Fabrication and Electrical Characterization of Correlated Oxide Field Effect Switching Devices for High Speed Electronics

Shriram Ramanathan
HARVARD COLLEGE PRESIDENT & FELLOWS OF

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Final Report

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Fabrication and electrical characterization of correlated oxide field effect switching devices for high speed electronics

None

The electronic properties of thin film correlated oxides was investigated via electrical transport measurements and electronic structure studies. Microscopic connection between insulator-metal switching, orbital occupancy, electron-phonon interactions was emphasized. The response of correlated oxides to strong electric fields and their dynamics was investigated. A few different oxide systems were considered during the course of the study: they include VO2, SmNiO3, and NbO2. The common aspects of these materials include their thermal insulator-metal transition.
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PI: Shriram Ramanathan, Harvard University
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Final Report

Report Summary
The electronic properties of thin film correlated oxides was investigated via electrical transport measurements and electronic structure studies. Microscopic connection between insulator-metal switching, orbital occupancy, electron-phonon interactions was emphasized. The response of correlated oxides to strong electric fields and their dynamics was investigated. A few different oxide systems were considered during the course of the study: they include (3d\textsuperscript{1}) VO\textsubscript{2}, (3d\textsuperscript{3}) SmNiO\textsubscript{3} and (4d\textsuperscript{5}) NbO\textsubscript{2}. The common aspects of these materials include their thermal insulator-metal transition. At the same time, the different crystal structure between the binary oxides and the perovskite nickelates and the nature of d-orbital filling leads to profound complexity in the electronic nature of the phase change. In the report below, particular emphasis on the orbital splitting effects and conductivity of NbO\textsubscript{2} is discussed in detail and compared with a model system of VO\textsubscript{2}. Optical properties from 0.2 to 6.5 eV of epitaxial NbO\textsubscript{2} (4d\textsuperscript{5} system) films in their insulating states were investigated by spectroscopic ellipsometry. We found a d\textsubscript{||}-e\textsubscript{8} orbital splitting energy of ~1.6 eV in NbO\textsubscript{2} compared to ~1.3 eV in VO\textsubscript{2}. The edge of the O2p-like valence band is estimated to be 3.2 eV below the Fermi level through x-ray photoelectron spectroscopy measurements, suggesting that electrons from O2p states do not contribute to optical absorption below this energy.

I. INTRODUCTION
Metal-insulator transitions (MITs) in oxides are an intriguing problem from both a fundamental materials physics and an applied technology perspective [1]. Though the precise roles of electron correlations and lattice distortions on the phase transition remains an active area of research, many recent theoretical studies have suggested intimate interplay among the orbital splitting/polarization, correlation effects, and Peierls dimerization in the 3d\textsuperscript{1} system [2-6]. Occupied states have been probed by x-ray photoelectron spectroscopy (XPS) [7], and a rough structure of unoccupied 3d-like states have been deduced by O K-edge x-ray absorption measurements [8-10]. NbO\textsubscript{2}, a 4d\textsuperscript{5} system, like VO\textsubscript{2} crystallizes in a distorted rutile-type structure with Nb dimers and undergoes a temperature-induced MIT, albeit at a considerably higher temperature of ~1083 K [11]. It is commonly accepted that because 4d orbital valence states are more dispersed in both space and energy, Mott physics is less important in 4d transition-metal oxides than in 3d ones. Along this line of reasoning, it is perhaps surprising that the insulating state of NbO\textsubscript{2} persists to higher temperatures than that of VO\textsubscript{2}. A proposed explanation for this difference is that the Peierls effect in NbO\textsubscript{2} is stronger due to larger Nb metal-metal overlap of 4d orbitals, leading to greater orbital splitting between occupied d\textsubscript{||} states and the unoccupied e\textsubscript{g} states [12]; however, given the many attempts to revise and improve theoretical and computational studies of VO\textsubscript{2} [2-5,13], the physical and electronic properties of NbO\textsubscript{2} also should be examined more thoroughly. Currently, there are few experimental studies that provide insight into the electronic structure of NbO\textsubscript{2}.

There have been diffraction [14,15], calorimetry [16], electrical [11,17-19], and magnetic [19] studies on bulk NbO\textsubscript{2}, which have shown that it transforms from a high-temperature rutile-structure metal to a low-temperature Nb-dimerized diamagnetic insulator at ~1083 K. Recently epitaxial NbO\textsubscript{2} thin films have been grown on (0001) Al\textsubscript{2}O\textsubscript{3}, (111) MgO, (111) MgAl\textsubscript{2}O\textsubscript{4}, and (111) perovskite oxide substrates [20,21]. The key to achieving epitaxy of (100) rutile-type compounds is exploiting substrate surfaces with eutactic planes [22].

1
II. EXPERIMENTAL DETAILS

Epitaxial NbO$_2$ films were grown on (0001) Al$_2$O$_3$ by DC reactive sputtering of a Nb metal target at 650 °C, 200 W, 10 mTorr, 7.5 sccm O$_2$, and 42.5 sccm Ar. An epitaxial (010) VO$_2$ film was grown on (0001) Al$_2$O$_3$ by RF sputtering a V$_2$O$_5$ ceramic target at 450 °C, 150 W, 5 mTorr, 1.3 sccm O$_2$, and 48.7 sccm Ar. Deposition conditions were optimized to both achieve stoichiometric phases as well as film smoothness for reliable ellipsometry measurements. X-ray reflectivity was used to measure the film thickness, and x-ray diffraction was used for phase and orientation determination. Raman spectroscopy was performed in a confocal microscope using a 532 nm laser source; a filter prevents the collection of signal <170 cm$^{-1}$.

Electrical transport measurements were performed in the van der Pauw geometry; contact pads of 5 nm of Ti and then 50 nm of Au were sputtered on the films. Ex-situ XPS scans were taken with Al K$_x$ radiation and with an electron flood gun that prevents charging, and the samples were grounded to the spectrometer. The energy scale of the XPS data is referenced so that Au4f$_{7/2}$ peak is at 84.0 eV.

Spectroscopic ellipsometry measurements were taken at incident angles of 50° and 70° with respect to the plane normal. These experiments were performed by collaborator at Woollam Inc. By checking data taken at different in-plane rotations, we confirmed that in-plane anisotropy is not present into our measurements, which is expected because the rutile-type thin films grow with rotational variants and hence 3-fold in-plane global rotational symmetry [20,22]. Furthermore, though our rutile-type films are oriented out-of-plane, we were able to fit all of our data at both incident angles assuming isotropic optical constants, which may be due to the small path length difference between the $p$ and $s$ polarized light within the thin films. Thus, our measurements are not sensitive to the possible crystal optical anisotropy of VO$_2$ and NbO$_2$. Our optical conductivity spectra should be thought of as polarization averaged. All data sets were fitted both point by point and also separately with analytical oscillators. Point-by-point fitting has the advantage that it does not impose a functional form to the dielectric functions, but analytical oscillator fitting has the advantage that the resultant dielectric functions are ensured to satisfy the Kramers-Kronig relations. Both types of fits for all of our data sets presented here gave quantitatively comparable results. We strove to use the minimum number of oscillators while maintaining high fidelity of fitting, so that fitted parameters of different samples can be fairly compared, but the choice of oscillators is not unique. We used a collection of Lorentz and Tauc-Lorentz oscillators; the imaginary part of the dielectric function has a functional form with respect to energy $E$ of:

$$\varepsilon_2 = \sum_i \frac{A_i B_i^2 E_i}{(E_i^2 - E^2)^2 + B_i^2 E^2} + \sum_j \frac{A_j C_j E_j (E - E_{gj})}{(E^2 - E_j^2)^2 + C_j^2 E^2} \Theta(E - E_{gj})$$

where $\Theta$ is the Heavyside step function. $A_{i(0)}$, $B_{i(0)}$, $E_{i(0)}$, $E_{g(i)}$, and $C_i$ are the fit parameters for the $i$th Lorentz oscillator and the $j$th Tauc-Lorentz oscillator.

III. RESULTS

The real optical conductivity of V1, N1, and N2 are shown in Figs. 1(a)-(c). Results of the point-by-point and oscillator fits are compared, and the contribution of each individual oscillator is also displayed. Fitted parameters are summarized in Table I. The lowest energy optical excitation feature can be fitted adequately mainly by a single Tauc-Lorentz oscillator. The center energy is 1.31 eV for V1 and 1.58 eV for both N1 and N2. Though N1 and N2 should be nominally the same in terms of deposition conditions, aside from a small difference in thickness, we can see that that higher-energy (>3.5 eV) features are different; in particular, N2 shows higher conductivity and more spectral features. Nevertheless, their low-energy spectra (<3.5 eV) are quite comparable, as captured by their respective Oscillators 1 and 3 in Table I.

Sum-rule analysis [Fig. 1(d)] can be performed on optical conductivity spectra to determine the effective number of electrons $n_{eff}$ per formula unit of NbO$_2$ accounting for optical excitation from 0 to a cutoff energy of $E$. 

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\[ n_{\text{eff}}(E) = \frac{2m_0}{N\pi\hbar^2} \int_0^E \sigma_1(E')dE' \]

where \( m_0 \) is the bare electron mass and \( N \) is the volume density of formula units of NbO\(_2\) or VO\(_2\).

X-ray diffraction scans of N1 and N2 reveal that the both of the films are (110)-oriented in using Miller indices of its room-temperature distorted \( \text{i}4_1/\text{a} \) unit cell [15], which corresponds to the pseudorutile (100) orientation [Fig. 2(a)]. The out-of-plane spacings, pseudorutile \( a \) lattice parameters, of both samples are 4.835 Å, which is within the range of reported values of bulk crystals [15,23,24]. Note that the film peak of N1 is broader and slightly asymmetric. There is a weak second NbO\(_2\) orientation in N2, but no other peaks for N1. We did, however, find slight differences in Raman peak positions, particularly for the mode near 390 cm\(^{-1}\), as well as weaker signal for the mode at 272 cm\(^{-1}\) in N1 [Fig. 2(b)]. Moreover, the Raman peaks of N2 are more intense and sharper of those of N1. Therefore, the contrast between the optical conductivity of N1 and N2 may be due to minor differences in point defect concentrations and/or in residual thin-film strain within the NbO\(_2\) phase.

XPS was employed to probe the energy positions of the occupied valence band states of V1, N1, and N2 [Fig. 3(a)]. There are two Stark differences: (1) emission from occupied valence \( d \) electron states is maximized at 0.85 eV for VO\(_2\) and \( \sim 1.25 \) eV for NbO\(_2\) (1.3 eV for N1 and 1.2 for N2), and (2) the emission edge of O2\( p \)-like states are estimated to be \( \sim 2.0 \) eV for VO\(_2\) and \( \sim 3.2 \) eV for NbO\(_2\). Because the samples are grounded to the spectrometer, the binding energies should be interpreted as the energies with respect to their Fermi levels. Our XPS spectrum of V1 matches closely to that of Shin et al. [7] The O2\( p \) band energies of N1 and N2 closely resemble recent \textit{in-situ} photoemission studies of epitaxial NbO\(_2\) films on (111) perovskite substrates [21]. Since XPS is surface sensitive, and both VO\(_2\) and NbO\(_2\) are susceptible to surface oxidation to their highest oxides, the intensity for transition-metal valence \( d \) peak depends on the degree of surface oxidation in ambient conditions. For example, surface oxidation on N2 is more pronounced than on N1. Nevertheless, for seven different NbO\(_2\) films measured, we find that though the relative intensity may differ, the position in energy of Nb\( 4d \) valence peak does not change to within \( \pm 0.1 \) eV, which is roughly the resolution limit of the XPS system (data not shown). The same is true for the position of the O2\( p \)-like band. The higher oxide and NbO\(_2\) differ mainly in 4\( d \) electron filling; thus despite some degree of surface oxidation, the valence band XPS nevertheless yields a good estimate of the O2\( p \) band position of NbO\(_2\). A core-level Nb3\( d \) XPS scan of N2 illustrates there is in fact some unavoidable sample surface oxidation once the sample is exposed to the ambient, showing Nb\(^{5+} \) 3\( d \) doublets [Fig 3(b)]. Regardless, there is also a clear signature of Nb\(^{4+} \). Core-level peak positions of N2 are listed in Table II, and they closely match reported values from bulk crystals [26,27]. After background subtraction, the Nb3\( d \) core-level XPS spectrum of N2 in Fig. 3(b) was fitted with two doublet pairs. Each pair corresponds to the spin-orbit-split 3\( d_{5/2} \) and 3\( d_{3/2} \) levels of two different Nb valence states, 5\( + \) and 4\( + \). For each pair, we constrained the relative integrated intensities between 3\( d_{5/2} \) and 3\( d_{3/2} \) to be 3:2 and possessing the same full-width at half maximum (FWHM) values. The FWHM value of fitted Nb\(^{4+} \) peaks was 1.28 eV and that of Nb\(^{5+} \) was 1.31 eV. The integrated intensity ratio between Nb\(^{4+} \) and Nb\(^{5+} \) was 31:69. However, we believe that the Nb\(^{5+} \) oxide is confined to the very surface, because in our experience, core-level Nb3\( d \) scans of even elemental Nb metal films show a comparable amount of Nb\(^{5+} \) signature due to surface oxidation in ambient conditions. Figure 3(c) reveals the activation energy for electrical conduction to be 0.16 eV for N1 and 0.135 eV for N2. The weaker temperature dependences exhibited by both samples at low temperatures may be indicative of hopping transport via defect states.

IV. DISCUSSION

Using Goodenough’s nomenclature [28], the antibonding \( d \)-like states that partake in bonding with surrounding oxygen are \( d_{\|} \) and \( e_6 \) (\( t_{2g} \) in octahedral symmetry), where \( d_{\|} \) refers to the orbitals that are also involved in direct metal-metal bonding. The two \( d \)-like orbitals that bond with oxygen are referred to as \( d \) (\( e_6 \) in octahedral symmetry). In the dimerized insulating states of both VO\(_2\) and NbO\(_2\),

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the $d_{||}$ further splits into $d_{||}$ metal bonding and $d_{||}^*$ metal antibonding states. For our discussion, we assume that the arrangement of lowest to highest energy orbitals is $d_{||} \rightarrow e_g \rightarrow d_{||}^* \rightarrow d$, which is supported by a number of computational studies [2,12,29,30]. However, we do acknowledge there should be band overlap, particularly between the $e_g$ and $d_{||}^*$ bands. For the purpose of our discussion, we will also assume that the lone $d$ electron resides solely in the $d_{||}$ state, but note that computational studies typically do not yield full orbital polarization in the insulating states [2,3,12].

Because binding energy edge of the O2p-like states deduced by XPS [Fig. 3(a)] is ~3.2 eV for NbO$_2$ and ~2.0 eV for VO$_2$, we assume that excitation of the one 4$d$ (3$d$) electron is mainly responsible for the optical conductivity below these energies for NbO$_2$ (VO$_2$). This assumption can be justified by the observation that $n_{off}$ is considerably less than 1 at the stated energies for each compound [Fig. 1(d)]. Table I shows that the center energies of Tauc-Lorentz oscillator used to fit the lowest energy absorption feature are 1.31 eV for V1 and 1.58 eV for N1 and N2. This center energy ranges from 1.56 to 1.67 eV for ten different NbO$_2$ thin films measured. In both experimental [31] and theoretical [32] studies of VO$_2$, similar optical excitation is thought to be indicative of a $d_{||} \rightarrow e_g$ transition, representative of the essential orbital splitting that is required to stabilize the insulating state. Experimentally, reported peak energies range from 1.1 to 1.35 eV for VO$_2$ [31,33-36]. Therefore, we assign the peak energy of 1.58 eV in N1 and N2 to be representative of the $d_{||}$-$e_g$ orbital splitting; the larger separation in NbO$_2$ appears to be consistent with its higher transition temperature.

The center energies of oscillators 1 in N1 and N2 are only slightly larger than the binding energy peak of the occupied $d_{||}$ band as determined by XPS, which suggests that the Fermi level is close to the conduction band edge and explains the small activation energy observed in electrical transport. Hence, the activation energy should not be interpreted as half of the band gap. In Jannick and Whitmore’s electrical transport study of bulk ceramic NbO$_2$, they found a higher activation energy of ~0.45 eV [18]. Furthermore, we believe that the center energies of Oscillators 3 in N1 (2.96 eV) and N2 (2.97 eV) are representative of the $d_{||} \rightarrow d_{||}^*$ transition. This assignment is close to the separation concluded in DFT calculations based on the LDA approximation, but it should be noted that any possible correlation effects were not accounted for [12]. On the other hand, we also note that an older calculation of the joint density of states of NbO$_2$ performed by Posternak et al. does not show a distinct peak at ~3.0 eV [37]. From Jiang and Spence’s O K-edge electron energy loss spectroscopy (EELS) studies of NbO$_2$ [38], they deduced that the octahedral crystal field splitting of unoccupied 4$d$-like and antibonding states to be ~3.5 eV. We assume this value to be the approximate separation between the $e_g$ and $d$ states. Therefore, any possible excitation to the $d$ states contributes minimally to that of the peak captured by Oscillator 3. Furthermore, considering the position of the O2p band as deduced by XPS, excitation of electrons from O2p states likewise should contribute insignificantly to the Oscillator 3 peaks of N1 and N2. Table I shows that Oscillator 3 of V1 peaks at 2.92 eV; however, in this sample, the origin is more difficult to isolate because O2p $\rightarrow e_g$ transitions contribute heavily at this energy range, as is suggested by previous studies [28,32,35] as well as by the lower O2p photoelectron band edge energy of V1 at 2.0 eV below the Fermi level [Fig. 3(a)]. In VO$_2$ thin films, Qazilbash et al. report an optical peak at 2.5 eV attributed to $d_{||} \rightarrow d_{||}^*$ transition [31], and Verleur et al. observe a peak at ~2.75 eV in bulk and ~3.0 eV in thin-film samples but did not assign them to any particular transition. Whether a discernable peak emerges in theoretical optical conductivity calculations of VO$_2$ depends on the model used and computational details [32].

For NbO$_2$ at photon energies >3.2 eV, it is clear that a combination of transitions from occupied O2p and $d_{||}$ states are involved, so we do not attempt to make any further assignments of optical features to specific transitions. If excitonic and other excited-state correlation effects can be ignored, Fig. 4 represents a rough schematic of the energy ordering of the different bands (orbitals) with respect to the Fermi level of our NbO$_2$ samples, as deduced from our optical conductivity and XPS measurements. The position of the $d$ states was inferred from Jiang and Spence’s O K-edge EELS measurements in addition to our data [38]. A recent ab initio study on niobium oxides suggest that a Hubbard $U$ of 2 eV on Nb 4$d$
orbitals may be appropriate [39]. Given that recent work has suggested correlation effects are sizeable even in 5d transition-metal oxides [40], their contribution in the 4d transition-metal oxide NbO₂ needs to be re-examined.

V. SUMMARY

we have reported on the optical conductivity and orbital thermodynamics of NbO₂ films with epitaxial variants deposited on (0001) Al₂O₃. XPS measurements indicate that emission from the occupied d∥ band states peaks at 1.2 eV below the Fermi level, and O2p band edge is ~3.2 eV below the Fermi level. A comparison of the spectral features of NbO₂ and VO₂ states reveals a d∥-e₈ orbital splitting that is ~0.3 eV larger in NbO₂, which is consistent with its higher MIT temperature. We are able to determine approximate energy separation among Nb 4d-like and O2p-like electronic states based on experimental data.

TABLE CAPTIONS

Table I. Fitted parameters used to calculate the optical conductivity spectra [Fig. 1(a)-(c)] from spectroscopic ellipsometry. B, C, E, and Eₖ are in units of eV, while A is dimensionless.

Table II. Core-level binding energies of N₂ in eV.

Table III. The 1s XPS peak positions in eV of adventitious carbon and oxygen of V₁, N₁, V₂, and the Au and Ag references. Several different Au samples were measured, and the range of C1s peak positions is noted.

FIGURE CAPTIONS

FIG. 1. Real optical conductivity 1 of (a) V₁, (b) N₁, and (c) N₂, showing the spectra fitted point by point (symbols) as well as by Lorentz and Tauc-Lorentz oscillators (solid lines). The optical conductivity contributions from individual oscillators are shown in the dashed lines. (d) The effective number of electrons neff involved in optical processes as a function of photon cutoff energy.

FIG. 2. (a) X-ray diffraction 2 - scans and (b) Raman spectra of N₁ and N₂. The Miller indices used for the NbO₂ peaks refer to its Nb dimerized tetragonal unit cell. The 440 and 222 reflections correspond to the pseudorutile 200 and 101 reflections, respectively.

FIG. 3. (a) Valence band XPS spectrum of V₁ and N₂, (b) core-level Nb3d spectrum of N₂, and (c) temperature-dependent electrical transport of N₁ and N₂.

FIG. 4. Proposed, approximate energy arrangement of electron levels of NbO₂ based on the ordering of orbital states suggested by the theoretical study of Ref. [12] and our measured experimental optical conductivity and valence band XPS features. The position of the d states was inferred by an EELS study in Ref. [38].

FIG. 5. Ellipsometry data (a) and (b) of N₁ taken at two different incident angles. The raw data are shown as open symbols, and fits derived from an oscillator model are shown as lines.

FIG. 6. The spectra of n, k₁, and k₂ of (a) V₁, (b) N₁, and (c) N₂ attained by oscillator fits.
FIG. 7. (a) The optical conductivity of N1 modeled as a homogenous 54 nm film versus a 52 nm film with an additional 2 nm Nb$_2$O$_5$ surface layer attained by point-by-point fits. (b) The optical constants of Nb$_2$O$_5$ used in the fitting of (a).

Table I

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Figure 1
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Photoelectron Yield

Binding Energy (eV)

Photoelectron Yield

Binding Energy (eV)

Resistivity ($\Omega \text{ cm}$)

$1000/T (K^{-1})$

Figure 3
\[ d_\sigma \quad +3.9 \text{ eV} \]

\[ d_{\parallel}^* \quad +1.8 \]

\[ e_g^{\pi} \quad +0.4 \quad E_f = 0 \]

\[ d_{\parallel} \quad -1.2 \]

\[ \text{O}_2p \quad -3.2 \]

\[ \text{---} \quad -10.0 \text{ eV} \]

Figure 4
Figure 5
Figure 6
REFERENCES