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Effect of oxygen stoichiometry on the insulator-metal phase transition in vanadium oxide thin films studied using optical pump-terahertz probe spectroscopy

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Using optical pump-terahertz probe spectroscopy, we studied the dynamic behaviors of photoinduced insulator-metal phase transition in vanadium oxide thin films with different oxygen stoichiometry. We found that the insulator-metal phase transition of vanadium dioxide is very sensitive to oxygen stoichiometry: the increased oxygen content in vanadium oxide will reduce the magnitude of phase transition and change the dynamics of the phase transition. The transient complex photoconductivity of vanadium oxide thin films is investigated and analyzed with Drude-Smith model, supplying insight of the dynamic process of phase transition in vanadium oxide thin films. © 2013 AIP Publishing LLC. [http://dx.doi.org/10.1063/1.4824834]

Vanadium dioxide (VO₂) exhibits insulator-metal phase transition at Tc ~ 67°C, in which the electrical conductivity changes up to 5 orders of magnitude.1–3 The ultrafast first-order phase transition in VO₂ is accompanied not only by a structural phase transformation but also by a significant modification of the optical absorbance: VO₂ is transparent over the infrared region of the electromagnetic spectrum below the phase transition temperature, while the metallic phase of VO₂ is opaque at most spectral frequencies above the phase transition temperature. The extraordinary near-room-temperature changes in electrical and optical properties make this material very attractive for versatile potential applications such as switching devices, Mott field-effect transistor, optical waveguides, sensing components, and optical storage devices.4–8 However, the insulator-metal phase transition is very easily affected even annihilated by the material properties, such as crystalline quality, structural dimension, strain, and morphology.9–12 In a recent report, the phase transition behavior has been demonstrated to be also sensitive to the vanadium or oxygen related vacancies.13,14 Ramanathan et al.13 carried out detailed measurements for vanadium oxide thin films, prepared by reactive sputtering of a vanadium target, to correlate electron transport properties to the band structures obtained from near-edge X-ray absorption fine structure spectroscopy (NEXAFS). Another study carried out by Nazari and co-workers14 investigated the effect of oxygen deficiency related to native doping concentration on the phase transition magnitude and temperature. These works have discovered that the insulator-metal phase transition and the electron correlations involved in the phase transition sensitively depend on the oxygen stoichiometry, even a deviation in the anion stoichiometry by a few percent can result in several orders of magnitude difference in the phase transition behaviors or the phase transition temperature shift. However, little work has been devoted to the effect of oxygen stoichiometry on photoinduced insulator-metal transition, which has important applications in optoelectronic devices. Here, we present an optical pump-terahertz probe (OPTP) spectroscopy study of the photoinduced ultrafast metal-insulator phase transition in three vanadium oxide thin films with near VO₂ stoichiometry prepared under similar conditions. We found that the photoinduced metal-insulator phase transition behavior vary dramatically in the VO₂ thin films with oxygen stoichiometry. OPTP spectroscopy has been proven to be a powerful tool for the investigation of the ultrafast metal-insulator phase transition on time scales from subpicosecond to nanosecond.15–18 Measuring the transient photoconductivity with OPTP will provide direct information on the dynamic behaviors of the insulator-metal phase transition. The present work helps improve the understanding of the physics of the photoinduced phase transition in VO₂ and optimize the design of optical device based on VO₂.

Vanadium dioxide thin films were prepared by the pulsed laser deposition (PLD) on c-plane sapphire substrates. A V₂O₅ target was ablated by a KrF excimer laser operated at the wavelength of 248 nm. The substrate was kept at 800°C and oxygen partial pressure was maintained at 12 mTorr during the deposition. The employed laser energy were 340 mJ, 330 mJ, and 300 mJ for sample 1 (S1), sample 2 (S2), and sample 3 (S3), respectively. The photoinduced insulator-metal phase transition of VO₂ thin films were characterized with an OPTP system, which has an useable bandwidth from 1 to 5 THz as described elsewhere.18 In brief, the ultrafast optical pump was generated by a Ti:sapphire regenerative amplifier laser system, which provides ~35 fs optical pulses at the center wavelength of 800 nm with a repetition rate of 1 kHz. The THz probe was generated using a two-color air-plasma technique19 and detected by a THz Air-Biased-Coherent-Detection (THz-ABCD) method.20 Optical pump fluences ranging from 150 to 750 μJ/cm² were used to excite the samples. The entire OPTP setup is enclosed in a chamber purged with dry nitrogen to reduce water vapor absorption. All the measurements were carried out at room temperature.
X-ray diffraction (XRD) and Raman scattering spectroscopy were employed to characterize the composition and crystallinity of the three VO$_2$ thin films used in this study. Figures 1(a)–1(c) show XRD patterns of the three VO$_2$ thin films. The peaks at 41.69° represent the diffraction of c-plane sapphire substrates, and the peaks located at 39.80°, 39.75°, and 39.52° attribute to the diffractions from either (002) or (020) plane of the three VO$_2$ samples S1, S2, and S3, respectively. The fact that the XRD peak of VO$_2$ samples shifts to smaller angles from S1 to S3 is due to the extension of crystal lattice, since the film is under a compressive strain due to the lattice mismatch at the interface between the film and the substrate. The Raman spectra of the three samples are shown in Figures 1(d)–1(f), respectively. The representative peak positions of Raman shift from VO$_2$ thin films used in this study and single crystal VO$_2$ from Ref. 21 are summarized in Table I. It can be seen that the peak positions shift to high frequencies from S1 to S3. Previous Raman studies have shown that the presence of V$^{5+}$ in nonstoichiometric VO$_2$ (Ref. 22) and/or strain$^{23}$ of VO$_2$ could lead to an increase in the energy of optical phonons in VO$_2$. As a consequence, the slight increase in the Raman shift is likely to be a result of presence of V$^{5+}$ and/or the compressive strain as evidenced by X-ray photoelectron spectroscopy (XPS) and XRD results.

Figures 2(a)–2(c) depict the dynamics of differential transmittance $\Delta T/T_0$ at various excitation fluences for S1, S2, and S3, respectively, where $T_0$ is the peak intensity of transmitted THz probe pulse through unexcited samples, $\Delta T = T - T_0$, and $T$ is the peak intensity of transmitted THz probe pulse through the excited samples. The excitation fluences used in the experiment are labeled in Figure 2. The open circles are experimental data, and the solid lines are least square fitting with a biexponential function, $A_1 \exp(-t/\tau_1) + A_2 \exp(-t/\tau_2)$. The biexponential behavior suggests that there are two processes (a fast process and a slow process) during the insulator-metal

![Fig. 1](image1.jpg)

**FIG. 1.** Typical XRD patterns from (002) or (020) plane of VO$_2$ and c-plane sapphire of (a) S1, (b) S2, and (c) S3. Raman spectra of (d) S1, (e) S2, and (f) S3 with 532 nm laser excitation.

![Fig. 2](image2.jpg)

**FIG. 2.** Transient differential transmission ($\Delta T/T_0$) of the THz wave through (a) S1, (b) S2, and (c) S3 with different excitation fluences. The excitation fluences are labeled correspondingly. The open circles are experimental data, and the solid lines are least square fitting with a biexponential function for S1 and S2, a single exponential function for S3. Excitation fluence dependence of $\Delta \sigma$ of (d) S1, (e) S2, and (f) S3 at different delay time $\Delta t = 5$ ps (red triangles), 25 ps (blue squares), 100 ps (orange circles), and 300 ps (green diamonds).

<table>
<thead>
<tr>
<th>$\omega_{V1}$</th>
<th>Ref. 21</th>
<th>S1</th>
<th>S2</th>
<th>S3</th>
</tr>
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<tr>
<td>191</td>
<td>194</td>
<td>196</td>
<td>201</td>
<td></td>
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<tr>
<td>$\omega_{V2}$</td>
<td>221</td>
<td>221</td>
<td>223</td>
<td>226</td>
</tr>
<tr>
<td>$\omega_{O}$</td>
<td>612</td>
<td>616</td>
<td>618</td>
<td>623</td>
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phase transition. The THz transmittance decrease significantly within 1 ps after the photoexcitation, followed by a gradual drop in a time scale of \(~100\) ps to achieve the maximum differential transmittance. The abrupt decrease of THz transmittance indicates the conductivity of VO2 thin films has a sharp increase due to the photodoping and occurrence of metallic domains. The subsequent gradually decrease in THz transmittance suggests that the metallic phase domains grow and coalesce from spatially separated sites or from the surface of the thin film to the thin-film-substrate interface. Thus, as described in our previous report,16 the fast process is assigned to the photodoping and nonthermal nucleation of the metallic phase and the slow process can be attributed to the growth and coalescence of the nonmetallic phase domains in the VO2 thin films. The heat accumulation effect from multiple pulse excitations can be ignored because the decrease of THz transmittance can recover practically in the laser pulse period of \(1\) ms, i.e., before the arrival of next pump pulse. For sample S3, the temporal evolutions can be well fitted by a single exponential function and the decrease of THz transmittance is much smaller at lower fluences, but it grows rapidly and nonlinearly at higher fluences, indicating the onset of insulator-metal phase transition. The transient complex photoconductivity spectra at different delay times can provide detailed information on the dynamics of the insulator-metal phase transition in VO2 thin films. In order to study the transient conductivity spectrum \(\Delta \sigma(\omega)\), the entire transmitted THz probe pulse through the unexcited sample E and the pump-induced change of the entire THz probe pulse transmitted through the excited sample \(\Delta E\) were recorded by probe scans at certain pump-probe delays. The \(\Delta \sigma(\omega)\) can be obtained by using equation59

\[
\Delta \sigma(\omega) = \frac{1}{C_0} \int \frac{I_s - I_0}{I_0} d\omega
\]

used to determine the different V cation oxidation states in vanadium oxides. Figure 3 shows the XPS spectra focusing on O1s and V2p3/2. Two broad peaks at around 523.6 eV and 516.3 eV, corresponding to the V2p1/2 and V2p3/2 core levels, respectively, are exhibited in addition to the O1s peak. After subtracting the Shirley background, each of the measured XPS peaks could be deconvoluted into several peaks: both V2p1/2 and V2p3/2 can be described by a combination of a V5\(^+\) peak and a V4\(^+\) peak. The V4\(^+\)/V3\(^+\) peak and V5\(^+\)/V3\(^+\) peak are located at 515.9 eV and 517.1 eV, respectively, which is in agreement with reported results of vanadium oxides with mixed valence states.26,27 From the ratio of the integrated areas of V4\(^+\) and V5\(^+\) peaks, \(I_{V^+}/I_{V^{5+}}\), we could estimate the ratios of oxygen to vanadium by \((2I_{V^+} + \frac{1}{2}I_{V^{4+}})/(I_{V^{4+}} + I_{V^{5+}})\). Thus, we obtain the ratios of oxygen to vanadium are 2.16, 2.18, and 2.22 in S1, S2, and S3, respectively. It should be noted that the surface of VO2 thin film is usually oxidized to V2O5 phase as reported previously.28 As a result, the oxygen content at the surface is higher than that at the inner of the thin films. Nevertheless, it is obvious that S3 is over-oxidized and more contribution to the V2p3/2 originates from V5\(^+\) than the other two samples. The phase transition amplitude is strongly affected by the oxygen stoichiometry.14 Thus, as oxygen content is remarkably excessive, the insulator-metal phase transition vanishes in S3.

The transient complex photoconductivity spectra at different delay times can provide detailed information on the dynamics of the insulator-metal phase transition in VO2 thin films. In order to obtain the transient conductivity spectrum \(\Delta \sigma(\omega)\), the entire transmitted THz probe pulse through the unexcited sample E and the pump-induced change of the entire THz probe pulse transmitted through the excited sample \(\Delta E\) were recorded by probe scans at certain pump-probe delays. The \(\Delta \sigma(\omega)\) can be obtained by using equation59

\[
\Delta \sigma(\omega) = \frac{1}{C_0} \int \frac{I_s - I_0}{I_0} d\omega
\]

As shown in Figs. 1(d)–1(f), the XRD peak of VO2 shifts to smaller angles from S1 to S3. The shift indicates the extension of crystal lattice, revealing the extent of the oxygen nonstoichiometry increases from S1 to S3.25 In order to have a quantitative characterization on the oxygen content, XPS was conducted to detect the degree of oxidation in the three samples. As the binding energy of the V2p3/2 core level is dependent on the oxidation state of the V cation, the peak positions of the V2p3/2 and corresponding V-O signal can be

FIG. 3. The XPS spectra of (a) S1, (b) S2, and (c) S3. The measured spectra are shown as black circles and the reproduced curves are shown as red solid lines.
The optical penetration depth of 800 nm optical pump in VO$_2$,
in which the inverse of absorption coefficient $n$ is taken as the inverse of absorption coefficient $1/\alpha \approx 100$ nm in our measurement. $n(\approx 3.02)$ is the refractive index of sapphire substrate at THz frequencies and measured by THz-time domain spectroscopy. The transient complex conductivity spectra of the three VO$_2$ samples in the frequency range from 1 THz to 5 THz measured at 20, 36, 200, and 500 ps after photoexcitation are shown in Figure 4, S1 (see supplementary materials), and 5, respectively. As shown in Figure 4, S1, and 5, the transient complex conductivity of the three samples can be well fitted using the Drude-Smith model, given by

$$\Delta \sigma(\omega) = \frac{n + 1}{Z_0 d} \left[ \frac{1}{1 + \Delta E(\omega)/E(\omega)} - 1 \right],$$  \hspace{1cm} (1)$$

where $Z_0 = 377\, \Omega$ is the impedance of free space, $d$ is the optical penetration depth of 800 nm optical pump in VO$_2$, and $\Delta E(\omega)$ is the frequency-dependent effective energy gap.

As shown in Figures 4(a), 4(b), and 4(c), the real and imaginary parts of the transient complex conductivity of S1 at different probe delays: $\Delta t = 20$ ps (black circles), 36 ps (red triangles), 200 ps (blue squares), and 500 ps (yellow diamonds). The solid lines are best fits with the Drude-Smith model.

Typical atomic force microscopy (AFM) images of the three VO$_2$ thin films were captured in order to investigate the quality of the three samples. As described in previous studies, metallic domains emerge and coalesce in the phase transition process. Therefore, the electrons would localize in the metallic domains and backscattering would occur at the domain boundaries, which explains the non-zero $c$ value. With the domain size changes, the $c$ value will correspondingly change. Therefore, by monitoring the temporal evolutions of parameter $c$, a clear picture about the dynamics of photoinduced insulator-metal phase transition can be obtained. Before delay time $\Delta t = 20$ ps, optical pump has induced small domains of metallic rutile phase in the sea of insulating monoclinic phase. The free carriers have backscattering at boundaries of the metallic domains and the parameter $c$ has relatively large values. During period from $\Delta t = 36$ ps to 200 ps, parameter $c$ shows a quite small value approaching zero. During this time period, the metallic domains grow and coalesce to form a continuous metallic film, reducing domain boundaries and the possibility of backscattering. Thus, the parameter $c$ is close to zero. At $\Delta t = 500$ ps, the phase transition begins its reverse process: metal-insulator phase transition. In this process, the metallic VO$_2$ thin film begins to convert to insulator gradually. The insulating domains emerge and coalesce, and the metallic phase becomes discontinuous. Thus, the value of parameter $c$ increases again. However, the parameter $c$ of sample S3 shows relative big values ($\sim -0.80$) at all delay times. The strong carrier localization and backscattering effect are mainly attributed to the crystal quality of the samples. Typical atomic force microscopy (AFM) images of the three VO$_2$ thin films were captured in order to investigate the quality of the three samples, as shown in Figures 4(c), S1(c), and 5(c). Samples S1 and S2 have smooth and uniform
surface, while sample S3 exhibits a relatively rougher surface. The average surface roughness (Ra) for S1, S2, and S3 are 0.297 nm, 0.809 nm, and 2.68 nm, respectively. The sample S3 has the roughest surface in the three samples due to the existence of many grains. Carrier backscattering would occur at the grain boundaries and carriers would localize in these small grains, explaining the large values of the parameters $c$ during all the delay times. Compared to S3, S1, and S2 have smoother surface, and the change of parameter $c$ is caused by the evolution of metallic domains. The changing of the $c$ value clearly reveals the dynamics of the phase transition process in VO$_2$ thin films.

In conclusion, the dynamic behavior of the photoinduced insulator-metal phase transition of the vanadium oxide thin films with near VO$_2$ stoichiometry has been investigated using OPTP spectroscopy. We observed a correlation between photoinduced phase transition and oxygen stoichiometry. The excessive oxygen content in vanadium dioxide will reduce the magnitude of phase transition. The transient photoconductivities of the three samples are well fitted with the Drude-Smith model. The temporal evolution of fitted parameter $c$ clearly reveals the dynamics of the phase transition process. Our results help improve the understanding of the physics of the photoinduced insulator-metal phase transition, optimize the growth condition of VO$_2$ thin films, and are useful for the design of VO$_2$ based optical devices.