Applied Surface Science 268 (2013) 556–560

Contents lists available at SciVerse ScienceDirect

Applied Surface Science

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

# Effect of annealing temperature on thermochromic properties of vanadium dioxide thin films deposited by organic sol–gel method

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ARTICLE INFO

*Article history:*
Received 27 April 2012
Received in revised form 3 December 2012
Accepted 2 January 2013
Available online 9 January 2013

*Keywords:*
Organic sol
$VO_2$ thin films
Thermochromic
Annealing temperature

ABSTRACT

This paper described the synthesis of vanadium dioxide ($VO_2$) thin films on mica substrates with different annealing temperatures by an organic sol–gel method. We performed X-ray diffraction, scanning electron microscope and optical transmission measurements to investigate the effect of the annealing temperature on the crystalline structure, morphology, and phase transition properties of these films. The results showed that a polycrystalline structure with high crystallinity and compact surface at the annealing temperature of 500 °C. The film exhibited a $V_6O_{13}$ phase and a flat surface with small grain size at 440 °C. By contrast, the $V_nO_{2n-1}$ appeared when the annealing temperature at 540 °C, and the film surface split into segregation of spherical grain and aggregates of continuously dendritic particles. Accordingly, the optimal annealing temperature was 500 °C using the organic sol–gel method. And it turned out that the films mainly contained $VO_2$ (M) phase at room temperature with high content of $V^{4+}$ valence. Particularly, the films showed different changes in the infrared transmittance and hysteresis width during the phase transition. The largest transformation of the infrared transmittance before and after MIT was 73%, while the narrowest temperature hysteresis width was 8 °C at 500 °C.



## 1. Introduction

Vanadium dioxide ($VO_2$) is a functional material that undergoes a reversible metal-insulator phase transition (MIT) at a critical temperature (*Tc*) of 68 °C, accompanying the structural transition from high-temperature rutile to low-temperature monoclinic phases [1,2]. The semiconductor to metal transition exhibits abrupt changes in optical, electrical and magnetic properties [3]. Therefore, these characteristics make $VO_2$ a promising material for a wide variety of applications including thermal sensors, uncooled microbolometers, and electrochromic switching devices [4–10].

Many methods have been developed to deposit $VO_2$ thin films with high performance, including physical vapor deposition [11,12], chemical vapor deposition [13–15] and sol–gel method [16–18]. Sol–gel method is used widely because of many advantages. It can be coated on complex shape or large substrate surface. It is easy to introduce other elements for doping [19–21]. Furthermore, special organic–inorganic multiple coating can be obtained by sol–gel method. Inorganic sol–gel method makes use of ordinary raw materials. However, it needs rigorous experimental condition because of high annealing temperature [22]. Meanwhile, organic vanadium alkoxides such as $VO(OC_3H_7)_3$ [15,23], $VO(i\text{-}OC_2H_5)_3$ [24] and $V(C_5H_7O_2)_3$ [17] were used as precursor to prepare $VO_2$ thin films in organic sol–gel method, they are expensive by commercial purchase.

In order to solve this problem, the $V_2O_5$ powder, isobutyl alcohol (IBA) and benzyl alcohol (BA) have been utilized to prepare organic precursor sol and vanadium oxide thin films [25]. In this paper, we presented the realization of $VO_2$ thin films on mica substance by this organic sol–gel method. Some simple equipments and procedure were utilized. It could save the cost for the organic precursor obtained at low temperature. Meanwhile, Part of $V^{5+}$ ions were reduced to $V^{4+}$ ions in organic precursor, which could simplify the subsequent heat treatment process. Lipophilic organic solvents were in favor of sol rapidly spreading out on mica substrate and improving adhesive force. All the results indicated that the $VO_2$ thin films prepared by this organic sol–gel method exhibited good properties.

## 2. Experimental procedures

### 2.1. Organic vanadium sol preparation

Vanadium pentoxide powder was suspended in a mixed solution of IBA ($C_4H_{10}O$) and BA ($C_7H_8O$) at a certain molar ratio ($V_2O_5$:$C_4H_{10}O$:$C_7H_8O$ = 1:80:8) with a process of refluxing at 110 °C for 4 h. A clear sol of the organic vanadium was obtained after filtration of insoluble residue by pumping filter.

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http://dx.doi.org/10.1016/j.apsusc.2013.01.007

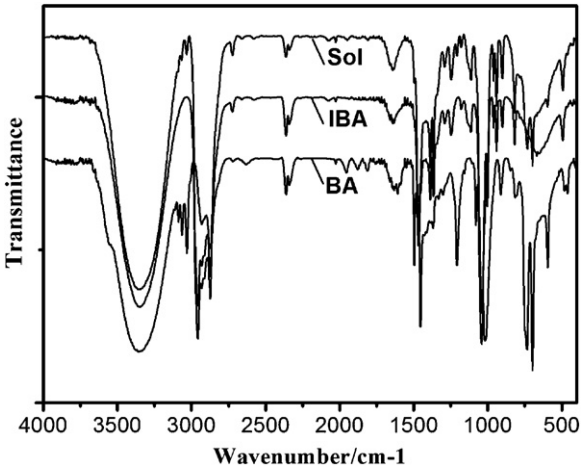


**Fig. 1.** FTIR spectrum of the organic solvents and sol on KBr plates.

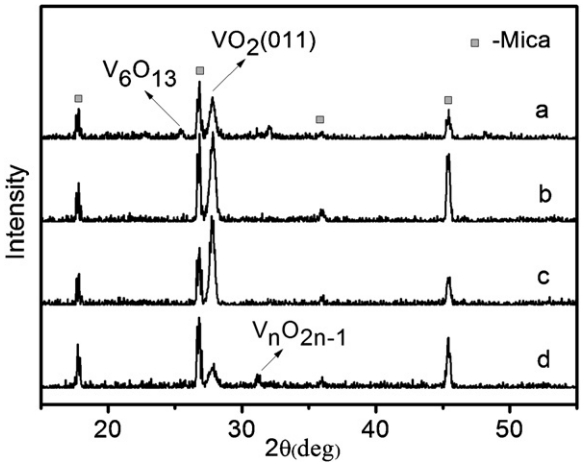


**Fig. 2.** XRD patterns of $VO_2$ films on mica plate annealed at (a) 440 °C, (b) 460 °C, (c) 500°C and (d) 540 °C.

### 2.2. Thin films preparation

Mica substance were sequentially pretreated acid solution ($HCl:H_2O_2:H_2O = 2:2:5$) and alkaline solution ($NH_3{\cdot}H_2O:H_2O_2:H_2O = 2:2:5$) [26]. It was cleaned with deionized water, soaked in ethanol for several hours, and then dried at 50 °C.

The spin-coated sol was prepared on mica substance at 1000 rpm for 9 s which repeated five times in order to obtain the films with a certain thickness. Xerogel films were annealed in the tube furnace at 440 °C, 460 °C, 480 °C, 500 °C, 520 °C and 540 °C under the heating rate of 8 °C/min, respectively. Nitrogen was introduced into the tube furnace for getting rid of air about 30 min at the beginning of annealing process and the flow velocity of nitrogen was 50 ml/min. During the annealing process, the system was hermetic and the films was annealing hermetically in static nitrogen atmosphere. And then $VO_2$ films were obtained after cooling to room temperature with the same velocity of nitrogen.

### 2.3. Characterization methods

Samples were characterized by X-ray diffraction (X'Pert, Philips, Holland) with Cu Kα radiation. The compositions of the films were detected by X-ray photoelectron spectroscopy (X'sam, Kratos, UK). The morphology of thin films was determined by scanning electron microscopy (JSM-5900LV, Electronics Co. Ltd, Japan). Fourier transform infrared spectroscopy (Tensor 27, Bruker, Germany) with a heating temperature control device was utilized to analyze the transmittance the thermo chromic characteristics of the films in the mid-infrared range.

## 3. Results and discussion

### 3.1. FTIR spectrum of sol

Fig. 1 shows the FT-IR spectra of the organic solvent and sol on KBr plates in the spectral range at 4000–400 $cm^{-1}$. Two strong absorption peaks near the wavenumber of 3300 $cm^{-1}$ and 3000 $cm^{-1}$ were corresponding to the O—H vibration of alcohol and bending vibration of $—CH_2—$, respectively. Moreover, peaks at 1500 $cm^{-1}$ were connected to $—CH_3$ and C—H stretching vibration. The large absorption around 1000 $cm^{-1}$ was in accordance with $—CH_3$ bending vibration, C—O stretching vibration and O—H plane bending vibration. Furthermore, absorption peaks at 700–800 $cm^{-1}$ were related to the $—(CH_2)_n—$ plane rocking vibration or the single replace of the C—H on benzene ring [27].

All vanadium-related peaks in Fig. 1 could not been judged in the presence of organic precursor due to the high content and strong absorption peaks of organic solvents. However, characters and color of the precursor prepared could be identified that reaction procedure probably occurred as follows [28].

Generation of organic vanadium precursor solution:

$$4C_4H_{10}O + V_2O_5 \rightarrow 2VO(i\text{-}OC_4H_9)_2 + 2H_2O \quad (1)$$

$$Or6C_4H_{10}O + V_2O_5 \rightarrow 2VO(i\text{-}OC_4H_9)_3 + 3H_2O \quad (2)$$

Hydrolysis reaction of the precursor solution of vanadium:

$$2VO(i\text{-}OC_4H_9)_3 + 2H_2O \rightarrow 2V(OH)O\text{-}(C_4H_9)_2 + 2\,C_4H_{10}O \quad (3)$$

Condensation of organic precursor of vanadium:

$$2V(OH)O\text{-}(C_4H_9)_2 \rightarrow V_2O_3(—OC_4H_9)_2 + H_2O \quad (4)$$

### 3.2. XRD investigation

Fig. 2 shows the XRD patterns of films annealed at different temperatures. It could be seen that all samples exhibited three strong diffraction peaks at $2\theta = 17.8°$, 26.87°, 35.9°, 45.49° assigned to the mica substrate (JCPDS 07-0042). A typical crystalline diffraction pattern of monoclinic structure of $VO_2$ is observed at $2\theta = 27.86°$ (JCPDS 09-0142), which indicated that crystalline $VO_2$ was successfully prepared after annealing. Particularly, the peak around $2\theta = 27.86°$ exhibits the (0 1 1) preferred orientation. In addition, other kinds of vanadium oxide diffraction peaks are not found in Fig. 2(b) and (c) of the samples prepared at 460 °C and 500 °C. This fact indicates that most of $V^{5+}$ ions are reduced to $V^{4+}$ ions. However, a diffraction peak appears at $2\theta = 25.42°$ in Fig. 2(a) corresponding to $V_6O_{13}$ probably due to the insufficient reduction of $V^{5+}$ at low annealing temperature. The XRD pattern of Fig. 2(d) reveals a peak at $2\theta = 31.2°$ which could be attributed to various forms of $V_nO_{2n-1}$ such as $V_2O_3$. Therefore, it can be concluded that the annealing temperature range of 460–500 °C is more suitable for preparing the $VO_2$ thin films. The relatively low annealing temperature could be explained with deoxidizing part of $V^{5+}$ in the organic sol preparation process. Although all of the films exhibit polycrystalline structures, the full width at half-maximum (FWHM) of the (0 1 1) peaks is quite different from each other, which is 0.465°, 0.449°, 0.401°, and 0.408° from (a) to (d), respectively. The optimal crystallinity was obtained at 500 °C.