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Optimization and preparation of the high-efficiency solar selective absorber based on double W-SiO_2 cermet layers

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Abstract: To improve optical absorbance in the solar spectrum region as well as to reduce solar emittance in the infrared region, a new solar absorber structure based on the double W-SiO_2 cermet layers was proposed and optimized. The factors which affect the spectral selectivity of the solar absorber such as the IR reflectance property of metal, and the volume fraction of the absorption layer were investigated. A series of W-SiO_2 cermet films with different values of volume fraction were prepared onto Si and K9 glass substrates. The measured optical constants as well as those deduced from the data fitting were used to optimize performance of the selective solar absorber. Based on the optimized parameters, the solar absorber structure with the layer parameter, consisting of that W (~150 nm) / W-SiO_2 (94 nm, 0.67HVF) / W-SiO_2 (34 nm, 0.27LVF) / SiO_2 (47 nm), was fabricated using a magnetron sputtering system at room temperature. The experimental results agree well with the simulated ones, showing an average optical absorption of 95.3% in the wavelength region of 250~1500 nm, and a low thermal emittance of about 0.124 at 600 K in the broad wavelength region of 0.25~25 μm. Due to the simple components and high efficiency, the solar selective absorber based on the structures consisting of double W-SiO_2 cermet layers shows a good potential for practical applications in the future.

Key words: solar selective absorber, W-SiO_2 cermet layer, high solar absorbance, low thermal emittance
PACS: 78.20.Bh, 78.20.Ci, 78.20.Nv

基于W-SiO_2双金属陶瓷结构的高效率太阳能选择性吸收薄膜的优化和制备

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摘要：理论优化并成功制备了一种以W-SiO_2双金属陶瓷作为吸收层的太阳能选择性吸收薄膜,同时提高了薄膜在太阳辐射波段的吸收并降低了在红外波段的热辐射。研究了包括金属反射层材料、吸收层金属体积分数等因素对薄膜整体吸收效率的影响。基于对Si和K9玻璃基底上生长的不同金属体积分数的W-SiO_2陶瓷薄膜光学常数的研究,利用磁控溅射方法制备出如下膜系:W (~150 nm) / W-SiO_2 (94 nm, 0.67HVF) / W-SiO_2 (34 nm, 0.27LVF) / SiO_2 (47 nm)。膜系实际测量结果与仿真结果完全吻合,在250~1 500 nm宽光谱波段实现了高达95.3%的吸收率,并且在600 K温度下达到0.124的低热辐射率。该四层膜系结构简单,易于制备,有很强的实际应用前景。

关 键 词：太阳能选择性吸收薄膜;W-SiO_2金属陶瓷;高太阳能吸收率;低热辐射率

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Introduction

With the consciousness of human beings to improve environmental protection with increasing consumption of traditional energy, the demand for renewable energy resource has been more concerned recently. Among all these renewable energy sources, solar energy is considered to be an ideal one as it is green, non-polluting, available everywhere and inexhaustible [1-2]. Solar radiation usually can be transformed into usable energy forms such as the electrical and thermal energies in which the photo-thermal conversion is the simplest and most efficient way. In order to achieve the best solar-to-heat conversion efficiency, the collectors should have an exceptional spectrally selective solar absorber surface with a high solar absorption in the solar spectrum region and very low emittance in the infrared region according to Kirchhoff's law.

To meet the basic characteristics of the spectrally selective solar absorber mentioned above, six typical structures have been studied, including (a) intrinsic absorbers, (b) semiconductor-metal tandems, (c) multilayer absorbers, (d) cermets (Ceramic-Metal), (e) textured absorbers, and (f) photonic crystals [3-4]. Among the various models applied for the selective solar absorber structures, most of the commercial selective solar absorber surfaces are based on metal-dielectric composites known as cermets. Several cermets based on various metals and dielectrics have been reported [5-7]. One possible structure is a cermet film with a graded metal concentration profile, in which the metallic concentration is higher at the top than that at the bottom of the film [8]. The other possible structure is formed by two homogeneous cermet layers (double cermet layers): one layer with a LMVF (low metal volume fraction) cermet is put on the top of layer with a HMVF (high metal volume fraction) cermet deposited onto an infrared reflector layer. The later one has higher photothermal conversion efficiency than the surface using only a single cermet layer or a graded film structure [9]. In double cermet layers, solar radiation is effectively absorbed internally by additional phase interference mechanism. Concerning the fabrication of such cermets, several techniques such as electroplating, metal pigmented anodized oxide, physical vapor deposition, chemical vapor deposition and so on, have been developed. However, among these various techniques, sputtering approach, one of the physical vapor depositions, is the most commonly and widely used [10-11].

With respect to the dielectric components, the cermet absorber commonly consists of SiO_2, Al_2O_3, Cr_2O_3 and AlN matrix [12]. Various metal, such as Pt, Ni, Cr, V, Mo and so on has been embedded in the dielectric host matrix with the optical properties evaluated in advance. By taking the merit of the high melting point and high reflectivity of metals in the long wavelength range, W (tungsten) is usually considered to be a suitable metal material for photo-to-heat conversion and has been widely used in selective solar absorbers [13-15]. But as we know, W-SiO_2 double cermet selective solar absorber coating has not been studied so far. The research carried out in this work, therefore, not only will show the characteristics and optical properties of W-SiO_2 cermet layer with different metal volume fraction, but also will present the optimal feature of both solar absorption and thermal emittance for the selective solar absorber based on the double W-SiO_2-cermet-layers structure by using the sputtering method.

1 Experimental details

The solar selective absorbers based on the double W-SiO_2-cermet layers were deposited on the Si or K9 glass substrate by using an electron beam assisted sputtering system (INFOVION, Seoul, Korea) at room temperature with a background pressure of 4.5×10^{-6} Torr. Before deposition, the substrates were ultrasonically cleaned and dried by nitrogen gas. The cleaned substrates were put on a rotating sample holder at a rate of 10 rpm to improve uniformity. The growth pressure was fixed at 1×10^{-3} Torr by a throttle valve with the argon (Ar) gas flow rate of 10 sccm (standard cubic centimeter per minute). As shown in Fig. 1, the multiple layers were deposited to be consisting of, in order from the bottom up, a W infrared reflection layer, a W-SiO_2 HMVF layer, a W-SiO_2 LMVF layer, and finally a SiO_2 antireflection coating on top. The direct current (DC) sputtering was used to deposit W, while SiO_2 was deposited by the radio frequency (RF) sputtering method. The complete experimental processing conditions for the multilayer structures are listed in Table 1.

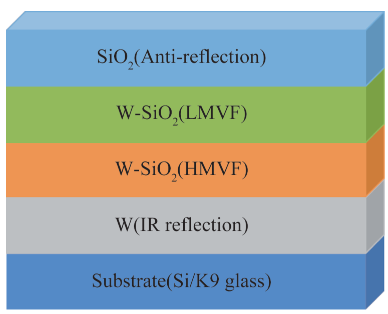

Fig. 1 Schematic of the solar absorber consisting of double W-SiO_2-cermet layers
图 1 基于W-SiO_2双金属陶瓷层的太阳能吸收薄膜示意图

Table 1 Growth parameters of the W−SiO_2 double cermet solar selective absorber
表 1 W−SiO_2双金属陶瓷选择性吸收薄膜的生长参数

Layers	DC power /W	RF power /W	Thickness /nm	Metal volume fraction
W	50	–	150	1
W−SiO_2 (HMVF)	60	200	94	0.67
W−SiO_2 (LMVF)	10	200	34	0.27
SiO_2	–	150	47	0

W-SiO_2 cermets with different metal volume fraction were deposited by varying the deposition power of tungsten at 0 W, 10 W, 20 W, 30 W, 40 W, 50 W and 60 W, respectively, while maintaining a constant deposition power of SiO_2 at 200 W. A step-profiler was used to calibrate the sputtering rate of each layer, and a variable-angle spectroscopic ellipsometer (J. A. Woollam VASE) was applied to precisely determine the optical constants and thickness of the nanocomposite solar absorber coatings. The reflectance spectrum studies were carried out with a UV - Vis - NIR spectrophotometer (UV 3600 plus, Shimadzu) in the wavelength range of 250~2 500 nm and a Fourier-transform infrared spectrometer (Nicolet Nexus 470 FT-IR spectrometer) in the wavelength range of 2.5~25.0 μm. The absorbance of the sample was calculated from the measured reflectance data according to the conditions of $T = 0$ and $A = 1-R$, since the transmittance T of the sample with the thick W reflection layer can be omitted.

2 Results and discussion

2.1 Infrared (IR) reflection layer

For the high reflectance in the infrared region and high temperature resistance, noble and transition metals are often considered to be the appropriate materials for IR reflection layer. The infrared reflectance characteristics of pure Cu, W, Ni, Pt and Cr metals were studied by measuring the reflectance spectra of each thick metal layer deposited onto the Si substrate. The selection criteria will depend on the required reflectance spectra that the metal should reflect low in solar radiation region while high in the infrared region to achieve low emittance. The measured reflectance spectra of the various metals are shown in Fig. 2.

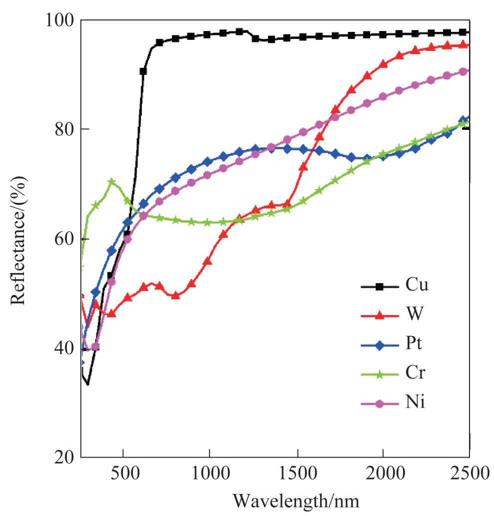

Fig. 2 Measured reflectance spectra of the thick W, Ni, Pt, Cu, and Cr films deposited onto the Si substrate.
图2 沉积于Si衬底上的厚W、Ni、Pt、Cu、Cr层的测量反射光谱

It can be seen in Fig. 2 that chromium exhibits a spectral feature of low reflectance of about 65% in the entire 400~2 500 nm wavelength region, resulting in higher thermal emittance. On the contrary, copper shows a highly uniform reflectance of about 95% in the Vis-NIR range of 700~2 500 nm, which could decrease the solar absorption in the visible region. Overall, tungsten has an average reflectivity lower than 50% in the UV-Vis region of 300~800 nm and higher than 90% in the infrared region. This is supposed to be helpful to improve the solar absorbance and to reduce the thermal emittance at the same time. Additionally, tungsten has a high melting point, which can act as a diffusion barrier between the substrate and the cermet layer. Considering W-SiO_2 as the absorption layer, choosing tungsten as the base layer also has its advantage in the process of film growth. Thus, tungsten was chosen as an ideal IR reflection layer for the solar selective absorber consisting of double W-SiO_2 cermet layers.

2.2 W-SiO_2 cermet layer

Since the solar radiation is mainly absorbed in the two cermet layers, it is important to study the characteristics of single W-SiO_2 cermet layer with different W volume factor in the SiO_2 dielectric matrix. By changing the deposition power of W while keeping constant of the SiO_2 deposition power, the films with varying W concentration were prepared. Spectroscopic ellipsometry (SE) was used to investigate the optical constants of the sputtered W-SiO_2 nanocomposite thin films affected by the composition. The ellipsometric parameters (Ψ, Δ) were measured in the wavelength range of 300~1 200 nm at three incident angles: 65°, 70° and 75°.

In data fitting, effective medium approximation (EMA) is usually used to depict the dispersing function of a macroscopic inhomogeneous medium [16]. The EMA model is suitable for many compositional materials, including the metal-dielectric composites. A widely used EMA theory for nanocomposite systems proposed by Bruggeman and Maxwell-garnet is expressed as [17-18]:

$$\frac{\varepsilon_{M-G} - \varepsilon_b}{\varepsilon_{M-G} + 2\varepsilon_b} = f_a \frac{\varepsilon_a - \varepsilon_b}{\varepsilon_a + 2\varepsilon_b} \quad , \quad (1)$$

where ε_{M-G} is the effective dielectric function of the mixture, ε_a is the dielectric function of the guest material (inclusions), ε_b is the dielectric function of the matrix or host and f_a is the volume fraction of the a component.

The measured and fitted ellipsometric parameters at the incident angle of 65° are presented in Fig. 3. The fitted ellipsometric data of the W-SiO_2 composites with different concentrations of W are in good agreement with the experimental ones over the entire measured spectral range, demonstrating the accuracy and reliability of the fitting procedure.

The optical constants deduced from the ellipsometric data using the EMA model are shown in Fig. 4. It can be seen clearly that with the increasing deposition power of W in the process, the values of both n and k in the spectral range of 300~1 100 nm increase with deposition power of W, due to increasing fraction of metal W. The results indicate that by varying the concentration of W in the W-SiO_2 nanocomposites, both the refraction index n and the extinction coefficient k can be properly tuned to satisfy the required optical properties of materi-

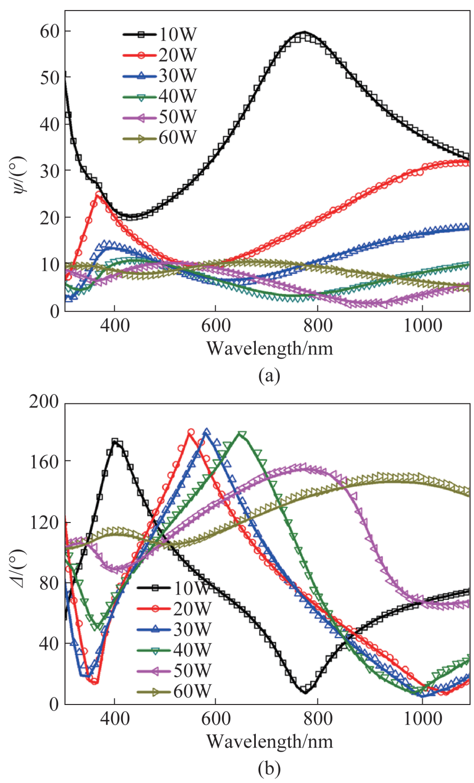

Fig. 3 Experimental (symbol) and fitted (line) ellipsometry data Ψ (a) and Δ (b) of the composite films with varying deposition power of W as measured at the incident angle of 65°

图3 不同W溅射功率下的复合薄膜在65°入射角时实际测量(符号)和拟合(实线)分别得出的椭偏参数Ψ(a)和Δ(b)

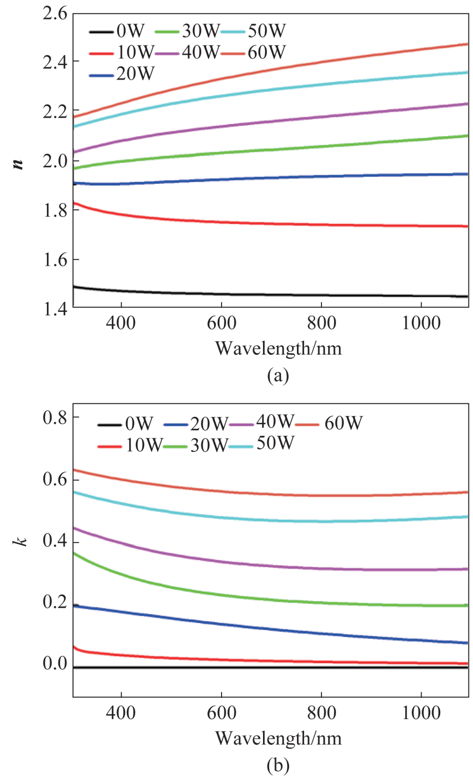

Fig. 4 Refractive index n (a) and extinction coefficient k (b) of the W-SiO_2 nanocomposite thin films with different deposition power of W

图4 不同W溅射功率下获得的W-SiO_2纳米薄膜的折射率n(a)和消光系数k(b)

als for the photonic device design and applications in broad spectral regions.

The structure with double-cermet absorber layers has higher absorbance than that of using only single absorber layer because solar energy can be gradually absorbed layer by layer in the structure. To achieve the best efficiency of absorption, the most differentiated two composites with sputtering power of tungsten in 10 W and 60 W were chosen as the LMVF and HMVF absorption layer, whose metal volume fraction were 0. 27 and 0. 67 respectively.

2. 3 Absorption property of solar selective absorber consisting of two W−SiO_2 cermet layers

In terms of the optical constants and thickness of each layer determined, the solar absorption of a multilayered film can be calculated by using the transfer matrix method (TMM). Reversely, the film parameters of absorber containing double W-SiO_2 cermet layers were obtained by data fitting procedure assuming A=1 in the wavelength range of 250～1 500 nm with the modified Levenberg-Marquardt optimization method, using the optical parameters of W-SiO_2 absorption layer obtained in advance. In terms of the schematic structure of the solar absorber as shown in Fig. 1, the optimal parameters are achieved as: SiO_2 (47 nm)/W-SiO_2 LMVF (0. 27VF, 34 nm)/W-SiO_2 HMVF (0. 67VF, 94 nm)/W (~150 nm). The reflectance spectra of the simulated and as-deposited solar selective absorber are shown in Fig. 5. It can be seen that the measured results agree well with the simulated ones, and the reflectance is very low with the average optical absorbance of about 95% in the wavelength range of 250～1 500 nm, increases rapidly in the long wavelength region of 1 500～5 000 nm, and keeps very high in the IR region of 5~20 μm.

The experimental results for the optical absorbance, reflectance and transmittance spectra of the samples are shown in Fig. 6. The performance of solar selective absorber is characterized by solar absorbance α and thermal

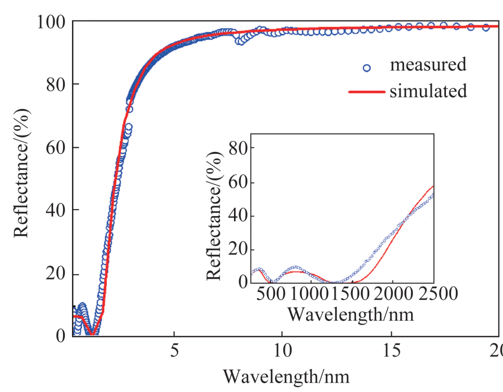

Fig. 5 Measured and calculated reflectance spectra of the solar selective absorber containing double W-SiO_2 cermet layers with optimal structure parameters

图5 最优化结构的W-SiO_2双金属陶瓷选择性吸收薄膜的实测反射光谱和理论反射光谱

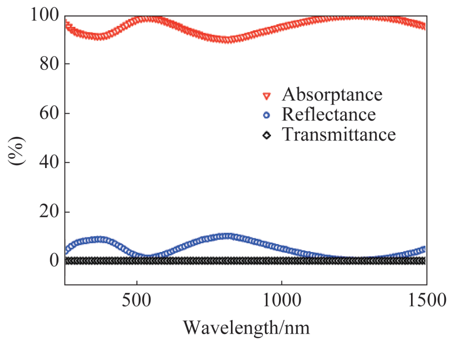

Fig. 6 Measured spectra of the absorbance, reflectance and transmittance under the near normal-incidence condition in the wavelength region of 250~1 500 nm
图6 在近正入射条件下测量的250~1 500 nm波长范围内的吸收、反射和透射光谱

emittance . It can be presented as [19]:

$$\alpha = \frac{\int_{\lambda_1}^{\lambda_n} A(\lambda) L_{sun}(\lambda) d\lambda}{\int_{\lambda_1}^{\lambda_n} L_{sun}(\lambda) d\lambda} \quad , \quad (2)$$

where $A(\lambda)$ and $L_{sun}(\lambda)$ represent the optical absorbance and standard AM 1.5 solar radiation spectrum respectively. Based on the measured absorbance spectrum, the solar absorbance α was determined to be approximately 95.3%, indicating the high and broad solar absorption properties of the double cermet film structure.

The thermal emittance ε, depending on the incident angle θ and temperature T can be given as follows [20]:

$$\varepsilon(\theta,T) = \frac{\int_0^{\infty} E(T,\lambda)[1 - R(\theta,\lambda)] d\lambda}{\int_0^{\infty} E(T,\lambda) d\lambda} \quad , \quad (3)$$

$$E(T,\lambda) = \frac{8\pi hc}{\lambda^5}\left[\exp\left(\frac{hc}{\lambda k_B T}\right) - 1\right]^{-1} \quad , \quad (4)$$

where $E(T,\lambda)$ is Planck's blackbody radiation and $R(\theta,\lambda)$ is the reflectance spectrum at incident angle θ. Then the thermal emittance $\varepsilon(0,T)$ of the proposed double cermet sample can be figured out under the assumption that the optical constants of W and SiO_2 are not changed significantly when the working temperature is much lower than the melting point. The results are listed in Table 2. It can be seen at temperature of 600 K, the thermal emittance is about 0.124, implying the low thermal radiation of the proposed solar selective sample.

Table 2 Thermal emittance $\varepsilon(0,T)$ of the solar selective absorber based on the double-W-SiO_2-layered structure

图2 基于W-SiO_2双金属陶瓷结构的太阳能选择性吸收薄膜的热辐射率$\varepsilon(0, T)$

T/K	300	400	500	600
$\varepsilon(0, T)$	0.050	0.073	0.099	0.124

3 Conclusions

In this work, optimal structures of the solar selective absorber consisting of the double-W-SiO_2-cermet layers were designed and constructed. The factors which affect the spectral selectivity of the solar absorber, such as the IR reflector, volume fraction of metal, and thickness of individual layers, and so on have been studied, respectively. By changing the deposition power of metal W, films with varying metal volume fraction were prepared. The Bruggeman and Maxwell-garnet EMA model was applied to fit the complex refractive index of the samples. The optical constants deduced from the fitting procedure as well as those measured by ellipsometry were used as a database to optimize the absorption performance of the solar absorber. Using the transfer matrix method for the structure design, the optimal layer thickness and W volume were obtained as: W (~150 nm) / W-SiO_2 (94 nm, 0.67HVF) / W-SiO_2 (34 nm, 0.27LVF) / SiO_2 (47 nm). The solar absorption device was fabricated using a combined DC-RF sputtering system. The experimental results were highly consistent with the simulated ones. A solar absorbance of 0.95 and thermal emittance of 0.12 at 600 K were achieved, implying the high absorption of the device in broad wavelength region and low thermal emittance at high working temperature. Since only two elemental compositions were used, the design will have its advantage in device fabrication and actual applications.

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