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Sol–gel preparation and characterization of SiO_2 coated VO_2 films with enhanced transmittance and high thermochromic performance

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ABSTRACT

Vanadium dioxide (VO_2) films prepared at low-temperature with a low cost are considerable for energy-saving applications. Here, SiO_2 coated VO_2 films with clearly enhanced visible transmittance by introducing antireflection coatings (ARCs) and excellent thermochromic performance were present. The VO_2 films have been prepared via a stable and low-cost sol–gel synthesis route using vanadium pentaoxide powder as precursor, and their structural, morphological, optical and electrical properties and thermochromic performance were systemically characterized. The resistance of VO_2 films varies by 4 orders of magnitude and the transmittance changes from 11.8% to 69.3% at 2500 nm while no significant deviation appears in the visible region during metal–insulator transition (MIT). Nanoporous SiO_2 coating with good optical transparency was coated on the surface of VO_2 film via sol–gel dip-coating technique to enhance its optical transmittance, and the visible transmittance is increased by 14.6% due to the significantly decreased reflectance. The critical transition temperature (63 °C) and infrared switching properties of VO_2 films are not much deteriorated by applying SiO_2 layer. The synergistic effect of antireflection and thermochromism on SiO_2 coated VO_2 films was investigated.

1. Introduction

Vanadium dioxide (VO_2) materials undergo a well-known reversible metal to insulator transition (MIT) at 68 °C (critical transition temperature, T_c) and have been extensively studied for many years [1–13]. MIT in VO_2 materials is accompanied with a crystallographic transformation from monoclinic structure (VO_2 (M)) to tetragonal rutile structure (VO_2 (R)) and abrupt changes of electrical, magnetic, thermal and optical properties [2–5]. Based on these properties, the VO_2 materials have been widely used in infrared bolometers and detectors [6,7], temperature-sensitive elements [8], gas sensors [9], optical storage media [10,11] and thermochromic smart windows [12,13].

VO_2 films have been usually fabricated by dry deposition techniques, such as vacuum evaporation deposition [14,15], pulsed laser deposition [2,16], chemical vapor deposition [17,18] and reactive sputtering [19], which can precisely control the stoichiometry of films by monitoring oxygen partial pressure. However, the complex deposition processes and expensive equipments greatly limit their practical applications. In general, wet chemical processes, such as electrochemistry deposition [20], water-quenching approach [8,21] and sol–gel method [13,22–24], are able to resolve the above problems. Among these methods, sol–gel method is more advantageous because of its low-temperature synthesis for both homogeneous and co-doped films with a low cost [25]. The precursor is crucial for the sol–gel process, and vanadium alkoxides (e.g. $VO(OC_3H_7)_3$) has been widely used to synthesize a vanadic sol, however, its expensive and needs a dry atmosphere protection during coating process. A developed sol–gel process using vanadium pentaoxide (V_2O_5) powder as precursor was previously reported to prepare vanadic precursor solution [26], and the VO_2 films prepared via sol–gel method using this precursor solution would be promising to be a stable and low-cost way, which has been not extensively reported.

Moreover, the low visible transmittance of VO_2 films (about 30%) due to strong absorption and reflection also limits their practical applications. Various methods have been developed to achieve higher visible transmittance of VO_2 films, such as fluorination of VO_2 films [27], doping of metal oxide into VO_2 films [28], core–shell structure of nanospheres and VO_2 films [29,30], preparation of VO_2–SiO_2 composite films [13] and formation of VO_2 porous films

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via assembly of VO_2 nanoparticles [31]. However, there still exist some problems including insufficient increase of visible transmittance (less than 10% usually), negative influence of dopants on thermochromic properties and decreased optical transmittance contrast of MIT. The introduction of antireflection coatings (ARCs) on the surface of VO_2 films attracts much attention for many years by using SiO_2 [16,32,33], TiO_2 [34], ZnO [35] or ZrO_2 [36], etc., and is still a promising way to improve the visible transmittance, which is especially useful in industrial applications [37–40]. The ARCs prepared by dry deposition followed by additional heating processes may lead to the change of VO_2 crystalline properties and then destroy the thermochromic performance [18,34,36]. Therefore, a few attempts have been indispensable requirements to obviously increase the transmittance by coating ARCs on VO_2 films at low temperature and simultaneously maintain their excellent thermochromic properties.

In this paper, the VO_2 films were prepared via a stable and low-cost synthesis route using vanadium pentaoxide powder (V_2O_5) as precursor, and the structural, morphological, optical and electrical properties and thermochromic performance of the VO_2 films have been systemically characterized. Nanoporous SiO_2 ARCs prepared good optical transparency was prepared on the surface of VO_2 films by sol–gel dip-coating technique. The synergistic effect of antireflection and thermochromism on VO_2 films by introduction of ARCs was investigated.

2. Experimental

2.1. Preparation of VO_2 films

All chemical reagents in the experiment were purchased from Sinopharm Chemical Reagent Co. Ltd. and used without further purification. The vanadic precursor solution was prepared according to the developed sol–gel process using V_2O_5 powder. V_2O_5 powder was added into the mixed solution of benzyl alcohol and isopropanol under stirring condition, followed by refluxing process at 85 °C for 2 h. The molar ratio of V_2O_5 powder, benzyl alcohol and isopropanol is 1:5:50 as optimized proportion. A transparent organic vanadic sol was obtained by removing the residues and used to prepare V_2O_5 film. The films were prepared via dip-coating technique (Dip Coater, WPTL0.01, MTI Co., China) at a controlled speed range of 3–200 mm/min. The as-prepared vanadic sol was dip-coated on quartz substrates at a typical speed of 50 mm/min and a smooth film of V_2O_5 gel with the thickness of approximate 100 nm was obtained. The V_2O_5 film was heated to 410 °C with a rate of 2.5 °C min^{-1} and hold for 3 h under Ar/H_2 (H_2: 4%) ambient to reduce the V_2O_5 film to VO_2 phase.

2.2. Preparation of SiO_2 coated VO_2 films

The silica sol with a concentration of 0.4 mol L^{-1} was synthesized using tetraethyl orthosilicate (TEOS, AR) as precursor, ammonia as catalyst and ethanol as solvent with a molar ratio of 1:2:40. The silica sol can maintain high stability during long-term storage after removing the catalyst by refluxing process. The as-prepared VO_2 films were dip-coated with silica sol followed by heating at 50 °C for 30 min and the SiO_2 coated VO_2 films were obtained.

2.3. Characterization

The crystalline structure of films was characterized by X-ray diffraction (XRD, Bruker D8 Advance). Surface and cross-section morphologies of films were investigated by field emission scanning electron microscopy (FE-SEM, Hitachi S-4800) with backscatter electron detector (BED). Structure and electron diffraction of films were examined by transmission electron microscopy (TEM, JEM2100F) attached with energy dispersive spectrometer (EDS). Atomic force microscopy (AFM, Seiko II SPI3800V and spa300HV) with a profilometer (Dektak 150) was used to evaluate the surface morphologies and roughness. The distribution and mean values of particles in sols were illustrated by laser scattering particle-size-distribution analyzer (Model LB-550, Horiba). The pore size distribution was obtained by applying Barret–Joyner–Halenda (BJH) model to the adsorption branch of isotherm. Refractive index and extinction coefficient of films were measured by spectroscopic ellipsometer (SC620UVN) prepared on silicon substrates. A double beam spectrophotometer (Hitachi U4100) in the spectral range of 240–2500 nm was used to record transmittance and reflectance spectra of films with control of the temperature interval using a resistively heated tubular holder. The resistivity of film at different temperatures was measured using four-probe technique.

3. Results and discussion

3.1. Structural and morphological properties of VO_2 films

The crystal structure and orientation of VO_2 films were investigated as shown in Fig. 1a. A clear diffraction pattern attributed to the (0 1 1) monoclinic phase of crystalline VO_2 (VO_2 (M), $P21/c$) can be identified while the broad signal is from the substrate. Measurements taken on different parts of the sample show the same characteristics, indicating the homogeneity in their composition and crystallization.

The micrographs of the VO_2 films are also shown in Fig. 1. From the AFM measurement (Fig. 1b), it seems that the surface of the VO_2 films is composed of many grains with average diameter of 103 ± 5 nm. The surface roughness (root mean square, RMS) of VO_2 films is 8.02 nm. According to the SEM image (Fig. 1c), it can be seen that the film has fine nanostructure with well-formed grains uniformly spreading over the entire substrate surface. To further determine the nature of the VO_2 films, the films were observed by TEM as it is shown in Fig. 1d. There are some particulate clusters and interconnected pores among particles, and the crystalline particle surfaces were smooth. The high-resolution TEM (HTEM) image is shown in Fig. 1e, which reveals clear grain boundaries. The composition of the VO_2 films can be analyzed by EDS (Fig. 1f). The elements of V, O, Cu and C are observed where the C and Cu are from the sample holder (e.g. carbon film and copper net). The weight percent of V and O from the selected area are 38.46% and 61.54%, respectively, in other words the molar ratio of V and O is 1.99, which indicates the composition of the VO_2 films agrees well with the stoichiometry.

3.2. Thermochromic performance of VO_2 films

The optical performance of the VO_2 films was measured by spectrophotometer at normal incidence. The optical transmittance spectra of VO_2 films at different temperatures during heating and cooling process were given in Fig. 2a and b, respectively. During heating process, the transmittance of VO_2 film almost decreases with increasing temperature in the infrared region. When cooling down the system, the transmittance increases again showing the reversibility of transition. The transmittance exhibits strong temperature dependence in the infrared region and is practically temperature independent in the visible region. Comparing the transmittance of the film at 20 °C (below T_c) and 90 °C (above T_c) (Fig. 2a), there is almost no change in the visible range (36.0%) while an abrupt decrease of transmittance from 69.3% (at 20 °C) to 11.8% (at 90 °C) at 2500 nm appears. VO_2 film undergoes a MIT at 68 °C from the high-temperature VO_2 (R) phase to a VO_2