Temperature-dependent Optical Characterization of VO₂ Thin Film Prepared from Furnace Oxidation Method

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Abstract

Thermochromic vanadium dioxide (VO₂) thin films have been deposited on quartz substrates via a two-step furnace oxidation method. First pure metallic vanadium thin films are deposited on quartz substrates using electron beam evaporation. Then the vanadium films are oxidized in an atmospheric tube furnace to produce stoichiometric VO₂. X-ray diffraction measurements confirm the composition of the prepared films. Temperature-dependent spectral transmittance measurements within the optical range reveal a 57% change upon transition at a wavelength of $\lambda = 2.5 \mu\text{m}$, indicating good potential for energy applications. The heating and cooling behaviors of the VO₂ thin films on quartz are also investigated, and the VO₂ transitions from an insulator to a metal at 345 K upon heating. There is approximately 20 K of hysteresis between the heating and cooling curves. The dielectric constants of the furnace oxidized VO₂ for both the insulating and metallic phases are fitted to a dispersion model for the visible and near-infrared regime. Excellent thermal stability of the fabricated VO₂ thin film from cryogenic to high temperatures is shown with in-situ optical measurements.

Keywords: Vanadium dioxide; Thermochromic; Optical characterization; Property fitting

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1. Introduction

Vanadium dioxide (VO₂) is a thermochromic material that undergoes a dramatic change in optical properties near its insulator-to-metal phase transition temperature of 68 °C.¹ At temperatures below its transition, VO₂ is a monoclinic insulator, whereas at temperatures above its transition the VO₂ is a rutile metal. Due to its considerable shift in optical properties upon phase transition, VO₂ has been investigated for a variety of tunable devices in the near-infrared and mid-infrared wavelength regimes, including smart windows,^{2,7} absorbers/emitters,^{8,9} spacecraft thermal control coatings,^{10,11} and thermal diodes.¹² In nearly every near-IR application, a large change in the VO₂ transmittance is desired to facilitate the tunable behavior. For example, smart window coatings based on VO₂ seek to have high near-infrared transmittance when the temperature is low to allow sunlight to pass through the window. On the other hand, when the temperature is high, the near-infrared transmittance should be comparably lower to prevent heating of the room. The properties of the VO₂ in the visible spectrum are also of interest for many tunable devices, including visible transmittance for smart windows and solar absorption for thermal control devices.^{2,13}

Given the multitude of potential applications for VO₂ in the visible and near-infrared ranges, it is critically important to develop a facile way to fabricate VO₂ films with a high degree of thermochromism. VO₂ is commonly fabricated via magnetron sputtering,^{6,14-16} which requires careful control of the chamber conditions,

including substrate temperature, oxygen and argon partial pressures, and power. Another challenge is that the VO₂ is typically reactively sputtered or post-annealed at high temperatures, typically greater than 450 °C, however significant progress has been made recently on the low temperature fabrication of VO₂ films. Malarde *et al.* fabricated VO₂ on floating glass substrates via APCVD deposition which showed a 58% change in transmittance at a wavelength of $\lambda = 2.5 \mu\text{m}$ for smart window applications.¹⁷ Similarly, Taha *et al.* also fabricated VO₂ on several substrates using DC magnetron sputtering and were able to achieve a 50% change in transmittance for their VO₂ on quartz samples at $\lambda = 2 \mu\text{m}$.¹⁸ Chang *et al.* also fabricated Cr₂O₃/VO₂ bilayers via a low-temperature DC sputtering process with a V₂O₅ ceramic target which achieved a ~55% change at $\lambda = 2 \mu\text{m}$.¹⁹ In addition to the development of new fabrication techniques, the optical properties of the fabricated thin film VO₂ need to be extracted in each relevant wavelength to accurately predict the performance of designed devices. The behavior of VO₂ at cryogenic and high-temperatures, is also of interest for a variety of space applications, including spacecraft thermal control and optical propulsion.

In the present work, vanadium dioxide thin films are prepared on quartz substrates using a simple two-step thermal oxidation technique.²⁰ The film composition is investigated using X-ray diffraction (XRD) and Raman spectroscopy, and the temperature-dependent visible and near-infrared transmittance is measured to provide a comparison to VO₂ fabricated via other methods. Moreover, the heating and cooling curves of the VO₂ thin film on quartz are characterized to illustrate the transition temperature, transition width, and hysteresis characteristics of the fabricated VO₂ thin films. Models of the dielectric constants in the visible and near-IR regimes are presented for VO₂ at both the insulating and metallic phases. Finally, the optical behavior of the VO₂ at cryogenic and high temperatures is investigated to elucidate the thermal stability of the fabricated films. This furnace oxidation technique along with the optical property models will be useful for developing VO₂

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based tunable optical coatings.

2. Sample preparation and characterization

A 60-nm-thick VO_2 thin film was fabricated on a 0.75" diameter, 0.50-mm-thick double side polished Z-cut quartz wafer (Precision Micro-Optics). First, 30-nm-thick pure vanadium was deposited onto the quartz substrate using electron beam evaporation (Lesker PVD75 Electron Beam Evaporator) from 99.99% pure 1/4" diameter 1/4" long vanadium pellets (Kurt. J. Lesker Co.). The deposition rate and chamber pressure were maintained at 0.7 Å/s and 3×10^{-6} Torr, respectively, during the deposition process. After the pure metal deposition, the precursor film was oxidized at 300 °C for 3 hours in a Thermco Minibrite ambient pressure tube furnace to produce a 60-nm-thick VO_2 thin film. Throughout the oxidation process, a mixture of 0.5 SLPM of pure O_2 and a 60 SLPM N_2 was flowed through the quartz tube. After the oxidation, the sample was allowed to cool in a pure N_2 purge flow for

10 minutes in the cold end of the furnace. The composition change of the thin film from metallic vanadium to insulating VO_2 is accompanied by a visual color change from grey to yellow. Fig. 1(a) shows a photo of an unoxidized 30-nm-thick pure vanadium thin film on quartz substrate (left) before oxidation, which appears opaque metallic grey, and that of vanadium dioxide film on quartz substrate (right) after oxidation, which looks yellow with good transparency to the text " VO_2 " underneath it.

The composition of the prepared thin film sample was characterized by XRD and Raman spectroscopy. Fig. 1(b) shows the XRD pattern for VO_2 prepared on quartz substrate, where the peaks at the 2θ angles of 28°, 37°, 43°, 56°, and 65° are typical of polycrystalline vanadium dioxide.²¹ There are no additional XRD peaks indicating the presence of other vanadium oxides, such as vanadium pentoxide (V_2O_5) or vanadium sesquioxide (V_2O_3), which do not contribute to the thermochromic switch of the fabricated thin film.

Fig. 1 (a) Photos of the pure vanadium metal film on a quartz substrate (left) and the yellow oxidized vanadium dioxide thin film on a quartz substrate (right). (b) XRD pattern and (c) Raman spectrum for the oxidized film with typical peaks for vanadium dioxide (VO_2).

Fig. 2 (a) Temperature-dependent spectral transmittance of the fabricated VO_2 thin film on quartz in the visible and near-infrared wavelength ranges. (b) Heating and cooling transmittance curves for the fabricated VO_2 at the wavelength $\lambda = 2.5 \mu\text{m}$.

Similarly, the Raman spectrum of the fabricated film as shown in Fig. 1(c) was also measured with a 488 nm laser source and 100× objective (Renishaw InVia spectroscopy system), which was also consistent with polycrystalline VO₂.²⁰ The thin film thicknesses of both the pure V metal (30 nm) and the VO₂ (60 nm) were determined using a contact profilometer (Bruker Dektak) to measure the height of a step prepared on the quartz substrate during the sample fabrication before and after the furnace oxidation process.

Temperature-dependent spectroscopic characterizations have been successfully used to study composition and optical properties of materials such as Al_{0.5}Ga_{0.5}N alloy from 300 K to 823 K²² as well as to directly measure spectral emissivity for experimentally demonstrating high-temperature polaritonic radiation from ceramic nanotube antennas²³ and coherent thermal emission from grating metamaterials due to magnetic polaritons.²⁴ Here, the temperature-dependent spectral transmittance of VO₂ thin film at normal incidence was measured by a Fourier-transform spectrometer (Thermo Scientific, Nicolet iS50) with extended spectrum from mid-infrared to near-infrared and visible range enabled by a white light source and a quartz beam splitter. A silicon detector was used for the wavelengths from 400 nm to 1 μm, while a DTGS detector captured the spectra at longer wavelengths from 1 to 2.5 μm, with each spectral measurement averaged over 32 scans at a resolution of 16 cm⁻¹. The sample was mounted on the cold finger inside a variable-temperature cryostat (Janis, VPF-800-FTIR) optically coupled through quartz windows with the spectrometer, and the sample temperature was accurately controlled in a wide range from 77 K to 800 K by a temperature controller (Lakeshore 335) along with liquid nitrogen and a built-in heater. Throughout the measurement the cryostat chamber was maintained at a vacuum pressure less than 1 × 10⁻⁴ Torr.

Fig. 2(a) shows the transmittance at room temperature when the VO₂ is insulating, and also at 100 °C when the VO₂ is metallic. Both the metallic and insulating VO₂ have 40-50% transmittance in the visible wavelengths, with the transmittance of the metallic phase 7% greater than the insulating phase. In the longer wavelengths, the fabricated VO₂ achieved a transmittance change of 57% at λ = 2.5 μm. This large change in near-infrared transmittance suggests that the furnace oxidized VO₂ would have considerable potential as a switching material for near-IR device applications. To investigate the nature of the insulator to metal phase transition of the furnace oxidized VO₂ sample, the heating and cooling curves were also measured. The in-situ temperature-dependent transmittance spectra were taken incrementally between room temperature and 370 K. After each set-point temperature was reached, 15 minutes were allotted for the sample temperature to stabilize at the set-point. Fig. 2(b) shows the heating and cooling curves at a wavelength of λ = 2.5 μm for the VO₂ thin film fabricated on quartz. The transition temperature was determined as the temperature at which the transmittance reaches the midpoint of the transmittance curve, i.e., 45%. Therefore, the heating curve shows a typical VO₂ transition temperature of 345 K, while the cooling curve shows a considerably lower transition temperature of 325 K, yielding a hysteresis of 20 K.

3. Dielectric models of fabricated VO₂ thin films for both phases

The dielectric constants for both the insulating and metallic VO₂ are fitted to a dispersion model²⁵ via a least-squares method by minimizing the objective function as:

$$F = \sum_{k=1}^N (T_{\text{exp}} - T_{\text{theo}})^2 \quad (1)$$

where T_{exp} is the experimentally measured transmittance data at each wavelength with index k and T_{theo} is the theoretical transmittance calculated by considering the sample as a thin film on an incoherent slab with ray-tracing optics:^{26,27}

$$T_{\text{theo}} = \frac{\tau_a \tau_s \tau}{1 - \rho_s \rho_b \tau^2} \quad (2)$$

where τ is the internal transmittance of the slab, τ_a is the transmittance from the air through the thin film layer, τ_s is the transmittance between the substrate and air below, ρ_s is the air-substrate reflectance, and ρ_b is the reflectance for the slab-air interface. τ_a and ρ_s are determined from Fresnel's equations, while τ_s and ρ_b are determined from thin-film optics.²⁶ The optical properties of the quartz substrate are taken from Palik's Handbook,²⁸ while the VO₂ optical properties are fitted to a Drude-Lorentz dispersion model:²⁵

$$\varepsilon(\omega) = \varepsilon_{\infty} - \frac{\omega_p^2}{\omega^2 + i\omega\omega_c} + \sum_{j=1}^N \frac{S_j}{1 - \omega^2/\omega_j^2 - i\gamma_j \omega/\omega_j} \quad (3)$$

where ε_{∞} is the high-frequency dielectric constant, ω_p is the density parameter and ω_c is the collision frequency for free carriers. S_j , ω_j , and γ_j are respectively the high-frequency dielectric constant, phonon strength, phonon frequency, and damping coefficient for each oscillator. Eight oscillators were used for the Lorentz term to achieve a satisfactory fit for both the metallic VO₂ and insulating VO₂. The least-squares parameter F was minimized according to ε_{∞} , ω_p , ω_c , ω_j , S_j , and γ_j using a genetic algorithm routine subject to bounds for each parameter. ε_{∞} was constrained to be between -10 and 10, ω_p and ω_c were limited between 500 and 30000 cm⁻¹, and S_j and γ_j were set to be between 0 and 10. The phonon frequency was bounded between 500 and 30000 cm⁻¹.

The fitted parameters for both the insulating and metallic VO₂ are summarized in Tables 1 and 2, respectively. Fig. 3(a) and 3(b) show the comparison of the experimental data from optical measurements and the calculation results from the fitted model the spectral transmittance for wavelengths from 0.4 to 2.5 μm for the insulating and metallic phases, respectively, where excellent agreement is clearly seen. The real and imaginary parts of the dielectric constants calculated from the dispersion model are shown in Fig. 3(c) and 3(d) for both insulating and metallic VO₂. Note that the optical properties of VO₂ strongly depend on its morphology from different fabrication methods,²⁵ and hence the dielectric constants should be determined based on the optical spectroscopic measurements for accurate modelling to facilitate the design of novel optical devices based on VO₂ films fabricated using this simple furnace oxidation process.

4. Cryogenic and high-temperature stability of VO₂ thin films

The thermal stability of VO₂ films across a wide temperature range from cryogenic to high temperatures is of great interest for a number of applications, in particular for space applications like radiative thermal control and optical force modulation, however it has not been studied. The temperature-dependent spectral transmission provides a viable way to experimentally study the optical properties at different temperatures. First, the behavior of the insulating VO₂ thin film on quartz sample at cryogenic temperatures was investigated with the customized cryostat coupled with the spectrometer using liquid nitrogen to cool the sample down to the lowest temperature of 77 K. With a built-in heater, the sample temperature was sequentially held at 77 K, 150 K, 250 K, and 300 K for 15 minutes at each temperature to ensure that the steady state

Fig. 3 (a) Comparison between the fitted model (solid black) and the experimental data for insulating VO₂ (dashed red). (b) Comparison between the fitted model (black) and the experimental data for metallic VO₂ (dashed red). (c) Real part of the dielectric function for insulating and metallic VO₂. (d) Imaginary part of the dielectric function for insulating and metallic VO₂.

Fig. 4 In-situ optical spectroscopic transmission measurements of 60-nm-thick VO₂ thin film on quartz substrate from cryogenic to high temperatures in the wavelengths from 0.4 μm to 2.5 μm . Note that the VO₂ is in the insulating phase from 77 K to 300 K, and in the metallic phase from 373 K to 750 K.

Table 1 Model Parameters Fitted for Insulating VO₂.

Insulating VO ₂ Properties						
ε_{∞}	ω_c	ω_n	Oscillator Index j	S_j	ω_j	γ_j
5.16	27876	993	1	0.2711	25948	1.1436
			2	0.2946	23277	0.0787
			3	0.5720	16158	1.3605
			4	0.7577	27127	0.7264
			5	0.5052	29574	0.6017
			6	0.0065	7733	0.9867
			7	0.0189	24330	1.1995
			8	0.6293	8652	0.7314

Table 2 Model Parameters Fitted for Metallic VO₂.

Metallic VO ₂ Properties						
ε_{∞}	ω_c	ω_n	Oscillator Index j	S_j	ω_j	γ_j
5.08	7197	24410	1	0.06352	22043	0.6738
			2	0.82578	4639	0.8577
			3	0.75794	22149	0.2311
			4	0.09844	21208	1.8399
			5	0.85808	4715	0.4489
			6	1.63554	1634	1.7125
			7	0.20847	24103	0.3586
			8	1.16358	4292	1.0351

was reached. Similarly, the VO₂ on quartz sample was heated beyond the phase transition at 373 K, 450 K, 550 K, 650 K and 750 K, where VO₂ is in the metallic phase, to inspect its high temperature behavior. Fig. 4 shows the temperature-dependent spectral transmittance in wavelengths from 0.4 μm to 2.5 μm for cryogenic to high temperatures. As it can be seen, the spectral transmission for the insulating VO₂ exhibits little change with less than 3% variation from 77 K to 300 K within the visible and the near-infrared. The metallic phase behaves similarly with little changes in spectral transmission, no more than 10% at high temperatures from 373 K up to 750 K. The results clearly demonstrate the excellent thermal stability of VO₂ thin films of both phases prepared from furnace oxidation method from cryogenic to high temperatures in vacuum conditions from visible to near-infrared regime. Note that there is a jump at the wavelength of 1 μm for the transmittance spectra at all temperatures. This is due to the fact that different detectors are used at wavelengths above and below 1 μm , at which both detectors have low responsivity with relatively larger Error about 5%.

5. Conclusion

In summary, the optical properties of VO₂ thin film prepared by the furnace oxidation method were investigated in a wavelength range between 400 nm and 2.5 μm , which is of interest for applications such as smart windows, optical filters, and optical force coatings for spacecraft attitude control. The fabricated 60 nm VO₂ on quartz films exhibited a 57% change in transmittance at a near-infrared wavelength of $\lambda = 2.5 \mu\text{m}$ and a 7% change in transmittance in the visible wavelengths. The VO₂ transition temperature was 345 K upon heating and 325 K upon cooling, yielding a hysteresis of 20 K. The dielectric constant of the insulating and metallic VO₂ was fitted to a dispersion model to assist with device design with furnace fabricated VO₂. Finally, the VO₂ thin film was shown to be thermally stable in a wide temperature range from 77 K to 750 K. The VO₂ thin film with large change in optical transmittance and excellent thermal stability achieved by the furnace oxidation process is promising as a switching material for tunable optical filters, smart windows, and thermal control applications.

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