EFFECT OF ANNEALING TEMPERATURE AND AMBIENT ON CRUCIAL PHYSICAL PROPERTIES OF SOL-GEL DERIVED VANADIUM OXIDE THIN FILMS

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ABSTRACT

The vanadium oxide thin films were deposited by sol-gel method using vanadyl acetylacetonate as a starting precursor for vanadium source. The precursor was deposited onto cleaned glass substrate by conventional dip coating process with drawing speed of 80 mm/min. The coating process was repeated 5 times with baking process at 60°C during each coating followed by annealing process. In order to extensively study the influence of annealing temperature and ambient on crucial properties of the deposited films, the annealing process was conducted at different temperatures ranging from 200°C to 400°C under different ambient including air and nitrogen atmosphere. The crystalline structures and phases of the annealed films were observed and analyzed by mean of X-ray diffraction technique meanwhile their morphological features were investigated by scanning electron microscope. The optical properties of the prepared films were measured by UV-Vis NIR spectrometer. The extensive studies and results acknowledge that both temperature and atmosphere during annealing process play significant roles on pivotal properties of the films, especially optical characteristics which are highly essential for specific thermochromic applications.

KEYWORDS: *Vanadium oxide; Annealing process; Sol-gel method*

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INTRODUCTION

Vanadium dioxide (VO_2) is one of transition metal oxide materials which is known to undergo a phase transition around 68°C from a semiconductive monoclinic phase to a metallic rutile phase [1]. This phase transition is accompanied by abrupt change in electrical conductivity, optical transmittance and reflectance in near-infrared region [2–3]. Therefore, this exceptional characteristic make VO_2 being widely used in surface coating in various technological applications such as thermochromic smart window, thermal sensor and switching devices [4–9].

VO_2 thin films have been prepared by various methods including chemical-vapor deposition (CVD) [10, 11], sputtering deposition [12], pulsed-laser deposition (PLD) [13, 14] and sol-gel method [15–17]. Among these methods, sol-gel method has been commonly used to synthesize VO_2 because of the simplicity and cheapness. In addition, it can be coated on large substrate surface that can meet commercial purpose. There are different precursors used for preparing vanadium oxide-based thin films via sol-gel method, such as V-alkoxide [18–20], V_2O_5[21] and V-halide[22]. In general VO_2 film deposition via sol-gel route, annealing process is one of crucial processes used to obtain desired thin films. Guo et al. [23] investigated the effect of annealing time period on structural evaluation and electrical properties of vanadium oxide thin films deposited by sol-gel method. It was acknowledged that the annealing time highly affected the phase structure and morphology of the films. Li et al. [24] investigated the effect of annealing in air at different temperatures on thermal stability of VO_2 films synthesized by sol-gel method. It was reported that air annealing above 300 °C resulted in the oxidation of VO_2 to V_2O_5.

In this work thin films of vanadium oxide have been deposited on glass substrate by sol-gel method using the vanadyl acetylacetonate $VO(acac)_2$ as starting material. The precursor solution was used for thin film dip coating after aging a week or more. The effect of annealing

temperature and ambient on morphology, structure and optical property of the films were investigated.

MATERIALS AND METHODS

Preparation of precursor solution

The vanadium oxide thin films were deposited by sol-gel method using an acetylacetonate as a precursor for vanadium source. First, 1.65 g of vanadyl acetylacetonate $VO(acac)_2$ was added into methanol (50 ml) with a designated concentration of 0.125 mol/l. The solution was stirred at room temperature for 1h until a homogeneous deep blue/green color precursor was reached. The precursor was then aged for 20 h that made the color change to red-brown.

Preparation of vanadium oxide thin films

The precursor solution became usable for thin film dip coating after aging for a week. Prior to coating, glass substrates were cleaned in acetone and deionize water. The film was dip-coated onto the substrate with drawing speed of 80 mm/min. The coating process was repeated 10 times with baking process at 60 °C for 5 min to remove some solvent. Then, Annealing process was carried out under different ambient in air and nitrogen atmosphere at different temperatures ranging from 200 °C to 400 °C.

Characterization

The samples were characterized by X-ray diffraction technique for the crystalline structure and phase identification of the films. (Rigaku, Smartlab) The oxidation states of vanadium were detected by X-ray photoelectron spectroscopy. The measurement was conducted at Beamline 5 of Synchrotron Light Research Institute, Nakhon Ratchasima, Thailand.

The surface morphology of deposited films was investigated by Field EmissionFE-SEM S-4700 Hitachi). The optical properties of the prepared films were measured by UV-Vis NIR spectrometer (PG, T90+). The structure deformation of precursor during aging was analyzed by FT-IR (Thermo Scientific Nicolet 6700).

RESULTS AND DISCUSSION

XRD

The crystalline structures and phase of annealed films were analyzed by X-ray diffraction technique. Fig. 1 shows the XRD patterns of the prepared films annealed at different temperatures ranging from 200 °C to 400°C under different ambient including air and nitrogen atmosphere. In Fig. 1(a), there is no shape peak, which means that the sample had not yet crystallized. The broad XRD pattern observed in the 20°- 40° is originated from typical diffraction pattern of glass substrate. On the other hand, as noticed in Fig 1(b), there are two noticeable diffraction peaks positioned at 37.2° and 43.2° appears the annealing temperature at 300 °C under nitrogen atmosphere that can be indexed to the (200) and (003) lattice plane of VO_2 (M) (JCPDS 43-1051) and V_2O_5(JCPDS 89-0611) phase. Correlated results indicate that the annealing temperature beyond specific point of around 300 °C under nitrogen ambient could considerably improve its crystallinity and crystal orientation of the films. As annealing temperature elevates to 400 °C, the corresponding XRD peak intensities of the film become sharper and more intense, suggesting the enhancement in its grain growth and crystallinity due to thermal energy assisted nucleation.

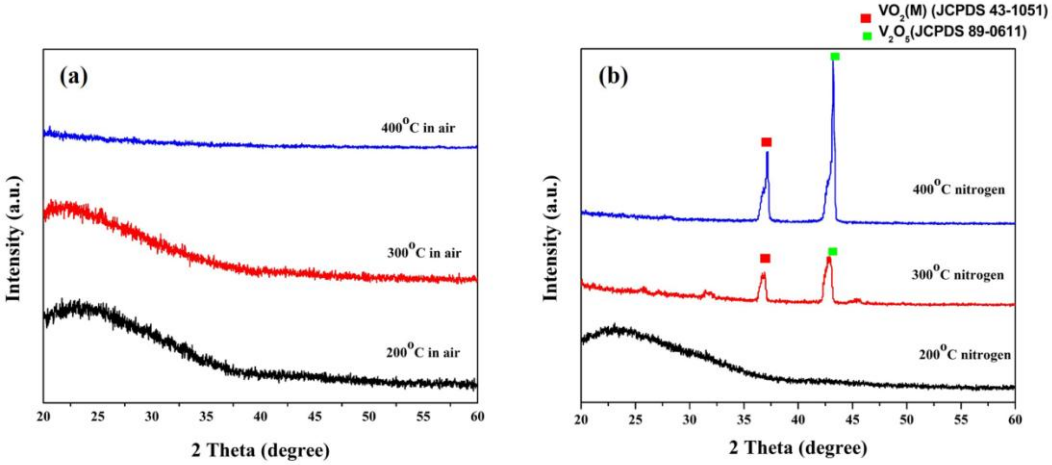

Fig. 1 XRD patterns of the vanadium oxide thin films on glass substrate annealed at different temperature under different ambient (a) air atmosphere and (b) nitrogen atmosphere.

Valence state of vanadium

The oxidation states of vanadium oxide thin film were investigated by X-ray photoelectron spectroscopy. The measurement was conducted on the film annealed at 400 °C for 3 h in ambient air. The wide scan spectrum and core-level spectra between 510 eV and 528 eV of the film are shown in Fig. 2. In Fig. 2(a), the XPS results indicate the existence of five major elements including carbon, sodium, silicon, vanadium and oxygen. The sodium and silicon signals typically originate from the glass substrates. The C1s is used for reference.

The V_{2p} XPS spectra of the vanadium oxide V_2O_5, VO_2 and V_2O_3 vanadium were characterized to determine the V_{2p} XPS fit parameters, (binding energy (BE)) for the vanadium oxidation states;V^{5+}, V^{4+} and V^{3+}. The binding energy of the $V_{2p3/2}$ core-level for each vanadium oxidation state is presented in Fig. 2 (b). The core-level spectrum of V_{2p} explicitly indicates three vanadium valence states, V^{5+} with a binding energy of 516.90 eV [25], V^{4+} with a binding energy of 516.25 eV [25] and V^{3+} with a binding energy of 514.86 eV [25].

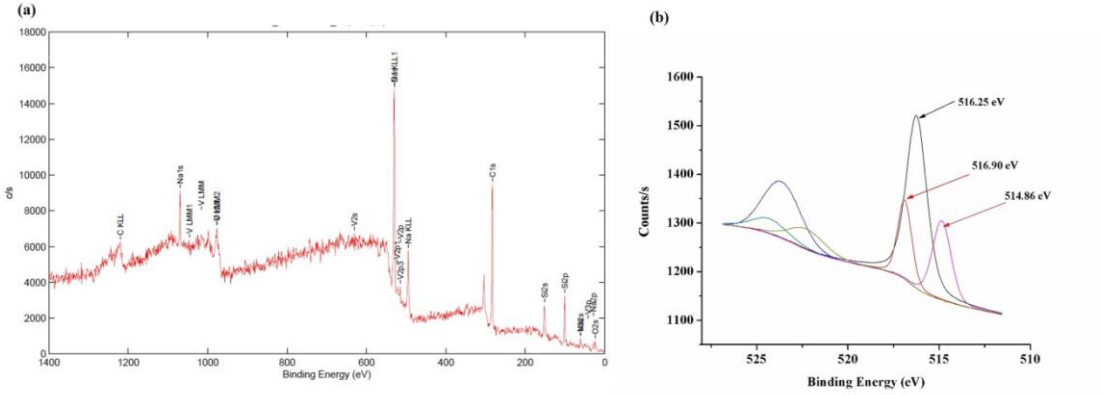

Fig. 2 XPS spectrum of the vanadium oxide thin film under air-annealed at 400 °C for 3h (a) surface spectrum and (b) the corresponding V_{2p} peaks.

Optical properties

The optical transmittance of the films was studied by UV-Vis spectroscopy within a range of 300 to 600 nm conducted at room temperature as shown in Fig. 3. In Fig. 3 (a) and (b), the transmission of film annealed in nitrogen atmosphere is much higher than the film annealed in air. This occurrence is probably originated from the truth that the film annealed in nitrogen atmosphere may enhance surface roughness and limit the supplied oxygen species for oxidization. The optical band gap energy of the film was evaluated using the Tauc relation [27].

$$(\alpha h\nu) = A\,(h\nu - E_g)^{1/2} \qquad (1)$$

Noted here that, $h\nu$ is a photon energy, α is the absorption coefficient, Eg is band gap energy, A is a constant. The band gap energy was can be evaluated from the plot of $(\alpha h\nu)^{1/2}$ and hv at different temperatures and different ambient as shown in Fig.4 (a) and (b), respectively. The band gap energies were estimated for each film and indicated in Table 1. As seen in the table the optical band gap energy increases with annealed in nitrogen ambient the optical band gap energy decreases with increasing temperature.

In addition, the film annealed in nitrogen atmosphere possesses direct energy band gap of approximately 2.9 to 3.4 eV due to the band edge transition for the band gap of V_2O_5 [28–30]. The band gap energy of the V_2O_5 films were found to increase with decreasing temperature as shown in Fig. 3 (b), which may be because of the lattice dilation effect with decreasing temperature.

Table 1 Temperature dependence on optical band gap energy of thin films

Temperature (°C)	Band gap energy (eV) in air atmosphere	Band gap energy (eV) in nitrogen atmosphere
200	2.98	3.36
300	3.15	2.26
400	3.18	1.17

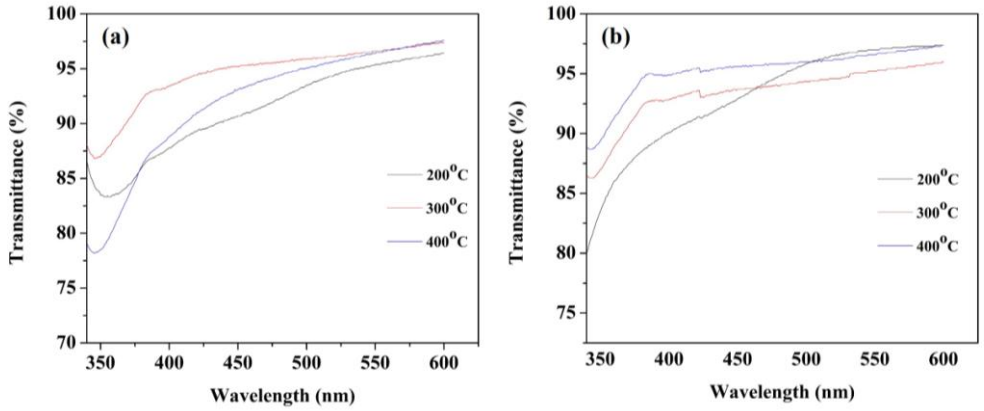

Fig. 3 Transmittance spectra of the vanadium oxide thin films annealed at different temperature under different ambient (a) air atmosphere and (b) nitrogen atmosphere.

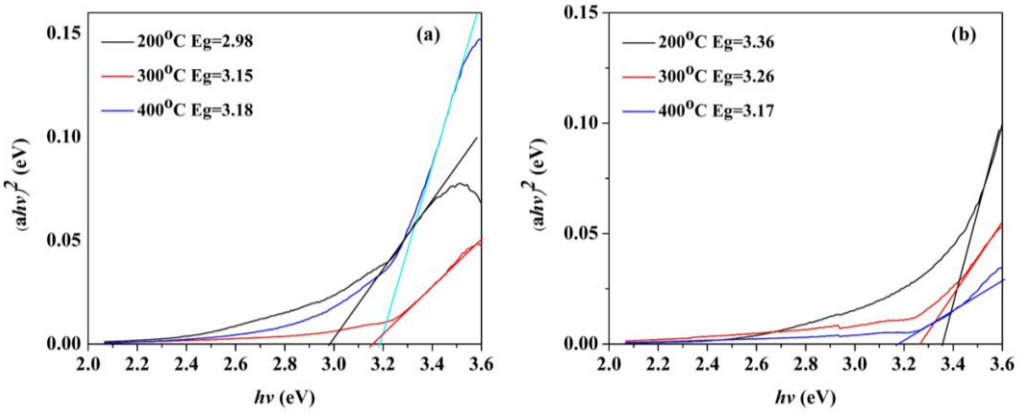

Fig. 4 Energy band gap of the films annealed at different temperature under different ambient (a) air atmosphere and (b) nitrogen atmosphere.

Surface morphology

The scanning electron micrographs of the films on glass substrates are presented in Figure 5. The thickness of films are measured to be about 51–52 nm in air and nitrogen atmosphere as shown in Fig.5(c) and (d). In Fig.5 (a), the grains of films annealed in air atmosphere is greater than the film annealed in nitrogen since the film annealed in nitrogen ambient may restrain grain growth. In addition Fig.5 (b), the film annealed in nitrogen atmosphere shows a flat surface that was formed closely connected. Results indicate that the annealing process significantly affects the morphologies of the films.

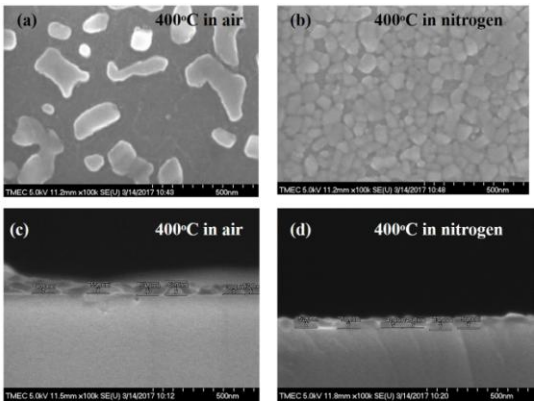

Fig. 5 SEM images of the films annealed at different ambient at 400 °C for 3 hours: (a) annealing in air atmosphere, (b) in nitrogen atmosphere. Cross-section images of VO films in (c) air atmosphere and (d) nitrogen atmosphere.

IR vibration

The infrared spectra of the films deposited on glass substrate annealed at different temperatures and different ambient are shown in Fig. 6 (a) and (b). As observed in all annealed films, the peaks situated around 900 cm^{-1} can be assigned to the VOH_2 stretching vibrational mode indicating the formation of coordination bonds with vanadium atoms. [31–32]. In addition, the pronounced band located at wave number lower than 500 cm^{-1} is typically assigned to metal-oxygen interaction confirming the formation of vanadium oxide compound of the deposited films.

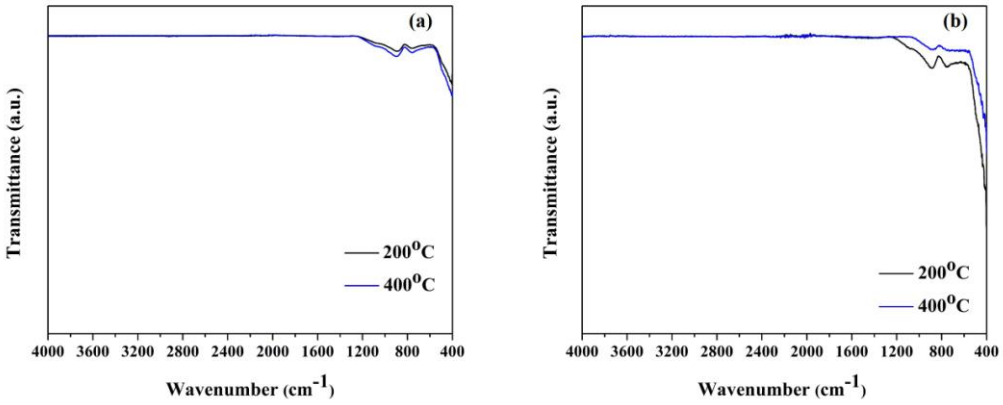

Fig. 6 FTIR spectra of the films annealed at different temperature under different ambient (a) air atmosphere and (b) nitrogen atmosphere.

CONCLUSION

In summary, the vanadium oxide thin films were prepared on glass substrates by sol-gel dip-coating process. Under nitrogen atmosphere, the XRD and SEM results showed the phase structure with quite crystallinity and compacts surface as the annealing temperature at 400 °C. The optical analysis indicated that the transmission of film annealed in nitrogen atmosphere is higher than the film annealed in air at the annealing temperature of 400 °C. From all results, the annealing temperature and ambient affect to the crystalline structure of VO thin films.

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