Thin Solid Films 543 (2013) 157–161

Contents lists available at ScienceDirect

Thin Solid Films

journal homepage: www.elsevier.com/locate/tsf

A low cost preparation of VO_2 thin films with improved thermochromic properties from a solution-based process

Lili Zhao [a,b], Lei Miao [a,*], Sakae Tanemura [a,c,d,**], Jianhua Zhou [a], Lihua Chen [a], Xiudi Xiao [a], Gang Xu [a]

[a] Key Laboratory of Renewable Energy and Gas Hydrate, Guangzhou Institute of Energy Conversion, Chinese Academy of Sciences, Guangzhou 510640, China
[b] Graduate University of Chinese Academy of Sciences, Beijing 100049, China
[c] Powder Technology PJ Lab., Nagoya Institute of Technology, Gokiso-cho, Showa-ku, Nagoya 466-8555, Japan
[d] Japan Fine Ceramic Center, 2-4-1 Mutsuno, Atsuta-ku, Nagoya 456-8587, Japan

ARTICLE INFO

Available online 11 January 2013

Keywords:
VO_2 thin films
Solution-based route
Annealing temperatures
Thermochromic property
W-doped
Phase transition temperature

ABSTRACT

This paper describes a solution-based route to synthesize vanadium dioxide (VO_2) thermochromic thin films on glass substrate by spin-coating technology followed by nitrogen-annealing with vanadium pentoxide (V_2O_5) and oxalic acid ($H_2C_2O_4$) as source material, which is fairly economical and practical. Surface morphologies indicate that the films obtained by this method are homogeneous and particulate, irregular prisms emerge as the annealing temperatures increase. X-ray diffractions show that films annealed at relatively low temperature are pure monoclinic phase with a preferred orientation of (011). NaV_4O_7 and NaV_6O_{15} form along with raising the heating temperatures. VO_2 films obtained exhibit excellent visible transparency and switching property at near-infrared wavelengths across the metal–semiconductor transition. Transmittance change at $\lambda = 2000$ nm of VO_2 thin film annealed at 450 °C attains as high as 41.5% and its solar modulation efficiency reaches up to 8.8%. The W-doped VO_2 film at a doping level of 1 at.% exhibits a thermochromic switch at 37 °C with a narrow hysteresis, which will greatly favor the practical application of VO_2-based smart windows.

1. Introduction

Since Morin first discovered the metal–semiconductor transition (MST) of vanadium dioxide (VO_2), this new frontier has intrigued many researchers for several decades [1]. VO_2 undergoes a thermal-induced reversible first-order phase transition at approximately 68 °C. Above the phase transition temperature, it has a simple tetragonal lattice with the $P4_2/mnm$ rutile space group (R phase) and exhibits metallic property. Below the phase transition temperature, it transforms to a narrow gap (0.7 eV) semiconductor with the $P2_1/c$ space group (M phase) [2,3]. This structure transition is accompanied by significant changes in electrical conductivity, optical transmittance and reflectance in near infrared region. Those properties make VO_2 as a candidate material for a variety of potential advanced applications such as temperature sensing devices, optical switching devices, modulator, data storage medium and smart windows for building/housing energy management, etc. [4–6]. The phase transition temperature (T_t) of VO_2 is one of the most important factors for the technological applications. Different methods, such as doping and strain control, have been proposed to modify the transition temperature closer to the ambient temperature. So far, tungsten is known as the most efficient dopant [2,6], with T_t lowering of 20 °C per 1 at.% in a typical value. Its range of distribution is summarized in the report [7] depending on various films fabrication techniques.

Various approaches have been explored to fabricate VO_2 thin films such as pulsed laser deposition, RF-sputter deposition, ion implantation and chemical vapor deposition [8–13]. These methods reveal superior quality compared to other film deposition techniques, including conformal coverage, high growth rate, high packing density and strong adhesion to underlying layer [14]. However, these methods are usually complex and expensive, which certainly increase the costs for high-throughout manufacturing. Alternatively, chemical solution deposition process such as sol–gel [15,16] and thermolysis [17,18] are preferred for their low cost and large-scale deposition. However, specific raw materials or complex treatments required during the deposition greatly limit their practical application [19]. Therefore, a facile and practical solution-based method is urgently needed. VO_2 thin films can be achieved under convenient procedures via this environment-friendly method.

In order to exploit VO_2 in a practical building envelope as fenestration application, it is important to deposit VO_2 films with excellent thermochromic properties on glass substrates, which are frequently used in industry due to their good transparency and low cost [20]. In our paper, an attempt was made to fabricate VO_2 thermochromic thin films with high visible transmittance and excellent optical

* Correspondence to: L. Miao, Key Laboratory of Renewable Energy and Gas Hydrate, Guangzhou Institute of Energy Conversion, Chinese Academy of Sciences, Guangzhou 510640, China. Tel.: +86 20 87035351.
** Correspondence to: S. Tanemura, Key Laboratory of Renewable Energy and Gas Hydrate, Guangzhou Institute of Energy Conversion, Chinese Academy of Sciences, Guangzhou 510640, China.
E-mail addresses: miaolei@ms.giec.ac.cn (L. Miao), fwhy7074@mb.infoweb.ne.jp (S. Tanemura).

0040-6090/$ – see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.tsf.2012.11.154

modulation in near infrared region on amorphous glass substrates by a simple solution-based route. The effect of annealing temperatures on the morphology, structure and optical properties of VO_2 films were investigated in detail. W-doped VO_2 film was also synthesized to decrease the phase transition temperature (T_t).

2. Experimental details

2.1. Starting materials

Vanadium pentoxide (V_2O_5, AR) and oxalic acid ($H_2C_2O_4$, AR) were used as starting materials to prepare the vanadium precursor solution. Ethyl alcohol was used as the solvent. Ammonium tungstate hydrate ($(NH_4)_5H_5[H_2(WO_4)_6]\cdot H_2O$, AR) was chosen for tungsten doping. All of these reagents were used without further purification.

2.2. Preparation of VO_2 films

The precursor solution of VO_2 films was prepared by the following procedures: 4.55 g V_2O_5 was reduced by $H_2C_2O_4$ under reflux in ethyl alcohol at 120 °C for 10 h, then a transparent blue solution of $VOC_2O_4\cdot xH_2O$ was formed. The reaction occurred as follows [21]:

$$V_2O_5 + 3H_2C_2O_4 = 2VOC_2O_4 + 2CO_2 + 3H_2O.$$

The tungsten-doped VO_2 film was synthesized by the addition of $(NH_4)_5H_5[H_2(WO_4)_6]\cdot H_2O$ aqueous solution to the $VOC_2O_4\cdot xH_2O$ solution. The amount of the additive was carefully controlled for the realization of a fixed W doping level up to 1 at.%. The precursor solutions were aged for 2 h at room temperature before spin coating.

Slide glasses (25×25 mm^2) were cleaned ultrasonically in acetone, ethanol and deionized water to remove organic and cation contaminations on the surface of the glass. This treatment was necessary for the formation of uniform and adherent films. Films were deposited on the glass substrate by spin coating using the precursor solutions at 600 rpm for 10 s and then 3000 rpm for 20 s. After drying at 60 °C for 10 min to remove the excess solvent, smooth films were formed. Then the as-prepared films were transformed to VO_2 films after annealing at various temperatures between 400 and 550 °C by the step of 5 °C/min in nitrogen atmosphere.

2.3. Characterization

The surface morphology of the VO_2 thin films were investigated using a field emission scanning electron microscope (FESEM, S-4800, Hitachi Japan) under the operating voltage of 2 kV. X-ray diffraction patterns were recorded by an X-ray diffractometer (XRD, PANalytical X'pert Pro MPD) in the 2θ range of 10–80° with the step of 0.0083° using Cu-Kα radiation ($\lambda = 1.54178$ Å). The accelerating voltage is 40 kV and the current is 40 mA. Ultraviolet–visible-near infrared spectrophotometer (UV–Vis–NIR, Lambda 750) was employed to characterize the optical switching properties of the films, from 250 to 2500 nm at temperature 30 °C and 100 °C, respectively. Temperature was measured with the assistance of a sensor in contact with the films which was connected with FP23 temperature controlling unit. Hysteresis loops were measured by collecting the transmittance of films at a fixed wavelength (2000 nm) at an approximate temperature interval of 2 °C.

Detail parameters of the hysteresis loops are obtained as follows. Plots of d(Tr)/d(T) & T are obtained from the hysteresis loops. Fitting each of the d(Tr)/d(T) & T curves by Origin pro 8.0 software, and a peak with well-defined maxima is yielded. The temperature ($T_{c,h}$ and $T_{c,c}$) corresponding to the maxima is defined as the phase transition temperature (T_c) of the heating and cooling branch with additional suffix *h* and *c*, respectively. The phase transition temperature (T_t) of VO_2 thermochromic films is defined to be $T_t = (T_{c,h} + T_{c,c})/2$ [22].

3. Results and discussion

3.1. XRD

Fig. 1 shows the X-ray diffraction patterns of VO_2 films annealed at different temperatures. A broad amorphous background peak, which stretches from 15 to 38°, is attributed to the amorphous glass substrates [20]. All of the film samples exhibit apparent diffraction peaks at $2\theta = 27.86°$ and 55.65° (denoted by star (☆)), which can be indexed to (011) and (220) planes of M-phase VO_2 (JCPDS card No. 72-0514, $P2_1/c$, $a = 0.574$ nm, $b = 0.452$ nm, $c = 0.538$ nm, and $\beta = 122.61°$), respectively [3]. In addition, the (011) peak is dominant, while the (220) peak is weak, indicating that the film has a strong preferred orientation [23]. The intensity of the (011) plane significantly increases as enhancing the annealing temperature, indicating that the crystallinity of film is improved.

For films annealed at 450, 500 and 550 °C, the film samples exhibit an additional weak diffraction at ~18° (denoted by inverse triangle (▼)), which is assigned to NaV_4O_7, and this peak intensifies as raising the annealing temperature from 450 to 500 °C. Two new peaks (denoted by empty rhombus (◇)) appeared in the XRD spectrum of the film annealed at 550 °C are identified to be NaV_6O_{15} (curve (d) in Fig. 1), but the diffraction intensity of NaV_4O_7 decreases simultaneously. The emergence of NaV_4O_7 and NaV_6O_{15} could be particularly attributed to Na ion diffusion from the glass substrate as increasing the temperature of post-annealing.

3.2. SEM

The thin films obtained from our method are observed to be yellowish-brown, which is the characteristic color of monocline/rutile phase VO_2. With increasing the annealing temperature, the characteristic yellow-brown color bleaches out slightly, which might be attributed to the formation of NaV_4O_7 and NaV_6O_{15}. The morphology and microstructure of VO_2 films annealed at 400, 450, 500 and 550 °C are presented in Fig. 2, respectively. The distinctive morphological changes have been observed due to the different annealing temperatures. For film annealed at 400 °C (Fig. 2(a)), the homogeneous film with uniform particulates covers the glass substrate entirely and exhibits a porous structure in nano-scale. The average grain size is estimated to be 30–40 nm. As seen in Fig. 2(b), slight grain growth is displayed in film treated at 450 °C, and a trace of irregular prisms appear at the same time. The amount of prisms increases as the annealing temperature increases to

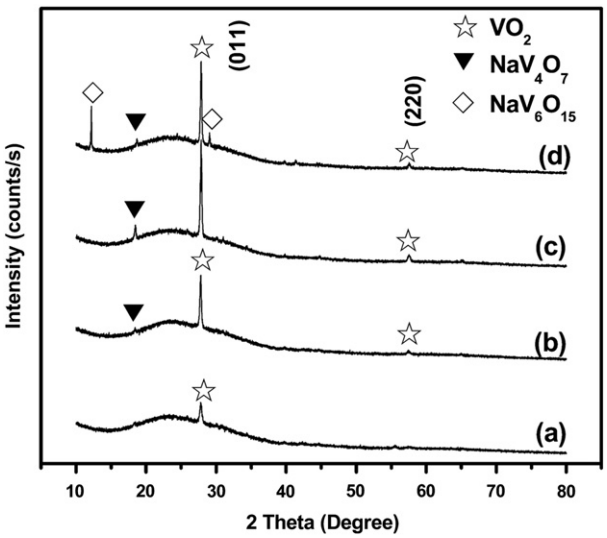

Fig. 1. XRD patterns of VO_2 films prepared at different annealing temperatures on glass substrates. (a) 400 °C; (b) 450 °C; (c) 500 °C; and (d) 550 °C.