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Full Length Article

Transformation of crystalline structure and photoelectric properties in VO_2/glass thin films by inserting TiO_2 buffer layers

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ABSTRACT

Vanadium dioxide (VO_2) with reversible metal–insulator transition (MIT) is a promising energy-saving material for next-generation smart windows and infrared devices. However, the specific applications are largely limited by controllable preparation with different polymorphs on common glass substrates. Herein, VO_2 thin films were prepared on transparent amorphous glass substrates by inserting TiO_2 buffer layers using pulsed laser deposition (PLD) technique. The results showed that B-VO_2 film would be formed on the amorphous glass substrate at 400 °C. While after inserting TiO_2 buffer layer, pure M-VO_2 films with clear phase transition properties were obtained. Based on the analysis of X-ray Diffraction (XRD) and Energy Dispersive Spectrometer (EDS) characterization, the crystalline transformation was attributed to the template effect of TiO_2 layer and Ti ions diffusion. The characteristics of VO_2/TiO_2/glass thin films were closely associated with the thickness of TiO_2 buffer layer. With 60 nm TiO_2 buffer layer, the VO_2/TiO_2/glass film showed the sharpest resistance change with more than 2.5-order of magnitude across the MIT, and the *T-vis* value is as high as 53% with the ΔT_{sol} up to 5.2%. Our current results demonstrated the importance of TiO_2 buffer layer to the formation of M-VO_2 film on amorphous glass substrate, which was very meaningful for the production of energy efficient smart windows in the future.

1. Introduction

Vanadium dioxides VO_2 are well-known energy-related materials and have extensively been used for interpreting correlation effects in solids since their origination in the 1950s [1,2]. Monoclinic/rutile VO_2 (M/R) undergoes a reversible metal–insulator transition (MIT) between VO_2(M) and VO_2(R) at approximately 68 °C with dramatic changes in the oxide's electronic and near-infrared (NIR) optical properties[3,4]. In view of the low critical temperature of MIT, VO_2 has attracted much attention because of its applications in solid state memory devices [5–7], sensors [8] and smart-windows [9–11].

VO_2 thin films could be made by many different techniques, for instance, molecular beam epitaxy [12], pulsed laser deposition [13], magnetron sputtering [14], sol–gel deposition [15], chemical vapor deposition [16], etc. Due to the MIT features are closely associated with the quality of VO_2 films, the preparation of high quality VO_2 films has become one of the most important issues over the past decades. It is known that the characteristics of the substrate material plays a major role to the thermochromism of VO_2 films [17–19]. Nowadays, some rigid crystals have been employed to act as the growth substrates, such as Titanium dioxide (TiO_2), silica (SiO_2), sapphire (Al_2O_3) and magnesium fluoride (MgF_2). While the introduction of rigid crystals brings about the high cost of the device preparation and hence extensively restricts its applications. Direct deposition of high quality VO_2 film on common glass substrates is potentially promising for the applications of smart windows and other transferable infrared devices. However, VO_2 films directly deposited onto common glass substrates are polycrystalline structure and often performed poor MIT properties [20,21]. Thus, it is highly desirable to find a way to improve the crystalline structure and photoelectric properties in VO_2/glass thin films. Moreover, Besides the M and R phases, there are several other VO_2 polymorphs. For specific application, VO_2 thin films should have a series of characteristics including purposefully chosen polymorphs, accurate stoichiometry, phase stabilization, and the work for controllable preparation of VO_2 films with different polymorphs is also desirable.

Previous reports usually grew different phase films of VO_2 (B and M) by controlling the vanadium arrival rate or oxidation of the V atoms. VO_2 (B) could be fabricated at lower temperature and transformed to the more stable R phase upon heating to 550 °C or more [22–24]. Recently, Liu et al. [25] reported that control of the stoichiometry of VO_2

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by designing a “sandwich structure” of a V_2O_5/metal (V, W)/V_2O_5 multilayer precursor. Through controlling the thickness of the middle metal layer, the polymorph switch from VO_2 (B) to VO_2 (M) can be achieved because of the difference between the diffusion length of the oxygen in V_2O_5 and in metal V and W. Despite these studies, a simple method of precisely controlling VO_2 (B) and VO_2 (M) and the fully understanding of electronic and optical properties of VO_2 (M) thin films still need further study. Finding ways to synthesize specific VO_2 polymorphs with defined properties will open up channels for new device designs.

To date, some researchers reported that TiO_2 buffer layers were employed for VO_2 thin films growth on glass substrate by means of reactive magnetron sputtering or chemical solution [26–31], and they focused mainly on improving the crystal quality and the electrical photoelectric properties of VO_2 films. However, the effect of the TiO_2 buffer layer on selecting different morphology was rarely noticed.

In this paper, TiO_2 thin film was used as buffer layer between VO_2 films and amorphous glass substrates by PLD technique. The effect of the TiO_2 buffer layer on selecting morphology and crystalline transition was illustrated and the VO_2/TiO_2/glass composite films with impressive photoelectric properties were obtained. The achievements may provide an insight into the role of TiO_2 buffer layer played during the formation of VO_2 films on glass substrate and some experiment basis for preparing advanced applications of VO_2-based devices.

2. Experimental section

2.1. Film preparation

The VO_2/glass and VO_2/TiO_2/glass films with different thickness of TiO_2 buffer layer were fabricated by Pulsed laser deposition (wavelength 248 nm, pulse width 25 ns) using a TiO_2 ceramic target (99.99% purity, 40-mm diameter, 5 mm-thickness) and a V target (99.95% purity, 25-mm diameter, 3 mm-thickness). The amorphous glass substrates (BF33) were ultrasonically cleaned in an ethanol/acetone solution, rinsed in deionized water, and then dried with nitrogen sequentially. Prior to all deposition, the base pressure was evacuated to 1.0×10^{-4} Pa. The spacing between the targets and substrates was kept at 6 cm. The laser beam was irradiated keeping an angle of 45° onto the target surfaces. During the deposition of TiO_2 buffer layers, the laser was operated at room temperature with a repetition rate of 5 Hz and the output pulse energy of 200 mJ, without oxygen inlet. The VO_2 thin films were prepared at a substrate temperature of 400 °C and an oxygen pressure of 0.9 Pa with the flow of 25 sccm while the output parameters of the laser were keeping constant. To improve the thin film uniformity, the target and substrate were driven to be rotating with a speed of 18 rpm. The film thickness was controlled by deposition time and corrected by Step Profiler (DektakXT, Bruker). In VO_2/TiO_2/glass samples, the thickness of VO_2 thin films was fixed at 60 nm and that of the TiO_2 buffer layers were 30 nm, 60 nm and 120 nm respectively. For comparison, VO_2 thin film grown directly on amorphous glass substrate was also prepared at the same conditions as those of VO_2/TiO_2/glass films. Here, four thin film samples were labeled as VO_2 (60 nm)/glass, VO_2(60 nm)/TiO_2(30 nm)/glass, VO_2(60 nm)/TiO_2(60 nm)/glass and VO_2(60 nm)/TiO_2(120 nm)/glass respectively.

2.2. Film characterization

The crystallographic properties of the films were characterized by X-ray diffraction (XRD) in regular θ-2θ scanning mode using LabXRD-6000 (Cu Kα: λ = 0.15406 nm). Raman spectroscopy equipped with a 514 nm laser wavelength was employed to measure the lattice vibration of the films. The surface morphology of the samples was studied by atomic force microscopy (AFM) in contact mode with a profilometer (Dektak 150). Then the surface roughness values (root mean square) were obtained by averaging the total surface area in the AFM images. SEM images were acquired by scanning electron microscopy (Zeiss Supa 50VP, Germany) equipped with EDS analysis measurement. Using Hall Effect Measurement System (HMS-5300, Ecopia), the temperature-driven MIT properties were investigated by measuring the sheet resistance during heating and cooling process within the temperature ranging from 20 to 120 °C. The temperature interval of all sheet resistive-temperature graphs is 2 °C and the sweeping rate were the same for all the samples. A double beam spectrophotometer (Shimadzu, UV-3600) with a spectral range of 200–2650 nm was used to record the transmittance spectra of films, and the temperatures were controlled by a resistively heated tubular holder.

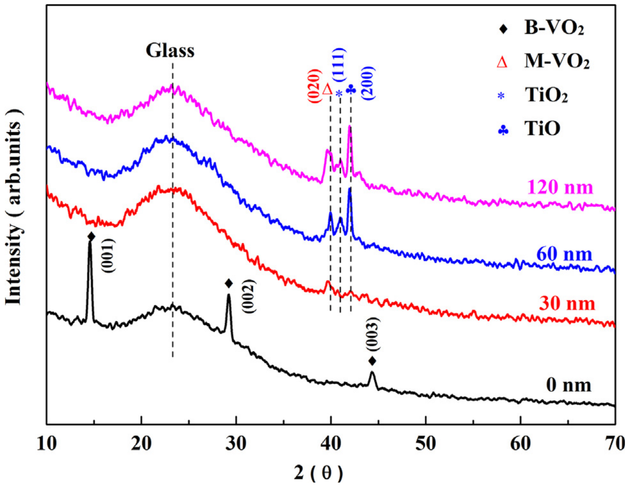

Fig. 1. XRD patterns of VO_2 films deposited on TiO_2 buffer layers with different thicknesses.

3. Results and discussion

3.1. Structure and microstructure characterization

Fig. 1 shows the XRD diffraction patterns of VO_2/glass film and VO_2/TiO_2/glass films. The broad diffraction valley corresponding to a 2θ degree ranging from 15° to 30° suggest the glassy nature of the substrates. For the VO_2/glass film, the peaks located at $2\theta = 14.49°$, 29.16° and 44.40° are assigned to B-VO_2 (0 0 1), B-VO_2(0 0 2) and B-VO_2 (0 0 3) diffraction respectively (JCPDS No. 31-1438), indicating that the B-phase VO_2 films with a single orientation were deposited directly on the glass substrate. B-phase VO_2 films (not discussed in detail in this paper) could be used in uncooled infrared (IR) detectors and electrodes for lithium-ion batteries on account of its high temperature-coefficient of resistance and large capacity for Li^+ intercalation [32,33]. For XRD patterns of the VO_2/TiO_2/glass films, it can be seen that the diffraction peaks appear at 39.96°, 41.08° and 41.97°, of which the peak located at 41.08° belongs to the TiO_2 (1 1 1) plane (JCPDS No. 82-0514), implying that the TiO_2 films exhibit the characteristics of rutile crystal. The peak located at 41.97° is assigned to TiO (2 0 0) diffraction. The appearance of TiO might due to Ti ions diffusion and incorporation with oxygen during VO_2 growth. The another peak located at 39.96° is assigned to M-VO_2 (0 2 0) diffraction (JCPDS No. 43-1051), implying the formation of M-phase VO_2 assisted by the TiO_2 buffer layer. Furthermore, with the increase of the buffer layer thickness, the intensity of diffraction peaks of TiO (2 0 0) and VO_2 (0 2 0) exhibit an increasing trend. Compared with that of VO_2(60 nm)/TiO_2(60 nm)/glass, the diffraction peak of VO_2 (0 2 0) of VO_2(60 nm)/TiO_2(120 nm)/glass has wider FWHM (full width at half maximum). It indicated that the crystallization quality of VO_2 thin films firstly got better and then became worse with the increase of the buffer layer thickness. Moreover, with increasing TiO_2 layer thickness, the VO_2 (0 2 0) diffraction peak exhibits a clear shift (2θ are 39.8°, 39.9° and