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Letter

Thermochromic VO_2 films by thermal oxidation of vanadium in SO_2

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ABSTRACT

Thermochromic films of VO_2 were prepared by a two-step procedure: Sputtering was first used to deposit metallic vanadium, and such layers were subsequently oxidized in SO_2 at a temperature in the 600–650 °C range. X-ray diffraction, Raman spectroscopy, measurements of temperature-dependent electrical resistance, and spectrophotometric transmittance data at different temperatures were employed to demonstrate that the films consisted of polycrystalline VO_2 with good thermochromism, especially when oxidized at the highest temperature. Oxidation in SO_2 is able to produce VO_2 without the stringent process control that can be an obstacle for making VO_2 by oxidation in O_2.

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1. Introduction

Vanadium dioxide has thermochromic (TC) properties and exhibits a reversible metal–insulator transition at a "critical" temperature τ_c of about 68 °C [1]. The material is monoclinic and semiconducting at $\tau < \tau_c$, where τ denotes temperature, while it is tetragonal and metallic-like at $\tau > \tau_c$. Thin films of VO_2 on transparent substrates can have a higher throughput of near-infrared radiation below τ_c than above this temperature, and therefore they are able to provide temperature-dependent control of solar energy transmittance while the luminous transmittance remains almost unaltered and high [2,3]. Such coatings onto glass or polymers are of much interest for TC glazings in energy-efficient buildings [4–8], especially (i) if τ_c is brought to the vicinity of room temperature as is easily done by tungsten doping [5,9], (ii) if the luminous transmittance is enhanced as is possible by doping with Mg [10–13], other alkaline earth metals [13], Zn [14], or F [15], (iii) if the solar energy transmittance modulation at τ_c is boosted by having a film comprising VO_2 nanoparticles [16,17], and (iv) if the further oxidation of VO_2-based films or particle deposits to V_2O_5 is impeded by protective top layers for example of Al oxide or Al nitride [18,19]. The practical manufacturing of VO_2 films—by direct deposition or by controlled post-deposition oxidation or reduction of a vanadium-based material—is challenging and may require judiciously controlled deposition or annealing parameters. However, as shown in the present paper, post-treatment of metallic vanadium deposits in gaseous SO_2 can yield TC films in a generous range of preparation parameters, and our new technique therefore offers some advantage with regard to practical manufacturing of VO_2-based thin films or particle composites.

2. Thin film preparation

We prepared VO_2 thin films by a two-step process: Metallic vanadium films were first deposited onto 1-mm-thick glass plates by DC magnetron sputtering in a system based on a Balzers UTT 400 unit. A 5-cm-diameter vanadium metal plate (99.95% purity) served as sputter target. The deposition chamber was initially evacuated to $\sim 10^{-5}$ Pa, and argon (99.99%) was then introduced so that the pressure became 1.2 Pa. Pre-sputtering was performed for a few minutes in order to clean the target, and vanadium films were deposited without substrate heating at a discharge power of 172 W. The film thickness was 40 ± 5 nm, as recorded by a Bruker Dektak XT surface profilometer, and a deposition rate of ~8 nm/min was estimated from film thickness and sputtering time.

For the second step of film preparation, the vanadium coated glass plates were transferred to an in-house built tubular reactor consisting of a 40-mm-diameter quartz tube inserted in a furnace, and the samples were exposed to SO_2 gas (99.98%) flowing at ~100 sccm in order to oxidize a number of metal films. Nitrogen gas (99.99%) was constantly flushed at ~100 sccm through the reactor. The total pressure in the reactor was ~0.02 atm, and the SO_2 partial pressure was ~0.01 atm. The reactor was heated at ~20 °C/min and the temperature was stabilized at a value in the $600 < \tau_s < 650$ °C range. Annealing in a gas mixture of N_2 and SO_2 took place at τ_s for ~1 h, and the sample was then cooled to room temperature overnight in nitrogen. This oxidation is predicted to

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increase the film thickness by a factor 2.25 [20], which is consistent with prior experimental data [21]. The VO_2 films in the present work are expected to have a thickness of 90 ± 10 nm. It is important to note that the preparation parameters for making the VO_2 films were not accurately controlled. 9

3. Structural and compositional characterization

VO_2 films that had been formed by the two-step procedure described above were characterized by scanning electron microscopy (SEM), x-ray diffraction, and Raman spectroscopy. For SEM studies, we used a LEO 1550 FEG Gemini instrument with an acceleration voltage of 3 kV. Fig. 1, recorded on a sample prepared at $\tau_s \approx 650$ °C, demonstrates that the film surface has a nanostructure with compact rounded grains that are 50–100 nm in size.

Grazing incidence x-ray diffraction data were taken by use of a Siemens D5000 θ–2θ diffractometer operating with CuK_α radiation and 40 kV acceleration voltage. Diffractograms were acquired in the $20 < 2\theta < 80°$ range at a glancing angle of 5°. Fig. 2 shows x-ray data for films prepared at the shown values of τ_s and demonstrates that the peak positions agree with those for the monoclinic M1 phase of VO_2 (Joint Committee of Powder Diffraction Standards Card no. 00-043-1051); no evidence was found for any other structure. Clearly the films are polycrystalline. The intensity of the diffraction peaks became higher when τ_s was increased. The main feature at $2\theta = 27.8°$ emanates from the (011) lattice planes and was used to assess the crystallite size D from Scherrer's equation [22]. D was found to increase from ~14 to ~19 nm as τ_s went from ~600 to ~650 °C.

Raman spectroscopy measurements were performed using a Renishaw micro-Raman system 2000 with an argon-ion laser line at the wavelength 514 nm. Fig. 3 reports Raman spectra of films prepared at τ_s being ~600 and ~650 °C. All of the peaks can be associated with VO_2 vibrational modes previously reported in the literature [23–28]. No other features than those due to the M1 structure of VO_2 could be identified, which indicates a phase-pure character of our films.

4. Electrical and optical properties

The sheet resistance of the films was determined by a four-point method using wires attached with silver glue. Data shown in Fig. 4 were obtained during heating from 20 to 130 °C followed by cooling. The resistance was found to change by about two orders of magnitude and the thermal hysteresis is ~12 °C. Spectral optical transmittance $T(\lambda)$ was measured in the $300 < \lambda < 2500$ nm wavelength range by use of a Perkin-Elmer Lambda 900 instrument equipped with integrating sphere. Fig. 5 shows data taken at 25 and 100 °C, i.e., well below and above τ_c. Pronounced thermochromism is manifest and $T(2500\text{ nm})$ is 68% at 25 °C and 16% at 100 °C. Our efforts to make TC films at $\tau_s < 600$ °C were not successful.

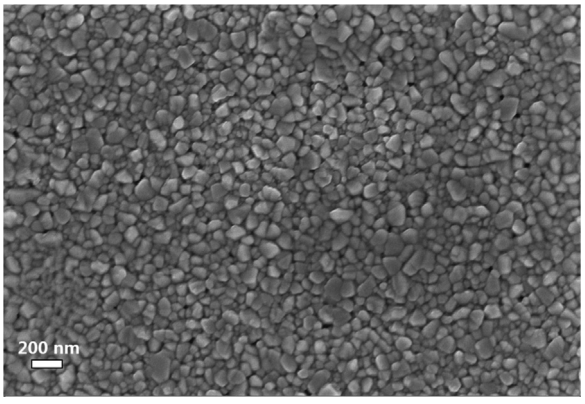

Fig. 1. Scanning electron micrograph of a VO_2 film made by oxidation of metallic vanadium in SO_2 at ~650 °C.

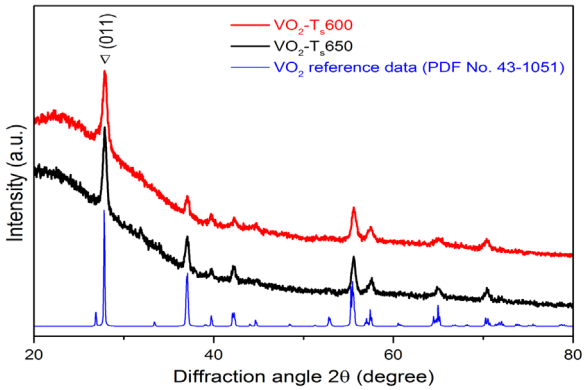

Fig. 2. X-ray intensity (in arbitrary units, a.u.) versus diffraction angle 2θ for VO_2 films made by oxidation of metallic vanadium in SO_2 at ~600 and ~650 °C. The peak corresponding to the (011) lattice planes was used for crystallite size estimation and is highlighted. Also shown is a reference diffractogram for the monoclinic M1 phase of VO_2, according to JCPDS Card no. 00-043-1051.

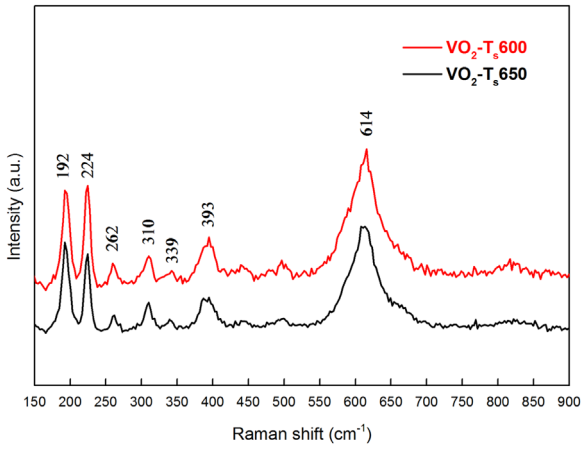

Fig. 3. Raman spectra, with intensity in arbitrary units (a.u.), of VO_2 films made by oxidation of metallic vanadium in SO_2 at the shown temperatures. Peaks occur at the shown wavenumbers.

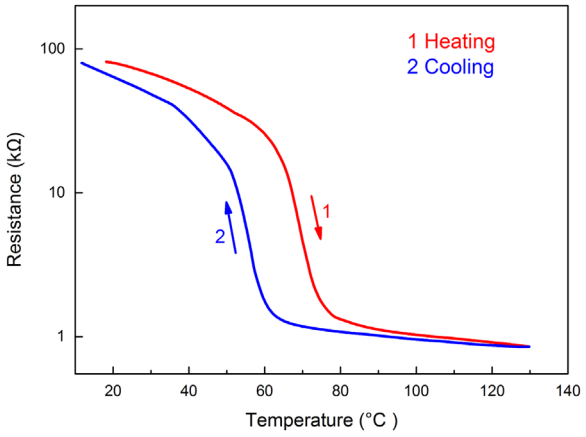

Fig. 4. Temperature-dependent electrical resistance during heating and cooling of a ~90-nm-thick VO_2 film made by oxidation of metallic vanadium in SO_2 at ~650 °C.

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