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Tungsten-doped vanadium dioxide thin films as smart windows with self-cleaning and energy-saving functions

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ABSTRACT

A simple and cost effective sol-gel process is developed for producing thermochromic tungsten-doped thin films of vanadium dioxide (VO_2). The precursor is first prepared by the reaction of vanadyl acetylacetonate, methanol, and tungsten chloride in a beaker. The precursor is then spin-coated on the substrate and, finally, annealed at 600 °C in argon gas. The resulting vanadium dioxide thin films are characterized by X-ray diffraction, X-ray photoelectron spectroscopy, scanning electron microscopy, variable temperature UV/Vis spectroscopy, and contact angle measurements. The results indicate that the particles of tungsten-doped vanadium dioxide thin films range from 30 to 150 nm, and the thin films show excellent hydrophilicity with a water contact angle (WCA) of 12°. According to optical tests, the tungsten-doped vanadium dioxide thin films exhibit satisfactory optical properties with an applicable integrated luminous transmittance ($T_{lum,s}$ = 80.75%, $T_{lum,m}$ = 79.24%) and excellent solar regulation efficiency ($\triangle T_{sol}$ = 9.10%, from $T_{sol,s}$ = 81.40% to $T_{sol,m}$ = 72.30%). The VO_2 films exhibit an applicable transition temperature of the semiconductor-to-metal phase change: at a W-doping level of 2 at.%, the transition temperature was measured to be 32 °C. The simple and low-cost method is a noteworthy addition to literature on the synthesis of nanostructured materials towards applications in energy-saving smart windows.

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1. Introduction

Recent economic development has been accompanied by worldwide attention to global warming, the harmful consequences of which must be addressed urgently "Green" nanotechnologies can offer many ways to reduce the energy consumption in buildings [1], which contribute 30–40% of the total energy consumption [2,3]. Hence, new and improved construction technology can have a significant effect in combating global warming [4]. The potential energy savings are huge and, as noted recently [5], can be accomplished without sacrificing comfort and amenities. The latter aspect is important because in most industrialized countries, 80%–90% of time is spent indoors, in buildings, and in vehicles [6]. Furthermore, improved energy performance can have financial benefits, and a recent study of market transactions in the USA showed that "green" buildings command higher rental rates and selling prices than comparable "non-green" buildings [7].

Intelligent energy-saving windows, especially "smart windows" based on thermochromic materials are considered to be suitable candidates for energy-saving devices, and have thus attracted considerable attention [8–10]. Smart windows can automatically adjust optical transmittance to balance room temperature and to save solar energy. Vanadium dioxide (VO_2) is a most interesting material, which shows an automatic reversible semiconductor-metal phase transition (SMT) and has intrigued researchers for over five decades since the existence of thermochromic properties was first discovered [11–13]. At ~67 °C, vanadium dioxide thin films undergo an automatic, reversible semiconductor-metal phase transition [14,15]. When the temperature is increased beyond 67 °C,

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the monoclinic structure ($P2_1/c$, M1 phase, the most stable monoclinic phase at room temperature) is transformed to the tetragonal structure ($P4_2/mnm$, R phase, space group $P4_2/mnm$) [16,17]. Accordingly, the optical properties of VO_2 thin films change significantly in the infrared band but weakly in the visible band, resulting in a dramatic modification of the optical properties from infrared (IR)-transmitting to IR-reflecting, while maintaining the visible transparency [18–20]. Therefore, VO_2 thin films are gradually being considered as a promising candidate material for energy-efficient thermochromic smart windows in buildings, cars, and aircrafts, due to their ability to adjust infrared light [21]. However, pure vanadium dioxide thin films do not have much value for practical applications owing to their slightly higher transition temperature ($\mathbf{T_C}$) relative to room-temperature (RT) [22]. Therefore, $\mathbf{T_C}$ must be shifted to ambient temperatures. Recent research has demonstrated that doping metal ions into the VO_2 lattice is an effective approach to change $\mathbf{T_C}$. Particularly, $\mathbf{T_C}$ is shifted to RT by doping films with high-valence ions, such as molybdenum [23] and tungsten [24,25]; as well as silicon [26], fluorine [27,28] and boron [29]. Among these dopants, tungsten is found to be most effective, lowering $\mathbf{T_C}$ by 23 °C per 1 at.% [30]; while 15 °C per 1 at.% and approximately 19 °C per 1 at.% have also been reported for Mo [24] and F-doping [28,29], respectively.

Thin films of stoichiometric VO_2 are not easily fabricated because other vanadium oxides, such as V_3O_5, and V_2O_5, have stable structures in similar conditions as those used during VO_2 growth [30]. Currently, many methods are applied for VO_2 (M)-based film fabrication, such as sol-gel http://www.sciencedirect.com/science/article/pii/S0042207X15002183[31,32], hydrothermal synthesis http://www.sciencedirect.com/science/article/pii/S0042207X15002183[33], magnetron sputtering deposition [34,35], sputtering oxidation coupling (SOC) [36], wet chemical approaches [37,38], chemical vapor deposition (CVD) [39], and pulsed laser deposition (PLD) [40,41]. The authors found that tungsten doping vanadium dioxide could effectively reduce the phase transition temperature [42,43].

In this paper, we report results on synthesis of tungsten doped vanadium dioxide thin films using a sol-gel method. The vanadium dioxide thin films reported in the current work are shown high transmittance of visible light and strong solar adjustment ability. Additionally, tungsten-doping of vanadium dioxide thin films were found to effectively reduce the phase transition temperature to room temperature. Furthermore, the tungsten doped vanadium dioxide thin films exhibit small water contact angles, which have a good hydrophilic and self-cleaning function.

2. Experimental section

2.1. Preparation of vanadium dioxide precursor

Vanadium dioxide precursor was prepared by a sol-gel method as follows. In a typical procedure, 1.00 g of commercial Vanadyl acetylacetonate ($VO(acac)_2$, 99% AR. Aladdin Reagent (China) Co., Ltd) powder added to 30 ml of methanol (AR. Aladdin Reagent (China) Co., Ltd) to form a dark brown solution with a concentration of 0.125 mol L^{-1}. The solution was vigorously stirred for 24 h to ensure that the $VO(acac)_2$ had dissolved and was then allowed to stand for two days.

2.2. Preparation of vanadium dioxide films

Fused quartz with dimensions of 2 mm × 2 mm × 1 mm, and cleaned with acetone, ethanol, and water, was adopted as the substrate for the vanadium dioxide film, which was spin-coated at 400 rpm for 6 s, then at 3000 rpm for 30 s, and finally, dried on a stove at 100 °C for 30 min in a vacuum atmosphere to drive off excess solvent. This entire process including spin-coating and drying, was repeated 3 times. Finally, the samples were annealed at a certain temperature for a fixed time under Ar atmosphere through a programmed sintering process to obtain the vanadium dioxide films (see Scheme 1).

2.3. Preparation of tungsten-doped vanadium dioxide films

The tungsten-doped vanadium dioxide film could be obtained by adding a certain amount of tungsten chloride (99.9%, AR. Aladdin Reagent (China) Co., Ltd) to the dark brown 0.125 mol L^{-1} vanadium solution. The remaining process was identical to that used for the VO_2 thin films.

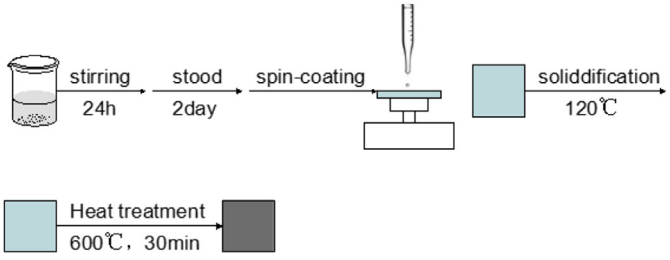
2.4. Characterization and measurements

The obtained samples were characterized by X-ray diffraction (XRD) using a D/MAX-IIIC X-ray diffractometer (Akishima-shi, Tokyo, Japan) with Cu Kα radiation (λ = 0.15406 nm), from 5° to 80°. The X-ray tube voltage and current were set at 35 kV and 25 mA, respectively. The data was used to determine the phase structures and crystallite sizes of the obtained samples. The morphology of samples was observed on a JSM-5610LV scanning electron microscope (SEM, JEOL, Japan) at an accelerating voltage of 20 kV. The valence state and content of vanadium and tungsten were studied by X-ray photoelectron spectroscopy (Thermo Fisher Escalab 250Xi, America). The wettability of the vanadium dioxide thin films were measured by the KRUSS DSA100 contact angle system. UV–visible diffuse reflectance spectra (UV–vis DRS) of the as-prepared samples were obtained by a UV–visible spectrophotometer (UV-3600, Shimadzu Corp., Tokyo, Japan).

3. Results and discussion

3.1. Film structure

Fig. 1 shows the typical XRD patterns of VO_2 films with various amount of W-doping and the typical diffraction peaks could be perfectly indexed to the VO_2 (M). Without W^{6+} doping, the XRD pattern in Fig. 1a exhibits one sharp diffraction peak at about $2\theta = 27.8°$, which matches with the (011) plane of the pure vanadium oxide monoclinic structure (JCPDS File no: 43–1051). The spectrum shows peaks at 38.6°, 45.1°, 55.5°, and 57.5°, which are related to the reflections from planes (200), (210), (220), and (022), respectively. Additionally, no evidence can be observed for other crystalline phases, such as V_2O_5, V_2O_3, or $V_{13}O_6$, indicating the purity of the composite films. And also there are not any additional diffraction peaks with W^{6+} doping (as seen in Fig. 1b and c). However, the intensities of the diffraction peaks significantly weaken with increasing molar ratio of W/(W + V). This is attributed to the formation of a solid solution of tungsten in VO_2, with



Scheme 1. Preparation procedure for vanadium dioxide films.

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