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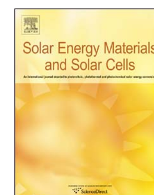

Low-temperature deposition of VO_2 films with high crystalline degree by embedding multilayered structure

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ABSTRACT

It is a long-standing challenge in the fabrication of single-phase VO_2 films at low temperature on Si substrate or glass substrate due to their thermodynamic phase-instability and the polymorphic structures. Recently, the demand for high-quality thin films deposited at low temperature is strongly pushed by their applications on devices and smart windows. Thermochromic films of VO_2, as well as multilayer films of VO_2/ZnO and VO_2/TiO_2/ZnO, were made by magnetron sputtering method and characterized by X-ray diffraction (XRD), atomic force microscopy (AFM), UV–visible-NIR spectrophotometer, (scanning) transmission electron microscopy ((S) TEM) and Electron energy loss spectroscopy (EELS). Films with high crystalline degree VO_2 single crystal phase were obtained at a fairly low temperature of 300 °C without subsequent annealing by embedding ZnO and TiO_2 layers between VO_2 and substrates. It is demonstrated that VO_2/TiO_2/ZnO films could display higher luminous transmittance and better semiconductor to metal transition (SMT) performance. Our data can serve a promising point for industrial production with high degree of crystallinity at a low temperature.

1. Introduction

Vanadium dioxide (VO_2) has attracted the interest because of its thermochromic semiconductor-to-metal transition (SMT) that exhibits tremendous contrast in optical, electrical and magnetic properties upon heating and cooling. VO_2 thin films are excellent materials for technological applications such as thermochromic coatings [1], ultra-fast switching devices [2], sensors and micromechanical systems [3,4], etc. In particular, transparent VO_2-based thin films provide an attracting application in smart windows, that is, windows that capable of regulating solar/heat transmission for energy efficiency and comfort [5–7].

Physical deposition method plays a dominant role in VO_2-based thin films manufacture and there are numbers of specific methods for VO_2 film deposition [8–10]. However, most of them have the problem of co-deposition of impurity vanadium oxides (VO, V_2O_3, V_2O_5) [10–12], causing degradation of thermochromic films properties. Generally, VO_2 film is deposited with substrate temperature of 350–500 °C for crystallization [1,8,10,13,14], which makes it difficult to produce with the present industrial production lines. Therefore, it is very meaningful to lower the temperature deposition of VO_2 films. Wang et al. reported a fabrication method of vanadium oxide films at a relatively low growth temperature of 200 °C, but it required post-growth annealing at 450 °C to get the VO_2 (M) films [11]. Melnik et al. investigated low-temperature method for thermochromic high ordered VO_2 phase formation, which is also need two steps including post annealing process [12]. In our consideration, the post annealing treatment is not recommended for the easier nucleation of impurity vanadium oxides (enthalpy of formation ΔH_{V2O5} =− 1557 cal/mole, ΔH_{V2O3} =− 1219 cal/mole, ΔH_{VO2}=− 713 cal/mole) and increasing mechanical stress due to the difference in thermal expansion coefficient α between film and substrate (α_{VO2} =2.1×10^{-5}/°C, α_{glass} =3.3–8.5×10^{-6}/°C). Zhang et al. proposed a 200 °C magnetron sputtering method for VO_2 thin film, where post annealing was inessential but a substrate bias voltage of −160 V was required [15]. Specific substrate bias voltage control can only be realized in small laboratorial sputtering devices but difficult in industrial production lines. Another low temperature (300 °C) method was proposed by Aijaz et al. [16], where the special equipment of high power impulse magnetron sputtering (HiPIMS) was applied. The inherent defects of high energy consumption and low

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deposition rate may keep HiPIMS away from practical application, thus new method for lowing sputtering temperature is still needed.

Differ from previous work, our paper proposed a novel low temperature (300 °C) preparation method without any post treatment process for high crystalline degree VO_2 films deposition by embedding multilayered structure. Since crystalline ZnO thin film can be relatively easily deposited among wide temperature range [17–19] and TiO_2 thin film always acts as buffer layer and growth template of VO_2 (M) films due to their similar lattice parameters [5,20,21], ZnO and TiO_2 thin film come to be the first choice of embedding layer. In our research, we systematically explored the possibilities of benefiting from SMT performance in multilayer stacks of the types VO_2/ZnO and VO_2/TiO_2/ZnO. Scanning transmission electron microscopy (STEM) and Electron Energy Loss Spectroscopy (EELS) results exhibited the good growth of VO_2 films and the interfaces. Some interesting results were found and this work can provide some good suggestions for low-temperature depositing VO_2 films with high performance.

2. Experimental

Films of VO_2 with single layer, bilayer (VO_2/ZnO), and trilayer (VO_2/TiO_2/ZnO) structure were fabricated on Si (100) or 50×50 mm^2 flat glasses substrates by magnetron sputtering deposition. Single stoichiometric phase VO_2 thin films were synthesized by means of dc sputtering from a VO_2 ceramic target. Compared to traditional reactive V metallic target sputtering, sputtering from a VO_2 ceramic target has an advantage of the stability of the deposited VO_2 stoichiometry being determined mainly by V-O stoichiometry in sputtering target. ZnO and TiO_2 layers were formed at bottom of VO_2 by rf magnetron sputtering from ZnO and TiO_2 ceramic target, respectively. All substrates were kept at elevated temperature 300 °C during sputtering, the sputtering temperature of 300 °C was chosen based on our early explorative experiments, in which the lower temperature (250 °C) sample showed poor crystallinity in STEM images and poor optical properties. The base pressure in sputtering chamber was 3×10^{-4} Pa, the dc gun power was 65 W, rf gun power was 80 W for both ZnO and TiO_2, sputtering time was 10 min for ZnO, 30 min for TiO_2, 60 min for VO_2 and the sputtering gas was supplied at 44 sccm for Ar and 1 sccm for O_2 to maintain 1.0 Pa. Schematic structure of the proposed multilayer structure is presented in Fig. 1.

The optical properties of the films were characterized by UV–visible-NIR spectrophotometer (HITACHI U-3100). The crystallinity and top morphology of the films were characterized by X-ray diffraction (XRD, Rigaku Ultima IV) and atomic force microscopy (AFM, SII Nano Technology Ltd, Nanonavi Π). The crystal structure and chemical composition concerning the thin film growth and interface engineering were studied by STEM (JEOL-2100F). The bright field imagining (BF) and high angle annular dark field imaging (HAADF) were obtained along with STEM tests. EELS in the Cs-corrected scanning transmission electron microscope (NION USTEM200) were also taken.

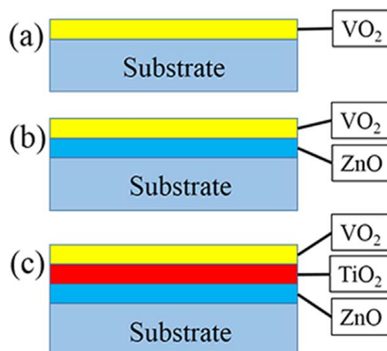

Fig. 1. Schematic structure of the proposed multilayer thin films with (a) single layer, (b) bilayer (VO_2/ZnO), and (c) triple layer (VO_2/TiO_2/ZnO) structure.

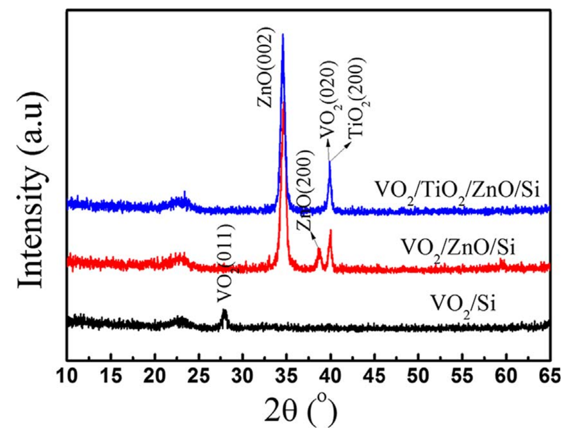

Fig. 2. XRD patterns VO_2 films with multilayer structure.

3. Results and discussion

3.1. Structure and surface analysis of VO_2-based multilayered films

Fig. 2 gives the XRD patterns of deposited films. The observed diffraction peaks in each pattern are successfully indexed to the ZnO, TiO_2 or VO_2(M) without impurity phase, confirming the purity of all the samples. VO_2 mainly shows (011) plane in single layer sample but (020) plane in bilayer and triple layer samples, which proves the influence on VO_2(M) orientation of embedding layer. XRD results also indicate the poor crystalized VO_2(M) in single layer sample and enhanced crystalline degree in triple concluding from the related peak intensity. ZnO displays main orientation of (002) and secondary orientation of (200) in bilayer sample but only (002) orientation remain in triple layer sample. It is probably attributed to the longer sputtering time in triple layer sample, ZnO keep the process of arrangement during TiO_2 sputtering and get a more uniform orientation. TiO_2 should appear as rutile TiO_2 (TiO_2 (R)) and show (200) plane, which can later be proved by TEM results, but the diffraction angle of 39.2° (PDF: 21-1276) is hidden by (020) of VO_2(M) (PDF: 43-1051). AFM test was taken on the surface of the samples for calculating root mean square roughness (RMS). The RMS results are 5.47 nm for single layer, 3.98 nm for bilayer and 1.86 nm for triple layer sample. It reveals that VO_2 film in triple layer sample becomes relatively flat and the size of crystal grains becomes more uniform.

The microstructure analyses for these three sets of samples are shown in Figs. 3–6, respectively. For all three samples, there exhibit an amorphous layer of SiO_x between deposited layers and Si substrate, so we consider that the deposited layers show no epitaxial growth relationship with substrate. For single layer VO_2 sample (Fig. 3), it can be noticed that the VO_2 layer is nearly amorphous, only few crystal grain with the size of 10–20 nm can be found near the substrate. The crystalline is confirmed by high-resolution TEM images in Fig. 3(b). Therefore, the microscope results demonstrate the poor crystallinity of single layer VO_2 sample deposited with 300 °C, as coincident with XRD results (Fig. 2).

Fig. 4 is the STEM-BF and HAADF images for bilayer VO_2/ZnO sample. Compared with Fig. 3, by embedding 20 nm ZnO layer, both ZnO and VO_2 appear to be polycrystalline and better crystalized. It can be noticed that there is a clear transition layer with the thickness of ~ 2 nm between ZnO and VO_2 film (yellow lines in Fig. 4(b)), but the transition layer is not smooth and there are regions of poor crystallization or even amorphous near it. Poor crystallization or amorphous regions exhibit darker contrast in HAADF image of Fig. 4(a). The size of domain in ZnO is counted as ~15 nm in wide while ~10 nm in VO_2 layer, which means the grains of VO_2 and the grains of ZnO are not well corresponded. The out-of-plane orientation is considered mainly to be the (001) plane in ZnO and (010) plane in VO_2 based on the XRD

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