Terahertz spectroscopy studies on epitaxial vanadium dioxide thin films across the metal-insulator transition

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We present results on terahertz (THz) spectroscopy on epitaxial vanadium dioxide (VO2) films grown on sapphire across the metal-insulator transition. X-ray diffraction indicates the VO2 film is highly oriented with the crystallographic relationship: (002)VO2//(0006)sub and (010)VO2//(2110)sub. THz studies measuring the change in transmission as a function of temperature demonstrate an 85% reduction in transmission as the thin film completes its phase transition to the conducting phase, which is much greater than the previous observation on polycrystalline films. This indicates the crucial role of microstructure and phase homogeneity in influencing THz properties. © 2011 Optical Society of America

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Vanadium dioxide (VO2) experiences a sharp metal-insulator transition (MIT) near room temperature accompanied by impressive changes in the electrical conductivity [1], optical reflectance [2], and dielectric properties [3]. In recent years, there has been tremendous interest in exploiting such effects in novel solid state devices, such as, but not limited to, electronic switches [4], temperature sensors [5], and metamaterials [6].

Studies on functional materials in the THz frequency range are growing rapidly. Anticipated applications include security and novel optoelectronic device technologies [7]. Also, for exploring MIT phenomena in VO2, THz techniques are relevant, such as time-resolved optical studies and THz apertureless near-field optical microscopy experiments [8,9].

The dielectric properties of VO2 thin films at high frequencies have been investigated and the results were analyzed on the basis of effective medium theories (EMTs) considering the presence of a mixture of conducting and dielectric phases in the VO2 films [2,10]. Choi et al. conducted temperature-variable midinfrared spectroscopic characterizations on VO2 thin films grown by pulsed laser deposition on sapphire substrates [2]. The dielectric properties were described by an EMT based on the Bruggeman approximation that includes percolative behavior [2,11]. Jepsen et al. investigated transmission in polycrystalline VO2 films prepared from annealing amorphous films by THz time-domain spectroscopy (THz-TDS), which enables monitoring high-frequency conductivity without electronic contacts to the sample, and found that the THz response could be modeled with a Maxwell–Garnett (MG) EMT where the percolation aspect is excluded [10,12].

While there is great interest in understanding THz response of VO2, to the best of our knowledge there are no prior THz-TDS studies on epitaxial VO2 films. It is known that the electrical properties of single crystalline VO2 can be dramatically different from that of polycrystalline films or films with nonstoichiometric phases [13], however, no such literature exists for THz spectroscopy. Here, we present THz-TDS studies on highly oriented VO2 films spanning the MIT phase boundary.

VO2 thin films of nominal thickness ~200 nm were grown by RF-sputtering from a VO2 target onto ~500 μm-thick (0001) sapphire substrates. The sputtering gun power was set as 270 W and the chamber pressure and substrate temperature were controlled to be ~10 mTorr and 550 °C, respectively, during synthesis. The films were characterized by x-ray diffraction (XRD) 2θ–ω scans, q-scans, rocking curve measurements, and electrical resistance measurements as a function of temperature in an environmental probe station.

THz-TDS studies were conducted on the samples as a function of temperature using a custom-designed setup. THz-TDS relies on the generation and detection of ultrashort electromagnetic transients, which in our setup have pulse widths of less than 1 ps, spectral content from 0.1 to 1.0 THz, and average power of 375 μW [14]. Femtosecond optical pulses from an 80 MHz KMLabs Chinook titanium: sapphire oscillator are split with 450 mW being used to generate the THz radiation by exciting a semi-insulating GaAs photoconductive switch biased at 2 kV/cm using aluminum strip lines with a gap of 1 mm. The remaining 5 mW is used to detect the THz radiation by measuring the polarization rotation of the probe pulse from induced birefringence within a ZnTe crystal resulting from the electric field of the incoming THz pulse. Off-axis parabolic mirrors are used to focus the generated THz radiation onto the VO2 sample and then refocus the transmitted radiation back onto the ZnTe detector.

The VO2 sample was mounted in a holder whose temperature was controlled by a Peltier element heater and monitored by a platinum resistance temperature detector. To ensure a minimum temperature gradient across the sample, the sample block was covered by expanded foam insulation, which creates minimal absorption of the incoming THz radiation. To account for any temperature effects of the sapphire substrate, the sample holder holds both a sapphire substrate coated with a VO2 thin film as well as a bare substrate. All data points are normalized to the transmission through the bare substrate. The THz-TDS system measures the amplitude, A, and phase, δ, of the transmission function Eν0/Er = A exp(iδ) where Eν,ref and Eν,0 indicate the transmitted electric

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fields through the bare substrate and the VO$_2$ thin film sample, respectively. This function is linked to the dielectric functions of the VO$_2$ thin film and the substrate, and can be calculated analytically [15]. Reflections within the substrate are removed experimentally by stopping the time delay scan before the reflected pulse arrives from the sapphire substrate 10 ps after the nonreflected pulse. The transmission function in this configuration is given by

$$E_{\text{VO}_2}/E_{\text{ref}} = (1 + n_{\text{substrate}})/(1 + n_{\text{substrate}} + Z_0 \sigma(\omega_f)d). \quad (1)$$

where $\omega_f$ is the angular frequency, $Z_0 = 377 \Omega$ is the vacuum impedance, $d$ is the thickness of the VO$_2$ film, and $\sigma = \sigma_1 + i\sigma_2 = -i\varepsilon_0\omega_f(\varepsilon - 1)$ is the complex conductivity of the VO$_2$ thin film [16].

Representative XRD $2\theta - \omega$ scan of the film shows reflections only from (002) and (004) planes of VO$_2$ phase as displayed in Fig. 1(a), indicating that the single phase and epitaxial VO$_2$ thin film with the c-axis perpendicular to the substrate surface was successfully grown on c-sapphire. In addition, as shown in the Fig. 1(a) inset, the full width at half-maximum (FWHM) of the rocking curve was estimated as $\sim$0.03° at the (002) reflection peak verifying a high crystalline quality of the VO$_2$ thin film. The XRD $\varphi$-scan displayed in Fig. 1(b) shows six off-axis reflections at $\Psi = 45^\circ$ and $2\theta = 27^\circ$, corresponding to (011) orientation of VO$_2$. This sixfold symmetry is due to the presence of three orientation variants of VO$_2$ that are rotated in-plane by 60° about [020] direction of the VO$_2$. These energetically equivalent orientations arise because of different symmetries of monoclinic VO$_2$ and rhombohedral (0001) sapphire across the interface with the orientation relationship: (002)$_{\text{film}}$//(0006)$_{\text{sub}}$ and [010]$_{\text{film}}$//[2110]$_{\text{sub}}$. Electrical measurements on the identical film showed nearly 4 orders of magnitude resistance change across the transition, indicating very high-quality films. The onset temperatures for the transition were estimated to be $\sim$68°C and $\sim$64°C during heating and cooling, respectively, consistent with typical observations on VO$_2$.

THz-TDS data were collected as the temperature, $T$, is slowly increased and then decreased, as shown in Fig. 2. Part (a) shows that, as $T$ increases, the transmitted electric field directly measured by the ZnTe detector is reduced through both reflection and absorption due to the increased conductivity of the VO$_2$ thin film. This data is then Fourier transformed and normalized to the bare substrate at the same $T$. As expected, there are no changes seen in the transmission through the bare sapphire substrate as a function of $T$. Parts (b) and (c) show the amplitude and phase of the transmission function, respectively. The transmitted amplitude is flat as a function of frequency, $\nu$, and decreases with increasing $T$ as expected; the phase is relatively insensitive to both $T$ and $\nu$ except for the peak at 0.1 THz, which corresponds to reflections within the substrate and suggests that the temporal cutoff of this reflection is not complete. Reflections within the substrate also explain the increased phase shift with $T$ at 0.1 THz as this reflection will become larger as the VO$_2$ film becomes more conductive, increasing the amplitude of the pulses from multiple reflections.

Figure 3 shows the $T$-dependence of the average conductivity calculated from 0.3 to 0.95 THz. In comparison, previous results with polycrystalline films on a 150 μm-thick glass by Jepsen et al. are shown as dashed curves [10]. The highly oriented VO$_2$ samples show much greater real conductivity but no susceptibility change.

The much greater conductivity is likely due to the epitaxial nature of the film. The blue and magenta curves in Fig. 3 show the predictions of the MG and Bruggeman EMTs for the VO$_2$ dielectric constant as the film is driven through the phase transition [11,12]. At the $T$ extremes, the film is assumed to be either entirely in the insulating phase with $\tilde{\epsilon} = 9$ or in the metallic phase with dielectric function where $\tilde{\epsilon} = \tilde{\epsilon}_m - \omega_p^2/\omega_f(\omega_f + i\Gamma)$ given by the Drude model. Here we take the high-frequency value, $\tilde{\epsilon}_m$ to be given by the insulating phase value, $\omega_p^2 = ne^2/\varepsilon_0m^* \Gamma$ is the plasma frequency, and the scattering rate is $\Gamma = e/m^* \mu$. We have used previously measured values of these parameters as estimates [2]. In particular, the effective mass is $m^* = 2m_e$, with $m_e$ the free electron mass, the best fit carrier density is $n = 0.87 \times 10^{22}$ cm$^{-3}$, and the carrier mobility is $\mu = 2$ cm$^2$/V·s. The excellent agreement with the measured values at both the low and high $T$ extremes indicates that these parameters describe the film components well. To calculate the behavior of the dielectric constant through the MIT, we have assumed the microscopic domains can be replaced by an effective medium where the fractional metallic part is given by $f = 1 - (1 + \exp((T - T_0)/\Delta T))^{-1}$. For the Bruggeman EMT, the best fit is given for $T_0 = 70^\circ$C and $\Delta T = 6^\circ$C, while for the MG EMT, $T_0 = 41^\circ$C and $\Delta T = 6^\circ$C. The significantly better agreement with the Bruggeman EMT is not surprising as the MG EMT only models dilute mixtures properly. The agreement also suggests that the phase transition is continuous in order for it to be modeled properly by an EMT. In contrast the nanogranular film measured by Jepsen et al. may produce a non-Drude-like conductivity from the existence of metallic islands and, thus, show the observed significant change in susceptibility [10].
In summary, we have conducted THz-TDS on VO$_2$ epitaxial thin films as a function of temperature spanning the MIT. From the 85% reduction in transmission across the phase transition, our results indicate that the transition to the metallic phase is much closer to completion in epitaxial films. The results could be of potential relevance in designing epitaxial phase transition oxides for novel THz applications and nanophotonics.

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References