For progress in natural science: Materials international investigations of structural phase transformation and THz properties across metal–insulator transition in VO$_2$/Al$_2$O$_3$ epitaxial films

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Abstract
Vanadium dioxide (VO$_2$) epitaxial thin films on (0001)-oriented Al$_2$O$_3$ substrates were prepared using radio frequency (RF) magnetron sputtering techniques. To study the metal-insulator-transition (MIT) mechanism and extend the applications of VO$_2$ epitaxial films at terahertz (THz) band, temperature-dependent X-ray diffraction (XRD) and THz time domain spectroscopy of the VO$_2$ epitaxial films were performed. Both the lattice constants and THz transmission exhibited a similar and sharp transition that was similar to that observed for the electrical resistance. Consequently, the MIT of the VO$_2$/Al$_2$O$_3$ epitaxial films should be co-triggered by the structural phase transition and electronic transition. Moreover, the very large resistance change (on the order of $\sim 10^3$) and THz response (with a transmission modulation ratio of $\sim 87\%$) in the VO$_2$/Al$_2$O$_3$ epitaxial heterostructures are promising for electrical switch and electro-optical device applications.

Keywords: VO$_2$; Epitaxial thin film; THz-TDS; Metal-insulator transition; Structural phase transition

1. Introduction
Vanadium dioxide (VO$_2$), a prototype of giant metal-insulator-transition (MIT) materials, was first discovered by Morin in 1959 [1]. Generally speaking, VO$_2$ transformed from a monoclinic (P$\overline{2}$_1/c) to a tetragonal (P$\overline{4}$-mnm) crystalline structure at approximately 68 °C, always accompanying with abrupt several-orders-of-magnitude changes in the optical and electrical properties. This phase transition behavior can be triggered not only by temperature [2] but also by electric field [3], light [4,5], and strain [6,7]. Therefore, these excellent properties make VO$_2$ a promising candidate for fundamental researches and industrial applications, such as smart windows [8], sensor devices [9], metamaterials [10] and memory devices [11,12]. Recently, considerable efforts have been focused on exploring the phase transition phenomena in VO$_2$ thin films and their applications in the terahertz (THz) frequency range [13–16]. In particular, the enormous and ultrafast phase-transition properties of VO$_2$ thin films are promising for potential applications in THz switches [17] and modulators [18].
Many researchers have focused on VO\(_2\) thin films and investigated the structure, electrical and THz transmission properties, including the hysteresis and phase transition temperature. For example, Brassard et al. [19] fabricated a series of VO\(_2\) films with different thickness and found that the microstructural and semiconductor metal transition characteristics were apparently affected by the thickness. Cui et al. [20] reported on synthesis and phase transition characterization of VO\(_2\) films grown on various single crystal substrates and found that VO\(_2\) films on (0001)-oriented Al\(_2\)O\(_3\) shown four order of resistance change between 25 °C and 100 °C. Mandal et al. [21] presented results on terahertz spectroscopy on epitaxial VO\(_2\) films grown on Al\(_2\)O\(_3\) across MIT and demonstrated an 85% reduction in transmission as the VO\(_2\) films transformed to metal phase.

On the other hand, the MIT mechanism of VO\(_2\) thin films is still debated among the prominent theories involving a thermal-driven structural phase transition (Peierls transition) [22], an electron-correlation-driven Mott transition [23] and coactions of these two mechanisms [24]. In 2004, Cavalleri et al. found the evidence for a structure-driven MIT in VO\(_2\) by ultrafast spectroscopy and declared that the mechanism of MIT was not the Mott–Hubbard transition [25]. However, Kim et al. observed that the tetragonal metallic phase did not occur simultaneously with MIT by the ultrafast pump-probe technology—they ascribed the MIT to the Mott mechanism illustrated by photo-assisted hole excitation [26]. Thus, the mechanism of MIT remains controversial. This finding makes us re-examine and further understand the mechanism of the MIT for VO\(_2\) thin films.

In this work, VO\(_2\) epitaxial films of thickness ~60 nm were grown on Al\(_2\)O\(_3\) substrates using RF-magnetron sputtering technique. Al\(_2\)O\(_3\) is a good choice as the substrate because it is widely available for fabricating high quality epitaxial VO\(_2\) films and is highly transparent in the THz range. Furthermore, we discussed the mechanism of the MIT of VO\(_2\)/Al\(_2\)O\(_3\) films based on the results of temperature-dependent XRD and THz time domain spectroscopy (THz-TDS). The giant modulation of the THz transmission, accompanying with a structural phase transition, is consistent with the sharp increase in the electrical conductivity across the MIT. Our results may have potential applications for VO\(_2\)-based THz devices such as THz modulators.

2.2. Structure characterization

The structure and quality of the VO\(_2\) films were characterized by high-resolution XRD with Cu K\(_{\alpha1}\) (\(\lambda = 1.5406\) Å) radiation (Rigaku SmartLab Film Version). The structural phase transition across the MIT of the VO\(_2\) thin films was investigated by in situ temperature-dependent XRD. XRD scans were performed when the temperature was stable.

2.3. Electrical transport measurements

The electrical transport measurements were performed using a home-made heat platform. The hysteresis loops of the resistivity as a function of temperature (R-T curves) were measured by typical two-probe method in the temperature range of 25–110 °C.

2.4. THz time domain spectroscopy

To study the transmission of VO\(_2\) films in the THz frequency range, a homemade THz-TDS system was used. As illustrated in Fig. 1, we used the photo-switching sampling technique with a low-temperature-grown GaAs (LT-GaAs) as a THz emitter. The femtosecond laser pulses delivered from the mode-locked Ti: sapphire laser (center wavelength of 800 nm; pulse width of 30 fs; repetition rate of 80 MHz) was impinged on the photo-switching device made on the LT-GaAs with a dipole antenna (namely, a photoconductive antenna, PCA). The radiated THz pulse was collimated and focused by a pair of 90° off-axis paraboloidal mirrors and interacted with samples placed on the focus of the second off-axis paraboloidal mirror. Then the THz pulse was also collimated and focused on another PCA which serves as the THz detector. The induced photocurrent was monitored in time domain by changing the arrival time of the probe femtosecond laser pulse. In this setup, the photocurrent was collected by a lock-in amplifier with the reference signal modulated by a chopper. To characterize the THz signals across the MIT of the VO\(_2\) films, a simple homemade heat platform was used as the in situ sample holder between the off-axis paraboloidal mirrors. All

2.1. Film growth

Commercial single (0001)-oriented Al\(_2\)O\(_3\) substrates were used as substrates to fabricate VO\(_2\) thin films via RF-magnetron sputtering. The vanadium which sputtered out from a vanadium metal target (99.99% purity) reacted with O\(_2\) under the sputtering pressure of 0.43 Pa and then the VO\(_2\) films were fabricated. The RF power was 60 W and the growth temperature was set to 350 °C [27]. The sputtering time was set to 30 min and the corresponding thickness of the VO\(_2\) film was ~60 nm by X-ray reflection (XRR, not shown here) [27].
the THz signals were obtained when the temperature was stable.

3. Results and discussion

3.1. The electrical transport measurements of the (010)-VO₂/Al₂O₃ thin film

Fig. 2(a) shows the resistance changes of the VO₂ thin film during the heating and cooling processes. It can be seen that the resistance jumps above three orders at the transition temperature of 64 °C as indicated by the differential curves as shown in Fig. 2(b). The giant resistance changes demonstrate the excellent electrical properties of the (010)-VO₂/Al₂O₃ thin film.

3.2. Correlations between the MIT and structural phase transition

Fig. 3(a) presents the temperature-dependent XRD patterns that show the VO₂ (020) peaks and the Al₂O₃ (0006) peaks. The substrate (0006) peaks do not move during the heating and cooling processes because of the rather weak thermal expansion. However, the VO₂ (020) peaks shift to lower angles upon heating and recover to their original high angles after the subsequent cooling process. The shifts in the (020) peaks are indicated by the guide line shown in Fig. 3(a). Fig. 3(b) indicates that the monoclinic VO₂ (020)_M peaks shifted to the (020)_R peaks of the rutile phase during the heating process, which is consistent with the atomic structure models at low and high temperature presented in Fig. 3(c). According to Bragg’s law, the lattice constants were calculated based on the 2θ diffraction angles and plotted in Fig. 3(d). As can be seen in Fig. 3(d) and the inset, the lattice constant also exhibits a
hysteresis property and a sharp transition at the critical temperature of 62 °C, which is consistent with the MIT, as indicated by the R–T curves shown in Fig. 2(b). Therefore, it is concluded that the MIT of the VO₂/Al₂O₃ thin films is a first-order transition accompanied by a structural phase transition.

3.3. THz spectroscopy studies of the MIT

To study the transmission of the VO₂ film in the THz frequency range, we measured the THz-TDS of the VO₂ thin film using our homemade temperature-dependent THz-TDS system (see Fig. 1), which was introduced in the experimental section. A typical THz time-domain spectrum (Fig. 4(a)) and the temperature-dependent THz time domain spectra (Fig. 4(b)) are presented together. The amplitude of the main peak was modulated with temperature and decreased sharply at about 68 °C. For the sake of brevity, the selected THz time domain spectra and their corresponding fast Fourier-transform (FFT) frequency domain spectra at 30 and 100 °C during the heating process are presented in Fig. 4(c) and (d). It is observed obviously that the transmission at 30 °C is much greater than that at 100 °C.

Since almost all the dielectric insulators are transparent and the metal is opaque in the THz band, it can be concluded that the VO₂ film is in an insulator state at 30 °C and a metal state at 100 °C. The THz pulses transmitted through the VO₂/Al₂O₃ thin film should carry some electronic structural information. In Fig. 5(a), the THz pulse is transmitted almost without any loss, thus indicating that a band gap \( E_g \) may appear and that the VO₂ should now be in an insulator state, as illustrated in Fig. 5(c). However, the THz signals decrease dramatically in Fig. 5(b) as the temperature increases above the critical temperature, thereby implying that the band gap disappeared and the VO₂ is now in a metallic state. The corresponding band structure is shown in Fig. 5(d). Therefore, the temperature-dependent THz-TDS can sensitively probe the MIT in the VO₂/Al₂O₃ thin films and provide some useful predictions about the electronic structure [14–16].

Based on the temperature-dependent THz-TDS results, the transmission vs. temperature curve in Fig. 6(a) was obtained by plotting the maximum value of the time domain spectra at various temperatures. Then, the differentiation of the transmission for the heating and cooling transition curves were calculated and plotted in the inset of Fig. 6(a). From Fig. 6(a), the phase transition temperature was evaluated to be 68 °C in the cooling transition, which is also consistent with the transition temperature shown in Figs. 2(b) and 3(d). Therefore, it is concluded that the MIT of the VO₂/Al₂O₃ thin films may be closely related to the electronic phase transition. Furthermore, the THz transmission modulation ratio can be calculated to be approximately 87% from Fig. 6(a), and this value is attractive for electro-optical device applications.

3.4. Theoretical simulations of THz transmission spectroscopy

The decrease in the THz field amplitude upon transition of the VO₂ films from insulator to metal is primarily associated with changes in the frequency (\( \omega \))-dependent complex conductivity, \( \sigma(\omega) \) and film thickness (\( d_f \)) through the expression [28–32]

![Fig. 4. (a) A typical THz time domain spectrum, (b) the temperature-dependent THz time domain spectra, the guide lines show the corresponding relationship of the main peak, (c) the selected 30 and 100 °C THz time domain spectra during the heating process, and (d) the corresponding Fast Fourier-transform (FFT) frequency domain spectra.](image-url)
\[ \frac{\tilde{E}_{f^+}(\omega)}{\tilde{E}_s(\omega)} = \frac{1 + n_s}{1 + n_s + z_0 \delta(\omega)d_f} , \]

where \( \tilde{E}_{f^+}(\omega) \) is the complex field amplitude transmitted through the VO\(_2\) film plus the substrate; \( \tilde{E}_s(\omega) \) is the complex field amplitude transmitted through the reference substrate (without the film); \( z_0 \) is the free space impedance, 377 \( \Omega \); and \( n_s \) is the refractive index of the sapphire substrate, which is 3.2 near 1 THz. Using the temperature-dependent film conductivity obtained from the DC electrical measurements shown in Fig. 2(a), the THz transmittance \( \tilde{E}_{f^+}(\omega)/\tilde{E}_s(\omega) \) was simulated and the results are presented in Fig. 6(b). Based on the inset of Fig. 6(b), the transmission transition temperature could be evaluated to be 65 °C in the cooling transition, which is in agreement with the experimental results presented in Fig. 6(a).

4. Conclusions

We deposited 60-nm-thick VO\(_2\)/Al\(_2\)O\(_3\) epitaxial films by RF magnetron sputtering and built a THz-TDS for the metal-insulator transition studies. Based on the \textit{in situ} temperature-dependent XRD and THz-TDS analysis, the MIT of the VO\(_2\) epitaxial films is thought to be co-triggered by the structural phase transition and electronic transition in the VO\(_2\)/Al\(_2\)O\(_3\) system. Moreover, the giant resistance change and transmission modulation in the THz range are promising for electrical switch and electro-optical device applications.

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