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Terahertz conductivities of VO_2 thin films grown under different sputtering gas pressures

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ABSTRACT

The terahertz (THz) conductivities in the metal-insulator transition process of VO_2 thin films on quartz substrates were investigated by using terahertz time-domain spectroscopy. It was found that the THz absorption and conductivity of the thin films are sensitive to the sputtering gas pressure, and the maximum THz amplitude modulation can reach as high as 75.9%. The complex THz conductivity in metallic state of the thin films can be well-fitted by the Drude-Smith model, and the temperature-dependent metallic domain fractions can be extracted by effective medium theory simulation. Based on these results, the metal-insulator transition of the VO_2 thin films can be characterized. The mechanisms of the THz transmission and conductivity were analyzed and discussed.

1. Introduction

Monoclinic vanadium dioxide (VO_2) is an attractive near-room temperature thermochromic material because of its remarkable change in optical and electronic properties during the reversible metal-insulator transition (MIT) [1–3], and can be potentially used in many areas, such as optical memory devices [4] and optic-electric switches devices [5,6]. Great progress has been made in the growth of high-quality VO_2 material [7–9], phase transition mechanism [10,11] and optimization of the thermochromic property [12–15] over the past few decades. The research on the basic interactions between VO_2 and electromagnetic wave in the terahertz ranges has attracted extensive attentions in recent years [16]. Especially, the coherent detection of the broadband THz pulse permits the direct access to the complex THz conductivity and dynamic metal-insulator transition by THz spectroscopy [11,17–20], providing an alternative to understanding the fundamental physical mechanism in strongly correlated systems. It has been demonstrated that the VO_2 thin films can behave as a tunable coating to support the active THz metamaterials [21,22], such as tunable polarizer, filter, switch and modulator with considerable dynamic range and multiple modulation ways, which can help us to develop some novel optics devices in the THz gap. In comparison with bulk crystal, the optical and electrical properties of the VO_2 thin film will be affected not only by the morphology but also by the complex interactions between strain field originating from the intergrain interaction and the substrate-film boundary as well [23]. And therefore, considerable efforts have been dedicated to regulate the morphology, grain size, crystal quality and thickness of VO_2 thin film by different growth conditions [24], substrate types [25,26] and substrate orientations [7,27]. Such methods make it possible optimize the modulation depth, the insertion loss and dynamic range in THz spectrum range. Different growth methods like sol–gel [10,28], solution-based process [29], thermolysis [30], pulsed laser deposition [31,32] and sputtering [12,26] have been explored to grow stoichiometric VO_2 thin film. Among them, the reactive

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sputtering technique is widely used method to grow VO_2 thin film with excellent crystal quality due to the diversiform controlling parameters like O_2 flow ratio, sputtering power and sputtering gas pressure that can normally control the stoichiometry, microstructure and crystal quality of the as-grown thin film. In previous work, we have studied the optical switching properties of VO_2 thin films by infrared (IR) spectrum [33], and it was found that the external growth factors like sputtering gas pressure and O_2 flow ratio can be employed to tailor the phase transition temperature, hysteresis width and the amplitude of the transition in IR range. In THz spectra region, the fundamental correlations between the THz conductivity and film growth parameters in reactive sputtering process that is essential to develop tunable VO_2 based THz device and understand the phase transition remain rarely explored. In this paper, we report the THz (0.2–1.3 THz) transmission and conductivity of the VO_2 thin films grown under different sputtering gas pressures. It was found that the complex terahertz conductivities of the VO_2 thin films in the metal-insulator transition process can be turned by growth parameters, and from which the metal-insulator transition of the VO_2 thin films can be well-characterized.

2. Experimental section

The VO_2 thin films were deposited on quartz substrate by radio frequency reactive magnetron sputtering. Our previous study found that the pure VO_2 thin films can be obtained only at the gas pressure of 0.2–0.4 Pa [33], and therefore, the VO_2 thin films used in this study were grown under the conditions of 0.2–0.4 Pa sputtering gas pressures, 3.5% of O_2 flow ratio, and 350 W of sputtering power. The film thickness is found to be about 350, 400, and 370 nm at the sputtering gas pressure of 0.2, 0.3, and 0.4 Pa, respectively. THz time-domain spectroscopy (TDS) was performed by using a standard transmission configuration, in which a mode-locked Ti:sapphire laser deliver the pulses with duration of 100 fs, center wavelength of 800 nm, and repetition rate of 76 MHz, which are divided into pump and probe beam. The pumping laser pulses are focused on LT-GaAs photoconductive antenna and generate the broadband THz pulse. The free-space electro-optic sampling technique via ZnTe crystal is employed to detect the electric field amplitude of the THz waveforms in time domain. The fast Fourier transformation (FFT) for the THz waveform is carried out to obtain the THz spectrum in frequency domain. The TDS measurements were undertaken under a dry nitrogen purge. The measuring temperature of the heater module lies in the range of 20–300 °C with the temperature accuracy of 1 K.

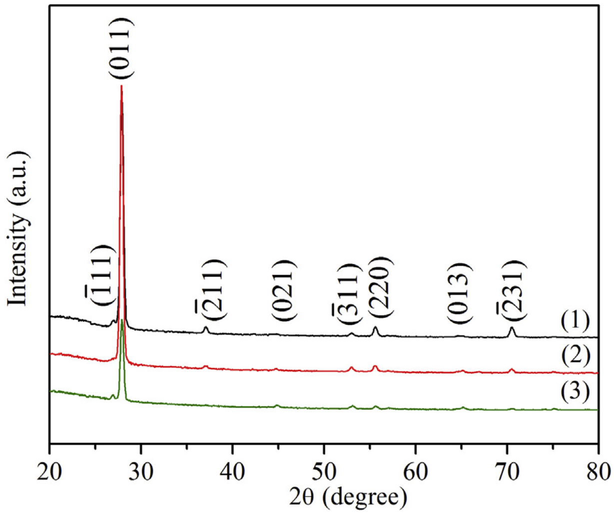

Fig. 1. XRD patterns of VO_2 thin films grown under sputtering gas pressure of (1) 0.2, (2) 0.3, and (3) 0.4 Pa.

Table 1
Some parameters calculated according to Scherrer's formula.

No.	(hkl)	FWHM	Grain Size	Avreage grain size (nm)
0.2 Pa	(011)	0.398	143.6	139.9
	$(\bar{2}11)$	0.44	164.3	
	$(\bar{3}11)$	0.49	125	
	(220)	0.43	126.5	
0.3 Pa	(011)	0.384	233.8	123.9
	$(\bar{2}11)$	0.45	83	
	$(\bar{3}11)$	0.46	80	
	(220)	0.44	98.7	
0.4 Pa	(011)	0.398	167.1	108.9
	(021)	0.44	94.4	
	$(\bar{3}11)$	0.49	63	
	(220)	0.43	110.9	

3. Results and discussion

Fig. 1 shows the XRD patterns of the as-grown thin films on the quartz substrate at different sputtering gas pressures. One can see that the diffraction peaks of the thin films at all sputtering gas pressures match well with monoclinic VO_2 (JCPDS card no. 01-072-0514), and a solo strong diffraction peak at $2\theta = 27.88°$ indicates that the VO_2 thin films are of [011] preferred orientation. The grain size can be estimated from XRD pattern using the Scherrer's formula [34]: $D = \frac{0.9\lambda}{\beta\cos\theta}$, where β is the full width at half maximum of a diffraction peak at 2θ corrected for instrumental broadening, and the corresponding arithmetic mean grain size of VO_2 based on the first four strong diffraction peaks is about 139.9, 123.9, and 108.9 nm at sputtering gas pressure of 0.2, 0.3 and 0.4 Pa, respectively (see Table 1). Obviously, the average grain size of the thin films decreases with increasing sputtering gas pressure. In the sputtering process, it is easy to generate the high-energy electrons and ions due to the less collision as the gas pressure decreases, which help to increase the energy of sputtered atom and the thermal effect of the substrate. The two factors can promote the growth of crystalline and increase the grain size. In addition, the crystallinity of the thin films was determined by the FWHM of the first four strong diffraction peaks, and normally, the lower the FWHM value the higher the crystallinity of the thin films [35]. Table 1 shows the FWHM value of the VO_2 thin films grown in 0.3 Pa is lowest compared with that of other samples, which demonstrates the VO_2 thin films grown in 0.3 Pa has high crystallinity. Fig. 2 shows typical FESEM images of the thin films grown at different sputtering gas pressures. One can see that the as-grown thin films are composed of random arrayed columnar particles. The particle size is larger than the mean grain size obtained by XRD analysis.

The transmitted THz pulse waveforms of the VO_2 thin films were measured at temperature range from 30 to 85 °C with the THz transmissions through the bare quartz substrates as references. It was found that all the VO_2 thin films at semiconductor-phase are highly transparent in the studied spectrum range. Fig. 3 shows the transmitted THz electric filed pulses through VO_2 thin films at temperature of 30 °C and 85 °C, corresponding respectively to semiconductor- and metal-phase VO_2. One can see that the THz transmission amplitude decreases pronouncedly after transition from semiconductor phase to metal phase. The THz modulation depth (calculated from the equation: $\Delta A = (A_i - A_m)/A_i$, where A_m and A_i are the THz field amplitudes at metal and insulating phase, respectively), is about 75.9, 72.1 and 60.5% for the VO_2 thin films at