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Niobium doped TiO_2: Intrinsic transparent metallic anatase versus highly resistive rutile phase

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We report on the structural, electrical, and optical properties of 5% niobium doped TiO_2 thin films grown on various substrates by pulsed laser deposition. The epitaxial anatase $Nb:TiO_2$ film on $LaAlO_3$ is shown to be an intrinsic transparent metal and its metallic property arises from Nb substitution into Ti site as evidenced by the Rutherford backscattering channeling result. In contrast, the rutile $Nb:TiO_2$ thin films show insulating behaviors with 2–3 orders higher room temperature electrical resistivity and ~30 times lower mobility. A blueshift in the optical absorption edge is observed in both phases, though of differing magnitude. © *2007 American Institute of Physics*. [DOI: 10.1063/1.2750407]

I. INTRODUCTION

In the field of electronics, considerable efforts have been dedicated to the study of transparent conducting oxides (TCO) due to the expanding demand for transparent electrodes in optoelectronic devices such as flat panel displays (FPDs), organic light emitting displays (OLEDs), etc.[1–3] Currently tin-doped indium oxide (ITO), with excellent conductivity ($\rho_{RT} \sim 10^{-4}$ Ω cm) and high transmittance (~90%) in the visible range, is in practical use for most transparent electrode applications. However, due to the cost and scarcity of indium, ITO may not be able to satisfy the demands in the future and, hence, the search for new TCO has become very significant.

TiO_2 has three different structural polymorphs: rutile, anatase, and brookite. The rutile phase, the most stable one, has been extensively studied[4–6] over decades because of its potential technological importance in catalysis,[7] electrochromism,[8] and photocatalysis.[9] In contrast, much less experimental work is reported on the anatase phase partly due to the difficulty in synthesizing good-quality single crystals.[10,11] The few reported studies have shown significant differences between the electrical, magnetic, and optical properties of the anatase and rutile phases.[12–14] Recently, the observation of high temperature ferromagnetism with some magnetic dopants into anatase TiO_2 has triggered great interest in this material in the field of spintronics.[15,16] However, there are hardly any detailed reports on the electrical properties of anatase TiO_2 doped by transition elements or other multivalent elements from a pure semiconductor technology point of view. Most recently, Furubayashi *et al.*[17] reported the discovery of Nb-doped anatase TiO_2 as a new TCO. It was shown that the room temperature (RT) resistivity of this material with Nb concentration >3% grown on a $SrTiO_3$ (001) single crystal is $2-3\times10^{-4}$ Ω cm and the transmittance in the visible range is ~90%. However, the origin and the precise nature of transparent metallic properties of $Nb:TiO_2$ invites further scrutiny because of the possibility of niobium diffusion into $SrTiO_3$ forming $Nb:SrTiO_3$, which also shows good conductivity at certain growth conditions.[18,19] Toward this end we have performed a systematic study of the structural, electrical, and optical properties of 5% $Nb:TiO_2$ (NTO) films grown on various substrates. Our results show that Nb-doped TiO_2 with a single crystalline anatase phase is indeed an intrinsic TCO and its metallic property arises from Nb substitution into the Ti site which provides electrons into the conduction band. However, its rutile phase shows insulating behavior with 2–3 orders higher room temperature resistivity. Possible reasons for these differences are addressed.

II. EXPERIMENT

The 5% $Nb:TiO_2$ thin films with a thickness of ~800 Å were grown on single crystal (001) $LaAlO_3$ (LAO), $SrTiO_3$ (STO), *r*-(*c*-)plane sapphire and quartz substrates, at the same growth conditions as reported by Furubayashi *et al.*[17] via pulsed laser deposition. X-ray diffraction patterns (as shown in Fig. 1) indicate that the films grown on (001) LAO and STO substrates were epitaxial with single phase anatase character and (00*L*) orientation. However, the films grown on *r*- and *c*-sapphire substrates are epitaxial and of rutile phase with the (101) and (*L*00) orientations, respectively. The NTO film on quartz (SiO_2) forms the polycrystalline rutile phase.

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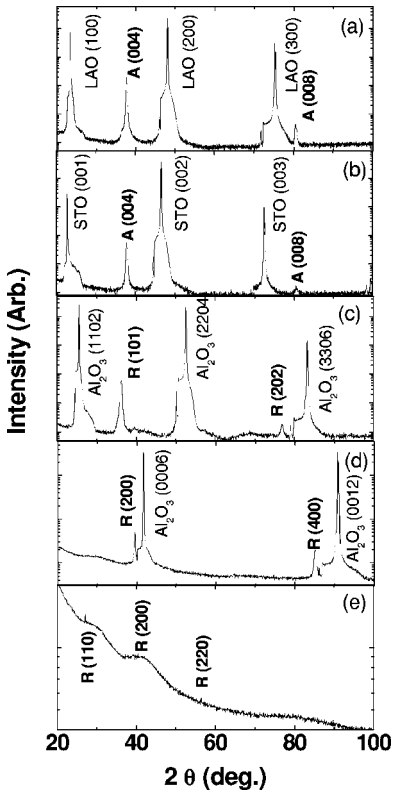

FIG. 1. X-ray diffraction patterns for (a) NTO/LAO, (b) NTO/STO, (c) NTO/r-Al_2O_3, (d) NTO/c-Al_2O_3, and (e) NTO/quartz thin films.

III. RESULTS AND DISCUSSION

Figures 2(a) and 2(b) show the Rutherford backscattering spectra (random and channeled) for 5% Nb:TiO_2 (NTO) films grown on (001) LAO and STO, respectively. The minimum channeling yield of Ti and Nb in NTO/LAO are both ~10%, indicating that about 90%Nb substitutes into the Ti site, while those for NTO/STO are about 50%, suggesting that NTO/LAO has a much better crystalline quality than NTO/STO. The better crystalline quality of NTO/LAO could

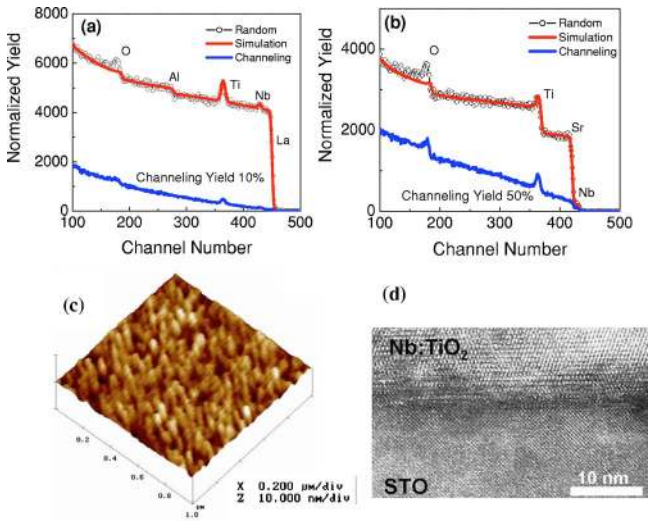

FIG. 2. (Color online) Rutherford backscattering-ion channeling spectrum obtaining from (a) NTO/LAO and (b) NTO/STO films and (c) AFM image of NTO/LAO film. (d) High-resolution TEM image at the interface of Nb:TiO_2 film and $SrTiO_3$ substrate.

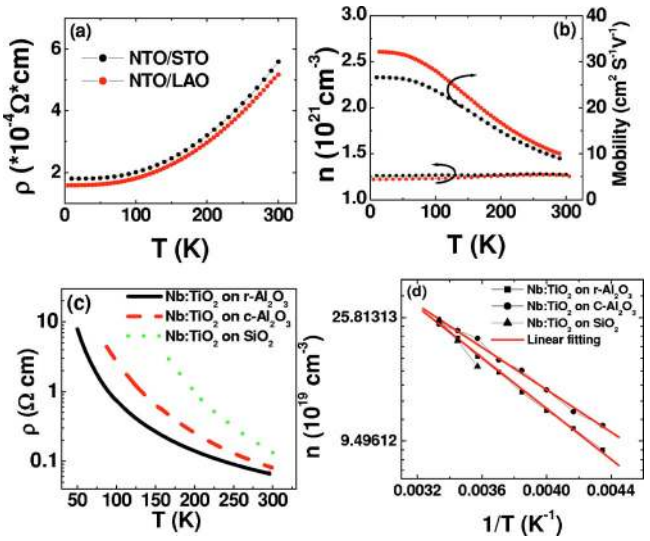

FIG. 3. (Color online) Temperature dependence of (a) resistivity and (b) carrier density and Hall mobility for NTO/STO (black curves) and NTO/LAO (red curves); (c) temperature dependence of resistivity for NTO/r-Al_2O_3 (black solid line), NTO/c-Al_2O_3 (red dashed line), and NTO/quartz (green dotted line). (d) Carrier density as a function of $1/T$ for NTO/r-Al_2O_3 (square dots), NTO/c-Al_2O_3 (round dots), and NTO/quartz (up triangle dots), red curves are fitting data.

be attributed to the lower lattice mismatch between TiO_2 and LAO (~−0.26%) than that between TiO_2 and STO (~−3.1%). This argument is further evidenced by the x-ray diffraction rocking curves (full width at half maximum of the anatase (004) peak are 0.42° and 0.93° for NTO/LAO and NTO/STO, respectively) and the atomic force microscopy (AFM) measurements. Figure 2(c) shows the AFM image of the surface of NTO/LAO, which is very smooth (mean roughness ~0.344 nm). While the film on STO (not shown) is much rougher, with a mean roughness of ~1.050 nm.

We investigate the interface nanostructure of NTO/STO by using high-resolution transmission electron microscopy (TEM). As shown in the Fig. 2(d) TEM cross-section image, the film is epitaxially grown as an anatase phase. The slightly distorted NTO nanostructure along the interface is caused by the misfit dislocations, stress at early stage deposition, and 2–3 atomic-level steps on the original STO substrate surface. We were unable to conclude whether there is any interdifussion of niobium in STO and contributing to the excellent conductivity of the NTO/STO sample. Since no extrinsic conducting layer forms when Nb diffuses into LAO and moreover our cobalt doped NTO/LAO has been shown not to exhibit interdiffusion even when grown at very high temperature (850 °C),[20] in the following we mainly focus on the properties of the films grown on (001) LAO substrate when we discuss the properties of anatase Nb:TiO_2.

Figure 3(a) compares the temperature dependence of resistivity for NTO/LAO and NTO/STO. Both samples show metallic behavior with the RT resistivity of 4.95×10^{-4} Ω cm for the NTO/LAO and 5.59×10^{-4} Ω cm for the NTO/STO (calculation based on the assumption that no interface Nb:$SrTiO_3$ contribution is present). These results confirm the report by Furubayashi *et al.*[17,19] As shown in Fig. 3(b), the carrier densities in the film on LAO are ~1.25 $\times 10^{21}$ cm^{-3} at room temperature and almost independent of

TABLE I. The comparison of room temperature resistivities, carrier densities, and Hall mobilities of NTO thin films grown at various substrates.

Samples	RT resistivity ρ_{RT} (Ω cm)	RT carrier density n_{RT} (cm^{-3})	RT Hall mobility μ_{RT} ($cm^2\ V^{-1}\ S^{-1}$)
Anatase 5% Nb:TiO_2 on LAO	4.95×10^{-4}	1.25×10^{21}	10
Anatase 5% Nb:TiO_2 on STO	5.59×10^{-4}	1.26×10^{21}	8.9
Rutile 5% Nb:TiO_2 on *r*-Al_2O_3	0.066	2.55×10^{20}	0.379
Rutile 5% Nb:TiO_2 on *c*-Al_2O_3	0.08	2.42×10^{20}	0.323
Rutile 5% Nb:TiO_2 on quartz	0.13	2.40×10^{20}	0.199

temperature. We can get the carrier density versus Nb concentration ~90%, which is identical to the Nb substitution rate (~90%) in NTO/LAO obtained from channeling. Figure 3(b) also shows the Hall mobilities μ_H, which increase from 10 to 33 $cm^2\ V^{-1}\ S^{-1}$ as temperature decreases from RT to 10 K. We also show the temperature dependence of the carrier density and Hall mobility data of our NTO/STO sample in Fig. 3(b) (again on the assumption that no contribution emanates from the interface Nb:$SrTiO_3$ layer) just for comparison with the NTO/STO data reported by Furubayashi *et al.*,[17] which show similar behavior.

Figure 3(c) shows the electrical properties of three rutile Nb:TiO_2 thin films grown on *r*-sapphire, *c*-sapphire, and quartz substrates. All the resistivity versus temperature ($R-T$) curves show negative slope indicating semiconducting (or insulating) properties. Figure 3(d) shows the carrier density n as a function of $1/T$ for these three samples (Hall measurements could only be performed above 230 K due to the high resistance at low temperatures, carrier density was obtained by simply assuming Hall mobility is amost equal to drift mobility). In contrast to the case of anatase, carrier density decreases quickly as temperature decreases and $\ln(n)$ is almost linear to $1/T$. By fitting the data, we can get the electron activation energy ε of ~0.075 and ~0.088 eV for NTO/*c*- and NTO/*r*-sapphire, respectively. This indicates that rutile NTO is a thermal activated semiconductor, while anatase NTO is a degenerate semiconductor. In Table I, we compared the room temperature resistivity, carrier density, and Hall mobility of all the samples. The room temperature resistivities are found to be 0.066 Ω cm for NTO/*r*-Al_2O_3, 0.08 Ω cm for NTO/*c*-Al_2O_3, and 0.13 Ω cm for NTO/SiO_2, all of which are 2–3 orders higher than the values for epitaxial anatase films grown on (001) LAO. These results are consistent with the report by Furubayashi *et al.*[19] However, it is found that the RT carrier densities (~2.4×10^{20} cm^{-3}) of these three rutile films are only five times lower than that of the single crystalline anatase phase, suggesting the origin of higher resistivity to be due to a significantly lower (~30 times) carrier mobility in the rutile phase.

The nonmetallic behavior of the rutile phase can be attributed to the small Bohr radius of the hydrogen-like donor state in this matrix. According to the Mott transition picture in semiconductors,[21] the critical donor concentration (n_{dc}) for Mott transition bears the following relation with the Bohr radius (a_H^*) of the hydrogen-like donor state

$$n_{dc} \sim (0.25/a_H^*)^3.$$

Using $a_H^* \sim 2.6$ Å (Ref. 13) of the rutile TiO_2, one can get the critical concentration n_{dc} of $\sim10^{21}$ cm^{-3}. However, the effective donor state Bohr radius for the anatase phase is ~15 Å, implying a much lower critical donor density (5×10^{18} cm^{-3}). Therefore, our rutile phase shows a thermally activated transport behavior while the anatase phase shows a metallic behavior.

In Fig. 4(a), we show the transmittance spectra of the anatase TiO_2 and NTO thin films together with LAO and STO substrates. The evaluated internal transmittance of all films is above 80% in the visible range, suggesting the NTO film grown on LAO is indeed an intrinsic transparent metal. Interestingly, the absorption edge of the film grown on LAO shows a blueshift with niobium doping. It is noticed that the similar result was also reported by Kurita *et al.* very recently.[22] This shift may be attributed to the well-known Burstein–Moss effect,[23] usually observed in degenerate semiconductors, where the transition occurs from the filled band to the lowest unfilled level in the conduction band. Based on the assumption of indirect optical transition in antase TiO_2,[13]

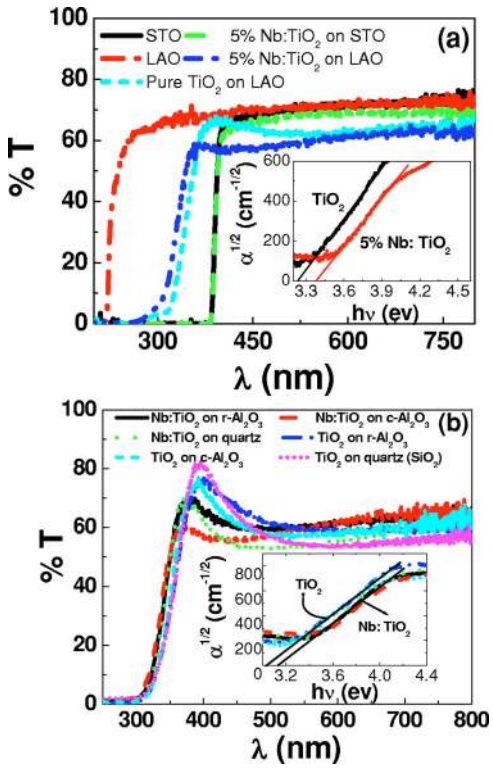

FIG. 4. (Color online) (a) Transmittance spectra of anatase TiO_2, NTO samples and LAO, STO substrates. Inset shows $\alpha^{1/2}$ vs $h\nu$ for TiO_2/LAO and NTO/LAO thin films. (b) Transmittance spectra of rutile TiO_2 and NTO samples. Inset shows $\alpha^{1/2}$ vs $h\nu$.

we plot $\alpha^{1/2}$ as a function of $h\nu$ in the inset of Fig. 4(a), where α is the absorption constant and $h\nu$ is the photon energy. The extrapolated optical absorption edge of TiO_2 and $Nb:TiO_2$ are found to be 3.22 and 3.37 eV, respectively. If assuming a single parabolic conduction band, one can roughly evaluate the effective mass of the conduction electrons. And our calculation shows this effective mass m^* is $\sim 2.5m_0$, where m_0 is the electron mass. For the sample grown on STO, the absorption edge is dominated by the band edge of the STO substrate itself, forbidding the observation of the expected similar shift in this case.

Figure 4(b) shows the transmittance spectra of the rutile samples with different substrates. We plot $\alpha^{1/2}$ as a function of $h\nu$ in the inset of Fig. 4(b), assuming the indirect optical transition of rutile TiO_2.[13,24] The extrapolated optical absorption edges of TiO_2 grown on *c*-sapphire, *r*-sapphire, and quartz are ~3.09 eV, while those of the NTO films are ~3.18 eV. We would like to point out that this shift of rutile NTO films with a magnitude of ~0.09 eV is surprising, given the low carrier density (2.5×10^{20} cm^{-3}) of these films. If this blueshift is also from the Burstein–Moss effect, calculation based on the simple conduction band assumption will give rise to a very small effective mass $m^*\sim 1.5m_0$, which is unexpected since the effective mass of rutile TiO_2 is usually about $8-20m_0$,[13] indicated also by the significantly low Hall mobility in our rutile samples. This large shift may arise from the widening of band gap with niobium doping, as indicated by x-ray photoemission studies.[6] However, the precise origin of this unusual blueshift requires further investigation.

IV. CONCLUSION

In conclusion, we have grown 5% $Nb:TiO_2$ films on LAO (001), STO (001), *r*-Al_2O_3, *c*-Al_2O_3, and quartz. Rutherford backscattering channeling data directly reveals the substitution of Nb into a Ti lattice (~90%) for the epitaxial anatase NTO/LAO film, which is found to be an excellent intrinsic conducting oxide ($\rho_{RT}\sim 4.95\times10^{-4}$ Ω cm). In contrast, the rutile phase of NTO shows much higher resistivity (2–3 orders higher room temperature resistivity than that of the anatase phase) and a considerably lower mobility. A blueshift in the optical absorption edge is observed in both phases and the magnitude of this shift in rutile is surprisingly large.

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