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Shape-dependent thermochromic phenomenon in porous nano-structured VO_2 films

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ABSTRACT

In this paper, we report the preparation of thermochromic porous nano-structured VO_2 films. The films with sphere-shaped, stone-shaped, and rod-shaped particles were derived from a sol–gel process with inorganic precursor and polyethylene glycol (PEG). The obtained porous nano-structured VO_2 films show tiny particles (about 20 nm), excellent optical property (light switching efficiency of 67%), and controlled hysteresis loop features (width and slope). The films can be obtained by simply controlling the N_2 flow rate during annealing process, providing an effective process for growing high quality thermochromic porous nano-structured VO_2 films with controllable hysteresis features, which is of great importance in achieving practical application.

1. Introduction

Vanadium dioxide (VO_2) exhibits a reversible semiconductor–metal (S–M) phase transition property at 68 °C, accompanied by dramatic changes in electrical and optical properties [1–3]. Particularly, the phase transition could be triggered thermally or optically [1]. Nano-structured VO_2 thin films are very attractive for optical data storage systems, fiber-optical switching devices, thermal relays and ultrafast optical switching [4–6].

In exploiting nano-structured VO_2 films as "smart material" for technological application, it is essential to understand the physical relation between the nanoparticle or film microstructure and the features of the phase transition, particularly the slope and hysteresis width.

So far, many efforts have been made to tune the hysteresis width and the slopes of individual branches [2,3]. However, some of these processes need high-temperature (1000 °C) annealing and special substrates (Al_2O_3 single crystals or fused silica), the rest of the process require some precision instruments [4,6,7], and the doping process is complicated. Therefore, the development of an easy process to make a thorough investigation of the relationship between microstructure and the S–M phase transition features of VO_2 films is a matter of both scientific and technological significance.

In our previous studies [8,9], we developed a simple process for the preparation of porous nano-structured VO_2 films. This process is rather competitive in practical application for the following advantages: low cost; good control of stoichiometry; easy doping and easy control of crystallinity and microstructure. In this paper, we report the preparation of thermochromic VO_2 films with controlled hysteresis loop features (width and slope) by adjusting the N_2 flow rate. Specifically, we addressed the effects of N_2 flow rate on microstructures, and consequently on S–M transition and hysteresis loop parameters. These phenomenons enable us to regulate the hysteresis loop parameters of VO_2 films wisely, which is of great importance in achieving practical application.

2. Experimental

2.1. Preparation of precursor solution

In a typical procedure of synthesis, 10 g vanadium pentoxide (M = 182, V_2O_5, 99.9% pure) powder was heated to 750 °C in a crucible until molten, and then poured it into 400 ml deionized water at room temperature. After vigorous stirring for 2 h, a brownish sol was formed. The sol was aged for 2 days, then a certain amount of polyethylene glycol (M_{av} = 2000, $HO(CH_2CH_2O)_nH$, PEG; AR) powder was homogeneously mixed with V_2O_5 sol (20 ml) as porous structure directing agent. The surfactant sphere colloids could be anchored to the surface of the V_2O_5 colloids by the combined electrostatic force and hydrogen bonding in the solution. A sticky solution was formed, 10 ml ethanol was

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then added in to dilute it and the blended sol was stirring for 24 h to get brick-red sol.

2.2. Preparation of VO_2 films

The muscovite substrates were pre-treated in ethanol, hydrochloric acid and aqueous ammonia to remove some organic contaminations on the surface of the natural substrates. The deposition was carried out by spin coating method, precursor films were formed on the treated muscovite substrates with a spin speed of 1400 rpm. Then, the films were dried at 90 °C for 20 min. This process was repeated thrice to increase the film thickness. Then the xerogel films were reduced by annealing at 505 °C under different N_2 flow rates for 1 h in a furnace, with a heating rate of 8 °C/min. The resulting films with a thichness of about 150 nm were obtained after cooling down from the annealing temperature. The obtained precursor gel films were reduced into thermochromic VO_2. The samples with different synthesis conditions were defined as sample 1 (under N_2 flow rate of 30 ml/min), sample 2 (under N_2 flow rate of 60 ml/min), sample 3 (under N_2 flow rate of 90 ml/min). The schematic flow chart of the synthesis procedures for porous VO_2 films is shown in Fig. 1.

2.3. Characterization

The morphologies of the films were studied by S-4800 scanning electron microscopy (SEM). The crystalline structure of the films was determined by X-ray diffraction (XRD) using X'Pert diffractometer with Cu Kα (λ = 0.15406 nm) radiation source at an X-ray grazing angle of 1.5°. The optical properties of the films were investigated by Tensor27 (Bruke, Germany) spectrophotometer to analyze the transmittance of the films in the infrared range below and above the phase transition temperature. The temperatures were measured with an appended temperature sensor in contact with the films and it was controlled via a temperature controlling unit. Hysteresis loops were measured by collecting the transmittance of films at a fixed wavelength (4 μm) at approximately 2 °C intervals.

3. Results and discussion

3.1. XPS

Fig. 2 records a typical XPS spectrum at room temperature for the porous nano-structured VO_2 film, and the insert is the enlarged spectrum between 510 eV and 535 eV. The spectrum clearly shows intense peak of V and O, as well as the C 1s at 287.2 eV that is caused by the carbon contaminant on the sample surface. The peak at 516.5 eV is attributed to the $V2p_{3/2}$, which is centered at the V^{4+} position, and the peak at 530.1 eV is associated to O 1s, the weak peak at 523.9 eV presents the $V2p_{1/2}$. The peak positions of O 1s, $V2p_{1/2}$ and $V2p_{3/2}$ are quite in agreement with the results of VO_2 reported by the previous work [10]. This result suggests that the valence of the vanadium in the film is +4. It can be seen from that there are no other impurities introduced to the films. The XRD

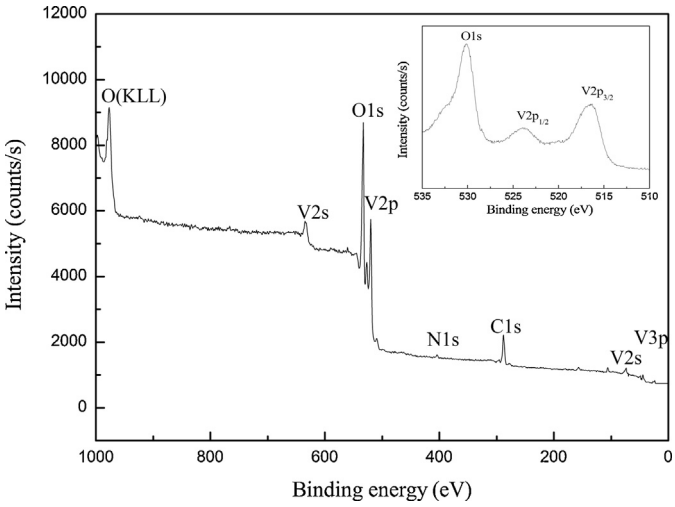

Fig. 2. Surface XPS spectrum of film on muscovite substrates after annealing, the insert is the enlarged spectrum between 510–535 eV.

result (discussed later) of the film also confirms that the obtained vanadium oxide films is stoichiometric and consists of pure VO_2.

3.2. XRD

Fig. 3 shows the XRD patterns for the porous nano-structured VO_2 films. The porous nano-structured VO_2 films are annealed at 505 °C at different N_2 flow rates. All the peaks can be indexed to monoclinic VO_2 (JCPDS Card No. 72-0541), which further verifies the phase purity of the VO_2 phase. Particularly, a sharp diffraction peak at about $2\theta = 27.7°$ is found for the samples, exhibiting (0 1 1) preferred orientation. The peaks at $2\theta = 17.76°$, 23.8°, 26.47°, 29.96°, 35.91°, 45.33°, and 50.06° correspond to different diffraction peaks of muscovite. No other vanadium oxides (such as V_2O_5 and V_2O_3) are detected. The mean crystallite size is calculated to be 17.8, 18.4, and 20.4 nm, respectively.

3.3. SEM

Fig. 4(a)–(c) shows the surface morphologies of the calcined films (calcined at 505 °C/1 h) annealed from the same V_2O_5 film containing PEG at N_2 flow rate of 30, 60, and 90 ml/min.

Our previous work showed that the decomposition of surfactant could enhance the crystallization of VO_2 and impede the crystal growth [8]. A large quantity of tiny particles of VO_2 may form firstly around the surfactant chains and induce the heterogeneous nucleation of VO_2. Thus, the addition of PEG could greatly reduce the mean particle size [2]. It can be seen from Fig. 4(a)–(c) that the particles of porous nano-structured VO_2 films are sphere-shaped, stone-shaped, and rod-shaped particles, respectively. The average crystal dimensions of sample 1 and 2 are nearly 20 nm, whereas the length and width of the nanorod are 50–800 nm and 10–30 nm, indicating that the rate of the N_2 flow rate had a strong effect on the morphology evolution of the porous

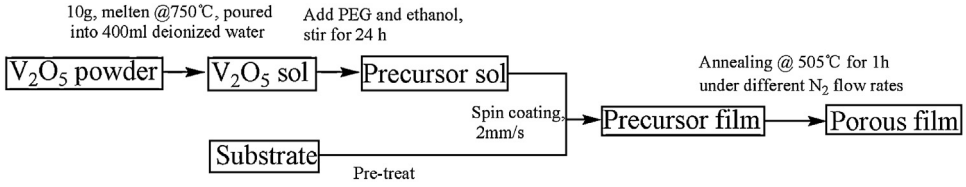

Fig. 1. Schematic flow chart outlines the synthesis procedures for porous VO_2 films.