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Microstructures and thermochromic characteristics of low-cost vanadium–tungsten co-sputtered thin films

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ABSTRACT

Tungsten–vanadium (W–V) co-sputtered thin films at a low cost were successfully synthesized on glass substrates by magnetron sputtering at room temperature and annealing under air atmosphere. The microstructures and optical properties of the thin films were characterized by four approaches, such as X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD), scanning electron microscopy (SEM) and spectrophotometer. XPS analysis demonstrated that W–V co-sputtered thin films were mostly composed of VO_2 and W^{6+}, with a little amount of V_2O_5 and other tungstovanadic compounds. XRD patterns illustrated that W–V co-sputtered thin films were polycrystal and W–V co-sputtered approach did not change the preferred orientation growth of the thin films. SEM micrographs displayed that VO_2 thin films were irregular in shape and distributed randomly, while W–V co-sputtered thin films had a rod-like morphology. Spectrophotometer spectra showed that W–V co-sputtered approach decreased the phase transition temperature from 68 °C to 40 °C, narrowed the thermal hysteresis loop from 6 °C to 3 °C, and made little influence on the infrared transmittance of pure VO_2 thin films.

1. Introduction

Global warming results in the growth of energy expenditure for air conditioning by the increasing needs of indoor comfort, and consumption of energy originating from the indoor–outdoor heat exchange is mainly carried out through the windows. Therefore, it is imperative for people to design a kind of smart window to save energy [1,2].

Making a kind of smart window can be accomplished by coating with a chromogenic thin film on normal glass [1,2], whose optical properties will be varied with the changes of external environment. A total of four types of chromogenic thin films are classified, e.g. electrochromic (depending on electrical voltage or charge), thermochromic (depending on temperature), photochromic (depending on ultraviolet irradiation), and gasochromic (depending on exposure to reducing or oxidizing gases) thin films [3–6]. Among four types of films, the vanadium dioxide (VO_2) thermochromic thin films have a great potential to be the materials to create smart window [7].

VO_2 is able to undergo a reversible phase transition, whose transition rate is able to achieve the order of picoseconds [8] at temperature of 68 °C or above. When the temperature below this critical temperature (68 °C), VO_2 is characterized as mono-clinic, semiconducting and high transmitting, while above this critical temperature, it is featured as tetragonal, metallic and high reflecting [2,9]. Furthermore, the transmittance mutation of VO_2 thin films emerges only in the infrared band, which contains around half total solar energy [10,11]. In contract, the transmittance is hardly changeable in the visible light band. Therefore, due to abovementioned optical properties, VO_2 thin films are greatly suitable to be used as smart window materials. However, the 68 °C phase transition temperature of VO_2 thin films is still higher than the room temperature, and the broad width of thermal hysteresis loop in VO_2 thin films will reduce the reversibility and reliability of phase transition. These two characteristics both intensively impede the application of VO_2 thin films and there is no any practical approach to remedy these defects up to now [12].

Recent studies show that the phase transition temperature of VO_2 thin films can be changed by doping impurity ions including W^{6+}, Mo^{6+}, Nb^{5+}, F^-, Cr^{3+}, etc. [13–16]. Especially, the phase transition temperature will be significantly reduced to near room temperature when W ions are doped into VO_2 thin films [7,17,18]. However, after doping impurity ions, the transmittance of VO_2 thin films will be decreased because VO_2 thin films form regional energy levels, where the electrons are stimulated to the conduction band and become delocalized electrons, absorbing the photon energy of different wavelengths at low-temperature semiconductor phase [19].

Despite many approaches have been explored to prepare undoped or doped VO_2 thin films, most of the reported methods are focused on the fabrication of VO_2 thin films. Obviously, these VO_2 thin films were

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prepared at a high cost in laboratory conditions [20–22]. Compared with the different fabrication approaches, the sputtering and CVD approaches are the relatively low-cost methods to be applied in the industry. Considering the price of the CVD equipment, we finally select the sputtering approach to make thermochromic window materials.

In order to solve these problems as well as to provide an effective technology in manufacturing low-cost, energy-efficient and practical smart window materials, we prepared the tungsten–vanadium (W–V) co-sputtered thin films by significantly minimizing the experimental limitations, such as depositing without substrate temperature and oxygen, sputtering with single mixed metal target and annealing in the air. Then the microstructures and morphologies of W–V co-sputtered thin films were analyzed and their optical properties were compared with that of pure VO_2 thin films.

2. Experimental details

In the experiment, thermochromic thin films were prepared by JC500-3/D magnetron sputtering coater (Chengdu Vacuum Machinery Plant, China) and the details of preparation procedures were described as follows. First, the glass substrates were cleaned in acetone, ethanol and de-ionized water sequentially for 3 to 5 min by ultrasonic cleaning equipment at frequency of 20 KHz. When the glass substrates were absterged, they were immediately dried with high-purity nitrogen (99.99%) to avoid being polluted in the air. Second, the dried glass substrates were placed in the chamber of direct current (DC) magnetron sputtering system equipped with a mixed metal target of W (1.4%) and V (98.6%) by weight. After the argon (99.999%) of 80 sccm flux was discharged with a fixed DC current of 0.3 A and DC voltage of 400 V for several minutes, the metal layers were deposited on the glass substrates. During the period of film deposition, the sputtering chamber was kept at room temperature, without adding curing voltage to heat substrates. Last, the prepared metal thin films were annealed to the thermochromic thin films in SX2-4-10 box-type resistance furnace (Shanghai Shengxin Scientific Instrument Company, China), with a temperature accuracy of ± 1 °C. In order to explore a low-cost technology, all samples collected from the thin films were annealed in the air atmosphere without any other gas.

The compositions of W–V co-sputtered thin films were examined by X-ray photoelectron spectroscopy (XPS, PHI-5000C ESCA, Perkin-Elmer Company, USA). MgKα radiation was served as photoelectron excitation source of XPS including 54° angle of incidence and sampling spot of 800 μm. Shift of binding energy caused by surface charge effect was adjusted by consulting the binding energy of C1s peak at 284.6 eV. X-ray diffraction (XRD, BD90, Beida Qingniao Corporation, China) was employed to reveal the crystal structures. CuKα was selected as target source of XRD including $\lambda = 0.15405$ nm with a working current of 30 A and voltage of 36 kV. The surface morphologies were characterized by field emission scanning electron microscope (SEM, NoVaTM Nano SEM 430, FEI Corporation, USA). Spectrophotometer (Lambda9, Perkin-Elmer Company, USA) with working wavelength of 280–3200 nm was adopted to observe the optical properties.

3. Results and discussion

3.1. XPS analysis

To understand the best annealing conditions on components and microstructures, the samples covered with metal thin films were cut into small pieces with the same size and consequently annealed at different temperature and time. The optical properties of W–V co-sputtered thin films under different annealing conditions at wavelength of 2 μm were summarized in Table 1, which reveals the best annealing parameters at temperature of 400 °C for 4 h. It also showed that W–V co-sputtered thin films were oxidized insufficiently and crystallized imperfectly at a lower annealing temperature or for short annealing time [23], resulting in either high phase transition temperature or low infrared transmittance of the thin films. While the grains of the thin films were integrated into structure-closed crystal group at a high annealing temperature [24], which also diminished the optical properties of the thin films. Therefore, all the samples in this paper were prepared at these best annealing parameters.

The comparison between the typical XPS spectra of W–V co-sputtered thin films and that of pure VO_2 thin films were performed (Fig. 1). Fig. 1(a) shows the photoelectron spectra of the W–V co-sputtered film and the pure VO_2 film. Fig. 1(b) shows V2p and O1s photoelectron spectra of the W–V co-sputtered film and the pure VO_2 film. Fig. 1(c) shows V4d photoelectron spectra of the W–V co-sputtered film and the pure VO_2 film. Fig. 1(d) shows W4f photoelectron spectra of the W–V co-sputtered film and the pure VO_2 film. According to the standard binding energy, the peaks at 37.2 eV and 35.0 eV were the binding energy for $W^{6+}_{4f5/2}$ and $W^{6+}_{4f7/2}$, respectively [25]. It implies that the valence of tungsten ions in the W–V co-sputtered thin films is $+6$. Additionally, the peaks at 516.4 eV and 524.0 eV were due to $V^{4+}_{2p3/2}$ and $V^{4+}_{2p1/2}$, respectively, and the peak at 517.2 eV was $V^{5+}_{2p3/2}$ [25]. It indicates that the vanadium of W–V co-sputtered thin films present predominantly as V^{4+} (VO_2) and V^{5+} (V_2O_5). Fig. 1(e) is the O1s photoelectron intensity fit by Gaussian–Lorenzian curve. It shows the proportion of the VO_2 and V_2O_5, from which we can see that V_2O_5 only accounted for a little in the vanadium oxides. XPS results demonstrated that W–V co-sputtered thin films mainly consisted of VO_2 and W^{6+}, with a bit amount of V_2O_5 and other tungstovanadic compounds.

3.2. XRD patterns of the thin films

The XRD patterns of both VO_2 and W–V co-sputtered thin films were analyzed (Fig. 2). It can be seen that two typical diffraction peaks appeared at nearly 28° and 56° were indexed to VO_2 (011) and VO_2 (220) phase, respectively. The peaks belonging to WO_3 were not observed in the consequence that tungsten was doped into vanadium oxide as the solute donor [24,26], which indicated tungsten entered into the crystal lattice of VO_2. Furthermore, it also discovered that the 2θ value (011) of W–V co-sputtered thin films and pure VO_2 thin films were 27.262° and 27.417°, respectively, based on calculation of Bragg law [27], the interplanar distance of W–V co-sputtered thin films and pure VO_2 thin films were 0.32683 nm and 0.32502 nm, respectively. It is because the ionic radius of W is longer than that of V [28], when W atoms substitute V atoms in VO_2 lattice, the interplanar distance of VO_2 will be enlarged, resulting in the lower diffraction angle. The FWHM of W–V co-sputtered thin films and pure VO_2 thin films were 0.198° and 0.176°, respectively. According to Sherry law, the mean grain diameters of W–V co-sputtered thin films and pure VO_2 thin films were 45.86 nm and 51.60 nm, respectively. Results of XRD illustrated that W–V co-sputtered approach did not change the preferred orientation growth of VO_2 thin films on glass substrates.

Table 1
Optical properties of W–V co-sputtered thin films under different annealing conditions at wavelength of 2 μm.

Annealing condition	Phase transition temperature	Infrared transmittance at 20 °C	Infrared transmittance at 70 °C
380 °C 2 h	49 °C	37%	14%
380 °C 4 h	46 °C	46%	14%
400 °C 2 h	44 °C	43%	15%
400 °C 4 h	40 °C	57%	15%
420 °C 2 h	53 °C	45%	22%
420 °C 4 h	49 °C	61%	29%