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VO_2 thin films with low phase transition temperature grown on ZnO/glass by applying substrate DC bias at low temperature of 250 °C

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ABSTRACT

High-performance vanadium dioxide films with low phase transition temperatures of 40–50 °C were successfully fabricated by applying various negative substrate bias voltages at a low substrate temperature of 250 °C. This low-temperature preparation method and the films' thermochromic properties may provide useful suggestions for industrial production of VO_2 films for smart window applications. The effects of the negative substrate dc bias voltage on the microstructure, surface morphology, and optical and electrical performance of the VO_2 films were characterized. X-ray diffraction showed that the residual compressive stress in the films increased as the substrate bias increased, and the maximum value can reach −576 MPa. Temperature-dependent sheet resistance measurement showed that the transition temperature (τ_c) and room-temperature sheet resistance decreased significantly with increasing substrate bias, and the lowest value of τ_c is 38.5 °C. The calculated solar energy modulation ability (ΔT_{sol}) of the VO_2 film fabricated under a substrate bias voltage of −175 V at 250 °C is approximately 9.73%, which may indicate strong potential for application in smart energy-efficient windows produced industrially at a low substrate temperature.

1. Introduction

Common chromogenic effects are photochromism, electrochromism, and thermochromism [1]. Among these, thermochromic materials have recently received increasing attention owing to their property of changing color with temperature. A typical thermochromic material is the metal oxide vanadium dioxide (VO_2), which is the most likely candidate for smart window applications [2–5]. VO_2 crystals exhibit an extremely sharp and ultrafast first-order phase transformation from the monoclinic to the rutile structure near 68 °C, which is accompanied by dramatic changes in the electrical conductivity and IR optical transmittance [6]. The rutile and monoclinic structures are illustrated in Fig. 1. Moreover, the phase transition temperature of VO_2 can be decreased to room temperature by doping with W [7], F [8], etc. These unique characteristics of VO_2 enable the development of next-generation memory [9], uncooled infrared (IR) microbolometers [10] and energy-efficient smart household or industrial windows [11]. Many researchers have fabricated high-quality VO_2 films by various technical methods, including the sol–gel method [12], pulsed laser deposition [13,14], molecular beam epitaxy [15], and magnetron sputtering [16]. Among them, magnetron sputtering has been widely used for many other types of thin films, and this method also shows great advantages for application in smart window fabrication owing to the high packing density, uniform large-area coating, and potential for industrialization [17–19].

However, a high substrate temperature of over 400 °C is required to prepare highly crystallized VO_2 films in conventional magnetron sputtering systems. The high substrate temperature may generally impose several limiting factors: (a) the high-temperature process is not useful for industrialization and low-cost production; (b) the high-temperature process may lead to diffusion of Na^+ from the soda-lime glass to the VO_2; (c) the high deposition temperature may limit the choice of substrate, such as polyethylene naphthalate and polyethylene terephthalate. Thus, it is necessary to lower the substrate temperature used for VO_2 film deposition. Some papers reported methods of fabricating VO_2 films at a low substrate temperature of approximately 200 °C, followed by high-temperature annealing [20,21]. Additionally, epitaxial growth technology was successfully used to prepare high-

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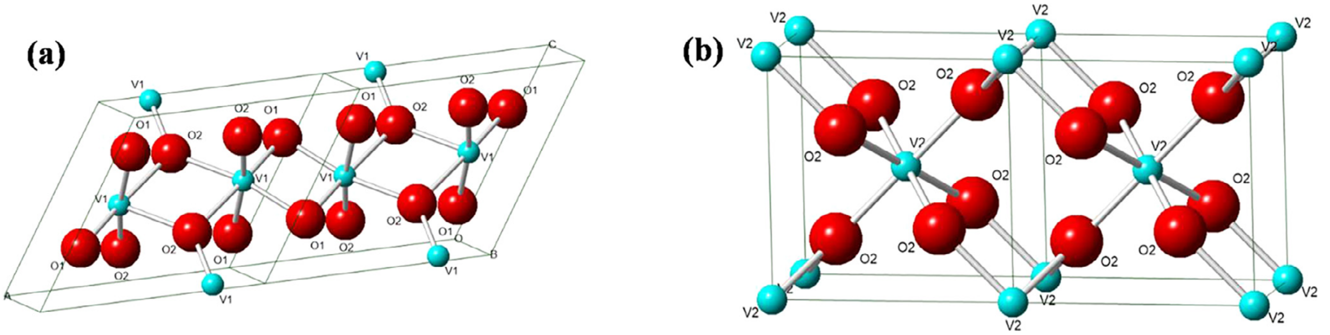

Fig. 1. Diagrams of the two kinds of VO_2 crystal structures; the large red balls and small blue balls represent oxygen atoms and vanadium atoms, respectively. (a) Monoclinic structure. (b) Tetragonal rutile structure. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

quality VO_2 films on a single-crystal substrate such as a sapphire or silicon wafer at low temperature, but this method relies on the use of an expensive and special single-crystal substrate [22].

In this paper, VO_2 films were deposited on ZnO/soda-lime glasses under various substrate bias voltages at 250 °C, on the basis of our previous work [17]. Many deposition parameters in the growth process of VO_2 films, such as the oxygen pressure, sputtering power, and sputtering temperature, have been considered, but few reports have focused on the effect of the substrate DC bias voltage on the thermochromism of VO_2 films. In general, the substrate bias voltage can generally attract Ar^+ cations in the plasma to bombard the growing films and provide external energy to enhance the film crystallinity; this energy may replace the energy provided by a higher substrate temperature and make low-temperature deposition possible. On the other hand, many Refs [23,24] have proved that a highly oriented oxide buffer layer of ZnO can be used to prepare high-quality VO_2 films with better visible transmittance and solar modulation ability due to the high degree of crystallization and high transparency respectively in a wide temperature and visible wavelength range. Additionally, a strong (0 0 2) preferred orientation ZnO films can be obtained in a wide range of sputter deposition conditions, which can help the formation of VO_2 [25]. In this paper, we attempted to combine a negative substrate bias voltage and a ZnO buffer layer to fabricate VO_2 films with good thermochromic properties at a low substrate temperature of 250 °C. The effect of the substrate bias voltage on the thermochromic properties of the VO_2 films was investigated.

2. Experimental

2.1. Deposition of VO_2 films

A ZnO buffer layer was first deposited on a glass substrate using a dc reactive magnetron sputtering system at 150 °C. High purity zinc target (99.99%) with diameter of 60 mm was used and the distance of target–substrate was about 100 mm. The power density of Zn target was 1.1 $W\,cm^{-2}$. The deposition chamber was pumped to a base pressure of 6×10^{-4} Pa by using a turbo molecular pump. Then pre-sputtering process was executed for 10 min to remove contamination from the target surface. The flow rate of O_2 and Ar were 5 sccm and 40 sccm, respectively. The deposition pressure was 0.5 Pa. The deposition time of ZnO films was about 30 min. The thickness of all ZnO films was controlled accurately to approximately 120 nm. Next, VO_2 films were deposited on the ZnO films by dc reactive magnetron sputtering at various negative substrate bias voltages at 250 °C. The substrate was connected to a dc source with a −300 to 0 V bias supply. A schematic of dc magnetron sputtering under a substrate bias voltage is shown in Fig. 2(a). A pure vanadium target (99.99%) of Φ60 mm was used as a sputtering target at a distance of 100 mm from the substrate. Then, VO_2 films were prepared on the 250 °C ZnO/soda-lime glass substrates at a 4.2 $W\,cm^{-2}$ target power density. The flow rate of O_2 and Ar were 1.8 sccm and 40 sccm, respectively. The deposition pressure was 0.5 Pa. The deposition time of VO_2 films was about 30 min. During the deposition process of VO_2 films, the bias voltage applied to the ZnO/soda-lime glass substrates ranged from −75 to −275 V. The samples fabricated under substrate bias voltages of 0, −75, −125, −175, and −275 V are denoted as S_0, S_{-75}, S_{-125}, S_{-175}, and S_{-275}, respectively. Detailed structure of the VO_2/ZnO/soda-lime glass is shown in Fig. 2(b).

2.2. Characterization

X-ray diffraction (XRD) measurements and Raman microscopy were used to determine the crystalline structures of the films. A Rigaku Ultima IV diffractometer in a 2θ geometry was used to investigate the crystallographic characteristics. The film thickness was obtained by means of low-angle X-ray reflectivity (XRR) with an angular resolution of 0.005°. The vibrational modes in the VO_2 films were determined using a Horiba Scientific XploRA PLUS Raman microscope with a 532 nm laser. The elemental analysis of vanadium and oxygen in films were obtained using the K-Alpha Thermo Scientific X-ray photoelectron spectroscopy. The relevant data was analyzed by commercial software of Casa XPS. The temperature-dependent sheet resistance of the VO_2 films was characterized using a four-point probe system with a Keithley 2400 source meter. A Peltier heating stage was used to control the temperature of the VO_2 films. During the measurement process, the film temperature was ramped up from room temperature to 70 °C and then ramped down to room temperature in 1 °C steps. The optical transmittance of the films at temperature above and below τ_c were measured using a PerkinElmer Lambda 950 UV–visible–near-IR spectrophotometer in 1 nm steps. The surface morphologies of the film samples were measured by a Zeiss Supra 5S Sapphire field-emission scanning electron microscope in secondary electrons mode. AFM images of the film samples were obtained by using Veeco Dimension 3100 atomic force microscope in tapping mode with a drive frequency of 283.487 KHz and a scan rate of 1.0 Hz at room temperature.

3. Results and discussion

3.1. Structure and composition

Fig. 3(a) shows the XRD patterns of the VO_2 films deposited without substrate bias and under substrate bias of −75 V. Both samples exhibit sharp diffraction peaks at 34.360°, which were indexed to the ZnO (0 0 2) planes (JCPDS No. 89-0511). Apart from the ZnO peak, some weak peaks appeared in the XRD pattern corresponded to V_2O_5 (JCPDS No. 89-0612), and the peaks located at 20.244°, 21.670°, 26.099° and 47.300° can be indexed as the reflections on the V_2O_5 (0 0 1), (1 0 1), (1 1 0) and (6 0 0) planes, respectively. This indicates that crystallizable