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Thermal aging effect of vanadyl acetylacetonate precursor for deposition of VO_2 thin films with thermochromic properties

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ABSTRACT

Thermochromic properties of vanadium dioxide (VO_2) have been studied extensively due to their IR reflection applications in energy smart windows. In this paper, we studied the optical switching property of VO_2 thin film, depending on the thermal aging time of the vanadyl acetylacetonate ($VO(acac)_2$) precursor. We found the alteration of the IR spectra of the precursor by tuning the aging time as well as heat treatments of the precursor. An aging effect of vanadium precursor directly affects the morphologies, optical switching property and crystallinity of VO_2 films. The optimum condition was achieved at the 7 day aging time with metal insulator transition (MIT) efficiency of 50%.

1. Introduction

Vanadium dioxide (VO_2) is a well known material for application in 'smart windows' [1,2] because it undergoes a fully reversible phase transition from a semi-conductive monoclinic phase (low temperature) to the metallic rutile phase (high temperature) at critical temperature (T_c, approximately 68 °C for pure bulk VO_2) with drastic change of electrical and optical properties [3–5]. This metal–insulator transition (MIT) is accompanied by a conductivity jump of up to 4–5 orders of magnitude and it causes reflection of infrared radiation [6]. Moreover, compared with other type of thermochromic materials including organic [7,8], organometallic and inorganic compound [9], VO_2 is most promising thermochromic window materials due to its good chemical stability, low phase transition temperature and visible light transparency. To fabricate the VO_2 thin films, various preparation techniques have been used, including chemical-vapor deposition (CVD) [10,11], pulsed-laser deposition (PLD) [12,13], sputtering deposition [14], and a sol–gel method [15,16]. Among them, the sol–gel method was most commonly used because of the simplicity and economic benefits. There are many different routes for the preparation of VO_2 film via sol–gel methods using various precursors including V_2O_5 powder [17], V-alkoxide [15,18,19], V-halide [20], and V-sulfide [21]. However, such precursors need reduction or oxidation and other complex steps such as transformation before use. In contrast, $VO(acac)_2$ has several advantages; it has relatively low toxicity, and has cost-effective, is highly stable against precipitation and hydrolysis [22], and it can be doped by various elements. Best of all, in this precursor the valence of vanadium is four, therefore a reduction process ($V^{5+} \rightarrow V^{4+}$) is not necessary. Despite these advantages of the precursor, there are few reports on preparation of VO_2 thin films by a sol–gel process using $VO(acac)_2$ as the precursor. According to the reports, the $VO(acac)_2$ precursor become usable for thin film coating after aging for a few weeks or more [22–24]. Such long term aging of the precursor could induce the time-consuming and it is economically inefficient. Therefore, more effective and faster aging processes are required to prepare the thermochromic VO_2 thin films with high MIT performance. In this work, we demonstrate the thermal aging of $VO(acac)_2$ precursor using a thermal reflux system at 80 °C. The structure, morphology, and thermochromic properties of the films were analyzed systematically with various aging times. By tuning the aging time of the precursor, structural transformation was observed through the FT-IR and UV–vis absorption analyses.

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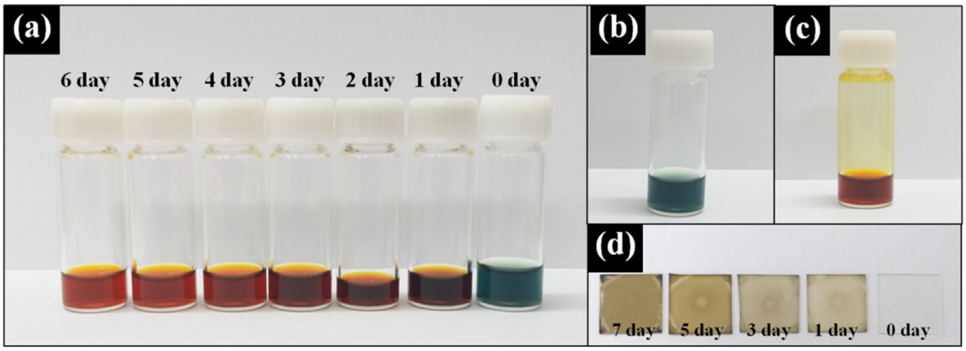

Fig. 1. Photograph of thermally aged $VO(acac)_2$ precursor with different aging times (a), and coating ability comparison between non-aged (b) and 7 day aged (c). Prepared VO_2 thin film after post-annealing with differently aged precursors (d). (For interpretation of the references to color in the text, the reader is referred to the web version of this article.)

2. Experimental details

2.1. Preparation of precursor solution

Vanadyl acetylacetonate ($VO(acac)_2$ (that is a V(IV) precursor), Sigma–Aldrich, 98%) and methanol (MeOH, DAEJUNG chemical, 99%) were used as starting materials to prepare a sol. First, 2.31 g of $VO(acac)_2$ were dissolved in 70 mL of 0.125 M MeOH and stirred for 1 h. After stirring, when a homogeneous deep blue/green color was formed, the solution was transferred to a 100 mL two-neck round flask connected with reflux condenser. The reflux system acts to maintain the total volume of solvent and oxidize the precursor through the reflux tube. The solution was stirred (500 rpm) and heated at 70 °C in an oil bath. And then, every 24 h, thermally aged sol was extracted from reactor.

2.2. Preparation of VO_2 thin film

The EAGLE XG glass (CORNING Inc.) substrate ($2.5 \times 2.5\ cm^2$) was cleaned ultrasonically with 1 M hydrochloric acid, deionized water, and ethanol for 20 min and dried with N_2. Then, O_2 plasma treatment (CUTE-MPR, UVFAB System Inc., 100 W for 5 min) was employed for the hydrophilic surface. Films were deposited on the substrate by spin coating each sol (100 μL) at 1500 rpm for 20 s. After drying on by hotplate for 10 min at 60 °C to remove the solvent excess, uniform films were formed. Finally, coated films were annealed for 5 h at 550 °C under vacuum (10.0 m Torr).

2.3. Measurements

The structural deformation of precursor during the thermal aging process was analyzed by FT-IR (Bruker, VERTEX 70). UV–vis absorption spectra of aged sols are collected by UV–vis spectrometer (Mecasys Corp., Optizen POP). The crystalline information of the films was determined using an X-ray (XRD) diffractometer (Bruker D8 Advance system) making $\theta/2\theta$ scans for phase identification. Diffraction patterns were collected for 2θ values between 10° and 80° with a 2° glancing angle, and scanned at 5°/min rate. The phases present were identified by comparing the peak intensities and their corresponding 2θ values to various vanadium oxide standards using the software PCPDFWIN ver. 2.1 (JCPDS-ICDD). Raman spectra were collected with a confocal Raman microscope (Witec, ALPHA 300 M) based on the 532 nm CO_2 laser. The surface morphology of films were determined by a field emission scanning electron microscope (FE-SEM, JEOL Corp., Model JSM-7100 F). Thermochromic properties of each film were

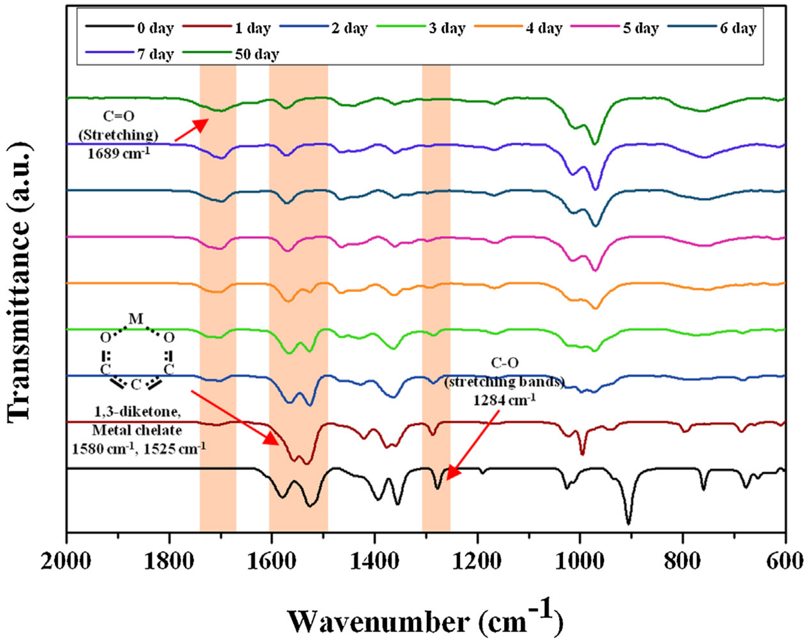

Fig. 2. FT-IR spectra of thermally aged $VO(acac)_2$ precursor with different aging times.