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Thermochromic VO_2 film deposited on Al with tunable thermal emissivity for space applications

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ABSTRACT

Thermochromic VO_2 thin films were deposited on various substrates, namely quartz, Si, and Al, using RF reactive magnetron sputtering deposition. IR thermometry measurements reveal that the emissivity properties of the system VO_2/substrate strongly depend on the IR optical properties of the substrate. VO_2 films deposited on a highly IR reflective substrate such as Al, present an emissivity dependence on temperature that is opposite to that of VO_2 deposited on an IR transparent substrate, like quartz and Si. XPS and Raman measurements show that VO_2 undergoes a crystalline structure transition from monoclinic to tetragonal when deposited on Al, quartz, and Si. They also confirm that the transition is accompanied by a change from an insulator or semiconductor state to a metallic state. The emissivity performance of VO_2/Al as compared to that of VO_2/quartz and VO_2/Si is attributed to the higher IR reflective properties of Al in comparison to quartz and Si. The increase of emissivity with temperature makes the VO_2/Al system of strong interest as a passive smart radiator device for thermal control of spacecraft.

1. Introduction

A passive smart radiation device (SRD) is a new type of thermal control material for spacecraft. Current space thermal control systems require heaters with an additional power penalty to maintain spacecraft temperatures during cold swings. Because its emissivity can be changed without electrical instruments or mechanical part, the use of SRD decreases the request of spacecraft power budget [1]. As an SRD, a thin film should have a low emissivity (ε_L) at low temperature to maintain the heat, whereas at high temperature its emissivity (ε_H) should be high to dissipate the additional unnecessary heat.

VO_2 is a thermochromic material that changes from a semiconductor to metallic with increasing temperature [2]. It is generally deposited on IR transparent substrates like Si, quartz, and Al_2O_3. The transition that occurs at about 70 °C is accompanied by an increase of IR reflectivity and a decrease of IR emissivity with increasing temperature [3–6]. Many works have discussed the possibility of lowering the transition temperature towards room temperature by doping VO_2 with W, Ti, Mg, and Al [3,7–10]. This flexibility makes VO_2 potentially interesting for optical, electrical, and electro-optical switches devices, and as window for energy efficiency buildings applications [8,11].

The systems VO_2/IR transparent substrate show an emissivity behavior with temperature opposite to that required for SRD applications [4–6]. Indeed, they are characterized by high emissivity at low temperature and low emissivity at high temperature. However, in previous work, members of our team have reported that the emissivity of VO_2/Al systems behavior with temperature is the opposite of that of VO_2/quartz, therefore complying with SRD requirements. In this preliminary work, no further characterization was however performed to understand this behavior. It was not even clear whether the VO_2 on Al substrate passes from a semiconductor phase either to another semiconductor phase or to a metallic state when temperature increases [1].

In the present work, we examine the changes encountered by VO_2 deposited on Al as compared to VO_2/quartz and VO_2/Si. We show that VO_2 deposited on Al has transition properties similar to those of VO_2 on quartz and VO_2 on Si. The reflectivity calculated at low and high temperature, using the measured optical constants of VO_2 on Al, is found to reproduce the observed opposite behavior of VO_2/Al as compared to that of VO_2/quartz.

2. Experimental details

2.1. Sample preparation

Samples of VO_2 films deposited on various substrates, namely Si, quartz, and polished mirror-like Al (roughness R_a less than

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40 nm) were prepared. The deposition was carried out by RF reactive magnetron sputtering of Vanadium target with 7.5 cm diameter in a mixture of Ar and O_2 gases. Before introducing the gases, the chamber was pumped down to 10^{-6} Torr. The flux ratio O_2/Ar was 4/40 and the total pressure was 4 mTorr. The RF applied power on the target was 550 W. The substrate temperature was maintained at 540 °C. The thickness of the deposited film was about 300 nm.

2.2. Characterization

The emissivity of the VO_2/substrate system can be obtained from the curve showing the sample temperature measured using IR thermometry (T_{IR}) as a function of its actual temperature (T_{act}). Measurements of T_{IR} were performed using an IR thermometer that provides a cumulative response sensitive in the 8–14 μm range. The IR thermometer provides the temperature of the sample for a blackbody of emissivity ε_{ref}=0.96. In contrast, T_{act} was measured using a thermocouple in contact with the sample. Then, the emissivity of the sample was estimated from the slope of the curves T_{IR} vs. T_{act} using the following equation:

$$\varepsilon \approx \varepsilon_{ref}(\delta T_{IR}/\delta T_{act}) \quad (1)$$

In order to investigate the behavior of VO_2 deposited on Al with temperature, we have examined the density of state at the Fermi level as a function of temperature. The V3d band of VO_2 was measured using X-ray photoemission spectroscopy (XPS). The incident radiation was Al K_α ($h\nu$=1486.6 eV). The binding energy was calibrated using the C1s peak. The phase transition of VO_2 deposited on Al was examined using the Raman spectroscopy. These measurements were performed with a micro-Raman system equipped with a laser (wavelength 514 nm, power of 25 mW at laser head), a grating with 1800 grooves/mm, and a CDD detector.

Specular IR reflectivity and ellipsometry measurements were carried out at an angle of 60° with a spectral resolution of 16 cm^{-1}. The reflectivity (R_p) reported in this work was measured using *p*-polarized light. A sample of 100 nm thick Au film deposited on Si was used as a reference. Measurements at low (30 °C) and high (100 °C) temperatures were performed using a setup allowing heating of the sample up to 100 °C. The emissivity of the materials can be calculated from the reflectivity value using the relation $\varepsilon(\lambda)=1-R(\lambda)-T_r(\lambda)$, where $R(\lambda)$ and $T_r(\lambda)$ are the materials reflectivity and transmission, respectively. Since the system VO_2/Al is opaque (Al is totally reflective in IR), its $T_r(\lambda)=0$ and therefore $\varepsilon(\lambda)=1-R(\lambda)$ at both low and high temperatures. The emittance (ε) is the global parameter averaging the spectral emissivity $\varepsilon(\lambda)$ weighted by the theoretical blackbody spectrum of emissivity at the operating temperature (T):

$$\varepsilon = \int_{\lambda_1}^{\lambda_2} (1-R(\lambda,T))M(\lambda,T)d\lambda \bigg/ \int_{\lambda_1}^{\lambda_2} M(\lambda,T)d\lambda \quad (2)$$

In Eq. (2), $M(\lambda,T)$ is the blackbody spectral distribution function, given by Planck's equation. The integration was performed over the infrared spectra λ_1=2 to λ_2=20 μm, following ESA's standard ECSS-Q-70–09A29 for emissivity measurements [12].

3. Results and discussion

We have examined the emissivity performance of VO_2 deposited on Al, quartz and Si. As explained in Section 2, the emissivity of the VO_2/substrate is obtained from the slope of the temperature measured using IR thermometry (T_{IR}) as a function of the actual temperature (T_{act}) of the sample, according to Eq. (1). The variation of T_{IR} *vs.* T_{act} for the systems VO_2/Si, VO_2/quartz, and VO_2/Al is presented in Fig. 1. It can be seen that for VO_2/Si the emissivity at low temperature, ε_L, is equal to 0.77, whereas at high temperature ε_H=0.41. In addition, the emissivity switch is $\varepsilon_H-\varepsilon_L=\Delta\varepsilon=-0.36$. For VO_2/quartz, ε_L=0.82, ε_H=0.51, with $\varepsilon_H-\varepsilon_L=\Delta\varepsilon=-0.31$. This negative emissivity switch ($\Delta\varepsilon$) makes these two systems unsuitable for SRD applications. In contrast, the VO_2/Al system is exhibiting an increase of the emissivity with temperature (ε_L=0.08, ε_L=0.34, and $\Delta\varepsilon$=0.26), a feature that complies with SRD applications.

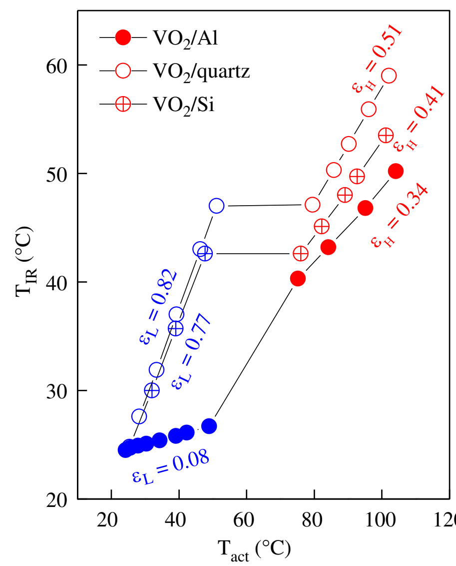

Fig. 1. Temperature determined from IR thermometry, (T_{IR}), as a function of actual temperature (T_{act}) of VO_2 films deposited on Si, quartz, and Al substrates.

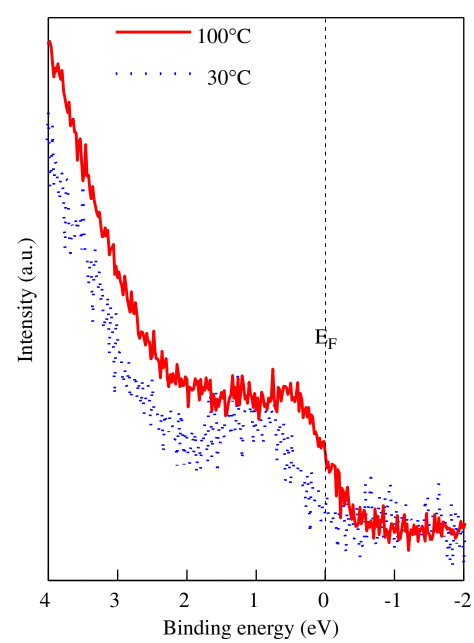

Fig. 2. XPS spectrum of the V3d band of VO_2 film deposited on Al substrate below (30 °C) and above (100 °C) the transition temperature.

In order to understand the reasons that make the behavior of VO_2/Al opposite to that observed for VO_2/quartz and VO_2/Si, we have investigated the characteristics of these various systems in the region of transition temperature. Fig. 2 shows the XPS spectrum of V3d band of VO_2 film deposited on Al substrate at two different temperatures, 30 and 100 °C, one below and the other above the transition temperature. Significant shift of the V

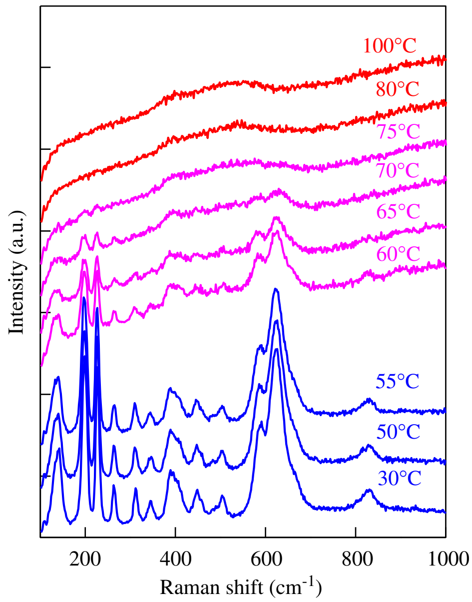

Fig. 3. Raman spectrum at various temperatures of VO_2 film deposited on Al substrate.

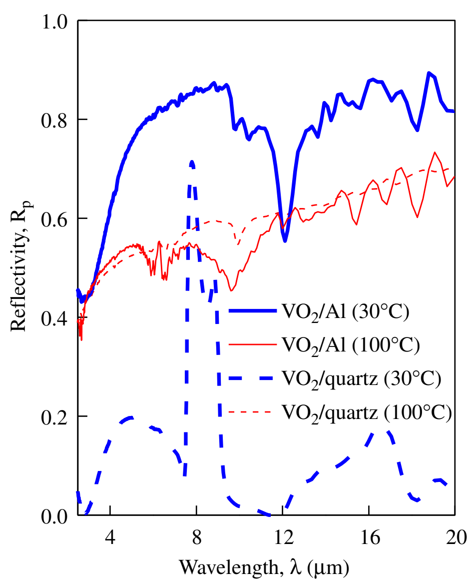

Fig. 4. Measured reflectivity (R_p) of VO_2 film on quartz and Al samples as a function of wavelength (λ) at low (30 °C) and high (100 °C) temperatures.

3d towards the Fermi level is observed in the metallic phase above the temperature transition. At 30 °C the spectral weight at Fermi level (E_F) is significantly low, which indicates the insulating or semiconducting nature of the VO_2 films. In contrast, at 100 °C, the spectral weight at E_F is high indicating a metallic state. These results are similar to those reported in the literature for VO_2 deposited on Si and quartz substrates [13–15].

Fig. 3 shows the Raman spectra of VO_2 films deposited on Al substrate for various temperatures. For temperatures between 30 °C and 55 °C narrow Raman peaks are observed. They are attributed to the monoclinic structure of VO_2 [16–19]. Further increase of temperature to 60–70 °C results in broader peaks. At temperatures higher than 70 °C, only a broad peak centered at about 560 cm^{-1} is observed, which is attributed to tetragonal structure [19]. The Raman spectroscopy clearly shows that deposited VO_2/Al exhibits a crystalline structure transition similar to that reported in the literature for VO_2/Si and VO_2/quartz [16–19].

The reflectivities (R_p) of VO_2/Al and VO_2/quartz were measured at 30°C and 100 °C temperatures. The results obtained at low and high temperature are shown in Fig. 4. For VO_2/quartz, R_p increases with temperature as already reported in the literature [4–6]. In contrast, for VO_2/Al, R_p decreases with increasing temperature. The emissivity determined from R_p for VO_2/Al using Eq. (2) increases from $\varepsilon_L = 0.20$ to $\varepsilon_H = 0.42$, yielding an emissivity switch of $\varepsilon_H - \varepsilon_L = \Delta\varepsilon = 0.22$, which supports the positive emissivity switch obtained from IR thermometry. The difference between the emissivity values determined using FTIR and IR thermometry can be attributed to a slight over estimation of the emissivity switch determined with Eq. (2), as well as to the difference in the measurement angles, to the *p*-polarized light in the FTIR measurements, and to the different wavelength domains considered.

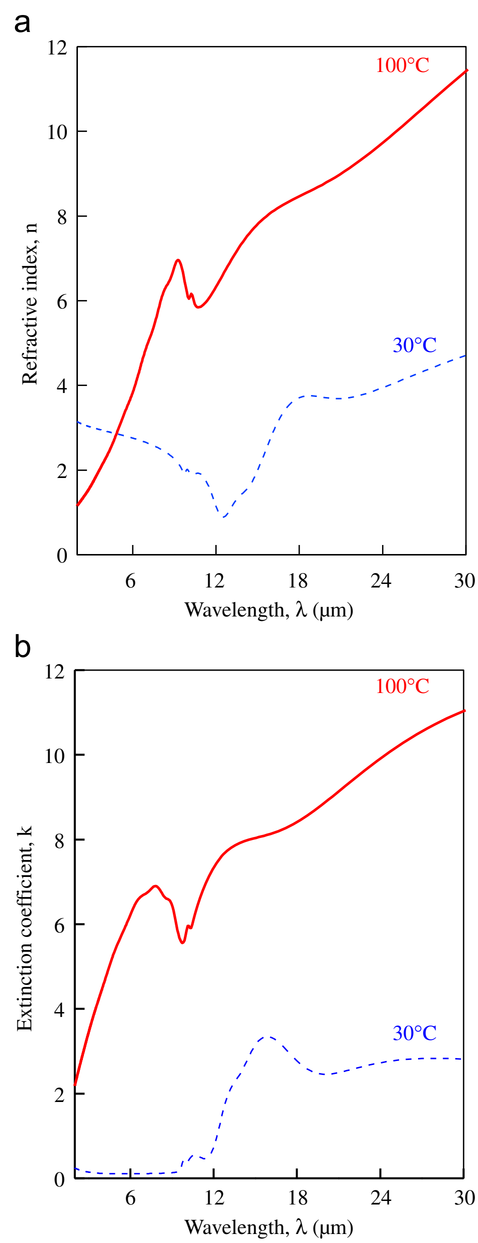

Fig. 5. Refractive index n (Fig. 5(a)) and extinction coefficient k (Fig. 5(b) of VO_2 films as a function of wavelength (λ) at low (30 °C) and high (100 °C) temperatures.

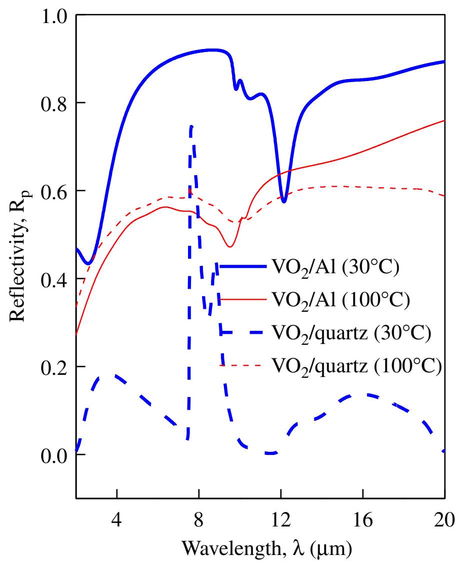

Fig. 6. Calculated reflectivities R_p of VO_2 film deposited on quartz and Al substrates as functions of wavelength (λ) at low (30 °C) and high (100 °C) temperatures.

In order to understand the behavior of the reflectivity for VO_2/Al as compared to that of VO_2/quartz, we calculated it using the optical constants derived from ellipsometry measurements (refractive index n and extinction coefficient k) for VO_2 film (see Fig. 5) and the optical constants of Al and quartz substrate obtained from the IR materials bank of *WVASE* 32 software (J.A.Woollam Co., Inc.). The optical constants of VO_2 were obtained by fitting the ellipsometric angles (Ψ and Δ) of VO_2 film, for wavelength range 2–30 μm [20]; n at 30 °C gradually decreases from about 3 to 1 with increasing wavelength from 2 to about 12 μm. Then, it increases, reaching 4 at about 20 μm. k is very small for 2–12 μm. Further increase of wavelength leads to an increase in k reaching 3 at about 16 μm. Only scant IR optical constant data were reported in the literature and it was for limited wavelength range from 2 to 10–15 μm [5,21,22]. While the behavior of k at 30 °C, in this work, agrees with that reported in the literature then that of n is different [5,21]. At 100 °C, behaviors of n and k are totally different compared with that at low temperature 30 °C; n increases rapidly from about 2 to 7 with increasing wavelength from 3 to 10 μm. Then, it decreases to 6 at about 12 μm. Further increase in wavelength leads to an increase in n; k has a similar behavior to that of n. Behavior of n and k at 100 °C in this work are in good agreement with that reported by Guinneton et al. [5] and differs from that reported by Petit and Frigerio [21] and Konovalova et al. [22].

The calculated reflectivities of VO_2/Al and VO_2/quartz at 30 °C and 100 °C, using the determined n and k for VO_2, are shown in Fig. 6. Clearly, VO_2/quartz is more reflective at high temperature than at low temperature, while the opposite is observed for VO_2/Al. These results are in agreement with the experimental results. It means that using the same optical constants for VO_2 on Al and on quartz; it is possible to reproduce the behavior of the reflectivity as a function of temperature. In other words, the properties of VO_2 remain the same on different substrates so that the dependence of emissivity on temperature is due to the higher IR reflectivity of Al as compared to quartz.

4. Conclusion

Thermochromic VO_2 films deposited on various substrates reveal emissivity properties of the system VO_2/substrate that strongly depend on the IR optical properties of the substrate. VO_2 films deposited on a highly IR reflective substrate such as Al show an emissivity dependence on temperature that is opposite to that of VO_2 deposited on an IR transparent substrate, like quartz and Si. XPS and Raman measurements show that VO_2/Al undergoes a crystalline structure transition from monoclinic to tetragonal. They also confirm that the transition is accompanied by a change from an insulating or semiconducting state to a metallic state. The emissivity performance of VO_2/Al as compared to that of VO_2/quartz and VO_2/Si is attributed to the higher IR reflective properties of Al in comparison to quartz and Si. Since its emissivity increases with temperature, the VO_2/Al system has very interesting tunable thermal emissivity properties. In particular, it holds a strong potential as a passive SRD for thermal control system in SRD applications.

Acknowledgments

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