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High-temperature solar-thermal conversion by semiconducting β-$FeSi_2$ absorbers with thermally stabilized silver layers

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ABSTRACT

In-situ high-temperature measurements of optical constants (refractive indices n and extinction coefficients k) for each layer of solar selective absorbing multilayers were carried out to simulate solar-thermal conversion efficiency at high temperatures. Conventional Mo layers showed a significant rise in infrared emissivity and a degradation of selective absorbing behavior with the increasing temperature. In contrast, thermally stabilized Ag layers maintained low emissivity even at temperatures below 700 °C. In these layers, agglomeration and vaporization were suppressed by SiN_x nano-particles dispersed in the Ag matrix and interfacial W adhesive layers, respectively. The interband absorption of β-$FeSi_2$ layers at higher temperatures revealed that larger n and k in the infrared region due to thermally excited electrons induced no rise in emissivity of the multilayers, and the narrower band gap based on Einstein's model shifted the absorptance cut-off wavelength closer to the ideal value and hence resulted in a higher solar absorptance. The solar-thermal conversion efficiencies of the multilayers consisting of low emissivity Ag layers with β-$FeSi_2$ absorbers were found to be greater than 75.9%, as estimated from the temperature dependence of n and k spectra.

1. Introduction

For the continuing development of concentrated solar power systems with efficient solar–thermal energy conversion [1], one of the most important issues is to reduce the energy costs by enhancing the system efficiency. Since an increase in the operating temperature is a possible way to enhance the thermodynamic efficiency, solar receiver tubes producing high-temperature heat are required. The evacuated receiver tubes used in proven linear focusing systems require solar selective absorber coatings offering both high and low absorptance in the visible-near-infrared (NIR) and NIR-infrared (IR) regions, respectively [2–4]. To achieve the spectrally selective absorption, absorbing multilayers consisting of solar absorbing layers stacked on a low emissive metallic base are used.

Solar absorbing layers in the conventional receiver tubes mostly consist of metal-dielectric composites such as cermet layers consisting of metallic Mo particles in SiO_2 or Al_2O_3 matrices [2–9]. To enhance the solar-thermal conversion efficiency at high operating temperatures, an absorptance spectrum with a steep transition curve from high to low absorptance at the cut-off wavelength $\lambda_{cut\text{-}off}$ (appropriate for the operating temperature) should be achieved. This is because at higher temperatures, black-body radiations with high intensity approach the solar spectrum and overlap each other. Thus, selective absorption of the solar spectrum is difficult without a steep cut-off. A promising approach to achieve a steep cut-off is to make use of the interband absorption of semiconducting materials [10–13]. In our previous study [13], semiconducting β-$FeSi_2$ [14–18] was used for the absorbing layers. The band-edge absorption of these layers resulted in a desirable selective absorptance with a steep transition curve in the NIR region [13]. Although the semiconducting nature of β-$FeSi_2$ is expected to show temperature dependence such as the variation of band gap due to electron-phonon interactions under enhanced lattice vibrations [19,20] and the change in carrier density in the conduction and valence bands with temperature [4]. This temperature dependence was not taken into account to evaluate the optical properties of the β-$FeSi_2$ absorbers in our previous study [13].

A silver (Ag) layer is one of the most promising low emissivity metallic bases showing the highest infrared reflectance (i.e., the lowest emittance). However, the upper limit of its operating temperature is around 400 °C because of thermal degradation such as agglomeration and vaporization [21,22]. Although there are many studies focusing on the thermal stabilization of Ag films by using additives [23–26], their

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objective temperatures were lower than 600 °C and the optical properties of stabilized Ag have not been discussed yet. Other candidates for low emissivity layer at high temperatures are refractory metals such as molybdenum (Mo) and tungsten (W), which have been used in some absorbers [2–9]. However, according to Seraphin [4], the increase in thermal emittance of Mo or W with the increasing temperature is remarkably larger than that of Ag. This is caused by the scattering of electrons from thermally induced phonon creation and the changes in electronic energy levels because of disorders. Although at high temperatures, the solar-thermal conversion efficiency of receiver tubes is dominated by the thermal emittance of their metallic bases, only a few reports [4,10,11] have discussed the optical absorptance measured at actual high temperatures.

This study focuses on the development of efficient solar selective absorbers operating at 650 °C or higher temperatures. In order to estimate the correct conversion efficiency from the absorption spectra at actual temperature, the abovementioned temperature dependence of optical properties for all the composing layers should be taken into account. Therefore, the objective of this study is to investigate the temperature dependence of optical constants (refractive index n and extinction coefficient k spectra) for each layer of solar absorbing multilayers and to utilize it for designing solar selective absorbers with higher conversion efficiency at high operating temperatures. To use Ag in low emissivity layers operating at high temperatures, a novel approach offering thermally stability at temperatures below 700 °C was discussed along with its influence on the infrared optical properties.

2. Experimental details

Each layer composing the solar-absorbing multilayers was prepared by a conventional sputtering technique. Sputtering targets consisting of 2-in.-diameter metallic Mo (> 99.99%), Ag (> 99.99%), Si (> 99.999%), W (> 99.95%), and β-$FeSi_2$ (> 99.9%) were placed in balanced magnetron sputtering sources. After evacuating the chamber to less than 1×10^{-6} Pa, sputtering gases were introduced into the chamber and the total pressure in the chamber was maintained at 0.4 Pa. For sputtering metallic or semiconducting layers, Ar gas was introduced, and Ar/O_2 or Ar/N_2 mixture was used for reactive sputtering of Si. Most of the layers were deposited on a rotating quartz glass substrate at room temperature, whereas Mo was sputtered on the substrate at 540 °C. For actual receivers, absorber coatings are deposited on metallic tubes covered with barrier layers such as SiO_2 and Al_2O_3. Since this study focused on the optical performance of developed multilayers, the absorbers layered on SiO_2 as a barrier were duplicated on quartz substrates to exclude the influence of inter diffusion between the absorbers and metallic tubes. A power source with a radio frequency of 13.56 MHz was attached to the Si target for stable reactive sputtering, and the power for producing the plasma was varied from 0 to 200 W. In contrast, the Ag, Mo, W, and β-$FeSi_2$ targets were sputtered using DC power ranging from 0 to 60 W. Composite layers consisting of a SiO_2 matrix with β-$FeSi_2$ were deposited by co-sputtering of the Si and β-$FeSi_2$ targets in Ar/O_2 ambient, and the composition was controlled by the sputtering power applied to each target. The thickness of each layer was adjusted by controlling the deposition time.

A spectroscopic ellipsometer (SEMILAB, GES5-E/IRSE) with a heating stage (Linkam) was used to analyze the temperature dependence of refractive index n and extinction coefficient k spectra from 250 to 25,000 nm along with the film thickness d. The temperature was varied from room temperature to 700 °C under Ar ambient. The incident angle of light at the surface of the measuring layers on the Si substrate was 70°. The optical constants for the metallic layers were evaluated using the dispersion model including Lorentz or Gaussian oscillators and the Drude model expression. Dispersion equations for the dielectric layers were expressed by the Cauchy model complemented by Gaussian oscillators. For the semiconducting β-$FeSi_2$ layers, the dispersion equation was based on the Tauc-Lorentz dispersion model combined with Lorentz and Gaussian oscillators, whereas only Lorentz oscillators were adequate to obtain the optical constants for SiO_2 with low concentration of β-$FeSi_2$.

Based on the measured n and k spectra, a computational simulation was performed using a software (Thin Film Center Inc., the Essential Macleod) to provide the absorptance spectrum of each single layer and to design the multi-layered structure.

To obtain the absorptance spectra in the 190–25,000 nm range, the optical reflectance and transmittance spectra were measured using a spectrophotometer (PerkinElmer, Lambda 950) and a Fourier transform infrared spectrometer (PerkinElmer, System 2000) each with an integrating sphere. Light was incident on the surface at 8 ° for both the reflectance measurements. Although we tried to measure the reflectance spectra at high temperatures by using a heating stage, thermal radiation from the heater caused optical disturbances and noise and hence loss of accuracy. In contrast, the abovementioned ellipsometric measurements can eliminate the harmful influence even under the heated conditions. Thus, more accurate absorptance spectra can be simulated by the n and k spectra measured at each elevated temperature. To confirm the reliability of the simulated absorptance spectra, the optical absorptance measured for the prepared multilayers only at room temperature was used as a standard of comparison.

Based on the simulated absorptance spectra, the solar absorptance α, the thermal emissivity ε, and the conversion efficiency η were calculated. These calculations have been described in detail elsewhere [13]. The solar absorptance α was derived based on the reference solar spectral irradiance ASTM G173-03 “Direct normal + circumsolar” [27]. The aperture width of the collector mirrors and the diameter of the receiver tubes were assumed to be 5.77 and 0.07 m, respectively.

The cross-sectional transmission electron microscopy (TEM) specimens were prepared using a focused ion beam (FIB) system. A 30 nm-thick platinum layer was coated on the solar-absorbing multilayers to prevent their charging-up. A small sample with a size of 10 μm × 20 μm × 3 μm was removed and was then pasted on an edge of an Al foil support using a micro-sampling system in a Hitachi NB5000 FIB system [28]. The sample was further thinned by Ga^+ with energy ranging from 40 to 2 kV. The thinned sample was irradiated using an Ar ion beam with an accelerating voltage of 1 kV to remove the damaged layers generated by Ga^+ on its surface. The specimen was examined in a Topcon EM-002BF at an accelerating voltage of 200 kV. The energy dispersive X-ray spectroscopy (EDX) spectra of the specimens were acquired by a Noran System Seven with twin EDS detectors in the TOPCON EM-002BF.

The formed crystal phases of these films were investigated by X-ray diffraction (XRD) based on $\theta/2\theta$ scans or grazing incidence 2θ scans using Cu K_α radiation (PANalytical, Empyrean). X-ray photoelectron spectroscopy (XPS) using Al K_α radiation (ULVAC-Phi, ESCA1800MC) was also used to confirm the chemical state of the elements and the chemical composition of the films.

3. Results and discussion

The measured temperature dependences of n and k spectra for Mo and thermally stabilized Ag films are shown in Fig. 1(a) and (b), respectively. The stabilization method used for the Ag film is illustrated in Figs. 2 and 3. Based on the optical constants, their reflectance spectra were calculated at each temperature, as indicated in Fig. 1(c) and (d). With an increase in the temperature, the n and k spectra of the Mo layer were found to change more drastically than those of the thermally stabilized Ag layer. The temperature dependence of the n and k spectra could be interpreted by a decrease in the electron relaxation time resulting from the enhanced phonon scattering in the Drude model, suggesting that the influence of temperature on the relaxation time was more pronounced in Mo than in Ag. Because of the change in the n and k spectra in Fig. 1(a), the simulated reflectance spectra of the Mo layer also showed a strong dependence on temperature. The higher