



Investigation on microstructures and phase transition characteristics of titanium/yttrium co-doped vanadium oxide thin films

Xin Zhou, Deen Gu*, Shiyang Xu, Haoxin Qin, Yadong Jiang

School of Optoelectronic Information, University of Electronic Science and Technology of China (UESTC), Chengdu, 610054, China



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ABSTRACT

Co-doping with two elements has recently attracted attention as a novel approach for tailoring the semiconductor-metal transition (SMT) characteristics of vanadium dioxide (VO_2). Here, we investigate the influence of titanium/yttrium (Ti/Y) co-doping on the microstructure and SMT characteristics of VO_2 thin films. At low Y concentration, Ti/Y co-doped VO_2 thin films exhibit a monoclinic structure similar to VO_2 but characterized by a smaller grain size, whereas, the $\text{VO}_2(\text{B})$ phase appears as the Y concentration is increased. Interestingly, even a complete amorphization of the film is obtained for co-doped VO_2 thin films. The strong dependence of the microstructure upon the co-doping level is ascribed to the conjugated influence from the simultaneous adjustment of V–V chains and V–O bonds due to the existence of Ti^{4+} and Y^{3+} ions in VO_2 lattice, respectively. As a result, the SMT feature of VO_2 thin films is strongly limited or even fully disappears.

1. Introduction

The first order semiconductor-metal transition (SMT) in vanadium dioxide (VO_2) has been investigated for decades due to the abrupt change of the optical and electrical properties during the SMT [1]. The SMT in VO_2 can be triggered by thermal, electrical, optical or magnetic fields [2,3], thus VO_2 is regarded as a potential material in many applications, such as tunable metamaterials [4], memory materials [5], smart windows [6], gas sensors switches [7] and field-effect transistors [8]. In order to meet the practical requirements, the SMT characteristics such as its temperature, hysteresis width and amplitude need to be adjusted. For example, different SMT temperatures are valuable for highly-tunable metamaterials [9]. A narrow hysteresis width is desirable for the applications in smart windows [10] and sensors [7], while a wide hysteresis width is favorable for optical data storage devices [11].

The doping with transition metal elements is a typical approach to modulate the SMT characteristics. The doping of VO_2 with high-valent transition metals such as niobium, molybdenum and tungsten was previously shown to decrease the SMT temperature [12–14]. Especially, the SMT temperature of VO_2 was shown to be reduced by 21–28 °C/at. % through W-doping [15], whereas doping with a low-valent metal (chromium, aluminium, etc.) increases the SMT temperature [16]. Besides, the hysteresis width can be obviously narrowed by Ti-doping [17]. Generally, mono-doping with one transition metal element hardly gives rise to desirable results for regulating the SMT characteristics of VO_2 . For example, W doping is an easy and effective approach for

adjusting the SMT temperature of VO_2 from about 68 °C to room temperature, however, the introduction of W outstandingly reduces the SMT amplitude [15]. So the co-doping with two elements has been recently attempted to further tailor the SMT characteristics, Mo/W co-doped VO_2 films prepared by a sol-gel process have shown a low SMT temperature of 35 °C but a wide hysteresis width of 22 °C [11]. Differently, K. Miyazaki et al. obtained a large temperature coefficient of resistance (TCR) value of 11.9%/°C in Cr/Nb co-doped VO_2 thin films, showing no thermal hysteresis [18]. Furthermore, W. Burkhardt et al. observed a simple superposition effect of W and F dopants in W/F co-doped VO_2 [19]. However, I. Takahashi et al. demonstrated an obvious interaction between W and Ti in W/Ti co-doped VO_2 films, resulting in enhanced optical and electrical properties [20].

It is well known that rare earth (RE) elements are effective dopants for improving the properties of oxides [21]. In fact, our previous work has shown that Y-doping can effectively regulate the SMT characteristics of polycrystalline VO_2 thin films [22]. However, the co-doping of VO_2 with a RE element and a transition metal element has been scarcely reported. In this article, we investigate the effect of Ti/Y co-doping on the microstructures and the SMT characteristics of VO_2 thin films. Interestingly, we observe a conjugated interaction between Ti^{4+} and Y^{3+} ions in Ti/Y co-doped VO_2 . Ti/Y co-doping gives rise to an obvious lattice distortion in VO_2 compared to mono-doping with only Ti or Y. The lattice distortion in Ti/Y co-doped VO_2 thin films results in the appearance of the $\text{VO}_2(\text{B})$ phase, or even the formation of a completely amorphous structure. As a result, the SMT feature of VO_2 is restrained,

* Corresponding author.

E-mail address: gudeen@163.com (D. Gu).

and even disappears due to Ti/Y co-doping.

2. Material and methods

A DC reactive magnetron sputtering system with a constant-current power supply was used for depositing Ti/Y co-doped VO₂ films based on a reactive sputtering process. Thin films were deposited on quartz substrates (23 × 23 × 1 mm³), which were cleaned in acetone and ethanol under ultrasonic bath, then rinsed with deionized water and dried by nitrogen. The substrates were fixed on a rotatable plate with a speed of 10 rpm during the whole process. Substrates were preheated in the chamber with base pressure lower than 1.0 × 10⁻³ Pa for 60 min at 100 °C, then the sputtering was performed at the same temperature at 0.320 A for 50 min with a O₂/Ar ratio of 1:50. After sputtering, the samples were annealed *in-situ* for 60 min at 400 °C in O₂ atmosphere with a pressure of 3.5 Pa. Finally, the samples were taken out as soon as the temperature was below 80 °C. The film thickness was controlled as about 320 nm according to the calibrated deposition rate. Yttrium doping was performed using V/Y alloy pieces (consisting of 10.0% Y and 90.0% V), while titanium doping was achieved using 99.9% purity Ti pieces (10 × 10 × 2 mm³). The Ti and V/Y pieces were symmetrically placed on the sputtered surface of a vanadium target (99.9% purity, 80 mm diameter, 5 mm thickness) [23]. The doping concentration was adjusted by varying the projected area of V/Y or Ti pieces on the vanadium target. For simplicity, the samples with different projected areas were denoted as VO, VTO, VYO, VTYO-1, VTYO-2, VTYO-3, VTYO-4 and VTYO-5, respectively.

The microstructures of films were determined by X-ray diffraction (XRD) and Raman analyses at room temperature (RT). XRD patterns were acquired on an X-ray diffractometer (D8 Advance, Bruker) with Cu K α radiation. RT Raman spectra were obtained on a confocal α -Raman spectrometer with the excitation wavelength of 514.5 nm (Ar⁺ laser) and an irradiation power of less than 1 mW (LabRAMHR800, Horiba Jobin-Yvon). The film compositions were probed by energy dispersive spectroscopy (EDS) in a field-emission scanning electron microscope (FESEM, S-4800, Hitachi). The surface morphologies were recorded by atomic force microscopy (AFM, Dimension Icon, Bruker). The thicknesses of VO₂ films were determined using a profilometer (XP-300, AMBios Tech). The temperature dependence of resistivity from RT to 90 °C was determined using a four-point probe (SX 1934) along with a hot plate at a heating/cooling rate of less than 1 °C/min. A high resistance meter (KEITHLEY 6517A) was used to measure the resistance of the samples with resistance higher than the measurement limit of the four-point probe. The chemical states of Y and Ti in the films were investigated by X-ray photoelectron spectroscopy (XPS, ESCALAB 250, Thermo) using Al K α radiation (1486.6 eV) after etching for 120s using Ar⁺ (3 keV). The binding energies (BEs) were calibrated based on the C 1s peak at 284.6 eV from adventitious carbon.

3. Results and discussion

Fig. 1a shows the XPS survey spectra of VO, VTO, VYO, VTYO-5, revealing the presence of Ti in VTO and VTYO-5 and Y in VYO and VTYO-5. As shown in Fig. 1b, the Ti 2p peak at about 485.5 eV for VTO and VTYO-5 indicates the Ti⁴⁺ oxidation state in Ti-doped and Ti/Y co-doped VO₂ thin films [24]. Fig. 1c shows the Y 3d XPS spectra for VYO and VTYO-5. The BE of about 158 eV suggests the presence of Y³⁺ oxidation state in VYO and VTYO-5 [25]. The effect of doping on the chemical state of V was further analyzed as Fig. 1d. The BE of about 516 eV for V 2p_{2/3} reveals that V exists in the form of V⁴⁺ in the undoped VO₂ thin film [24]. The BEs of V 2p_{2/3} in VTO and VYO are very close to the one in VO. This means that Ti or Y mono-doping scarcely influences the chemical state of V. However, the BE of V 2p_{2/3} in VTYO-5 (516.6 eV) is slightly higher than that in VO (516.2 eV). This implies that Ti/Y co-doping induces the further oxidation of V⁴⁺ compared with Ti or Y mono-doped VO₂ thin films [17,22].

The XRD patterns of undoped, Ti-doped, Y-doped, and Ti/Y co-doped VO₂ thin films are displayed in Fig. 2. Ti-doped and Y-doped VO₂ thin films show a polycrystalline monoclinic VO₂ (VO₂(M)) structure (PDF No. 76-0456) similar to the undoped VO₂ thin film [26]. However, Ti or Y mono-doping affects the grain size of monoclinic VO₂ crystals, which was estimated by using the Scherrer formula [26]. As indicated in Table 1, the grain size slightly increases for Ti-doping, while it obviously decreases for Y-doping. This indicates that Ti-doping promotes the grain growth, while Y-doping restrains it, in agreement with previous reports [17,22]. The crystalline structure in Ti/Y co-doped VO₂ depends on the Y doping level. The Ti and Y concentrations were obtained from EDS analysis (Table 1). As shown in Fig. 2, by combining Ti with a small amount of Y, the Ti/Y co-doped VO₂ thin films (VTYO-1 and VTYO-2) still keeps the same monoclinic structure as the undoped VO₂ (VO), but has smaller grain size. With the increase in the concentration of Y in Ti/Y co-doped VO₂ (VTYO-3), the intensity of (011) diffraction peak for VO₂(M) decreases and VO₂(B) phase appears as indicated by (110), (-401), (-311), and (312) diffraction peaks from VO₂(B) (PDF No. 31-1438) [27]. By further increasing the Y concentration in the Ti/Y co-doped VO₂, the intensity of each diffraction peak obviously decreases (VTYO-4), even no diffraction peak is anymore observed for VTYO-5, testifying an amorphous structure. These results suggest a strong interaction between Ti⁴⁺ and Y³⁺ ions in the co-doped VO₂, which leads to a stronger lattice distortion of VO₂ compared with mono-doping with Ti or Y. This is further demonstrated in the following Raman analysis.

Fig. 3 depicts the RT Raman spectra for all the samples. Y-doped and Ti-doped VO₂ thin films (VYO and VTO) have the same phonon modes as VO₂ (VO), which is consistent with XRD results. In Ti/Y co-doped VO₂, the Raman spectra vary with the Y concentration. At low Y concentration (VTYO-1 and VTYO-2), Ti/Y co-doped VO₂ exhibits similar Raman modes to mono-doped VO₂. The Raman intensities of typical modes decrease with the increase in the Y concentration. Although XRD analyses show that the VO₂(B) phase is present in VTYO-3 and VTYO-4 samples (Fig. 2), the main Raman peaks of VO₂(B), namely the V–O–V bending (263 cm⁻¹) and stretching (482 cm⁻¹) modes [28], are significantly weakened as only a weak signal around 482 cm⁻¹ is observed in VTYO-3 and VTYO-4 (Fig. 3b). This could originate from the strong effect of the Ti/Y co-doping on VO₂(B) Raman modes. A similar phenomenon has been observed in W-doped VO₂ films [29]. W-doped and undoped VO₂ films exhibited the same crystalline structure, but the characteristic Raman mode at around 220 cm⁻¹ disappeared in the doped film [29]. For VTYO-5, no Raman mode can be detected. This can be attributed to the amorphization of thin films as indicated by XRD data.

In order to further investigate the effect of doping on the microstructures of VO₂ lattice, two typical A_g modes were carefully followed. As indicated in Fig. 3c, the low-frequency A_g mode (ω_1) at 192 cm⁻¹ shifts to a lower frequency (187 cm⁻¹) for VTO. This suggests that Ti is incorporated into the VO₂ lattice in the substitutional form [17]. The ω_1 mode is generally ascribed to the motion of V ions along V–V chains [30]. The red-shift of ω_1 mode indicates that Ti-doping affects the local structure along V–V chains in VO₂(M) lattice. Substitutional Ti species induce a local anatase coordination structure around Ti site [31]. This causes a structural adjustment of V–V chains around Ti sites in the host VO₂ lattice [31], which results in the shift of ω_1 mode towards low frequency. Interestingly, there is no frequency shift of the high-frequency A_g mode (ω_2) at about 614 cm⁻¹ for Ti-doped VO₂ compared with undoped VO₂ as shown in Fig. 3d. This indicates that there is no effect of Ti-doping on V–O bonds in the monoclinic VO₂ lattice since ω_2 mode is related to the V–O stretching mode [32]. This could result from the same coordination number of Ti⁴⁺ ions as V⁴⁺ ions in the host VO₂ lattice.

In the Y-doped VO₂ (VYO) film, the ω_1 mode of slightly shifts to higher frequencies upon doping (Fig. 3c), which is consistent with the previous results [22]. This suggests that the presence of Y atoms in VO₂

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