Low-Temperature Synthesis of Vanadium Dioxide Thin Films by Sol-Gel Dip Coating Method

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1. Introduction

Vanadium oxide presents a partly-filled 3d orbital, leading to the formation of several oxides such as VO, V₂O₃, V₄O₇, VO₂, V₂O₅, and V₆O₁₃, which all belong to the series of Magneli (VₙO₂n₋₁) and Wadsley (V₂nO₅n₋₂) systems [1–3]. Among these oxides, monoclinic vanadium dioxide (VO₂ (M)) has gained most attention owing to its fascinating thermochromic property that can switch a phase structure reversibly between a monoclinic (semiconductor) and a rutile (metal) phase at about 68°C [3, 4] in response to external stimuli, leading to dramatic changes in the electrical and optical properties. The change of optical property from infrared-transmitting at low temperature to infrared-reflecting at temperatures higher than the monoclinic-rutile phase transition temperature, while maintaining the visible transmittance, makes the vanadium dioxide a promising candidate as thermochromic coating for a variety of devices such as smart windows, tunable absorbers and emitters, and thermal rectification [4, 5].

The thermochromic VO₂ (M) thin films have been prepared by several methods. The most typical methods include physical vapor deposition, chemical vapor deposition, and sol-gel method. The physical and chemical vapor depositions can precisely control the stoichiometry of films by monitoring oxygen partial pressure. However, the complex deposition processes and expensive equipment significantly limit their practical applications [6, 7]. The sol-gel method has been widely employed for material investigation because of several advantages. For instance, it can be coated on complex shape, large substrate. The process is of low cost, and there is easy control of reaction kinetics and
atomic doping. In addition, lower calcination temperature is typically required to obtain crystalline structure [8–10]. In a typical sol-gel process for VO₂ preparation, a V⁵⁺-containing precursor is firstly prepared, and then the precursor is deposited onto a clean, hydrophilic substrate through dip or spin coating. The obtained sample is dried and calcined typically at ≥600°C [11–13] to form an amorphous phase to a desired crystalline structure. Meanwhile, part of V⁵⁺ ions was reduced to V⁴⁺ ions [8, 11].

For commercial applications, such as smart window coating, glass is the desirable substrate. The soda lime glass is during calcination, to prevent film’s surface from oxidation methods reported in literatures employed low vacuum pressure, calcination temperature, and steps in the typical sol-gel process for VO₂ preparation, a V⁵⁺-containing precursor solution was prepared according to the literature [17, 18]. In a typical synthesis method, 0.3 g V₂O₅ powder (99.5%, Sigma-Aldrich Co., Ltd.) was dissolved in 30 mL 30% H₂O₂ (35%, Chem-Supply Co., Ltd.) with rigorous stirring for 30 min. At this step, the reaction was strongly exothermic, and the solution’s color changed from yellow to dark red sol upon a continuous stirring. After the two chemicals were mixed and aged for 2 days at room temperature, thin films were obtained by dip coating method using a dip coater (Model DC-150) performed at a dipping time of 2 min and a withdrawal rate of 6 mm/min on a glass slide substrate. The substrates were cleaned by means of ultrasonication for 30 min in deionized water, 20% acetone, 70% iso-propanol, and 20% ethanol, respectively. The as-deposited thin films were dried in ambient air for 24 h. The dried thin films were calcined at room temperature, 400, 450, and 500°C, in vacuum tube furnace at pressures of 2 × 10⁻² and 2 × 10⁻³ mbar. To investigate an effect of heat treatment, calcination was conducted by 1- and 2-step calcination, in which each step employed a heating rate of 2°C/min and soaking time of 3 h. For the 1-step calcination, the thin films were heated in a tube furnace to 400, 450, and 500°C, soaked at this temperature for 3 h, and cooled down to room temperature. The 2-step calcination was carried out in a tube furnace at 500°C using the same heating and cooling cycles, noted that the glass slide substrate employed in this work began to soften at a temperature of ~500°C; thus, calcination temperature did not exceed 500°C. Process parameters for film deposition are provided in Table 1.

2.2. Thin Film Characterization. Crystal structure characterization of the thin films was performed by using an X-ray diffractometer (XRD; Rigaku TTRAX III). Morphology and thickness were studied by using a scanning electron microscope (SEM; Quanta 400 FEI) performed in a top and tilted view, respectively. Films’ compositions, as well as an elemental mapping, were analyzed by using an energy dispersive X-ray spectrometer (EDS). Oxidation states of the elements were analyzed by using an X-ray photoelectron spectrophotometer (XPS; AXIS Ultra DLD). The binding energy was calibrated with carbon (C1s = 284.8 eV).

Electrical property of the thin film was determined by an AC four-point probe method. The measurement was conducted in a closed chamber with controlled temperature. During heating and cooling cycles, the film temperature was raised from room temperature to 100°C and subsequently reduced to room temperature step by step. The metal-to-insulator (MIT) phase transition temperature is defined as the average of the transition temperature (T_c) in the electrical property.

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T_c = \frac{T_c(\text{heating}) + T_c(\text{cooling})}{2}
\]

Transparency of the film coated on the soda lime glass was determined at 25 and 80°C by using a UV-Vis-NIR spectrophotometer (Shimadzu UV-3600 Plus) in a wavelength range 200–2500 nm. The bare soda lime glass was employed as a blank sample. Temperatures were controlled at 25 and 80°C with applied current electricity.

3. Results and Discussion

3.1. Synthesis of Vanadium Oxide Thin Films by Sol-Gel Dip Coating. It has been realized that it is difficult to fabricate pure monoclinic phase VO₂ thin film due to its instability under a general synthesis process. It is most likely that more stable vanadium oxides, such as V₂O₅, V₂O₃, and V₆O₁₃, are also present. These oxides block the reversible phase transition from metallic state to insulating state of the monoclinic VO₂. Among all of the V-O system, the V₂O₅ is a highly stable phase [20, 21]. Thus, in order to investigate the optimum synthesis condition, the presence of crystalline phases was initially considered. Figure 1 shows XRD
patterns of the vanadium oxide thin films after calcined at various conditions summarized in Table 1.

For the 1-step calcination (Figure 1(a)), the temperatures were controlled at 400, 450, and 500°C, respectively, and the pressure was fixed at $2 \times 10^{-2}$ mbar. XRD analysis of the dried thin film (denoted as “room temperature”) revealed amorphous nature signified by the absence of diffraction peak. XRD patterns of the thin films calcined at 400 and 450°C show diffraction peaks at 18.7°, 20.1°, 24.7°, 26.2°, 30.1°, 31.3°, 32.4°, 34.8°, 37.6°, 38.6°, 48.6°, and 51.1°, which correspond to the (001), (101), (201), (110), (301), (400), (111), (211), (401), (311), (302), and (012) planes.

**Table 1: Fabrication parameters of VO$_2$, V$_2$O$_5$, and V$_6$O$_{13}$ thin films.**

| Phase           | Furnace temperature (°C) | Vacuum pressure (mbar) | Calcination (step) |
|-----------------|--------------------------|------------------------|-------------------|
| Amorphous       | Room temperature         | $2 \times 10^{-2}$     | 1                 |
| V$_2$O$_5$      | 400                      | $2 \times 10^{-2}$     | 1                 |
| V$_2$O$_5$      | 450                      | $2 \times 10^{-2}$     | 1                 |
| VO$_2$+V$_2$O$_5$| 500                      | $2 \times 10^{-2}$     | 1                 |
| VO$_2$+V$_2$O$_5$+V$_6$O$_{13}$ | 500                      | $2 \times 10^{-3}$     | 1                 |
| VO$_2$          | 500                      | $2 \times 10^{-3}$     | 2                 |

**Figure 1:** XRD patterns of the vanadium oxide thin films prepared at various conditions: (a) $T=RT$, 400, 450, and 500°C ($P = 2 \times 10^{-2}$ mbar, 1-step calcination), (b) $P = 2 \times 10^{-2}$ and $2 \times 10^{-3}$ mbar ($T = 500°C$, 1-step calcination), and (c) 1- and 2-step calcination ($P = 2 \times 10^{-3}$ mbar, $T = 500°C$).
respectively, of the orthorhombic V\textsubscript{2}O\textsubscript{5} (ICCD card no. 04-015-2250). Increasing the calcination temperature results in an increased intensity of the XRD peaks, indicating an increase of film’s crystallinity. For the thin film calcined at 500°C, its XRD pattern reveals the peaks at 27.7°, 42.5°, 55.7°, and 57.8° corresponding to the (011), (210), (220), and (211) planes, respectively, of the monoclinic VO\textsubscript{2} (ICCD card no. 00-043-1051). Diffraction peaks of the V\textsubscript{2}O\textsubscript{5} at 18.7°, 37.6°, and 38.6°, which correspond to the (001), (401), and (311), planes, respectively, of the orthorhombic V\textsubscript{2}O\textsubscript{5} (ICCD card no. 04-015-2250) are also observed. This result indicates a coexistence of the V\textsubscript{2}O\textsubscript{5} and VO\textsubscript{2} phases by the 1-stepcalcination at 500°C. To further investigate the effect of calcination condition, the pressure of the vacuum tube furnace was varied to 2×10\textsuperscript{-3} mbar, while the temperature was maintained at 500°C. As shown in Figure 1(b), XRD patterns of the orthorhombic V\textsubscript{2}O\textsubscript{5} are dramatically reduced while those of the monoclinic VO\textsubscript{2} are enhanced. In addition, diffraction peaks at 17.9°, 25.7°, 30.3°, 32.6°, 36.3°, 45.8°, 50.1°, and 52.3° corresponding to the (002), (110), (400), (−402), (−113), (005), (020), and (220) planes, respectively, of the V\textsubscript{6}O\textsubscript{13} phase (ICCD card no. 04-008-4854) are present. This result indicates that lower vacuum pressure, the less amount of oxygen, promoted the formation of the VO\textsubscript{2}, as well as the V\textsubscript{6}O\textsubscript{13} minor phase. This reduction condition at a temperature above 400°C and a pressure below 2 Pa (2×10\textsuperscript{-2} mbar) which caused the conversion of V\textsubscript{2}O\textsubscript{5} thin films to VO\textsubscript{2} has been reported by Ningyi et al. [22]. It was observed that the reduction process followed the sequence as V\textsubscript{n}O\textsubscript{2n+1} (n = 2–4, 6) to VO\textsubscript{2}. Therefore, lower pressure favoured VO\textsubscript{2} formation caused by the oxygen deficiency [22, 23]. To further investigate the effect of calcination time, the calcination soaking time was increased from 3 to 24 h. It was found that the thin film consisted of only V\textsubscript{2}O\textsubscript{5} phase.

Figure 1(c) shows XRD patterns of the thin films prepared by means of 1-step and 2-step calcination in the vacuum tube furnace at 500°C with the pressure of 2×10\textsuperscript{-3} mbar. It is evident that only diffraction peaks of the monoclinic VO\textsubscript{2} are present in the film prepared by 2-step calcination caused by the reduction process of V\textsubscript{2}O\textsubscript{5} and V\textsubscript{6}O\textsubscript{13}.

SEM surface analysis of the VO\textsubscript{2} thin film prepared by the 2-step calcination process at 500°C with the pressure of 2×10\textsuperscript{-3} mbar (Figures 2(a) and 2(b)) reveals very fine VO\textsubscript{2} grains with irregular shape of ∼220–380 nm in size surrounded by an amorphous phase of anhydrous vanadium oxide from gelation [24]. Film’s thickness determined from a cross-sectional image (Figure 2(c)) is approximately 69–74 nm. Elemental composition analyzed by EDS (Figure 2(d)) reveals that the sample comprises of Si, O, Na, Ca, V, Mg, and Al at the amount of 30.1, 51.0, 8.5, 5.7, 1.5, 2.6, and 0.6 At.%, respectively. The V and O correspond to the VO\textsubscript{2} thin film, and the others (and part of O) correspond to the glass slide substrate. The elemental mappings of Si from the glass substrate and V from the VO\textsubscript{2} film (Figures 2(e) and 2(f)) reveal homogeneous distribution of the VO\textsubscript{2} grains in the thin film.

Typical surface XPS spectra of the VO\textsubscript{2} sample are depicted in Figure 3. Detail-scan spectra were employed to investigate the valence electron of the V and O and to confirm phase purity of the thin films. According to the standard binding energy, a typical two-peak structure (2p3/2 and 2p1/2) due to the spin-orbit splitting was observed [19]. The peaks at 517.6 eV and 525.2 eV correspond to VO\textsubscript{2}, as well as a small amount of V\textsubscript{2}O\textsubscript{3} [25, 26]. His result indicates that lower vacuum pressure, a number of less intense satellite peaks are also present. These V\textsubscript{2p} satellite peaks are attributed to the V\textsubscript{2}O\textsubscript{3}. The XPS composition analysis result confirms the presence of VO\textsubscript{2}, as well as a small amount of V\textsubscript{2}O\textsubscript{3} and V\textsubscript{2}O\textsubscript{5} [25, 26].

3.2. Electrical Properties of VO\textsubscript{2} (M) Thin Films. Figure 4(a) illustrates the temperature dependence of electrical resistance of the VO\textsubscript{2} thin films on the soda lime glass prepared by the 2-step calcination process at 500°C with the pressure of 2×10\textsuperscript{-3} mbar. The hysteresis loop indicates the metal-to-insulator transformation and the quality of the thin film. It was observed that surface resistance of the thin film decreased upon the heating process and increased upon the cooling process. The transition temperature, determined according to equation (1), was approximately 68°C (T\textsubscript{c} = (80°C + 56°C)/2). Furthermore, resistivity profile of the VO\textsubscript{2} thin films was nearly flat above the room temperature (semiconductor phase), indicating that the transition occurs at 68°C (metal-insulator transition phase) and constant at 80°C (metal phase), respectively [7, 27]. The VO\textsubscript{2} thin films were transformed from monoclinic to tetragonal (rutile) phase at the transition temperature.

3.3. Optical Properties of VO\textsubscript{2} (M) Thin Films. Figure 4(b) illustrates the optical transmittance spectra measured at 25 and 80°C of the VO\textsubscript{2} thin films. Visible optical transmittance remains at ∼40–50% when the sample’s temperature changes from 25 to 80°C. However, for a near infrared (NIR) region wavelength range of 800–2500 nm, the optical transmittance measured at 25°C is clearly
higher than that measured at 80°C. Moreover, the optical transmittance increases with increasing wavelength at 25°C, while it reduces with increasing wavelength at 80°C, indicating phase transition when the temperature is raised from 25 to 80°C. Thus, the thin film exhibits thermo-chromic properties [28–30].
4. Conclusions
A simple and effective synthesis method for the preparation of the vanadium dioxide thin films on the glass slide substrate has been demonstrated by a sol-gel dip coating at low temperature of 500°C in a vacuum tube furnace at a pressure of $2 \times 10^{-3}$ mbar. The calcination was performed by 2 steps, in which thin films were heated in a tube furnace to 500°C at a heating rate of 2°C/min, soaked for 3 h, and cooled down to room temperature, and the same process was repeated. The analyses revealed that the thin films consisted of monoclinic VO$_2$ phase and a small amount of V$_2$O$_5$ and V$_2$O$_3$ phases. The very fine VO$_2$ grains with irregular shape of $\sim$220–380 nm in size were homogeneously distributed on the surface. The film’s thickness was in a range of 69–74 nm.

The monoclinic to tetragonal (rutile) phase transition temperature was 68°C. The thin films exhibited good thermochromic properties. The low-temperature synthesis would be beneficial for thermochromic thin film coating on a conventional soda lime glass panel. In addition, as no intermediate gas was employed during calcination, the process would be suitable for large-scale fabrication.

Data Availability
The data used to support the finding of this study are included within the article.

Conflicts of Interest
The authors declare that there are no conflicts of interest regarding the publication of this paper.

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