



Enhancing thermochromic performance of VO₂ films via increased microroughness by phase separation

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ABSTRACT

Application of VO₂ to smart windows calls for an enhancement of both luminous transmittance (T_{lum}) and solar transmittance modulation (ΔT_{sol}). These two properties are related to optical constants, microstructure and film thickness. In this article, VO₂-based films with increased microroughness are prepared by polymer assisted deposition, and ZnCl₂ is added to the precursor solution to control the microstructure of the films. Addition of ZnCl₂ increases the microroughness of films through phase separation, which largely decreases the refraction index and the reflectivity of the films, resulting in enhanced luminous transmittance and solar transmittance modulation; two films with balanced optical performance show T_{lum} =50.5% and ΔT_{sol} =11.3%, and T_{lum} =59.3% and ΔT_{sol} =10.5%, respectively. Moreover, this kind of microstructure control has no influence on doping VO₂, which is proven by the deposition and characterization of W-doped VO₂-based films. By the formation of a W-doped VO₂/F:SnO₂/glass multilayer stack, a film shows excellent thermochromic properties and low emissivities; typically, a film with a phase transition temperature, T_{lum} , ΔT_{sol} of 43.4 °C, 30.0%, 8.82%, respectively, and emissivity of 0.20 for monoclinic and 0.33 for rutile phase is successfully prepared.

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1. Introduction

Reducing carbon dioxide emissions is necessary to solve the global warming problem and calls for new technologies that increase energy savings and generation [1]. Buildings consume 30–40% of the primary energy in the world, mainly due to heating, cooling, lighting and ventilation [2]. Energy-saving windows, which have spectrally selective coatings to control the transmittance of solar radiation, are of particular importance to decrease energy consumption in buildings. Thermochromic smart windows are one kind of energy-saving windows and help to increase the energy efficiency of buildings as they function to selectively regulate infrared transmittance in response to the environmental temperature [3,4].

Vanadium dioxide is a well-known thermochromic material [5–12]. VO₂ undergoes a first-order semiconductor-metal transition (SMT) at a critical temperature τ_c (68 °C for bulk VO₂), which is accompanied by a structural change between a high-temperature

rutile phase (P4₂/mnm, R) and a low-temperature monoclinic phase (P2₁/c, M₁) [5]. The distortion in the crystal structure results in severe changes in the optical properties. Monoclinic-phase VO₂ is semi conductive and is generally transparent to infrared solar radiation, whereas the rutile phase is metallic and reflects infrared solar radiation [13].

Properties of VO₂ can be adjusted to meet the application requirement of smart windows. SMT temperature can be effectively lowered to the vicinity of room temperature through doping, for example, tungsten [14,15]. The hysteresis loop width of a VO₂ film can also be narrowed down to 3 °C by doping of metal ions [13]. Still one lingering problem exists. For thermochromic VO₂-based films, it is difficult to achieve a sufficiently high luminous transmittance with preserved solar transmittance modulation [1]. Various methods have been applied to solve this problem. Anti-reflection coatings can effectively enhance both the luminous transmittance and solar transmittance modulation. Using reactive DC magnetron sputtering, Mlyuka et al. deposited a five-layer TiO₂/VO₂/TiO₂/VO₂/TiO₂ film with luminous transmittance of 45% and solar transmittance modulation of 12% [16,17]. Through an all-solution process, we have deposited a two-layer TiO₂/VO₂ film with a luminous transmittance of 49.5% and a solar transmittance modulation of 15.1% [18]. Calculations and experiments of Kang et al. suggest that porosity can also enhance the

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optical performance of VO₂ by lowering optical constants and the achievement of porosity is convenient with polymer assisted deposition [19]. Moreover, calculations using effective medium approximation method suggest that the solar transmittance modulation of VO₂-based nano-composites could reach 20% with acceptable luminous transmittances [20].

In this work, microstructure of films is controlled to enhance the optical performance of VO₂ films deposited by polymer assisted deposition [11]. We utilize the compatibility difference of inorganic salts with polyvinylpyrrolidone (PVP) to introduce phase separation and obtain films with large microroughness. The obtained films can be simply prepared and exhibit excellent optical performance. Doping can also be applied in this deposition process. By tungsten doping, we successfully lower down the SMT temperature to 25.4 °C. Moreover, emissivity of films is lowered 0.20 for monoclinic and 0.33 for rutile phase to by depositing VO₂-based films onto F:SnO₂ (FTO) glass.

2. Experiments

2.1. Starting materials

Vanadium oxide sulfate hydrate (VOSO₄·xH₂O, VOSO₄, 68% pure), ammonium tungstate ((NH₄)₁₀H₂(W₂O₇)₆, analytically pure), zinc chloride (ZnCl₂, analytically pure), and hydrogen peroxide solution (H₂O₂, 30% pure) were used as starting materials to prepare vanadium, tungstic, and zinc solution, respectively. Polyvinylpyrrolidone (PVP, K90) was added as a film-formation promoter. All the reagents were purchased from the Aladdin Reagent Co. Ltd. and were used without further purification.

2.2. Preparation of precursor solutions

2.2.1. Preparation of vanadium solution

The precursor solution of vanadium with PVP as an additive was prepared by adding 23.97 g of VOSO₄·xH₂O and 4 g of PVP to a 100-mL beaker containing 50 mL of deionized water. After stirring for 1 h, the solution was transferred to a 100 mL volumetric flask and then the volume was set to the mark using deionized water. The final concentration of the stock solution was 1 M for vanadium and 4 wt% for PVP.

2.2.2. Preparation of ZnCl₂ solution

ZnCl₂ (13.63 g) was carefully added to a 100-mL beaker containing 50 mL of deionized water. After stirring for 1 h, the solution was transferred to a 100 mL volumetric flask and then the volume was set to the mark using deionized water. The final concentration of ZnCl₂ was 1 M.

2.2.3. Preparation of tungstic solution

(NH₄)₁₀H₂(W₂O₇)₆ (2.580 g) was carefully added to a 100 mL beaker containing 50 mL of deionized water, and then 3 ml of hydrogen peroxide solution was slowly added to the breaker. After stirring and cooling down, the solution was transferred to a 100 mL volumetric flask and then the volume was set to the mark using deionized water. The final concentration of tungsten was 0.1 M.

2.3. Deposition of VO₂-based films and VO₂-based powders

Certain amounts (0–400 μL) of ZnCl₂ solution were added to 2 mL of the vanadium solution to obtain the precursor solutions. The volume of zinc solution was changed to adjust the Zn/V atomic ratio. The precursor solutions were mixed ultrasonically and were aged for 4 h at room temperature before spin coating. To deposit W-doped composite films, an appropriate volume of

tungstic solution (0–800 μL) was added to the precursor solution to adjust the W/V atomic ratio.

The films were deposited on fused-silica substrates (2 × 2 cm²) by spin coating the precursor solutions. The spin speed was changed to modulate the film thickness. After drying for 10 min at 60 °C to remove the excess solvent, smooth precursor films were formed. The procedure was repeated several times to further regulate the film thickness. After annealing for 1 h at 500 °C in a nitrogen atmosphere, the precursor gel films were transformed into thermochromic VO₂-based films.

VO₂-based powders were prepared using the precursor solutions. Precursor solutions were dried at 100 °C for 30 min to remove the excess solvent. The gel was annealed for 3 h at 500 °C under nitrogen atmosphere and transformed into VO₂-based powders.

2.4. Measurements

The crystalline phases of the films were determined using an X-ray diffraction (XRD) diffractometer (Philips Corp., Model Xpert, primary monochromatic Cu-K_α radiation). The optical transmittance was measured from 350 to 2600 nm at temperatures ranging from 25 to 100 °C by a spectrophotometer (Hitachi Corp., Model UV-4100). The morphology of the films was determined by a field-emission scanning electron microscope (FESEM, JEOL Corp., Model JSM-6700F). Low- and high-resolution transmittance electron microscopy (TEM) and energy dispersive spectroscopy (EDS) of films were obtained using a transmission electron microscope (JEOL Corp., Model JEM-2010). The thickness of the film was measured using a surface profilometer (Model Veeco-Dektak 150). The temperature was measured with a PT100 temperature sensor in contact with the film and was controlled by a temperature-control unit. The temperature errors were smaller than 1.5 °C based on repeated measurements. Hysteresis loops were measured by collecting the transmittance of films at a fixed wavelength (2000 nm) at an approximate interval of 2.0 °C. The optical constants of films at 632.8 nm were measured using an ellipsometer (Semilab Corp., Model EP20). Measurements of light scattering were carried out by a laser scatterometer at the wavelength of 632.8 nm, and scattering was characterized using the bidirectional transmittance distribution function (BTDF), which has been described in reference [21].

3. Results and discussion

3.1. Configuration of crystal structures

The XRD pattern of a film with Zn/V=0.12 is shown in Fig. 1(a). The monoclinic phase of VO₂ (JCPDF Card no. 72-0514) is identified as the main crystalline phase. Minor phase is not detected due to the weak signal-to-noise ratios (SNRs). The widening of the XRD peaks indicates that the film consists of very fine crystallites. However, due to the weak SNRs, the crystalline size is difficult to calculate from XRD data. Other films with 0 ≤ Zn/V ≤ 0.2 show similar XRD patterns.

To identify the minor phases, VO₂-based powders with similar Zn/V ratios were prepared, and the corresponding XRD patterns are shown in Fig. 1(b). Similar to films, the monoclinic phase of VO₂ is identified as the main phase within the research range (0 ≤ Zn/V ≤ 0.2). Diffraction peaks for ZnCl₂ (JCPDF Card no. 74-1752) is observed in the sample with Zn/V=0.1. Diffraction peaks for both ZnCl₂ and Zn₂VO₄ (JCPDF Card no. 73-1632) are detected in the sample with Zn/V=0.2. However, the weak peak intensities of Zn₂VO₄ and ZnCl₂ suggest that VO₂ is the main phase.

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