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W/Cu thin film infrared reflector for TiN_xO_y based selective solar absorber with high thermal stability

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The W/Cu thin film structure is deposited by magnetron sputtering to form the infrared reflector for the TiN_xO_y based selective solar absorber (SSA) that can be used in the low- and middle-temperature applications. The structural, chemical, and optical properties of the SSA layers that experienced thermal annealing at different temperatures for various durations have been investigated with the characterization techniques, including X-ray photoelectron spectroscopy, X-ray diffraction, atomic force microscopy, spectroscopic ellipsometry, and spectrophotometry. Without a W layer, the reflectance in both visible and infrared ranges of the SSA increases as a result of the crystallization of the Cu layer at elevated temperatures. With a W layer with appropriate film thickness, the increase of the reflectance in the visible range can be suppressed to maintain a high solar absorptance, whereas a high infrared reflectance can be maintained to achieve a low thermal emittance. It is shown that for the $\text{SiO}_2\text{-TiN}_x\text{O}_y\text{-W-Cu-Glass}$ SSA with a 15 nm W thin film, thermal annealing can significantly reduce the thermal emittance to a low value (e.g., 4.4% at the temperature of 400 °C for annealing at 400 °C for 6 h), whereas the solar absorptance can be maintained at a high value (e.g., 92.2% for the annealing at 400 °C for 6 h). *Published by AIP Publishing.*
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I. INTRODUCTION

As a key unit to collect the solar energy in the solar thermal energy systems, the selective solar absorber (SSA) should have low reflectance in the solar radiation range to absorb solar radiation energy as much as possible and high reflectance in the infrared radiation range to reduce the thermal emittance.^{1,2} In order to realize the specific selective reflectance spectra, an SSA usually includes an anti-reflection coating (ARC), a solar energy absorber, and an infrared reflector.³ When a glass substrate is used in a low cost application,^{4,5} a thick metallic thin film (i.e., Cu, Al, Mo, etc.) should be deposited on the glass substrate to serve as the infrared reflector.⁶

In order to reduce the reflectance in the solar radiation range, single layer or multi-layer dielectric thin film structures (e.g., SiO_2 , Al_2O_3 , AlN , etc.) can be used to form the ARC.^{7–9} Various types of solar energy absorber have been reported, such as transition metal oxynitrides,^{10,11} cermet (i.e., metal-dielectric composite),⁶ semiconductor-dielectric multi-layers,¹² and so on. Due to its good chemical and physical properties, titanium oxynitride (TiN_xO_y) has been commercially used as the solar energy absorber.¹³ Because the nitrogen can be replaced with oxygen in TiN_xO_y at high temperatures due to oxidation, the TiN_xO_y based SSA usually is

suitable for mid-temperature (i.e., <400 °C) application.^{14,15} With the advantage of low electrical resistivity ($\sim 1.7 \mu\Omega\text{-cm}$) and large thermal conductivity, Cu is a good candidate of infrared reflector to reduce the infrared emittance. However, Cu has a large atomic diffusion coefficient, particularly when the temperature is higher than 200 °C.^{16,17} In some commercial products, the titanium carbide (TiC) thin film is deposited on the top of Cu as a barrier layer because of its high thermal and chemical stabilities.¹⁸ The TiC thin film can be deposited by atomic layer deposition (ALD),¹⁹ plasma enhanced chemical vapour deposition (PECVD),²⁰ physical vapour deposition (PVD),²¹ etc. However, there are some disadvantages in using these methods, such as low productivity, high temperature process, and hard control of the process parameters to obtain desirable stoichiometric TiC_x , etc.²² In addition, the electrical resistivity of TiC is relatively high ($\sim 42 \mu\Omega\text{-cm}$).²³ Therefore, the infrared reflectance of TiC barrier layer is much lower than that of Cu, leading to a higher thermal emittance than that of Cu.

With their high thermal stability, refractory metals, such as tungsten (W), tantalum (Ta), titanium (Ti), etc., are also widely utilized as the Cu barrier layer.^{17,24} Particularly, due to its low electrical resistivity ($\sim 5.6 \mu\Omega\text{-cm}$), the W thin film can also be used as an infrared reflector,¹⁷ but it still has a higher thermal emittance than Cu. With the combination of highly thermal stable W and highly conductive Cu, it is possible to realize a high-performance infrared reflector with high thermal stability. In the W/Cu infrared reflector, the W

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layer must be thick enough to guarantee the barrier capability of the W layer but thin enough to achieve high infrared transmittance so that the Cu can play a dominant role in the infrared reflection of the structure. In the case of Cu thin film being used as the infrared reflector, the Cu thin film may undergo structural changes such as crystallization at elevated temperatures during the operation, leading to changes in its optical properties. The introduction of a more thermally stable W layer can suppress such changes as evidenced in this work. In this work, a W/Cu thin film infrared reflector is proposed for the TiN_xO_y based SSA for the low- and middle-temperature applications. The structure of the SSA is shown in Figure 1. In the SSA, the SiO_2 layer is used as a single-layer ARC, the TiN_xO_y film serves as the absorbing layer, the W/Cu thin film structure is utilized as the infrared reflector, and the glass is used as the substrate.

II. EXPERIMENTS

The SiO_2 - TiN_xO_y -W-Cu thin film structure was deposited on a glass substrate by RF magnetron sputtering (Denton Desktop Pro. Sputtering system) of 2-in. SiO_2 , TiN, W, and Cu targets (all the targets have a purity $> 99.9\%$), respectively. The chamber was pumped down to 9×10^{-6} Torr for all the deposition processes. The sputtering was carried out at room temperature, the sputtering power was maintained at 100 W, and the Ar gas flow rate was fixed at 10 sccm. The thickness of the Cu layer is $1 \mu\text{m}$, and the thickness of the SiO_2 , TiN_xO_y , and W layers for the optimized SSA are 73, 92, and 15 nm, respectively. In the study of its optical properties and chemical composition, the TiN_xO_y thin film was deposited on the Si substrate, and in the investigation of the thermal stability of the SSA, SiO_2 and TiN_xO_y thin films were also deposited sequentially on Cu/glass and Si substrates, respectively. In order to study the thickness effect of the W thin film, SiO_2 and W thin films were deposited sequentially on the Cu/glass substrate with the W thin film's thickness of 0, 15, 30, and 60 nm, respectively.

The chemical composition of the TiN_xO_y thin film deposited on the Si substrate was examined with X-ray photoelectron spectroscopy (XPS) (ESCALAB 250Xi). The optical properties of the thin films were characterized by spectroscopic ellipsometry (SE) (J. A. Woollam) with the incidence angle of 75° in the wavelength range of 300–1500 nm. The reflectance spectra of the as-deposited SiO_2 - TiN_xO_y -W-Cu-Glass, SiO_2 - TiN_xO_y -Cu-Glass, and SiO_2 - TiN_xO_y -Si were measured with an UV-Vis-NIR spectrophotometer (PerkinElmer Lambda 950) in the wavelength range of 250–2500 nm. The SiO_2 - TiN_xO_y -W-Cu-glass, SiO_2 - TiN_xO_y -Cu-glass, and SiO_2 - TiN_xO_y -Si samples

were annealed in a quartz tube furnace (Thermo Scientific tube furnace) with Ar gas flowing for 1 h at the temperatures of 200, 300, and 400°C , respectively. In order to examine the long-term thermal stability, the above-mentioned samples were further annealed for 6 h at the temperature of 400°C with the same conditions. The reflectance spectra were recorded each time after annealing. The XPS measurement combined with the etching with 1 kV Ar ion beam was used to characterize the atomic depth profiles of the as-deposited and 400°C -annealed SiO_2 - TiN_xO_y -Cu-Glass samples. The microstructures were analysed by using X-ray diffraction (XRD) (Bruker, D8 Discover) with the grazing angle of 1° . The surface morphologies were characterized with atomic force microscopy (AFM) (Bruker, Dimension Icon) in the tapping mode using a Si probe. The samples of SiO_2 -W-Cu with the W thicknesses of 0, 15, 30, and 60 nm were annealed in the quartz tube furnace with Ar gas for 1 h at 400°C . The reflectance spectra of the as-deposited and annealed SiO_2 -W-Cu samples were measured in the wavelength range of 250–2500 nm. Reflectance of the SSA in the wavelength ranges of $2.5\text{--}25 \mu\text{m}$ was measured with an FT-NIR/MIR spectrometer (PerkinElmer Frontier).

III. RESULTS AND DISCUSSION

The XPS result shows the existence of the Ti-O, Ti-N-O, and Ti-N states in the $\text{TiN}_x\text{O}_y/\text{Si}$ sample. Although the TiN_xO_y absorbing layer was deposited by sputtering a pure TiN target only with Ar gas, oxygen is still present in the films. There are three possible reasons for the existence of the oxygen content in the films. First, the residual oxygen and moisture in the deposition chamber provide the oxygen source for the reaction between oxygen and Ti during the TiN sputtering²⁵ (it should be pointed out that the environment humidity is high with a value in the range of 70%–80%). Second, oxygen is easier to react with Ti than nitrogen. Third, the sputtering deposition rate of the TiN is low ($\sim 2 \text{ nm/min}$) due to the low sputtering power ($\leq 100 \text{ W}$), which provides a long duration for the reaction between Ti and O. More details of the XPS analysis of TiN_xO_y thin films are reported in our previous work.²⁶

The optical properties of the TiN_xO_y thin film deposited on the Si substrate were characterized by using SE in the wavelength range of 300–1500 nm with the Drude-Lorentz model.²⁷ The optical constants including the refractive index and the extinction coefficient of the TiN_xO_y thin film in the wavelength range of 300–1500 nm were thus obtained from the SE analysis. The detailed methodology for the SE analysis has been reported in our previous work.²⁶ On the other hand, the optical constants of both SiO_2 and Cu can be obtained from the literature.^{28,29} With the known optical constants of SiO_2 , TiN_xO_y , and Cu, the reflectance of the SiO_2 - TiN_xO_y -Cu-glass SSA for given thicknesses of the SiO_2 , TiN_xO_y , and Cu thin films can be calculated in a wide wavelength range. To achieve the best performance of the SSA, the thicknesses of the SiO_2 and TiN_xO_y layers were optimized to obtain the lowest reflectance in the solar radiation range and highest reflectance in the infrared radiation range. The optimized thicknesses of the SiO_2 and TiN_xO_y layers are 73 and 92 nm, respectively (the thickness of the Cu layer was

FIG. 1. Schematic structure of the SSA with the SiO_2 - TiN_xO_y -W-Cu thin film structure on the glass substrate.

maintained at 1 μm). The calculated reflectance in the wavelength range of 250–2500 nm of the $\text{SiO}_2\text{-TiN}_x\text{O}_y\text{-Cu-glass}$ SSA with the optimized thicknesses is shown in Figure 2. Note that the refractive index and extinction coefficient of TiN_xO_y in the wavelength ranges of 250–300 nm and 1500–2500 nm were calculated using the Drude-Lorentz optical dispersion model with the model parameters yielded from the SE fitting in the wavelength range of 300–1500 nm.

The $\text{SiO}_2\text{-TiN}_x\text{O}_y\text{-Cu-Glass}$ SSA with the optimized layer thicknesses was fabricated. The reflectance spectra of the as-deposited and thermally annealed $\text{SiO}_2\text{-TiN}_x\text{O}_y\text{-Cu-Glass}$ SSA are shown in Figure 3(a). With the increase in annealing temperature from 200 to 400 $^\circ\text{C}$, the reflectance of the $\text{SiO}_2\text{-TiN}_x\text{O}_y\text{-Cu-Glass}$ SSA increases largely in the wavelength ranges of 300–800 nm and 1200–2500 nm but has a small decrease in the wavelength range of 800–1200 nm, which can be attributed to the crystallization of the Cu layer caused by annealing as discussed later. Because around 50% of the solar energy is in the wavelength range of 300–800 nm,³⁰ the large increase in reflectance in that wavelength range severely suppresses the absorption of solar energy. Table I shows the mathematical average reflectance over the wavelength range of 300–800 nm of the $\text{SiO}_2\text{-TiN}_x\text{O}_y\text{-Cu-Glass}$ SSA for different annealing temperatures/annealing durations. The average reflectance significantly increases from 5.2% for the as-deposited sample to 14.8% for the sample annealed at 400 $^\circ\text{C}$ for 6 h.

The solar absorptance (α) can be calculated using⁹

$$\alpha = \frac{\int_{\lambda=0.25\mu\text{m}}^{\lambda=2.5\mu\text{m}} P_{\text{solar}}(\lambda) \times (1 - R(\lambda)) d\lambda}{\int_{\lambda=0.25\mu\text{m}}^{\lambda=2.5\mu\text{m}} P_{\text{solar}}(\lambda) d\lambda}, \quad (1)$$

where λ is the wavelength, $P_{\text{solar}}(\lambda)$ is the intensity of the solar radiation (AM 1.5), and $R(\lambda)$ is the reflectance at specific wavelength. Table I shows the solar absorptance of the $\text{SiO}_2\text{-TiN}_x\text{O}_y\text{-Cu-Glass}$ SSA for different annealing temperatures/annealing durations. The solar absorptance significantly decreases with annealing temperature/annealing duration,

FIG. 2. Calculated reflectance of the $\text{SiO}_2\text{-TiN}_x\text{O}_y\text{-Cu-Glass}$ SSA with the optimized layer thicknesses and solar radiation intensity (AM1.5) in the wavelength range of 250–2500 nm. The inset shows the schematic structure of the $\text{SiO}_2\text{-TiN}_x\text{O}_y\text{-Cu-Glass}$ SSA.

FIG. 3. Experimental reflectance spectra of the $\text{SiO}_2\text{-TiN}_x\text{O}_y\text{-Cu-Glass}$ SSA (a) and $\text{SiO}_2\text{-TiN}_x\text{O}_y\text{-Si}$ structure (b) for different annealing temperatures/annealing durations.

which is mainly due to the increase in the reflectance in the wavelength range of 300–800 nm as a result of annealing.

To understand the increase in the reflectance and decrease of the solar absorptance of the $\text{SiO}_2\text{-TiN}_x\text{O}_y\text{-Cu-Glass}$ SSA caused by annealing, reflectance spectra of the as-deposited and annealed $\text{SiO}_2\text{-TiN}_x\text{O}_y\text{-Si}$ structures were measured, as shown in Figure 3(b). As can be observed in the figure, there is almost no change in the reflectance even after 400 $^\circ\text{C}$ annealing for 6 h, showing that the annealing did not cause significant changes in the SiO_2 and TiN_xO_y thin films. Therefore, it can be concluded that the changes in the reflectance and solar absorptance of the $\text{SiO}_2\text{-TiN}_x\text{O}_y\text{-Cu-Glass}$ SSA is related to the Cu thin film. There are two possible reasons for the changes: crystallization of the Cu thin film, which leads to changes in the optical properties of the Cu thin film, and or diffusion of the Cu atoms as Cu has a very large diffusion coefficient.³¹

The depth profiles of O, Si, Ti, N, and Cu elements in the as-deposited and 400 $^\circ\text{C}$ -annealed $\text{SiO}_2\text{-TiN}_x\text{O}_y\text{-Cu-Glass}$ SSA obtained from the XPS analysis are shown in Figures 4(a) and 4(b), respectively. It is observed that annealing did not produce significant changes in the atomic depth profiles. Therefore, Cu diffusion should not be the major factor responsible for the changes in the reflectance and solar absorptance of the $\text{SiO}_2\text{-TiN}_x\text{O}_y\text{-Cu-Glass}$ SSA.

XRD and AFM were used to examine the changes in the structural properties of the $\text{SiO}_2\text{-TiN}_x\text{O}_y\text{-Cu-Glass}$ SSA caused by annealing. Figure 5 shows the XRD patterns of the as-deposited and 400 $^\circ\text{C}$ -annealed $\text{SiO}_2\text{-TiN}_x\text{O}_y\text{-Cu-Glass}$

TABLE I. Average reflectance of $\text{SiO}_2\text{-TiN}_x\text{O}_y\text{-Cu-Glass}$ over the wavelength range of 300–800 nm and solar absorptance (α) of the $\text{SiO}_2\text{-TiN}_x\text{O}_y\text{-Cu-Glass}$ SSA for different annealing temperatures/annealing durations.

	As-deposited	200 °C for 1 h	300 °C for 1 h	400 °C for 1 h	400 °C for 6 h
Average reflectance (300–800 nm)	5.2%	6.3%	7.6%	10.9%	14.8%
Solar absorptance (α)	92.2%	90.9%	89.9%	87.5%	84.1%

FIG. 4. Depth profile of O, Si, Ti, N, and Cu in the as-deposited and 400 °C-annealed $\text{SiO}_2\text{-TiN}_x\text{O}_y\text{-Cu-Glass}$ SSA obtained from the XPS analysis combined with the etching with 1 kV Ar ion beam. The annealing was conducted at 400 °C for 1 h.

SSA, and the insets are the corresponding AFM images. The AFM images reveal that there is no significant change in the surface morphologies. However, the XRD patterns shown in Figure 5 indicate that there was crystallization in the Cu film during the annealing as the full width at half maximum (FWHM) of Cu (111) peak decreases from 1.39° to 1.00° after the annealing. The calculation of the Cu crystalline grain size with the Scherrer's equation³² shows that the grain size increased from 6.14 nm to 8.52 nm after the 400 °C annealing. The crystallization would lead to a lower electrical resistivity of the Cu layer. This argument is supported by the observation that the sheet resistance of the Cu thin film decreases from 115.6 m Ω /sq. to 42.9 m Ω /sq. after

the annealing at 400 °C for 1 h. It has been shown that a material with low electrical resistivity would exhibit high reflectivity.³³

To examine the influence of annealing on the optical properties of Cu thin film, SE was used to measure the refractive index and the extinction coefficient in the wavelength range of 300–1500 nm of the Cu thin film deposited on a glass substrate without and with 400 °C-annealing for 1 h, and the result is shown in Figure 6. It is obvious that the annealing process has a large impact on the optical properties of the Cu thin film. After the 400 °C annealing, the refractive index of the Cu thin film increases in the wavelength range of 300–350 nm but largely decreases in the wavelength range of 350–1500 nm. The extinction coefficient of the Cu thin film increases in the wavelength range of 300–1500 nm, especially in the infrared wavelength

FIG. 5. XRD measurements of the as-deposited and 400 °C annealed $\text{SiO}_2\text{-TiN}_x\text{O}_y\text{-Cu-Glass}$ SSA. The insets show the corresponding AFM images with the image size of $500 \times 500 \text{ nm}^2$. The annealing was conducted at 400 °C for 1 h.

FIG. 6. Refractive index and extinction coefficient in the wavelength range of 300–1500 nm of the as-deposited and 400 °C-annealed Cu thin films.

range, which could be attributed to the increase in the free electron mobility after the annealing. Therefore, the 400 °C-annealing process changes the optical properties of the Cu thin film significantly.

By using the data of the refractive index and the extinction coefficient of the Cu thin films with/without 400 °C-annealing, the reflectance spectra of the $\text{SiO}_2\text{-TiN}_x\text{O}_y\text{-Cu}$ structure with the Cu thin films with/without 400 °C-annealing were calculated in the wavelength range of 250–2500 nm, and the result is shown in Figure 7. It can be observed from the figure that the annealing of the Cu thin film leads to an increase in the reflectance in the wavelength ranges of 350–750 nm and 1350–2500 nm but a decrease in the wavelength range of 750–1350 nm. The result is consistent with the experimental observation of the annealing effect on the reflectance of the $\text{SiO}_2\text{-TiN}_x\text{O}_y\text{-Cu}$ -Glass SSA as shown in Figure 3(a). Therefore, the annealing effect on the reflectance of the $\text{SiO}_2\text{-TiN}_x\text{O}_y\text{-Cu}$ -Glass SSA can be attributed to the annealing-caused change in the optical properties of the Cu thin film. Note that there is a difference between the calculated reflectance data shown in Figure 7 and the experimental reflectance data shown in Figure 3(a). There are two possible reasons for the difference. First, the samples used in the two figures are not identical in terms of annealing treatment. In Figure 7, the Cu/Si sample was annealed at 400 °C for 1 h, and there was no further annealing. In Figure 3(a), the $\text{SiO}_2\text{-TiN}_x\text{O}_y\text{-Cu}$ -Glass sample was annealed at 200 °C, 300 °C, and 400 °C for 1 h, respectively, and 400 °C for another 6 h. The second reason is that the optical data of Cu in the wavelength ranges of 250–300 nm and 1500–2500 nm may be not very accurate because they were obtained from the calculation using the optical dispersion model with the model parameters for the Cu layer yielded from the ellipsometric analysis in the wavelength range of 300–1500 nm (note that the working wavelength range of our ellipsometer is only in the range of 300–1500 nm). However, the difference does not affect the conclusions of this study.

As shown in Figure 6, the optical properties of Cu changes largely after annealing. In order to overcome the problem, a W thin film with high thermal stability is inserted

FIG. 7. Reflectance of the $\text{SiO}_2\text{-TiN}_x\text{O}_y\text{-Cu}$ structure on the Si substrate in the wavelength range of 250–2500 nm calculated by using the optical constants of the as-deposited Cu thin film and the 400 °C-annealed Cu thin film.

between the TiN_xO_y layer and Cu layer. However, one major disadvantage is that W has a larger electrical resistivity than that of Cu. Therefore, in order to utilize the high reflectance of Cu thin film in the infrared range, it is important to find out a suitable thickness of the W thin film such that both high thermal stability and high infrared reflectance can be achieved for an SSA using the combination of W and Cu layers. Figure 8(a) shows the measured reflectance spectra in the wavelength range of 250–2500 nm of the as-deposited and 400 °C-annealed $\text{SiO}_2\text{-W-Cu}$ -Glass structures with the W layer thicknesses of 0, 15, 30, and 60 nm, respectively. A 73 nm SiO_2 layer is used in the structure to protect the W thin film from oxidation. Without W thin film (i.e., the thickness of W thin film is zero), there is a large difference in the reflectance in the wavelength range of 250–1500 nm between the as-deposited and 400 °C-annealed samples. With increase in the W film thickness, the difference in the reflectance is reduced rapidly, and when the W film thickness increases to 60 nm, the difference almost disappears. Therefore, the optical properties of W thin film are much thermally stable than that of Cu thin film.

It can also be observed from Figure 8(a) that with the increase in W film thickness from 0 to 60 nm, the reflectance of the $\text{SiO}_2\text{-W-Cu}$ -Glass structure in the wavelength range of 1500–2500 nm decreases significantly. For example, for the annealed samples, the reflectance at the wavelength of 2500 nm is 96.9% for the case of without W thin film, the reflectance slightly decreases to 93.6% for the case of 15 nm

FIG. 8. (a) Reflectance spectra of the as-deposited and 400 °C-annealed $\text{SiO}_2\text{-W-Cu}$ -Glass structure with the W layer thicknesses of 0, 15, 30, and 60 nm, respectively. (b) Calculated transmittance spectra in the wavelength range of 250–2500 nm of W thin film with the thickness of 15, 30, and 60 nm on glass.

W thin film, and it largely decreases to 61.7% for the case of 60 nm W thin film. The decrease in the infrared reflectance is due to the decrease in the infrared transmittance of the W thin film with the increase in W film thickness. The transmittance in the wavelength range of 250–2500 nm of W thin films with the thicknesses of 15, 30, and 60 nm on glass has been calculated, as shown in Figure 8(b). The average transmittance over the wavelength range of 1500–2500 nm of W thin film is 24.3%, 8.5%, and 1.8% for the W film thickness of 15, 30, and 60 nm, respectively. The 60 nm W thin film blocks almost all the infrared light, and thus, the infrared reflectance of the structure is determined by the W thin film. As the W thin film has a much lower infrared reflectance due to its higher electrical resistivity than that of the Cu thin film, the $\text{SiO}_2\text{-W-Cu-Glass}$ structure has a much lower infrared reflectance as compared to the structure without W thin film. In contrast, the much higher infrared transmittance of the 15 nm W thin film allows the Cu layer play an important role in the infrared reflectance of the $\text{SiO}_2\text{-W-Cu-Glass}$ structure, and thus, the infrared reflectance of the structure is not largely reduced due to the introduction of the W thin film. Therefore, to achieve high thermal stability, high thermal absorption, and low infrared emittance, 15 nm W thin film is utilized in the W/Cu infrared reflector in this work.

The reflectance spectra of the as-deposited and thermally annealed $\text{SiO}_2\text{-TiN}_x\text{O}_y\text{-W-Cu-Glass}$ SSA with 15 nm W thin film are shown in Figure 9. Annealing, even at 400 °C for 6 h, does not cause a significant change in the reflectance in the wavelength range of 250–900 nm. It leads to a small decrease and a large increase in the reflectance in the wavelength ranges of 900–1600 nm and 1600–2500 nm, respectively. The result suggests that annealing will not cause a large degradation in both the solar absorptance and thermal emittance of SSA. The reflectance changes in the infrared range are due to the change of the optical constants of the Cu film as a result of crystallization in the Cu film caused by thermal annealing. The comparison of the XRD patterns of the Cu phase between the as-deposited and 400 °C-annealed $\text{SiO}_2\text{-TiN}_x\text{O}_y\text{-W-Cu-Glass}$ samples shown in Figure 10 suggests that there is crystallization in the Cu film caused by annealing. The AFM images in the insets of

FIG. 9. Reflectance spectra of the $\text{SiO}_2\text{-TiN}_x\text{O}_y\text{-W-Cu-Glass}$ SSA under different annealing conditions.

FIG. 10. XRD patterns of the as-deposited and 400 °C-annealed $\text{SiO}_2\text{-TiN}_x\text{O}_y\text{-W-Cu-Glass}$. The insets are the AFM images of (a) as-deposited $\text{SiO}_2\text{-TiN}_x\text{O}_y\text{-W-Cu-Glass}$ and (b) $\text{SiO}_2\text{-TiN}_x\text{O}_y\text{-W-Cu-Glass}$ annealed at 400 °C for 1 h. The AFM image size is $500 \times 500 \text{ nm}^2$.

Figure 10 also show that the surface morphologies of the $\text{SiO}_2\text{-TiN}_x\text{O}_y\text{-W-Cu-Glass}$ SSA are stable after the 400 °C-annealing.

The average reflectance over the wavelength range of 300–800 nm and the solar absorptance of the $\text{SiO}_2\text{-TiN}_x\text{O}_y\text{-W-Cu-Glass}$ SSA under the different annealing conditions have been calculated, and the results are shown in Table II. Compared to the as-deposited sample, the sample annealed at 400 °C for 6 h causes only a slight increase (1.6%) in the average reflectance, and no significant change in the solar absorptance (α) (α remains above 92%). The situation of the $\text{SiO}_2\text{-TiN}_x\text{O}_y\text{-W-Cu-Glass}$ SSA is different from that of the $\text{SiO}_2\text{-TiN}_x\text{O}_y\text{-Cu-Glass}$ SSA. As shown in Table I, the average reflectance of the $\text{SiO}_2\text{-TiN}_x\text{O}_y\text{-Cu-Glass}$ SSA significantly increases from 5.2% for the as-deposited condition to 14.8% for the annealing at 400 °C for 6 h, whereas the solar absorptance decreases largely from 92.2% for the as-deposited condition to 84.1% for the annealing at 400 °C for 6 h. Obviously, the thermal stability of the $\text{SiO}_2\text{-TiN}_x\text{O}_y\text{-W-Cu-Glass}$ SSA is much better than that of the $\text{SiO}_2\text{-TiN}_x\text{O}_y\text{-Cu-Glass}$ SSA. This suggests that the W thin film not only has thermally stable optical properties, but is also able to prevent Cu diffusion into the TiN_xO_y layer.

Figure 11 shows the reflectance spectra in the wavelength range of 2.5–25 μm of the $\text{SiO}_2\text{-TiN}_x\text{O}_y\text{-Cu-Glass}$ SSA and $\text{SiO}_2\text{-TiN}_x\text{O}_y\text{-W-Cu-Glass}$ SSA of both as-deposited and annealed at 400 °C for 6 h. Except the as-deposited $\text{SiO}_2\text{-TiN}_x\text{O}_y\text{-W-Cu-Glass}$ SSA, the reflectance of all other samples is more than 90% in the wavelength range of 4–25 μm . It should be pointed out that the reflectance at the wavelength of 2500 nm in Figure 9 is lower than that in Figure 11. The discrepancy is due to the fact that the reflectance measurements in the wavelength ranges of 0.25–2.5 μm and 2.5–25 μm were conducted with two different systems, respectively. It is found that the system used for the measurement in the wavelength ranges of 0.25–2.5 μm has a lower accuracy. However, the discrepancy does not affect the conclusions of this study. Because the W thin film

TABLE II. Average reflectance over the wavelength range of 300–800 nm and solar absorptance (α) of the $\text{SiO}_2\text{-TiN}_x\text{O}_y\text{-W-Cu-Glass}$ SSA under different annealing conditions.

	As-deposited	200 °C for 1 h	300 °C for 1 h	400 °C for 1 h	400 °C for 6 h
Average reflectance (300–800 nm)	4.1%	4.3%	4.4%	5.0%	5.7%
Solar absorptance (α)	92.7%	92.5%	92.6%	92.5%	92.2%

FIG. 11. Reflectance in the wavelength range of 2.5–25 μm of the $\text{SiO}_2\text{-TiN}_x\text{O}_y\text{-Cu-Glass}$ SSA and $\text{SiO}_2\text{-TiN}_x\text{O}_y\text{-W-Cu-Glass}$ SSA of both as-deposited and annealed at 400 °C for 6 h. The black body radiation spectrum in the wavelength range of 1.5–25 μm at the temperature of 400 °C is also shown in this figure.

has a higher electrical resistivity than that of Cu, the as-deposited $\text{SiO}_2\text{-TiN}_x\text{O}_y\text{-W-Cu-Glass}$ SSA has a low reflectance. However, after 400 °C-annealing for 6 h, the reflectance of the $\text{SiO}_2\text{-TiN}_x\text{O}_y\text{-W-Cu-Glass}$ SSA has a comparable reflectance with that of the $\text{SiO}_2\text{-TiN}_x\text{O}_y\text{-Cu-Glass}$ SSA in the wavelength range of 2.5–25 μm . The thermal emittance (ε) can be calculated with Eq. (2),⁹

$$\varepsilon = \frac{\int_{\lambda=0.25}^{\lambda=25\mu\text{m}} P_{bb}(\lambda) \times (1 - R(\lambda)) d\lambda}{\int_{\lambda=0.25}^{\lambda=25\mu\text{m}} P_{bb}(\lambda) d\lambda}, \quad (2)$$

where $P_{bb}(\lambda)$ is the intensity of the black body radiation (the black body radiation spectrum at the temperature of 400 °C is shown in Fig. 11). The thermal emittance (ε) is calculated for the working temperature of 400 °C. After annealing at 400 °C for 6 h, the thermal emittance at the working temperature of 400 °C of the $\text{SiO}_2\text{-TiN}_x\text{O}_y\text{-Cu-Glass}$ SSA decreases from 7.7% to 2.9%, and the thermal emittance at the working temperature of 400 °C of the $\text{SiO}_2\text{-TiN}_x\text{O}_y\text{-W-Cu-Glass}$ SSA decreases from 17.2% to 4.4%. Therefore, for the $\text{SiO}_2\text{-TiN}_x\text{O}_y\text{-W-Cu-Glass}$ SSA with 15 nm W thin film, an annealing can significantly reduce the thermal emittance to a low value (e.g., 4.4% for the annealing at 400 °C for 6 h), whereas it is still able to maintain the solar absorptance at a high value (e.g., 92.2% for the annealing at 400 °C for 6 h).

IV. CONCLUSION

With the advantages of high thermal stability of W and low electrical resistivity of Cu, the W/Cu thin film infrared reflector has been utilized in the SSA with the structure of

$\text{SiO}_2\text{-TiN}_x\text{O}_y\text{-W-Cu-Glass}$, which is deposited by RF magnetron sputtering. When there is no W layer in the SSA, the reflectance in the wavelength range of 300–800 nm and 1500–2500 nm increases largely due to the crystallization of Cu after thermal annealing. In order to reduce the effect of low thermal stability of Cu, a W thin film with high thermal stability is inserted between the TiN_xO_y layer and the Cu layer. It is shown that for the $\text{SiO}_2\text{-TiN}_x\text{O}_y\text{-W-Cu-Glass}$ SSA with 15 nm W thin film, an annealing can significantly reduce the thermal emittance to a low value (e.g., 4.4% for the annealing at 400 °C for 6 h) while it is still able to maintain the solar absorptance at a high value (e.g., 92.2% for the annealing at 400 °C for 6 h).

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