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High performance mid-temperature selective absorber based on titanium oxides cermet deposited by direct current reactive sputtering of a single titanium target

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This article reports the design and fabrication of a new double cermet-based low-mid temperature solar selective absorber based on TiO_x cermet layers, which were deposited with a single Ti target by varying O_2 partial pressure in sputtering chamber as reactive gas. High metal volume fraction cermet 1 and low metal volume fraction cermet 2 were deposited with O_2 partial pressure of 0.15 mTorr and 0.25 mTorr, respectively, with direct current power density of 6.58 W cm^{-2}. The complex refractive indices from ellipsometry were used to design solar selective absorber. The reflectance, thermal stability, and morphology were studied in absorbers on Cu and stainless steel. The effect of TiO_2 and SiO_2 as anti-reflective coating layers was investigated. The absorber on Cu substrate has high absorptance of 90.8% and low emittance of 4.9% (100 °C), and changed to 96.0% and 6.6%, respectively, after annealing at 300 °C for 4 days. *© 2016 AIP Publishing LLC.*
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I. INTRODUCTION

Renewable energy is becoming more and more important in order to meet the global energy demand while keep the man-made pollution to earth at the minimum level. Compared with wind or water energy, solar energy is a much more reliable and abundant energy source. There are mainly two ways to use solar energy: photovoltaic (PV)[1] process and photo-thermal process. For photo-thermal process, solar energy can be first directly converted into heat then to electricity via traditional steam turbines, or to electricity via solar thermoelectric generators (STEGs)[2] or thermophotovoltaics (STPVs).[3] In order to effectively harvest solar energy, solar absorbers with spectrally selective property, which can absorb more solar energy while lose less by decreasing radiation, have been designed. Ideally, solar selective absorber should have absorptance (α) = 1 in strong solar spectral irradiance (0.3–2.5 μm) to increase the absorption and thermal emittance (ε) = 0 in longer wavelength infrared (IR) region (wavelength >2.5 μm) to reduce heat radiation loss. The transition around 2.5 μm should be where solar spectrum intensity meets the absorber blackbody radiation intensity at a certain temperature.[4]

To achieve high absorptance and low emittance, a sharp change of reflectance at the transition wavelength is required for solar selective absorbers. Cermet-based thin film solar selective absorbers stand out due to good optical properties, easy to manufacture, and long term stability. Quite a few designs with different film structures,[5] like single homogeneous cermet layer,[6] double cermet,[7–9] and triple cermet[10] based solar selective absorbers have been studied for many decades. With numerical modeling and co-evaporation technique, Zhang and Mills[7–9] demonstrated a series of double cermet structure selective absorbers with absorptance higher than 0.9 and emittance lower than 0.05 at 50 °C, which are much better than the performance of single cermet structures. Since thermal and electron beam evaporation cannot meet the large area deposition due to poor growth control,[11] more and more selective absorbers deposited by sputtering technique have been studied recently.[7,11–16] Yin *et al.*[10] reported direct current (DC) reactive sputtering of Cr-Cr_2O_3 low-high-low metal volume fraction (LHL) triple cermet layers based selective surface for hot water application, with absorptance in the range of 0.92 to 0.96 and emittance between 0.05 and 0.08. However, they reported troublesome repeatability in getting exactly the same reflectance spectrum.

Compared with chromium, which could pollute soil and water, and pose potential health risks, titanium (Ti) is more environmentally friendly and cost effective. Though environmentally friendly Al_2O_3[17] and SiO_2[18] based selective absorbers were well studied, they need to use at least two targets in fabricating cermet layers or multilayer stacks. Inspired by this, we tried to design and deposit a double cermet based structure with Ti target. We were able to get low/high partially oxidized TiO_x layers with accurate thickness through DC reactive sputtering of Ti with different O_2 partial pressures. Targeting for mid-temperature application, polished copper plate works fine as substrate without extra infrared reflector layer. With proper antireflection coating on the top, we achieved pristine absorptance of 90.8% and emittance of 4.9% (at 100 °C). After annealing at 300 °C for 4 days, the selective absorber became more stable with the absorptance increased to 96.0% and emittance changed to 6.6%. This solar selective absorber with good optical properties has good

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TABLE I. Sputtering parameters for cermet layers and optimized solar selective absorbers.

Sample	Substrate	Ti bonding layer (nm)	Cermet 1 (HMVF) (nm)	Cermet 2 (LMVF) (nm)	ARC
Cermet 1	Si wafer	NA	300	NA	NA
Cermet 2	Si wafer	NA	NA	300	NA
$SiO_2/TiO_x/Cu$	Cu	10	108	55	99 nm SiO_2[a]
$SiO_2/TiO_x/SS$	SS[b]	10	108	55	99 nm SiO_2[a]
$TiO_2/TiO_x/Cu$	Cu	10	108	55	64 nm TiO_2[a]

[a]SiO_2 ARC layer was deposited with RF power density of 9.87 W cm^{-2}.
[b]SS stands for stainless steel.

repeatability. A variety of structures can combine with this thin film solar selective absorber for different applications. For example, it can be fabricated with spectral splitter, for hybrid (heat and electricity) solar energy conversion applications. It can also be used for near-infrared radiation emission reduction.

II. EXPERIMENTAL DETAILS

The solar selective absorbers were deposited onto mechanically polished Cu and stainless steel (SS) substrates by magnetron sputtering system (AJA international, Inc.). Before deposition process, the chamber was evacuated to pressure lower than 5×10^{-7} Torr. High purity Ti (99.995%, 3 in. diameter) and SiO_2 (99.995%, 2 in. diameter) targets were used for deposition. DC power was supplied to Ti target to deposit Ti and TiO_x layers, while the SiO_2 dielectric layer was deposited by radio frequency (RF) power. During deposition, the pressure was kept at 3 mTorr with Ar flow rate of 28 sccm and different oxygen gas flow rates for different partially oxidized TiO_x and TiO_2. During the whole experiment, a DC power density of 6.58 W cm^{-2} was applied on Ti target. First, 10 nm of Ti was deposited on substrates as bonding layer. For cermet 1 (high metal volume fraction: HMVF) and cermet 2 (low metal volume fraction: LMVF), O_2 flowed at 1.5 sccm and 2.5 sccm, which generated partial oxygen pressure of 0.15 mTorr and 0.25 mTorr, respectively. Thicknesses of cermet 1 and cermet 2 were optimized to be 108 nm and 55 nm, respectively. On the top, SiO_2 or TiO_2 anti-reflective coating (ARC) layer was deposited. The TiO_2 ARC layer was deposited with DC powered Ti target and 6.5 sccm O_2 (oxygen partial pressure of 0.57 mTorr). The thickness of each layer was measured on the coating deposited onto partially covered Si wafers with an Alpha-step 200 profilometer (Tencor). Detailed preparation parameters were summarized in Table I.

Variable angle M-2000 spectroscopic ellipsometer (J.A.Woollam Co.) was used to collect data for dielectric function simulation of single cermet layers. To test the fabricated absorbers' thermal stability, the TiO_x-based solar absorbers on Cu and stainless steel substrates were annealed at 300 °C in vacuum of $\sim 5 \times 10^{-3}$ Torr in tubular furnace. Pristine and annealed samples were characterized in terms of their optical properties and morphology. Veeco Dimension 3000 Atomic Force Microscope (AFM) was used to measure the morphology and roughness of the films on Cu and SS substrates. The spectral directional-hemispherical reflectance was measured from 0.2 to 2.5 μm with a Cary 5000i spectrophotometer. From 2.5 to 25 μm, the bidirectional reflectance, which is the ratio of radiance along the outgoing direction to the irradiance along the incoming direction, was recorded with a Nicolet iS50 FTIR spectrometer with a reference/background sample of gold mirror (Thorlabs) at an incident angle of 10° from normal axis.

III. RESULTS AND DISCUSSION

Schematic of the solar absorber is shown in Fig. 1. It consists of a thin bonding layer of Ti, the double cermet layers of TiO_x with different metal volume fractions, and an ARC layer of SiO_2. The bonding layer of Ti is designed to overcome thermal expansion mismatch between substrates and cermet layer. By controlling O_2 flow rate and maintaining the same DC power density on Ti target, partially oxidized TiO_x layers were achieved.

A. Optical properties

The refractive indices of each layer are key to design solar selective absorber. In order to study the optical properties of partially oxidized Ti cermet, 300 nm of single cermet 1 and cermet 2 layers were separately deposited onto Si wafers. Those two samples were measured with the ellipsometer at an angle of 50°, 60°, 70°, and 80°. Their refractive indices were simulated in CompleteEASE software (J.A.Woollam Co.) with Tauc-Lorentz model, which is good to describe absorbing amorphous thin films and consistent with Kramers-Kronig relations.[19,20] The simulated results

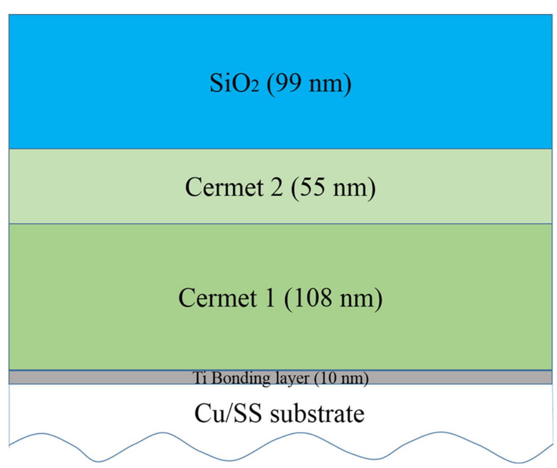

FIG. 1. Schematic of double cermet layers based solar selective absorber $SiO_2/TiO_x/Cu/SS$, consisting of one Ti bounding layer, two cermet layers by sputtering Ti with different O_2 gas flow rates, and one ARC layer of SiO_2 on mechanically polished Cu or stainless steel substrates.

were shown in Fig. 2(a). Since cermet 1 is oxygen poor, which is more metal-rich, it has higher extinction coefficient than cermet 2 in visible and near-infrared regions. Using the refractive indices (n, k) of the cermets, Ti and SiO_2, by tuning the thickness of each layer with the help of OpenFilters[21] software, double-cermet layer based solar selective absorbers ($SiO_2/TiO_x/Cu$ and $SiO_2/TiO_x/SS$) were designed and deposited onto Cu and SS substrates, as shown in Table I. The resulting reflectance was close to the simulated reflectance in Fig. 2(b). Quite low reflectance spectra in visible range were achieved in both simulation and experiments, which benefitted higher absorptance. Reflectance of $SiO_2/TiO_x/Cu$ and $SiO_2/TiO_x/SS$ in the full wavelength range was measured and shown in Fig. 2(c). In visible and near infrared range, the reflectance spectra are almost the same due to strong absorption of double cermet layers. At wavelength longer than 2 μm, substrates properties play an important role in the reflectance. The valley at about 9–10 μm is caused by Si-O vibration. Compared with SS, Cu itself is a good IR reflector with much lower emittance, so there is no need to deposit extra IR reflector layer for this absorber on Cu substrate.

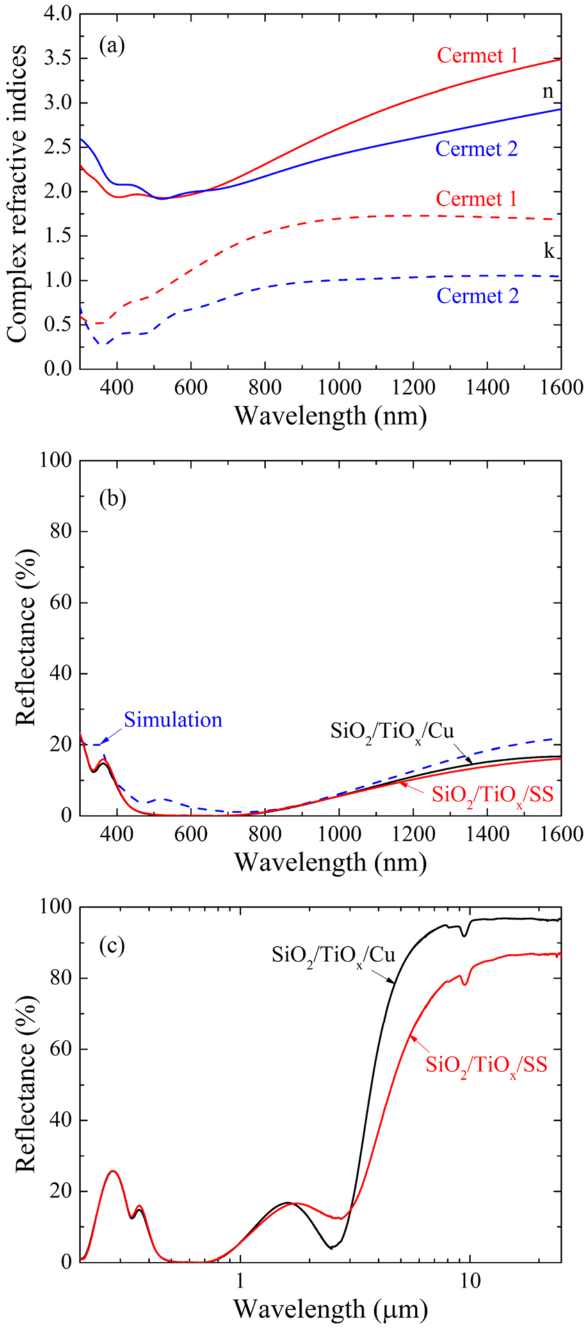

FIG. 2. (a) Simulated optical constants of cermet 1 and cermet 2. Solid lines represent the refractive index n and dashed lines represent extinction coefficient k. (b) Simulated reflectance of SiO_2/TiO_x solar selective absorber on Cu (dashed blue line) and experimental reflectance spectra of SiO_2/TiO_x on Cu (solid black line) and on SS (solid red line) in the wavelength range of 0.2 μm to 1.6 μm. (c) Full wavelength reflectance spectra of SiO_2/TiO_x on Cu (black line) and SS (red line) substrates.

B. Thermal stability test

To test the thermal stability of this solar selective absorber, $SiO_2/TiO_x/Cu$ samples were annealed at 300 °C in sealed vacuum tubes for 24 h and 96 h. The reflectance spectra of samples before and after annealing were compared in Fig. 3(a). Some changes in reflectance were observed between pristine and annealed samples. The reasons could be the increased particle sizes and roughness caused by crystallization during annealing, which leads to minor changes in refractive indices.[22] Surface morphology changes between pristine and two annealed samples were observed by AFM. The mean squared roughness increased from 6 nm (pristine sample, Fig. 3(b)) to 14.4 nm (annealed for 1 day, Fig. 3(c)) to 19.3 nm (annealed for 4 days, Fig. 3(d)). The groove structures caused by mechanical polishing were kept. While roughness increase is reasonable for prolonged annealing test, 3 more days of annealing did not increase the roughness too much for $SiO_2/TiO_x/Cu$. There was almost no change on the reflectance spectra of samples annealed for 1 day and 4 days, indicating good thermal stability up to 300 °C. The calculated absorptance based on AM 1.5 direct + circumsolar solar spectrum and emittance (at 100 °C) based on blackbody radiation spectrum at the evaluated temperature using reflectance data were shown in Table II. The solar selective absorber is good for applications below 300 °C. Also, it can be used for low-temperature such as solar hot water (no more than 100 °C) since the absorber is cost effective and non-toxic. Since solar selective absorber's performance depends on operation temperature and incident solar energy flux, we calculated its efficiency to be 91.4% as a typical solar hot water heater, which operates at near 100 °C with around 1 kW m^{-2} (1 sun) incident power. For higher solar concentration ratio, the absorptance becomes more important and the efficiency will be higher. The equation was discussed in detail by Cao *et al.*[4]

C. Comparison of anti-reflective properties of SiO_2 and TiO_2

Initially, our goal was to use single Ti target to form the solar selective absorber by controlling O_2 flowing rate even using TiO_2 as ARC layer, so we deposited TiO_2 by using DC reactive sputtering, with high O_2 flow rate of 6.5 sccm (partial pressure of 0.57 mTorr in sputtering main chamber). In this case, the whole solar selective absorber was deposited with a single target Ti by DC power, which will potentially reduce the cost in application. Since the solar spectral irradiance gets

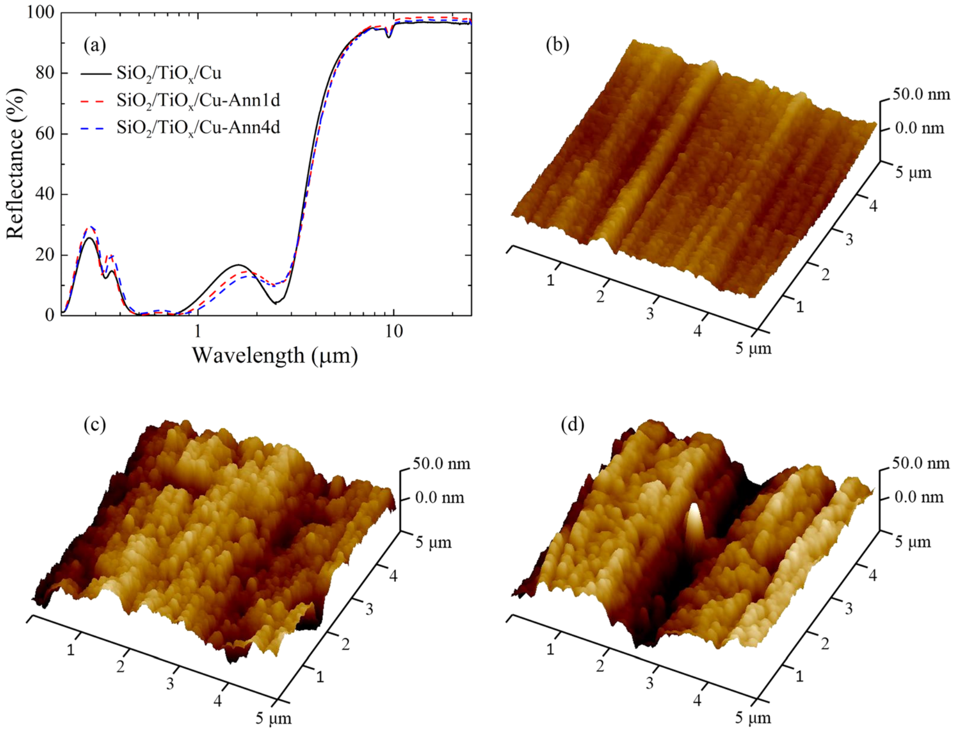

FIG. 3. (a) Reflectance of $SiO_2/TiO_x/Cu$ as pristine (solid black line), annealed at 300 °C for 1 day (dashed red line) and annealed 4 days (dashed blue line). AFM images of $SiO_2/TiO_x/Cu$ (b) pristine, (c) annealed 1 day, and (d) annealed 4 days.

maximum at around 550 nm, we targeted the best anti-reflective wavelength here to improve absorptance. A same optical thickness of TiO_2 with SiO_2 as top layer was used for simulation and experiment as proof, shown in Table I ($TiO_2/TiO_x/Cu$). The simulated and measured reflectance spectra were compared with $SiO_2/TiO_x/Cu$ in Fig. 4. However, at the targeted best anti-reflective wavelength around 550 nm, reflectance of $TiO_2/TiO_x/Cu$ had a peak instead of a valley. To compare the anti-reflective properties of TiO_2 and SiO_2 at wavelength of 550 nm, we did a simple simulation of reflectance spectra of those 2 ARC layers with different optical thicknesses on cermet 2, ignoring its extinction coefficient. The refractive index n of TiO_2 equals 2.65 at 550 nm, while the simulated cermet 2's real part of refractive index $n_{cermet\ 2}$ is 1.94, and that of SiO_2 is 1.46 at this wavelength. The reflectance spectra could be calculated by the following equation:[23]

$$R = \frac{r_1^2 + 2r_1r_2\cos 2\delta_1 + r_2^2}{1 + 2r_1r_2\cos 2\delta_1 + r_1^2r_2^2}, \tag{1}$$

where

$$r_1 = \frac{n_0 - n_1}{n_0 + n_1}, \quad r_2 = \frac{n_1 - n_2}{n_1 + n_2}, \quad and\ \delta_1 = \frac{2\pi}{\lambda}n_1d_1.$$

TABLE II. Calculated absorptance and emittance (100 °C). After annealing, $SiO_2/TiO_x/Cu$'s absorptance gets higher and emittance gets lower.

	Absorptance (%)	Emittance (%)
$SiO_2/TiO_x/Cu$	90.8	4.9
$SiO_2/TiO_x/SS$	95.3	21.0
$SiO_2/TiO_x/Cu$-ann 1d	96.0	5.8
$SiO_2/TiO_x/Cu$-ann 4d	96.0	6.6

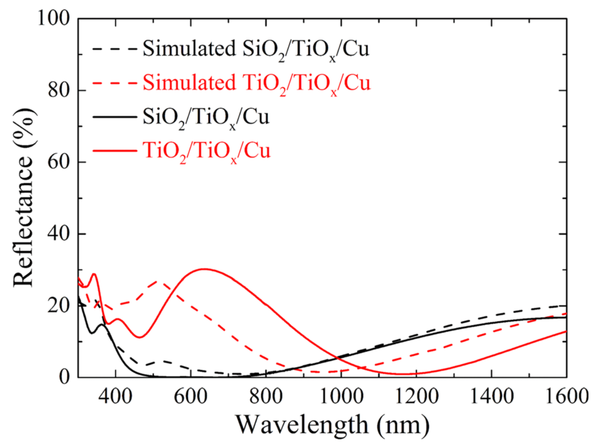

FIG. 4. Simulated and experimental reflectance spectra of $SiO_2/TiO_x/Cu$ (black) and $TiO_2/TiO_x/Cu$ (red).

In the calculation, n_0 represents refractive index of air and $n_2 = n_{cermet\ 2}$, while n_1 is replaced by refractive index of TiO_2 or SiO_2 at investigated wavelength. The optical thickness equals n_1d_1. The calculated reflectance of TiO_2 and SiO_2 as function of optical thickness was shown in Fig. 5. For effective anti-reflection it is required that the ARC layer needs to have lower refractive index than the top cermet layer in order to reduce reflectance. However, TiO_2 has higher refractive index than top cermet layer at visible and near infrared wavelength range. So TiO_2 has no anti-reflective effect on this selective absorber. In this sense, several other metals, like Mo, may be possible to form selective absorbers with single targets, which is beyond the scope of this work.

IV. CONCLUSION

We simulated and deposited partially oxidized TiO_x by DC reactive sputtering at different oxygen gas partial

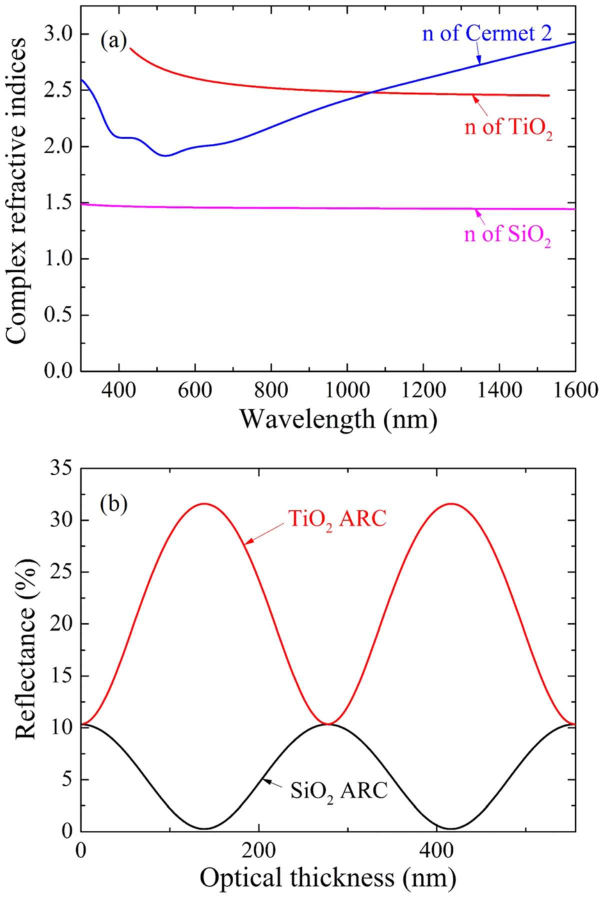

FIG. 5. (a) Optical constants of TiO_2, SiO_2, and top cermet layer (simulated). (b) Simulated anti-reflective properties at 550 nm of different optical thicknesses of TiO_2 and SiO_2. Assumption: top cermet layer is infinite thick and no absorption ($k = 0$).

pressures as a double-cermet based solar selective absorber on Cu substrate. The simulated optical constants of TiO_x indicate that they can be used as absorption layer in solar selective absorber. Double cermet-based selective absorber deposited on Cu substrate has lower total-directional emittance compared with that deposited on the SS substrate due to the intrinsic property of the mechanically polished Cu. It is also found that TiO_2 is not suitable as anti-reflective coating for this absorber. Finally, we demonstrate a solar selective absorber with high absorptance of 96.0% and low emittance of 6.6% at 100 °C after annealing at 300 °C, which has potential for low-mid temperature solar thermal applications.

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