Structural, transport, and ultrafast dynamic properties of V$_{1-x}$Nb$_x$O$_2$ thin films

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Abstract

We report the coherent study of structural, transport, and ultrafast dynamic properties of V$_{1-x}$Nb$_x$O$_2$ thin films. Films of a solid solution of V$_{1-x}$Nb$_x$O$_2$ (0 $\leq x \leq 1$) are prepared on (0001) sapphire substrates using reactive target ion beam deposition. We found that, at room temperature, the low-temperature lattice symmetry of pure VO$_2$ (monoclinic, $P2_1/c$) and NbO$_2$ (tетragonal, $I4_1/a$) is only maintained at low substituting levels ($x < 0.1$ and $x > 0.9$) and regular rutile lattices are adopted by films with higher substituting levels ($0.1 < x < 0.9$). We characterized the dc transport properties and the photoinduced ultrafast dynamics at the terahertz frequency range, both of which demonstrate strong dependence on the film composition. At $x \sim 0.5$, both the dc conductivity and ultrafast response diminish, which corresponds to a strong localization of free charge carriers in the system. The strong composition dependence of film transport, ultrafast dynamic, and insulator-metal transition properties promises approaches to improve the performance of devices based on transition metal oxides.

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I. INTRODUCTION

Vanadium dioxide (VO$_2$) undergoes an insulator-to-metal transition (IMT) from below to above $T_c = 340$ K, accompanied with a structural phase transition from a monoclinic to rutile lattice [1]. The IMT of VO$_2$ can be characterized by abrupt changes in electrical conductivity and optical transmittance/reflectivity in infrared (IR) and terahertz (THz) regions, making it a suitable candidate for ultrafast switching and optical sensing applications [2–4]. However, the performance of VO$_2$-based devices inevitably degrades when the operation temperature goes above $T_c$, which is commonplace in modern electronics. In contrast, NbO$_2$, a cousin dioxide of VO$_2$, exhibits IMT at a much higher temperature ($\sim$1081 K). It is also accompanied with a structural transformation from a body-centered tetragonal (bct) to a regular rutile lattice [5]. As demonstrated by previous limited investigations, NbO$_2$ also appears to be a good candidate for practical applications such as resistive memories and ultrafast switching using electric bias or optical excitation, especially for high-temperature operations [6–8].

Besides the transition temperature, the IMTs in VO$_2$ and NbO$_2$ demonstrate discrepancies in several other aspects. Compared with that of VO$_2$, the change in electrical conductivity of NbO$_2$ across IMT upon heating is less abrupt and much smaller in magnitude ($\sim$10$^4$ times in VO$_2$ versus $\sim$10$^1$ times in NbO$_2$) [9–11]. Moreover, for optically induced IMT, ultrafast experiments have demonstrated fast insulator-to-metal switching dynamics in both VO$_2$ and NbO$_2$ [8,12–14]. However, in VO$_2$ the long recovery time from the metallic phase back to the insulator phase has prohibited fast on/off switching applications [15]. Unlike other semiconductors where the recovery time governed by electron-hole recombination process can be modified by forming internal electric field or introducing moderate density of defects [16–18], effective tuning of response time and optical contrast between phases in correlated metal oxides is still lacking. In contrast, recent near-infrared pump-probe [8] and optical pump terahertz probe (OPTP) [14] studies of NbO$_2$ have shown that the recovery time can be orders of magnitude faster than those of VO$_2$. However, the photoinduced relative change of near-infrared (800 nm) reflectivity ($\Delta R/R$) and THz conductivity ($\Delta \sigma$) of NbO$_2$ are much smaller than those of VO$_2$ [8,14].

Therefore, one may achieve better device performance by alloying these two oxides together (e.g., optical switching with faster recovery rates and larger optical responses). In addition, studying this alloyed system is particularly interesting from the fundamental physical perspective. Both VO$_2$ and NbO$_2$ are formed by transition metals in the same column of the Periodic Table, resulting in the commonality of one d valence electron that is not engaged in metal (M)–oxygen (O) bonding. Both of their IMTs at respective critical temperatures are accompanied by structural transformations with similar distortion in the lattice. Thus, the investigation of the alloyed...
V$_{1-x}$Nb$_x$O$_2$ promises insights into the physics underlying the IMT in $d^1$ compounds.

II. EXPERIMENT

In this study, we prepare V$_{1-x}$Nb$_x$O$_2$ (0 $\leq x \leq$ 1) thin films by reactive bias target ion beam deposition (RBTIBD) with a full set of $x$ values ranging from 0 to 1. This technique has been employed to prepare high-quality epitaxial VO$_2$ [19] and NbO$_2$ [20] thin films on various substrates and its capacity of cosputtering allows for exploration of alloyed material systems [21]. The evolution of lattice structures, dc transport, and photoinduced THz dynamics of the films against composition is systematically investigated.

The V$_{1-x}$Nb$_x$O$_2$ thin films are deposited on sapphire (0001) substrates using RBTIBD. Detailed growth conditions can be found in Supplemental Material, Note 1 [22]. The Nb concentration, defined as $x = \text{Nb}/(\text{Nb} + \text{V})$ (at.%), is measured by Rutherford backscattering (National Electrostatics Corp. Pelletron). The film thicknesses are determined by the x-ray reflectivity (Smartlab, Rigaku Inc.). The film growth rate (nm/min) as a function of composition is plotted in Fig. S1 [22]. X-ray 2$\theta$ scans (Smartlab, Rigaku Inc.) are conducted to characterize phase composition, microstructures, and lattice parameters of the films. In addition, x-ray $\phi$ scans (Smartlab, Rigaku Inc.) are employed to confirm the identification of the 2$\theta$ diffraction peaks and to derive the orientation relationship between the V$_{1-x}$Nb$_x$O$_2$ films and the substrates. Raman spectra are measured with an inVia Raman spectroscope (Renishaw System Ltd.) using a 514-nm laser source. Temperature dependence of dc resistivity is measured using a VersaLab system (Quantum Design Inc.) from 200 to 400 K with a temperature ramp rate of 5 K/min. For dynamic properties, the static and photoinduced terahertz (0.2–2 THz) conductivity dynamics are characterized by applying the time-resolved optical pump (800 nm) terahertz probe spectroscopy with a pump power of $\sim$2 mJ/cm$^2$ (Details in Supplemental Material, Note 2) [22].

III. RESULTS

A. Microstructure

It is known that in their metallic phases, both VO$_2$ and NbO$_2$ take a regular rutile lattice ($P4_2/mnm$) by forming chains of edge-sharing MO$_6$ octahedra linked at their corners along the $c$ axis. For their semiconducting phases, VO$_2$ adopts a monoclinic ($P2_1/c$) lattice and NbO$_2$ takes a bct ($I4_1/a$) lattice, sharing essentially the same local deviation from the rutile lattice: formation of M-M dimers along the $c$ axis to yield alternating M-M bond lengths [23–26].

Raman spectra of all the V$_{1-x}$Nb$_x$O$_2$ films are shown in Fig. 1(a). Considering their similar lattice structures, it is not surprising that the pure VO$_2$ and NbO$_2$ films ($x = 0$ and 1) exhibit similar Raman features, which agrees well with previously reported results [27,28]. For VO$_2$ the two bands at low frequencies (194 and 225 cm$^{-1}$) correspond to the stretch and twist modes of the V-V dimers, respectively. The Raman spectrum of NbO$_2$ shows bands at 158 and 183 cm$^{-1}$, which can be related to the vibration modes of the Nb-Nb dimers caused by the heavier Nb atoms. Moreover, the band near 860 cm$^{-1}$ could be associated with certain vibration mode within the NbO$_6$ octahedra. As the composition moves from pure VO$_2$ or NbO$_2$ towards V$_{0.5}$Nb$_{0.5}$O$_2$, the two bands related to M-M dimers decrease rapidly in intensity and become absent for samples with...
compositions for $0.089 \leq x \leq 0.73$. As Nb(V) is substituted into VO$_2$(NbO$_2$), it is expected that the $M-M$ chains will be broken, leading to a decrease in $M-M$ chains tilting along the $c$ axis and the detwisting of MO$_6$ octahedra. Therefore, there is a transition of the surrounding lattice to a more symmetric, rutile structure [31,32]. The disappearance of the low-frequency Raman features could indicate the collapse of the respective low-temperature symmetry of VO$_2$ and NbO$_2$. The broad Raman band developed between 620 and 860 cm$^{-1}$ for samples with composition ranging from $x = 0.27$ to 0.73 is suspected to be related to certain $M-O$ vibration modes within MO$_6$ octahedra, with the strength of the vibration varied by the $M-O$ bond length and the local distortion of MO$_6$ octahedra. It is worth noting that no Raman feature of other oxide phases of vanadium or niobium is observed, suggesting that a solid solution has been maintained over the whole range of composition.

Figure 1(b) shows the out-of-plane x-ray $2\theta$ scans of the V$_{1-x}$Nb$_x$O$_2$ films, where $2\theta$ is the angle between the incident and diffracted x-ray beams. All samples exhibit diffraction peaks near $2\theta = 40^\circ$ and $2\theta = 86^\circ$. For clarity, all the samples are indexed on the basis of the rutile structure, although the rutile symmetry is distorted when $x$ is close to 0 (VO$_2$) or 1 (NbO$_2$). The diffraction peaks correspond to (200) and (400) peaks of the rutile lattice. [For the low-temperature lattices, they correspond to (020) and (040) diffractions of the VO$_2$ lattice, and (440) and (880) diffractions of the NbO$_2$ lattice, respectively.] No other diffraction peaks corresponding to any other vanadium-oxide or niobium-oxide phases are present, which further confirms that solid solutions instead of mixed phases are formed over the whole range of composition.

To confirm the assignment of out-of-plane $2\theta$ diffraction peaks, x-ray $\phi$ (the in-plane orientation of the sample stage) scans are conducted on (110) diffraction of rutile V$_{1-x}$Nb$_x$O$_2$ lattice at $2\theta = 26^\circ$ and $\chi = 45^\circ$ ($\chi$ is the tilted angle of the sample stage) based on the lattice symmetry, an example of which is shown in Fig. 1(c) (on the sample with composition $x = 0.55$). Furthermore, the observation of six diffraction peaks, combined with the x-ray $\phi$ scans of sapphire (0112) diffraction at $2\theta = 25.5^\circ$ and $\chi = 12.8^\circ$, indicates that the orientation relation between the deposited films and substrates is (001)/(100)$_{V_{1-x}Nb_x}O_2$ || (1010)/(0001)A$_2$O$_3$. This is the same as that between pure VO$_2$/NbO$_2$ films deposited by RBTIBD technique and (0001) sapphire substrates [20,33].

With the increase of $x$, film peaks shift towards lower $2\theta$ angles, corresponding to an increase of lattice constant along the $a$ axis of the rutile lattice ($a_R$). In Fig. 1(d), values of $a_R$ are extracted from the $2\theta$ peak positions of (200)$_R$ diffraction and plotted as a function of $x$, with the black line showing the linear fitting. The increasing trend of $a_R$ with the increase of Nb concentration is due to the larger size of the Nb ion, as the effective ionic radii of V$^{4+}$ and Nb$^{4+}$ in octahedral coordination are 0.58 and 0.68 Å, respectively [34]. In addition, previous studies have pointed out that the Nb (V) substitution introduced into VO$_2$(NbO$_2$) would exist as Nb$^{5+}$(V$^{3+}$), with V$^{3+}$(Nb$^{5+}$) resulting nearby. This is attributed to the instability of Nb 4d electrons compared with that of the V 3d electrons [9,35]. The effective ionic radii of V$^{3+}$ and Nb$^{5+}$ in octahedral coordination are both 0.64 Å [34]. Thus the deviation from the linear fitting can be accounted for by the variation in the size of ions.

### B. dc transport properties

Figure 2(a) shows the temperature dependence of dc conductivity in all V$_{1-x}$Nb$_x$O$_2$ samples from 200 to 400 K. First,
FIG. 3. Optically induced THz photoconductivity change ($\Delta \sigma$) as a function of time for $V_{1-x}Nb_xO_2$ samples with Nb concentration (a) below and (b) above $x = 0.27$. Measurement data are shown in circles while fitting curves in solid lines. (c)–(e) Composition dependence of fitted parameters describing (c) the rise term, (d) the fast decay term, and (e) the slow decay term. The dashed and dashed-dotted curves are guide to the eyes.

samples with Nb concentration up to $x = 0.089$ demonstrate the temperature-driven IMT. With the increase of $x$, IMT occurs at lower temperatures with smaller and less abrupt changes in the film conductivity across the IMT. The film conductivity of the semiconducting state is enhanced significantly by the Nb substitution, while that of the metallic state only exhibits a slight reduction. As Nb substitution is introduced into VO$_2$ films, it is expected that the breaking of Peierls distortion and the weakening of electronic correlation within the V-V dimers would result in a decrease of the band gap, leading to the decrease in transition temperature and the increase of conductivity (in the semiconducting phase) [31,36,37]. Similarly, for samples with compositions close to pure NbO$_2$ ($0.92 \leq x \leq 1$) which still maintain bct lattices, the conductivity increases as the V substitution level increases.

An interesting observation is that for those samples with intermediate Nb concentration ($0.27 \leq x \leq 0.73$), the films remain semiconducting despite the observed collapse in monoclinic (bct) symmetry of VO$_2$(NbO$_2$). In addition, the film with the composition closest to $V_{0.5}Nb_{0.5}O_2$ (the one $x = 0.52$) exhibits conductivity much lower than all the other samples. The composition dependence of the film conductivity at 300 K is summarized in Fig. 2(b). Similar composition-dependent behavior of conductivity has also been observed in bulk crystals previously [as is shown by the black line in Fig. 2(b)] [35].

C. Ultrafast THz conductivity dynamics

To investigate the effect of cation substitution on the ultrafast dynamics of the $V_{1-x}Nb_xO_2$ samples, time-resolved THz conductivity dynamics are characterized by OPTP spectroscopy, which are shown in Figs. 3(a) and 3(b). The time resolution of the OPTP measurement is limited by the bandwidth (response time) of the ZnTe detector crystal, which is $\sim 300$ fs. As is shown in Fig. 3(a), the samples with Nb content up to $x = 0.27$ demonstrate a long-lived conductivity upon the excitation of the pump pulse, while for other samples with higher Nb concentration the THz dynamics exhibit long-lived but slowly decaying conductivity after the initial fast partial decay [shown in Fig. 3(b)]. The magnitude and lifetime of the photoinduced THz conductivity strongly depend on the film composition.

To quantitatively describe the measured THz conductivity dynamics of these samples, the THz conductivity transient is fitted using the following equation:

$$\Delta \sigma(t) = \frac{A}{1 + e^{-[(t-a)/T_1]}},$$

in which there is only one rise term characterized by time $T_1$ with amplitude $A$, and two decay terms described by time constant $T_2$ with amplitude $B$ (fast decay) and time constant $T_3$ with amplitude $C$ (slow decay), respectively. The composition dependence of these fitted parameters is summarized in Figs. 3(c) to 3(e).

First, $T_1$ and $A$ are both suppressed with the increase of $x$, reaching a minimum at $x = 0.52$ and then raising at higher Nb concentration, as is shown in Fig. 3(c). For the THz conductivity transients shown in Fig. 3(a), only the rise term ($\frac{A}{1 + e^{-[(t-a)/T_1]}}$) is employed in the fitting as negligible decay is observed during the first 30 ps for samples with low Nb concentration. Thus, in Figs. 3(d) and 3(e) the fitted decay...
parameters ($B$, $T_2$, $C$, and $T_3$) are absent for $x \leq 0.27$ and only speculated trends are plotted. As shown in Fig. 3(d), the fast decay (for $x > 0.5$) takes place within $\sim 1$ ps after the photoexcitation and its magnitude takes an increasing percentage of the maximum photoinduced THz conductivity change as the Nb content increases. Compared with the fast decay, the slow decay term varies more dramatically against composition. The value of $T_2$ drops from several hundreds of picoseconds to a few tens of picoseconds as the film composition approaches pure NbO$_2$.

It is important to see that the sample $x = 0.52$ exhibits the smallest photoinduced $\Delta\sigma$ [Fig. 3(c)] and fastest “semiconductor-like” decay. This, together with the dc transport data in Fig. 2(b), again suggests the strong localization of carriers in the mixed valent oxide V$_{0.3}$Nb$_{0.7}$O$_2$, even with above-band-gap photoexcitation.

IV. DISCUSSION

A. Semiconducting dc transport behavior of V$_{1-x}$Nb$_x$O$_2$ samples with rutile lattice

VO$_2$ and NbO$_2$ have similar band structures near the Fermi level, which are composed of the $\pi$-type overlap between V 3$d$/Nb 4$d$ and O 2$p$ orbitals with $t_{2g}$ octahedral symmetry determined by the symmetry of MO$_6$ octahedra. In addition, as the MO$_6$ octahedra share edges along the c axis, the orthorhombic symmetry of the crystalline field further degenerates the antibonding $\pi$ band into the $d_{\parallel}$ and the $e_{\pi}^g$ band. For the metallic phase, the $d_{\parallel}$ band overlaps with the $e_{\pi}^g$ band with the Fermi level lying in between them. For the semiconducting phase, the $d_{\parallel}$ band splits into the bonding and antibonding band and the $e_{\pi}^g$ band is lifted up, giving rise to the band gaps [38–40]. Regarding the origin of the IMT or the nature of the semiconducting phase, for VO$_2$ the dispute centers about the relative contribution from the increased electronic correlation (Mott-Hubbard mechanism) and the metal dimerization (Peierls mechanism) [41–44]. For NbO$_2$ it is generally agreed that the latter should play a more important role due to the larger overlap of $4d$ orbitals/stronger Nb–Nb bonding [45,46], but electronic correlation also contributes to the band-gap formation, although to a lesser extent, as is revealed by recent density functional theory and cluster-dynamical mean-field calculations [47].

For samples with composition ranging from $x = 0.089$ to 0.73, it is expected that the Peierls insulation is destroyed because of the transformation in lattice structure due to cation substitution. Despite the rutile lattices, the semiconducting transport behaviors could be attributed to the electronic correlation (Mott-Hubbard mechanism) and the enhanced randomness of the film lattice (Anderson localization). A strong enough combination of Coulomb repulsion and lattice disorder could result in the localization of charge carriers and give rise to the observed semiconducting transport behavior [48–50]. In this scenario, the intrinsic electrical conduction could be realized by the electronic hopping of charge carriers. Since the cation substitution results in the formation of Nb$^{5+}$ and V$^{3+}$ in the V$_{1-x}$Nb$_x$O$_2$ system, the real structure of the film would be $V^{4+}_{1-x}$Nb$^{5+}_{x}$ for $0 < x < 0.5$ and $V^{3+}_{1-x}$Nb$^{5+}_{1-x}$Nb$^{4+}_{2x-1}$ for $0.5 < x < 1$. In principle, the charge-carrier hopping would occur between the same types of cations, manifesting as the position change of cations with the same type but different valences (V$^{4+}$/V$^{3+}$ or Nb$^{5+}$/Nb$^{4+}$). This might explain why the film exhibits conductivity enhancement around the composition where the amounts of V$^{3+}$ and V$^{4+}$ (Nb$^{5+}$ and Nb$^{4+}$) are close [35,50].

The change in the cations that conduct electricity, combined with the distribution of lattice disorder, could account for the observed variation in the dc transport features against the film composition. At last, the conductivity minimum that occurs at $x \sim 0.5$ can be interpreted as the complete demobilization of conduction carriers due to the valence states V$^{3+}$/Nb$^{5+}$ [9,35].

B. Ultrafast dynamics of V$_{1-x}$Nb$_x$O$_2$ samples

Since the pump energy (1.55 eV) is well above the band gap of VO$_2$ (0.6–0.7 eV) [51] and NbO$_2$ (indirect band gap of 0.7 eV and direct band gap of 1.24 eV) [46,52], the interband photoexcitation will lead to the generation of a large number of nonequilibrium carriers and thus the rise of THz conductivity. Previous studies of VO$_2$ have shown that when the excitation density (pump fluence) falls below a certain critical value, the full IMT cannot be triggered and the photoinduced carriers relax through various pathways in a few picoseconds, giving rise to the “semiconductor-like” decay features of $\Delta\sigma$ [53,54]. When the excitation density exceeds a certain threshold, the persistence of photocurrent change indicates that the film has transitioned to a uniform metallic state. It has been reported that the instantaneous modification of electronic correlation by optical excitation could cause subpicosecond band-gap collapse and metal-like optical response, while the establishment of the long-range rutile order may take up to several tens to hundreds of picoseconds [55,56]. Moreover, under certain pump fluence or certain external conditions (such as low temperature), the VO$_2$ films were found to transition to an electronic metallic state while maintaining monoclinic symmetry [53].

Regarding the measured photoinduced THz conductivity dynamics for the V$_{1-x}$Nb$_x$O$_2$ films, the long-lived THz conductivity observed for all the samples (except for the sample $x = 0.52$) indicates that a metastable metallic state is formed by the excitation of the pump pulse. For the samples maintaining the low-temperature lattice of VO$_2$ and NbO$_2$, the absence of a slow increase of the THz conductivity change over a timescale of $\sim 10^2$ ps suggests that the full structural transition to rutile lattice has not been triggered [53]. This observation is consistent with other OPTP studies on VO$_2$ and NbO$_2$ films, where the threshold pump fluence to trigger the structural transition is higher than what has been used in our study (2 mJ/cm$^2$) [14,53]. The metallic response can be attributed to the suppression of the Coulomb repulsion and the resulted collapse of the band gap, which essentially breaks the Mott insulation [43,57,58]. The fast partial decay shown in Fig. 3(b) can be ascribed to the electron-phonon interaction during which the energy is transferred to the lattice. Much shorter processes (within 1 ps) such as electron-electron scattering, localization or self-trapping of photocarriers can also be included [8,59,60]. The slow decay characterized by $T_3$ can be assigned to the recovery of the metastable metallic...
state to the initial semiconducting state, which is faster in Nb-rich samples. The magnitude of THz conductivity change and the recovery rate of the photoinduced metallic state differ more than one order of magnitude across films with different composition, exhibiting strong dependence on the doping concentration. The drastic modulation of the THz conductivity demonstrates a continuous series of the solid solution.

Structural characterization demonstrated that the whole system constituted a continuous series of the solid solution VO$_2$ and NbO$_2$ transitioned to more symmetric rutile lattices. Despite the changes in the lattice symmetry, the orientation relationship between the films and substrates remained unchanged by cation substitution as (001)$\parallel$V$_{1-x}$Nb$_x$O$_2$ $\parallel$ (1010)$\parallel$Al$_2$O$_3$. Temperature dependence of dc conductivity was examined from 200 to 400 K and temperature-driven IMT was observed for films with Nb concentration below x $= 0.089$. Films adapting rutile lattices still demonstrated semiconducting electrical transport behaviors across the measured temperature range. Drastic composition dependence of dc transport and ultrafast dynamics properties was observed and an “inert” substituting level at x $\sim 0.5$ was demonstrated to display a lack of both static and photoinduced conductivity. The high tunability of decay time makes V$_{1-x}$Nb$_x$O$_2$ a potential candidate for ultrafast optical switches in wire or wireless data transmission.

Y.W. and J.Z. contributed equally to this work.
