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Regulation of the phase transition temperature of VO_2 thin films deposited by reactive magnetron sputtering without doping

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ABSTRACT

Thin films of phase pure VO_2(M) were fabricated on quartz glass by reactive magnetron sputtering. Structural, morphological, electrical and optical properties of the prepared samples were characterized. Interestingly, it was found that the phase transition temperature can be regulated to a large scale from 46 °C to 72 °C only by precisely controlling the oxygen partial pressure without any element doping. It was assumed that changes in the amount of free electrons and internal strain introduced by the tiny change in the oxygen-to-vanadium ratio contributed to the significantly regulated phase transition behavior.

1. Introduction

Vanadium dioxide (VO_2), one of the most interesting thermochromic materials, exhibits a reversible first-order metal–insulator phase transition (MIT) at a critical temperature $T_c = 68$ °C (bulk single crystal VO_2) [1]. VO_2 has a monoclinic structure with the $P2_1/c$ space group (M phase) below the phase transition temperature; the M phase is an insulator with an energy gap of ~0.6 eV [2]. While above the phase transition temperature, it transforms to a simple tetragonal rutile lattice with the $P4_2/mnm$ space group (R phase) and the rutile phase is a conductor [2]. The metal–insulator phase transition mechanism of VO_2 can be thought of as an orbital-assisted concerted Mott–Peirls transition [3]. Dramatic changes in the electrical and optical properties occur accompanying the phase transition. Although the phase transition is accompanied by a change in the crystal structure, it results in only a small volume change (1%) in the unit cell [4] and the VO_2 thin films can survive stress changes above almost 10^8 cycles [5,6]. Consequently, VO_2 thin films are suitable for many applications, such as switching devices, sensors, and smart windows [7–9].

Various methods have been utilized to deposit VO_2 thin films, such as sputtering [10,11], ion implantation [12], pulsed-laser deposition [13], chemical-vapor deposition [14], and sol–gel method [15,16]. Compared to other thin film fabrication methods, magnetron sputtering is characterized by the following advantages: good adhesion of films on substrates, very good thickness uniformity, good controllability and long-term stability of the deposition process, and scalability to large areas.

The ability of oxygen to change the phase-transition properties of VO_2 was studied [4,17–20]. However, it is still a challenge to fabricate single phase VO_2 thin films due to the multiple chemical phases of the V–O system, such as VO, V_2O_3, VO_2, V_6O_{13} and V_2O_5. In this research, we thoroughly investigated the effect of oxygen on the structural, electrical and optical properties of pure single phase VO_2(M) thin films deposited on quartz glasses by reactive magnetron sputtering. Interestingly, the MIT temperature of the prepared samples can be regulated as much as ~26 °C without any element doping. Achieving carrier density and such a large regulation of T_c without any element doping has not been reported.

2. Experimental section

VO_2 thin films with a thickness of ~50 nm were deposited in a reactive rf magnetron sputtering system by sputtering water-cooled vanadium metal target (50 mm in diameter, 99.9% purity). Quartz glasses (20 × 20 × 1 mm) were used as substrates. Before being put into the deposition chamber, quartz glass substrates were ultrasonically cleaned in acetone and subsequently in ethanol for 15 min, respectively, and then dried with pure nitrogen flow.

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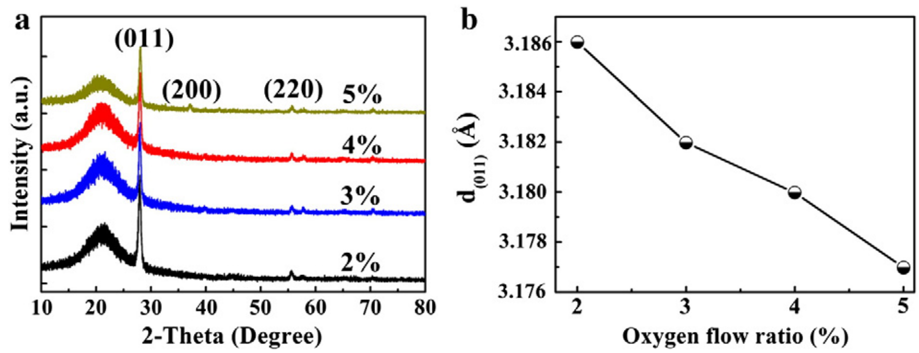

Fig. 1. a. The XRD spectra and b. (011) planar distance of VO_2 films fabricated with different oxygen flow ratios.

After being pumped down to a base pressure of 5×10^{-4} Pa, the deposition chamber was filled with high purity (99.999%) Ar and O_2 mixture gas. The oxygen flow ratios (oxygen flow rate/total flow rate) were fixed as 2%, 3%, 4%, and 5%, respectively. The total gas pressure was maintained at ~1.0 Pa. An r.f power of 200 W was applied to the V target. During deposition, the substrate temperature was kept at 450 °C for the better crystallinity of VO_2 thin films. To improve the film homogeneity, the substrates were rotated along the vertical axis at a speed of 10 rpm.

The crystalline structures of the deposited films were characterized by an X-ray diffractometer (XRD, Rigaku Ultima IV) with Cu K_α radiation ($\lambda = 0.15406$ nm) and glancing incidence angle of 1°. The film thickness was measured using a surface profilometer, model Veeco Dektak 150. The surface morphologies of the prepared films were observed by atomic force microscopy (AFM, Nanocute SII, Seiko, Japan). The room-temperature electrical resistance and carrier concentration were measured by a four-point probe in the van der Pauw configuration with a Lakeshore 7704A Hall System. The optical transmittance was measured at wavelength range of 250–2600 nm at 26 °C and 95 °C by a spectrophotometer (Hitachi Corp., Model UV-4100). Temperature was measured with assistance of a PT100 temperature sensor in contact with the films and was controlled via a temperature controlling unit. Heating was controlled through a temperature-controlling unit. Hysteresis loops were measured by collecting the transmittance of films at a fixed wavelength (2000 nm) at a temperature interval of ~2.0 °C. The normal incidence transmittance and reflectance in the region of 2.5–5 μm were measured using a Bruker Equinox 55 Fourier transform infrared (FTIR) spectrometer. An Au film was employed as a reference.

3. Results and discussion

3.1. Structural characterization

The XRD spectra for VO_2 thin films deposited on quartz glasses are shown in Fig. 1a. All peaks can be indexed to VO_2(M) and (011) was the prominent plane for the VO_2 thin film prepared by this method. No reflections due to other types of vanadium oxides were observed. The VO_2 (011) interplanar spacing $d_{(011)}$, which as an indicator of the strain in the films, was calculated from the VO_2 (011) peaks according to Bragg's law. Fig. 1b shows that the $d_{(011)}$ values of VO_2 films increase as the oxygen flow ratio decreases.

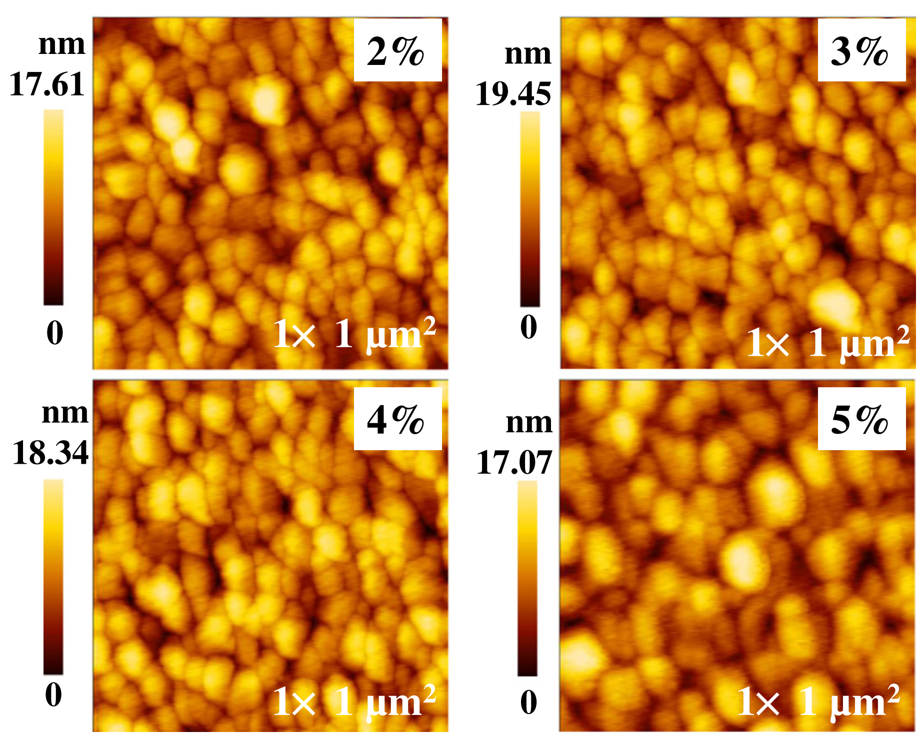

Fig. 2. AFM images of VO_2 films that were deposited at different oxygen flow ratios.