencing serious degradation of reflectivity, demonstrating their potential in applications for solar front reflectors.

1. Introduction

Solar thermal electric power systems are one of the major technologies for converting sunlight to electricity [1–5]. Owing to the widespread application of solar thermal electric power generation, the development of advanced solar reflector materials that maintain high performance for decades in outdoor service and are capable of being manufactured in large volumes at a competitive cost is urgently demanded [5–8]. For reflector materials in solar thermal applications, a high reflectivity in the entire wavelength range of the solar spectrum (300 to 2500 nm) is crucial as part of the optical requirements. Moreover, the performance of the reflector materials strongly depends on the films formed on the substrate [9].

In particular, metallic (or metallic compound) thin films formed on various substrates have received increased attention in the solar energy field because of their excellent properties, such as high conductivity, conspicuous reflectivity within long electromagnetic wavelengths and superior transmission [10–13]. Due to their high reflectivity (97% of the sunlight) and applicability as well as their flexibility that allows them to be molded into a variety of curved surfaces [14], metallic film reflective materials have recently attracted increasing scientific interest for their role in solar energy applications, such as solar reflectors. Based on their superior performance over traditional reflective materials such as glass, metallic thin films exhibit significant potential for future commercialization [15]. It has been reported that only free electron-like metals, which obey the Drude model, are suitable to be used as reflectors for solar thermal applications. Among the Drude metals, silver and aluminum [14], which are two important reflective metals with a hemispherical reflectivity of 97% and 92%, respectively, are recognized as the best solar reflectors. Nevertheless, the free electron-like metals, which exhibit limited corrosion resistance, are often used in back surface mirrors. These metals are always evaporated on the back of a glass or polymer substrate to protect the metal from oxidation. Among the state-of-the-art solar reflector materials, back-surface-silvered low-iron glass or polymethylmethacrylate (PMMA) [16,17] are the two established materials. However, glass mirrors tend to be brittle, heavy and fragile. Although front surface mirrors so far have been developed to be bendable and lightweight, their optical performance severely degrades in only a couple of months if the surface is not protected [18,19].

It is well known that approximately 80–85% of optical reflectivity is determined by the quality of the films that cover the solar reflectors. Therefore, it is desirable to use various alloys [20] or protective layers [17,21,22] to improve film adhesion, optical reflectivity and anti-corrosion behavior compared to pure metallic films [23]. Kennedy et al. [21] provides a basic knowledge of solar front reflectors with a structure of $A1_2O_3$ (4 μm)/Ag

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(70 nm)/Cu (40 nm) acting as the layers of protection, reflection and substrate, respectively. The results revealed outstanding optical performance with a reflectivity of 95% in an aging test over 3000 h. Their new structure highlights the development of new films for solar reflectors. However, the thickness of the $A1_2O_3$ protective layer is 4 μm, which markedly increases the cost. Thus, although many films have been reported to be suitable for solar reflector materials, few of them consist of novel structures that can maintain high reflectivity, continuously endure harsh conditions in outdoor environments and can be fabricated at a low cost. Such films for solar reflector materials are expected to have both academic and industrial significance.

The EMP was employed to conduct the simulation process to guide the design of the films for solar front reflectors. Because the program was previously applied primarily to the simulation of the optical parameters of thin films under single-wavelengths or center wavelengths, the simulation of the optical parameters for thin films under a wide range of wavelengths has not yet been reported. In a solar concentration system, it is very important that the simulation and calculation for reflectivity and transmission of the thin films focus on a wide range of wavelengths, such as the visible region (300–780 nm) and the sunlight region (300–2500 nm), and not just on the single wavelength.

In this paper, a novel structure composed of Ag film protected by SiO_2 was designed by EMP and fabricated using RF magnetron sputtering applied to the solar front reflector. Our films can be applied onto the surface of any substrates. Here, we choose glass as the substrate because it was free and easily accessible. The reflectivity of the obtained samples was tested and calculated under the light wavelengths ranging from 250 to 2500 nm with Ag and SiO_2 films of different thicknesses. To test the potential application in a high-temperature environment, harsh abrasion and aging resistance tests were conducted to verify the anti-corrosion behavior of the obtained films. The effect of different annealing temperatures on the reflectivity was also investigated to test the durability of the films. The aim of this paper is to determine how the annealing temperature and the thickness of the film together affect its optical and anti-corrosion behaviors.

2. Materials and methods

The experiments performed in this study are divided into sequent phases:

(1) preparing SiO_2/Ag/glass samples; (2) determining the optimum thickness for the protective and reflective layers; (3) simulating the SR and LR with the EMP; (4) testing the anti-abrasion and anti-aging performances; and (5) analyzing the influence of annealing temperature on the thin film reflective materials.

2.1. Preparation of SiO_2 protected Ag thin films

Ag and SiO_2 thin films are deposited with high vacuum multi-functional magnetron sputtering equipment (JPGP-450, Sky, China) using Ag (Φ=60 mm × 5 mm, 99.99% purity) and SiO_2 targets (Φ=60 mm × 5 mm, 99.99% purity) on glass (32 mm × 25.4 mm × 1.2 mm) substrates at room temperature. Prior to deposition, the substrates were ultrasonically cleaned with anhydrous ethyl alcohol and then washed with deionized water several times. The substrates were then soaked in a cleaning solution (a mixture of ammonia, hydrogen peroxide and deionized water with a mass ratio of 1:2:5) and then heated for 15 min. Finally, the substrates were cleaned with deionized water and placed in a vacuum oven for experimental use immediately after being dried with an air dryer. The high-purity working gas (argon, with 99.999% purity) was introduced into the sputtering chamber after it was evacuated to a pressure of 6.1×10^{-4} Pa. Before the films were deposited, all targets were pre-sputtered with argon ions for 5 min to identify samples with poor surface adsorption. During sputtering, the argon gas flow rate was kept at 22 sccm and the chamber pressure was maintained at 0.7 Pa. The Ag sputtering was performed in DC mode (40 W) [24], whereas the SiO_2 sputtering was performed in RF mode at a higher power of 280 W [25] due to the low sputtering yield of the SiO_2 ceramic target. The distance between substrate and target was kept at 75 mm for all depositions. The deposition rates of Ag and SiO_2 were 64.4 nm/min and 9.1 nm/min, respectively. All the prepared samples were then placed in petri dishes and then stored in a vacuum oven to avoid contamination.

2.2. Design and simulation of SiO_2 protected Ag thin films

For the optical characterization, the EMP was employed and the calculated results were compared with measured optical properties. The EMP is a comprehensive software package for the design, analysis, manufacture and troubleshooting of thin film optical coatings [26,27]. The simulation method for the EMP was performed by the adhering to the following steps. First, construction parameters such as the refractive index and the extinction coefficients of Ag and SiO_2, which were calculated using ellipsometry measurements, were input. Second, simulations with variable parameters such as the wavelength ranges (250 to 2500 nm) and the number of layers (glass/Ag/SiO_2/air), were designed. Finally, an analysis of each layer with a variable thickness of Ag and SiO_2 thin films under wavelengths ranging from 250 to 2500 nm was performed to determine the optical properties of each layer, and to determine whether each layer is appropriate for the optimal simulation with system modification.

2.3. Characterization

The thickness of the films was measured using an AS500 level meter, and a normal reflectivity measurement of the films under light wavelengths ranging from 250 to 2500 nm was conducted on a UV–vis–NIR spectrophotometer (PerkinElmer, Lambda 950), with a light injection angle set at 8°. The reflectivity of the prepared samples was calculated according to ISO 9050-2003. SR ρ_e and LR $\rho_{v,o}$ of films shall be calculated using the following two formulas (according to ISO 9050-2003: Glass in building–Determination of light transmittance, solar direct transmittance, total solar energy transmittance, ultraviolet transmittance and related glazing factors):

$$\rho_e = \sum_{\lambda = 300\ \text{nm}}^{\lambda = 2500\ \text{nm}} \rho_0(\lambda) S_\lambda \Delta\lambda \Big/ \sum_{\lambda = 300\ \text{nm}}^{\lambda = 2500\ \text{nm}} S_\lambda \Delta\lambda \tag{1}$$

$$\rho_{v,o} = \sum_{\lambda = 380\ \text{nm}}^{\lambda = 780\ \text{nm}} \rho_0(\lambda) D_\lambda V(\lambda) \Delta\lambda \Big/ \sum_{\lambda = 380\ \text{nm}}^{\lambda = 780\ \text{nm}} D_\lambda V(\lambda) \Delta\lambda \tag{2}$$

The chemical compositions of the surface of the films were analyzed through Axis Ultra DLD X-ray photoelectron spectroscopy (XPS) (X-ray with the Mono Al Kα energy of 1486.6 eV, 10 mA × 15 kV were used and calibrated internally by carbon deposit C 1s (285.0 eV). The full spectrum of the CAE scanning mode was performed at 160 eV).

The bilayer films comprised of Ag and SiO_2 were etched by a focused ion beam (FIB, 30 kV and 100 pA) through a hole with a diameter of 1 μm which was bombarded vertically. Then, the morphology and the grain size of the films were observed using a scanning electron microscope (Nova Nano SEM 430, 10 kV).

The films deposited on the substrates were scrubbed 100 times with a brown brush and then the films were subjected to the XPS to investigate the abrasion resistance [28]. For durability testing, a 10 cm × 10 cm sample was aged for 486 h in a Q-sun/Xe-3-HS