Nano-Cr-film-based solar selective absorber with high photo-thermal conversion efficiency and good thermal stability

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Keywords
Solar Energy, Thermo-optical materials, Multilayers, Thin films, optical properties

Disciplines
Atomic, Molecular and Optical Physics | Condensed Matter Physics | Physics

Comments
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Abstract: Optical properties and thermal stability of the solar selective absorber based on the metal/dielectric four-layer film structure were investigated in the variable temperature region. Numerical calculations were performed to simulate the spectral properties of multilayer stacks with different metal materials and film thickness. The typical four-layer film structure using the transition metal Cr as the thin solar absorbing layer [SiO2(90nm)/Cr(10nm)/SiO2(80nm)/Al (≥100nm)] was fabricated on the Si or K9 glass substrate by using the magnetron sputtering method. The results indicate that the metal/dielectric film structure has a good spectral selective property suitable for solar thermal applications with solar absorption efficiency higher than 95% in the 400-1200nm wavelength range and a very low thermal emittance in the infrared region. The solar selective absorber with the thin Cr layer has shown a good thermal stability up to the temperature of 873K under vacuum atmosphere. The experimental results are in good agreement with the calculated spectral results.

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OCIS codes: (160.6840) Thermo-optical materials; (230.4170) Multilayers; (310.6860) Thin films, optical properties.

References and links
1. Introduction

It is significant to improve the efficiency of solar thermal energy conversion systems which will strongly depend on the optical properties of solar selective materials and structure. Solar spectrally selective absorbers should have the feature to maximize the solar energy absorption by trapping the photons in the structures, and at the same time minimize the loss of thermal radiation emission. Ideally, these materials should perform as a perfect photon absorber over a wide solar spectral region and a perfect reflector in the thermal infrared (IR) region. The latter condition is in order to avoid heat loss due to the emission of radiation from the surface of the photon absorber according to Kirchhoff’s law.

The use of spectrally selective photon absorbers for efficient collection of solar energy in power generation systems was proposed about 50 years ago [1]. Since then, to achieve the spectral selectivity, various materials and structures such as the semiconductor, composite media, absorber-reflector tandem, and the materials with the rough or porous surface, cermet and multilayer films have been studied as the practical approaches for the solar selective absorber design and construction [2–15]. Among these materials and structures, the multilayer-film-based structures are of special interest because of their good spectral properties and high thermal stability [9, 10], which makes them particularly suitable for the photo-thermal solar energy conversion applied under the medium and high temperature conditions.

In this work, we studied the spectrally selective thin film structure with different kinds of transition metals composed of several layers, as schematically shown in Fig. 1. The typical film structure from surface to substrate is composed of: an optional antireflection layer composed of a transparent dielectric material that enhances solar absorption and protects the absorbing metal layer to avoid its oxidation as exposed in air; an thin solar absorbing transition metal layer, designed with a thickness such that solar radiation is effectively absorbed internally due to the intrinsic absorption and destructive interference; an transparent dielectric layer which has the proper optical constant and thickness to match the phase and amplitude of solar light propagated in the film; a metal reflecting layer composed of an excellent IR reflector such as aluminum or copper which significantly reduces the IR emittance by the substrate; a silicon or glass substrate.

By properly matching between amplitude and phase of the light entering into the structure through the multiple reflection, transmission and absorption processes these plan films with simpler coating structures can provide an alternative solution to realize higher efficiency of the photo-thermal conversion in the visible to near-infrared region with low thermal radiation in the IR region. Technically, these films can be deposited on the substrate by magnetron sputtering which is feasibly applied with relatively low coating cost in the industry. In terms of the data simulation in the study, the multilayer structure using the transition metal Cr as the thin solar absorbing layer [SiO2(90nm)/Cr(10nm)/SiO2(80nm)/Al(≥100nm)] was experimentally demonstrated and fabricated on the Si or K9 glass substrate by using the magnetron sputtering method with the results to show high photo-conversion efficiency and good thermal stability up to the temperature of 873K in the major solar radiation region.
2. Numerical simulation

We first simulated the spectral properties of the four-layer (dielectric/transition-metal/dielectric/metal) structure film deposited on the silicon or K9 glass substrate under the normal incident condition by numerical calculations based on the rigorous transfer matrix approach which derived from the basic principles of Maxwell’s equations. For the photon energy conservation, the general condition of $T + R + A = 1$ should be satisfied, where $T$, $R$ and $A$ represent transmittance, reflectance and absorptance, respectively, of the light entering into the material and structure, implying that the ideal solar absorber will correspond to the feature of that $T = 0$, $R = 0$ and $A = 1$. For simplicity, the absorptance $A$ can be deduced from the calculation of $T$ and $R$ in the data simulation process.

As a significant part in the metal/dielectric multilayer structure, the thin transition metal layer with the proper optical constant and thickness can be designed to achieve high efficiency of solar energy absorption. By fixing the layer thickness ($t$) of other materials as that: the anti-reflection dielectric layer SiO$_2$ ($t = 100$nm), the reflection metal layer Al ($t = 100$nm), and the transparent dielectric layer SiO$_2$ ($t = 90$nm), the absorptance spectra of the four-layer structure by using different transition metals (Cr, Ti, Co, Ni, W, Mn, Pt and Ir) [16–18] as the absorption layer are drawn in Fig. 2 for comparison. All of the calculated results display a high and wide absorption band in the 400-800nm wavelength region. As seen in Fig. 2, the four-layer structure using the transition metal Cr as the thin solar absorbing layer presents superior absorption performance than other transition metals in the 400-800nm wavelength region, and also the Cr metal element has the natural feature of being less chemically active and relatively more stable for the solar device to work in the environment, especially in the higher temperature conditions.

For the IR-reflection layer ($t = 100$nm) in the structure, we changed the metal (Al, Ag, Cu, Au and Cr) [16–18] in calculation by fixing the layer thickness of other materials as that: the anti-reflection dielectric layer SiO$_2$ ($t = 100$nm), the absorption transition metal layer Cr ($t = 10$nm), and the transparent dielectric layer SiO$_2$ ($t = 100$nm). The absorptance curve under the normal incidence condition is shown in Fig. 3. It can be seen clearly that Al, Ag, Cu, Au and Cr all can be chosen as the candidate for the reflection material used in the multilayer structure. The absorptance of the film stack is about higher than 95% in the 400-1200nm wavelength region. It can be seen that the absorption is less sensitive to the IR-reflection layer thickness within the condition in which the light cannot transmit through the film stack due to the high optical absorption properties of the metal layers in the metal/dielectric multilayer structure.

Next, we simulated the absorptance of the spectrally selective absorbers by varying the dielectric layer materials (Al$_2$O$_3$, SiO$_2$, CaF$_2$, BK7, KCl and MgF$_2$) with fixed thickness of $t = 100$nm. The fixed thickness of the absorption layer Cr and IR-reflection layer Al is 10nm and
100nm, respectively. The calculated spectral absorptance are shown in Fig. 4 to see the values which are higher than 95% in the 400-900nm wavelength region.

Fig. 2. Comparison of spectral absorptance of different transition metal layers (Cr, Ti, Co, Ni, W, Mn, Pt and Ir) with proper thickness used in the structure. The thickness of other layers is that: reflection layer Al (t = 100nm), transparent dielectric layer SiO$_2$ (t = 90nm) and the anti-reflection dielectric layer SiO$_2$ (t = 100nm).

Fig. 3. Comparison of spectral absorption of different metal reflection layer materials (Al, Ag, Cu, Au and Cr) with fixed thickness (t = 100nm).

Fig. 4. Comparison of spectral absorptance of different dielectric layer materials (Al$_2$O$_3$, SiO$_2$, CaF$_2$, BK7, KCl and MgF$_2$) with fixed thickness (t = 100nm).
The spectral characteristics of a typical four-layer structure using the transition metal Cr as the solar absorbing layer [SiO$_2$(90nm)/Cr(10nm)/SiO$_2$(80nm)/Al(100nm)] are in Fig. 5 to show that a very high optical absorption (>95%) over the wide wavelength range from 400nm to 1200nm can be achieved while the total physical and cost effective film thickness is less than 300nm. The results indicate that the metal/dielectric multilayer film structure has the ability to absorb the most part of the solar energy in the visible-to-near-IR wavelength region.

As mentioned above, the performance of a solar selective absorber is basically characterized by absorption and thermal emittance. The thermal emittance $\epsilon$, which can be calculated based on the reflection spectrum $R$ and Plank’s black body radiation $E(T, \lambda)$, is the function of the incident angle $\theta$ and temperature $T$, especially in the long wavelength ($\lambda$) region [3].

$$
\epsilon(\theta, T) = \frac{\int_0^\infty d\lambda E(T, \lambda)[1 - R(\theta, \lambda)]}{\int_0^\infty d\lambda E(T, \lambda)}
$$

(1)

where

$$
E(T, \lambda) = \frac{8\pi hc}{\lambda^3} \left[ \exp\left(\frac{hc}{\lambda k_b T}\right) - 1 \right]^{-1}
$$

(2)

We simulated the IR-reflection curve of the four-layer metal/dielectric film structure [SiO$_2$(90nm)/Cr(10nm)/SiO$_2$(80nm)/Al(100nm)] in the 1-30μm, and calculated the thermal emittance under the normal incidence condition by using Eq. (1). The simulated reflectance spectrum for the four-layer metal/dielectric film structure is shown in Fig. 6. Obviously, the structure can present a very high reflection in the IR region, indicating a good spectral property of low thermal emittance for practical application. Considering the application under the medium and high temperature condition, we also calculated the near-normal emittance in the 300-1000K temperature range with the result shown in the inset of Fig. 6. It can be seen that the film structure with the reflectance spectrum will have the normal emittance of 0.058 at 600K.
The calculated emittance values of the four-layer metal/dielectric film structure [SiO$_2$(90nm)/Cr(10nm)/SiO$_2$(80nm)/Al(100nm)] are summarized in Table 1 to show that the structure can present a very low thermal emittance in a wide incident angle and temperature region. This feature is required for the practical device application in the solar-thermal conversion system.

Table 1. Calculated Emittance Values of the Four-layer Metal/Dielectric Film Structure [SiO$_2$(90nm)/Cr(10nm)/SiO$_2$(80nm)/Al(100nm)]

<table>
<thead>
<tr>
<th>Temperature</th>
<th>0°</th>
<th>10°</th>
<th>20°</th>
<th>30°</th>
<th>40°</th>
<th>50°</th>
<th>60°</th>
<th>70°</th>
<th>80°</th>
</tr>
</thead>
<tbody>
<tr>
<td>300 K</td>
<td>0.034</td>
<td>0.034</td>
<td>0.037</td>
<td>0.041</td>
<td>0.048</td>
<td>0.056</td>
<td>0.068</td>
<td>0.088</td>
<td>0.123</td>
</tr>
<tr>
<td>400 K</td>
<td>0.040</td>
<td>0.041</td>
<td>0.044</td>
<td>0.049</td>
<td>0.055</td>
<td>0.064</td>
<td>0.076</td>
<td>0.094</td>
<td>0.125</td>
</tr>
<tr>
<td>500 K</td>
<td>0.048</td>
<td>0.049</td>
<td>0.051</td>
<td>0.055</td>
<td>0.061</td>
<td>0.068</td>
<td>0.079</td>
<td>0.095</td>
<td>0.128</td>
</tr>
<tr>
<td>600 K</td>
<td>0.058</td>
<td>0.059</td>
<td>0.060</td>
<td>0.063</td>
<td>0.067</td>
<td>0.073</td>
<td>0.081</td>
<td>0.095</td>
<td>0.129</td>
</tr>
</tbody>
</table>

3. Experimental details

3.1 Sample fabrication

It is shown above in data simulation that the four-layer metal/dielectric film structures will have a good spectral selectivity suitable for application of the selective absorbers under the high temperature condition. To demonstrate this experimentally, we have fabricated these multilayered thin films by magnetron sputtering in the Leybold LAB600SP chamber at room temperature. Since magnetron sputtering is an extremely flexible coating technique that can be used to deposit many kinds of materials on the substrate properly, it is possible to achieve the multilayer structure with the thickness to be precisely controlled in the nanometer scale. The metal and dielectric films with target purity of 99.99% were deposited by DC and RF magnetron on the Si or K9 glass substrate, respectively with a background pressure of 6.0 × 10$^{-6}$mbar. The optically polished Si or K9 glass substrate will provide a smooth surface to reduce the data analysis error arisen from the light scattering effect of the sample in the study. For the deposition of the SiO$_2$ layer, the power was 150W and the Argon gas flow rate was 25SCCM (SCCM denotes cubic centimeter per minute at STP). The Cr and Al metal layer was deposited at 200W and the Argon gas flow rate was 20SCCM.

The thickness of each layer is controlled by the deposition time according to the sputtering rate which was determined by the power and flux of Argon gas flow rate as calibrated by the ellipsometer and Kosaka Surfocorder ET300 in advance.
According to the data simulation as shown above, combination of different metals and dielectric materials can be chosen as the candidate of the spectrally selective absorbing films. By considering the cost-effective factor of the material and the solar-to-thermal conversion efficiency, however, the combination of Cr, Al and SiO₂ layers will be more suitable for them to be put into practical application with good spectral properties.

3.2 Characterization

The spectral property of the typical layered structure [SiO₂(90nm)/Cr(10nm)/SiO₂(80nm)/Al (≥100nm)] has been measured in experiment. The reflectance spectra of the samples have been measured in the 300-800nm and 1-5 μm wavelength ranges under the incidence angle of 35° by using the spectroscopic ellipsometers working in the visible and IR spectral regions, respectively. The spectrometer UV-3101PC Shimadzu was also used to measure the reflectance spectra of these samples in the 0.3-1.8μm wavelength region.

To evaluate the thermal stability, samples also were tested under the high temperature condition (up to 873K) for 6 hours with an electric heater in a vacuum chamber. After the heat treatment process, the spectral properties of the samples were measured for evaluation of the thermal stability and spectral selectivity of the samples.

4. Results and discussions

After optimization and fabrication of the spectrally selective film structure [SiO₂ (90nm)/Cr(10nm)/SiO₂ (80nm)/Al (≥100nm)], the samples show a very good photo-thermal conversion performance with the features of high solar energy absorption and low thermal emittance under the high temperature condition. Figure 7 shows a transmission electron microscope (TEM) image of the multi-layered sample structure deposited on the Si substrate with the interface between each layer to be clearly seen in the micro section of the sample. The thicknesses of each layer from top to substrate are about 95nm, 10nm, 90nm and 300nm, respectively, and are consistent with the simulated parameters and pre-set experimental data of the sample.

![Fig. 7. Transmission electron microscope (TEM) image of the four layer film sample with the structure [SiO₂ (90nm)/Cr (10nm)/SiO₂ (80nm)/Al (≥100nm)] deposited on the Si substrate.](image)

In the photo-thermal conversion multilayer structure, the thin Cr layer of about 10nm thick is sandwiched between two dielectric SiO₂ layers and plays the significant role to efficiently absorb the solar energy in a broad wavelength range. The transition metal layer of Cr has the relatively higher reflectance in the IR region and lower reflectance in the visible region [19]. By varying the thicknesses of the metal and dielectric layers, the bandwidth of the high absorption region can be adjusted and expended to best fit into the spectral region of solar radiation, resulting in high absorptance in the visible region and low emittance in the IR region.
The experimental absorption spectra of the sample are shown in Figs. 8 and 9, respectively. In comparison with the simulated results shown in Fig. 5, the absorptance of the multilayer film in the whole visible band is higher than 95% and even close to 100% at the wavelength of about 500nm. As seen in Fig. 10, the optically smooth surface (20x10mm²) of the sample deposited on the K9 glass substrate has a deep black color which is in good agreement with the measured spectra as shown in Figs. 8 and 9, and indicates the high photon absorption characteristics of the sample in the visible region. In the near IR region, the absorptance is also higher than 90% in the wavelength range shorter than 1.2μm. The absorptance decreases with increasing wavelength sharply down to about 60% at 1.8μm. The results are well in agreement with the calculated ones, indicating that this simpler metal/dielectric four-layer film structure can really capture the largest possible amount of solar energy over the major solar spectrum.

According to Kirchhoff’s law, the emittance ε(ω) of the heat-radiated body or surface at thermal equilibrium will be the function of the reflectance R as shown in Eq. (1). The experimental reflectance spectrum of the sample measured in the 1-5μm wavelength region is shown in Fig. 11. It can be seen that the reflectance increases with the wavelength and tends to be close to 100% in the longer wavelength region. The experimentally measured reflectance spectrum of the sample is in good agreement with the calculated result. Due to the experiment difficulty to measure the reflectance spectra of the sample in the far IR region at the moment, the emittance ε can be deduced from the calculated reflectance spectrum of the sample shown in Fig. 6, and reaches to the value lower than 0.06 under the normal incidence condition and in the wide temperature range as see the data given in Table 1. The result indicates that the metal/dielectric multilayer film structure can present a good spectrally selective property with very low thermal emittance in the infrared region.

![Absorptance and transmittance spectra of sputtered film sample](image)

Fig. 8. Absorptance and transmittance spectra of sputtered film sample [SiO₂(90nm)/Cr (10nm)/SiO₂ (80nm)/Al (≥100nm)] were measured in the 300-800nm wavelength region under the incidence angle condition of 35°.
**Fig. 9.** Absorptance of the sample measured by the spectrometer in the 0.3-1.8μm wavelength region under the near normal incidence condition.

**Fig. 10.** The optically smooth surface (20x10mm²) of the sample deposited on the K9 glass substrate has a deep black color, indicating the high photon absorption characteristics in the entire visible region.

**Fig. 11.** The comparison of reflectance spectra between measured and simulated ones in the 1-5μm infrared region for the film structure [SiO2(90nm)/Cr (10nm)/ SiO2 (80nm)/Al (≥100nm)].
Finally, in order to evaluate the thermal stability of the samples, we put the sample at the temperature of 873K in vacuum of $1 \times 10^{-5}$ mbar for 6 hours. After the heat treatment process, no remarkable change has been found on the sample surfaces through the macroscopic observation. In addition, the reflectance spectra after heat treatment process were also measured to see that the spectra are almost identical with the result shown in Fig. 12. The result indicates that the metal/dielectric multi-layer film structure has the good thermal stability and can be applied for selective solar absorbers under the high temperature condition reached up to 873K.

![Fig. 12. The measured absorptance spectrum of the sample before and after the heat treatment process at 873K.](image)

5. Conclusion

We have studied the four-layered metal/dielectric film structure which can be applied for the solar spectrally selective absorber under the medium and high temperature condition. The solar absorber has the simpler film structure to trap the photons with high photon-thermal conversion efficiency in the major solar spectral region and low thermal emittance in the IR region. In addition, the typical nano-Cr-film based solar spectrally selective absorber shows good thermal stability without spectral deterioration under the temperature up to 873K. Both simulated and experimentally measured results are in good agreement to each other. The metal/dielectric four layer film structures with suitable device fabrication technique are cost-effective with relatively simple procedure for production and quality control to show the potential application in the solar energy field.

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