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Metal–insulator transition properties of sputtered silicon-doped and un-doped vanadium dioxide films at terahertz range

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ABSTRACT

Silicon-doped and un-doped vanadium dioxide (VO_2) films were synthesized on high-purity single-crystal silicon substrates by means of reactive direct current magnetron sputtering followed by thermal annealing. The structure, morphology and metal–insulator transition properties of silicon-doped VO_2 films at terahertz range were measured and compared to those of un-doped VO_2 films. X-ray diffraction and scanning electron microscopy indicated that doping the films with silicon significantly affects the preferred crystallographic orientation and surface morphologies (grain size, pores and characteristics of grain boundaries). The temperature dependence of terahertz transmission shows that the transition temperature, hysteresis width and transition sharpness greatly depend on the silicon contents while the transition amplitude was relatively insensitive to the silicon contents. Interestingly, the VO_2 film doped with a silicon content of 4.6 at.% shows excellent terahertz switching characteristics, namely a small hysteresis width of 4.5 °C, a giant transmission modulation ratio of about 82% and a relatively low transition temperature of 56.1 °C upon heating. This work experimentally indicates that silicon doping can effectively control not only the surface morphology but also the metal–insulator transition characteristics of VO_2 films at terahertz range.

1. Introduction

Vanadium dioxide (VO_2) is famous for its metal–insulator transition (MIT) near room temperature accompanied by giant and abrupt changes in electrical and optical properties [1–8]. Especially, this MIT can be finished in ~80 fs in a photo-induced transition experiment [9]. Owing to the excellent MIT properties, VO_2 film has attracted great interest for a wide variety of potential applications such as optical storage devices, smart windows, switching elements [1–8]. More importantly, a giant change in terahertz (THz) transmission was observed when VO_2 film undergoes the MIT which can be triggered not only by temperature [10,11] but also by light [1] or THz field [12]. The near-room-temperature giant and ultrafast MIT characteristics make VO_2 film a promising candidate for THz switching and modulator, which is particularly significant for high bandwidth communication because the THz frequency range covers a wide bandwidth from 0.1 to 10 THz [10]. For switching-type device applications, VO_2 film is required to possess a small hysteresis width in order to operate the devices reliably [5,13,14]. In other words, the smaller the hysteresis width of VO_2 film is, the more reliable the switching-type devices are. In addition, a large transmission modulation ratio is essential to improve the sensitivity, efficiency and reliability of VO_2 switches [13]. Although the preparation methods, deposition conditions and substrates can modulate the MIT properties, previous studies indicate that the hysteresis width of polycrystallineVO_2 films in general is relatively large [4,10,11,14].

Great efforts have been focused on the effect of doping on the MIT properties of VO_2 films. The results show that doping is a compromise between hysteresis width and modulation efficiency. Generally, doping the VO_2 films with many elements such as W, or Mo can profoundly narrow the hysteresis loop at the price of a significant reducing of the modulation ratio [15,16]. On the other hand, Chen et al. [17] prepared the VO_2–SiO_2 composite films and the results show that the presence of SiO_2 in the VO_2 films enhances the

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transmittance without compromising the modulation efficiency. Doping the VO_2 films with silicon (Si) may narrow the hysteresis loop without compromising the modulation depth. To the best of our knowledge, however, the effect of Si doping on the MIT properties of VO_2 films has been rarely studied up to now.

In this work, we prepared Si-doped and un-doped VO_2 films on high-purity single-crystal Si substrates via direct current reactive magnetron sputtering followed by thermal annealing and investigated their MIT properties at THz range. Owing to the best transparency as well as the least dispersive medium at THz range [18,19], the high-purity single-crystal Si is particularly applicable as substrates for VO_2-based THz devices. In addition, direct current reactive magnetron sputtering is one of the most widely used film deposition techniques due to its low deposition temperature, good adhesion, high growth rate and low cost [5]. The structure, morphology and MIT properties of Si-doped VO_2 films at terahertz range were measured and compared to those of un-doped VO_2 films. Interestingly, high-quality Si-doped VO_2 films with a small hysteresis width of about 4.5 °C and excellent THz transmission modulation ratio of about 82% were obtained. The experimental results indicate that Si doping can effectively control not only the surface morphology but also the MIT characteristics of VO_2 films at terahertz range.

2. Experimental details

We prepared Si-doped and un-doped VO_2 films on high-purity single-crystal Si (1 1 1) substrates (~10,000 Ω cm resistivity, ~0.5 mm thickness) by direct current reactive magnetron sputtering technique using V:Si targets [20,21] comprising V metallic disk (99.9% purity, 80 mm diameter, 4 mm thickness) and Si chips (99.9% purity, 0.5 mm thickness). The Si chips were attached onto the V target. The Si contents in the deposited films are controlled by altering the effective sputtering area of Si-chips. In order to improve the uniformity, the substrates were kept rotating at a high speed of about 30 rpm. The high-purity Si substrates were cleaned according to the methods described in our previous work [5]. The base pressure for the system was superior to 1×10^{-3} Pa. The working gas Ar (99.99% purity) and the reactive gas O_2 (99.99% purity) are introduced separately into the chamber by using two mass flow controllers. The target was pre-sputtered in pure Ar for 10 min in order to get rid of any possible contaminations of the target surface. For convenience of discussion, the key preparation parameters and the designations of the corresponding films were listed in Table 1.

The compositions and valences of the films were analyzed by X-ray photoelectron spectroscopy apparatus (XPS, XSAM 800) equipped with a hemi-spherical mirror analyzer. The base pressure of the XPS system was lower than 3×10^{-7} Pa. X-ray photoelectron spectra were produced using a nonmonochromatized X-ray source ($h\nu$ = 51486.6 eV). Ar ions were used as the sputtering ion beams whose energy and current density were 1500 eV and 1 mA, respectively. The binding energies were determined by using C1s peak at 284.8 eV as a reference. The XPS peak was fitted by using a Shirley function with software XPS peak 4.1. Field emission scanning electron microscope (SEM, Hitachi S4800) was applied to characterize the morphologies of the deposited films. The Si contents of VO_2 films determined by energy dispersive spectrometer (EDS, OXFORD X-Max) were also listed in Table 1. The crystal structures of the VO_2 films were characterized by using X-ray diffraction (XRD) diffractometer, PANalytical Corp., Model X' Pert Pro (primary monochromatic Cu K_a radiation and glancing incidence angle of 1.0°). Raman spectra were performed on a Raman microscope spectrometer (Horiba Corporation, LabRAM HR800) using a 532.2 nm laser. The resolution of the Raman system and the overall uncertainty in the presented spectra are less than ±0.65 cm^{-1} and ±0.2 cm^{-1}, respectively. The THz transmission of VO_2 films at 4.8–5.4 THz was measured by using Fourier transform infrared spectroscopy (FTIR, PerkinElmer Spectrum) equipped with heating units.

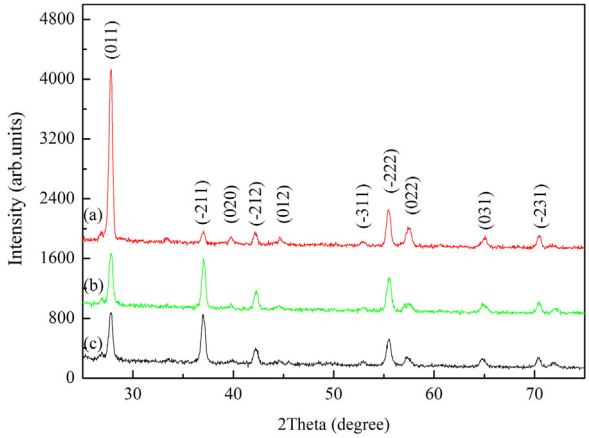

Fig. 1. XRD spectra for un-doped and Si-doped VO_2 films. (a) S1, (b) S2 and (c) S3.

3. Results and discussions

3.1. XRD analysis

Fig. 1 exhibits the XRD spectra for un-doped and Si-doped VO_2 films. One can find that all the deposited films show polycrystalline structures matching the monoclinic VO_2 well (JCPDS card no. 82-0661). For S1, an un-doped VO_2 film, a strong peak at $2\theta = 27.80°$ is found, corresponding to the (0 1 1) plane of VO_2 phase. The other peaks at $2\theta = 36.98°$, 39.78°, 42.17°, 44.62°, 52.89°, 55.42°, 57.51°, 65.08° and 70.44° are indexed to the diffractions from the (−2 1 1), (0 2 0), (−2 1 2), (0 1 2), (−3 1 1), (−2 2 2), (0 2 2), (0 3 1) and (−2 3 1) planes of VO_2 phase, respectively. Obviously, the intensity of VO_2 (0 1 1) peak is much larger than that of the others, indicating a polycrystalline nature with a (0 1 1) preferred orientation. One can also find that the Si-doped VO_2 films show a similar polycrystalline structure to that of un-doped films. In other words, all the peaks at the same locations as those observed in the XRD spectra for un-doped VO_2 film are also observed for Si-doped VO_2 films. However, the VO_2 (0 1 1) peak of Si-doped films is much weaker while the VO_2 (−2 1 1) peak is much stronger compared with that of un-doped VO_2 film. The Si-doped VO_2 films, S2 and S3, no longer show a (0 1 1) preferred orientation, since the VO_2 (0 1 1) peak has the same intensity as that of VO_2 (−2 1 1) peak. In addition, S2 and

Table 1
The key preparation parameters and the designations of the corresponding films.

Sample	Reactive oxygen flow rates (SCCM)	Substrate temperature (°C)	Deposition Time (min)	Annealing time (min)	Annealing temperature (°C)	Si contents in VO_2 films (at.%)
S1	1	100	40	45	330	0
S2	1	100	40	45	330	4.6
S3	1	100	40	45	330	10.6
S4	1	100	40	45	330	19.8