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# Growth parameter-property phase diagram for pulsed laser deposited transparent oxide conductor anatase Nb:TiO$_2$

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The authors performed a systematic study of the structural and electrical properties of Nb:TiO$_2$ thin films by varying the substrate temperature ($T_S$) and oxygen partial pressure ($P_{O_2}$). Niobium is found to incorporate easily and substitutionally into titanium lattice site as indicated by its low activation energy. By increasing $T_S$, the carrier concentration ($n$) increases in the same way that niobium substitution fraction ($s$) increases, and the mobility increases as the structural quality is improved. With increasing $P_{O_2}$, $n$ decreases dramatically though $s$ does not change considerably. This may indicate that a large number of $p$-type native defects form, which "kill" the electrons produced by the Nb donors. © *2007 American Institute of Physics*. [DOI: 10.1063/1.2785152]

Titanium dioxide (TiO$_2$) is probably the most important oxide in the current technology of catalysis,[1] pigment,[2] and sensor devices.[3] Most recently, there has been considerable interest in doping TiO$_2$ thin films by transition metal elements in order to achieve multifunctional application of this material in semiconductor technology.[4] Examples include realizing room temperature ferromagnetism in both rutile and anatase TiO$_2$ with various dopants (the so called diluted magnetic semiconductors).[4–6] Interestingly, anatase TiO$_2$ doped by niobium (NTO) grown on SrTiO$_3$ (STO) was reported as a new type of transparent metal with its room temperature conductivity comparable to that of the commercial transparent electrode In–Sn–O (ITO) used in optoelectronic devices.[7,8] This discovery is significant because ITO, with the indium scarcity issue, is not able to satisfy the future demands for the speedy development of flat panel displays, organic light emitting displays, etc.[9–11]

Given the growing significance of NTO as an electronic material, it is of interest to understand and optimize the corresponding film growth by exploring the growth parameter-property phase diagram. In the commonly used pulsed laser deposition technique, the deposition temperature and oxygen partial pressure are the crucial parameters in the context of optimization because they can modify the crystalline structure, native defects, and charge states. In this letter, we have performed a systematical study on the growth condition dependent on structural and electrical properties of Nb doped thin films. Rutherford backscattering measurements have revealed very low activation energy for niobium substitutional incorporation into TiO$_2$. We also find that the mobility of NTO film strongly depends on its crystal structural quality, while the carrier concentration strongly depends on oxygen partial pressure.

The Ti$_{0.95}$Nb$_{0.05}$O$_2$ thin films were grown on single crystal (001) LaAlO$_3$ (LAO) via pulsed laser deposition. We chose LAO instead of STO substrate for addressing the *intrinsic* electric properties of NTO since there is some possibility that niobium could diffuse into STO, thereby forming a thin layer of the well known conducting oxide Nb:SrTiO$_3$ (Ref. 12) which could contribute to the observed electric properties.[8] In the case of LAO, no such conducting layer can be formed even if some interdiffusion of Nb occurs. Moreover, NTO film grown on LAO shows better quality than the one grown on STO.[13] In our experiments, the laser energy density was kept at 2 J/cm$^2$. The substrate temperature was varied from 350 to 850 °C when oxygen partial pressure was kept at $10^{-5}$ Torr. The oxygen partial pressure was varied from $5\times10^{-6}$ to $1\times10^{-3}$ Torr when the substrate temperature was kept at 850 °C. The film grown at 350 °C and $10^{-5}$ Torr is polycrystalline and the one grown at 400 °C shows a mixture of anatase and rutile phases. All the other films show epitaxial anatase phase with (00$L$) orientation except the one grown at 850 °C and $5\times10^{-6}$ Torr which shows an impurity phase of Nb$_2$O$_5$.

Figure 1(a) shows the Rutherford backscattering (RBS) spectra of the NTO/LAO films grown at various temperatures, with the oxygen partial pressure of $10^{-5}$ Torr. From the simulation of the random spectra, we found that the thickness of these films is ~60 nm, closed to that of the one reported by Furubayashi and co-workers.[7] In their work, the high solubility of Nb was pointed out based on their x-ray diffraction data which showed a linear increase of lattice parameter with the increase of doping concentration. It is clearly noted [Fig. 1(b)] that the minimum channeling yields of both Ti and Nb, obtained from RBS spectra, decrease as the substrate temperature ($T_S$) is increased, which indicates the improvement of structural quality as well as substitutional fraction. We can obtain the absolute substitutional fraction of niobium using the formula of $S_{\text{Nb}}=1-\chi_{\text{minNb}}$, where $\chi_{\text{minNb}}$ is the minimum channeling yield of niobium. Figure 1(c) shows $S_{\text{Nb}}$ vs $1/T_S$ in NTO/LAO films (the same for the rutile NTO films grown on $c$ sapphire are also plotted for comparison). We can obtain the activation energy by fitting the data using the Arrhenius-like equation,

$$S_{\text{Nb}} \sim \exp(-E_A/RT_s),$$

where $R=8.62\times10^{-5}$ eV K$^{-1}$ atom$^{-1}$ is the universal gas constant. It is found that the activation energy for Nb incorporation into Ti site in anatase is ~0.068 eV/atom, while in rutile it is ~0.074 eV/atom. The activation energies are con-

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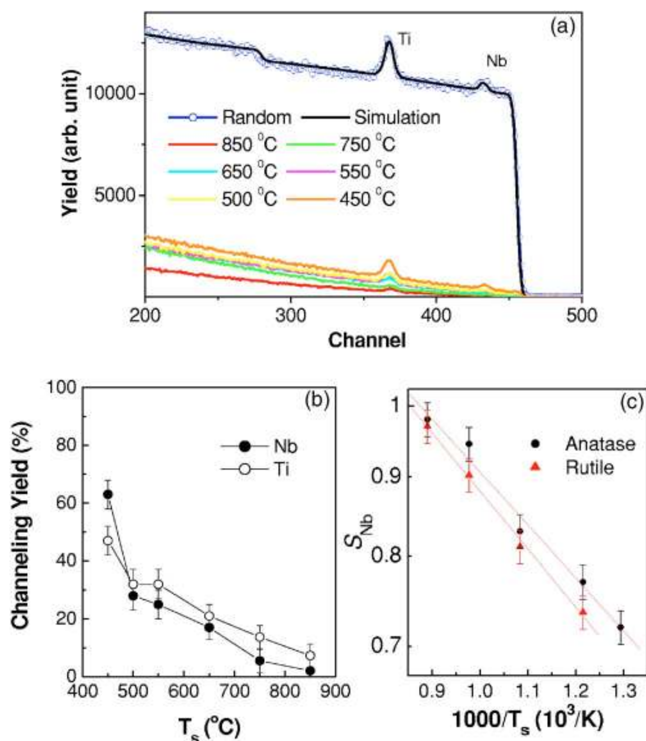


FIG. 1. (Color online) (a) 3.05 MeV $He^+$ Rutherford backscattering (RBS) random, simulation, and channeling spectra of the $Ti_{0.95}Nb_{0.05}O_2$ films grown on LAO substrate at various temperatures. (b) The $\chi_{min}$ of titanium and niobium as a function of $T_S$. (c) Nb substitutional fraction $S_{Nb}$ vs $1/T_S$ for both anatase NTO/LAO films and rutile NTO/*c*-sapphire films ($S_{Nb}$ is in $\log_{10}$ scale, black and red dots are experiment data, and solid lines are fitting data).

siderably low, which indicates that it is easy to substitute Nb into Ti for both phases even at low growth temperatures. This is in contrast to other transition metal doped $TiO_2$, such as diluted magnetic semiconductors, in which the dopants are found to be very difficult to incorporate substitutionally.[5,6] The high solubility of Nb may be attributed to the close ionic radius of $Nb^{5+}$ (0.78 Å) and $Ti^{4+}$ (0.75 Å) in the octahedral coordination.

Figure 2 shows the temperature dependence of resistivity for NTO/LAO film grown at 850 °C and oxygen pressure of

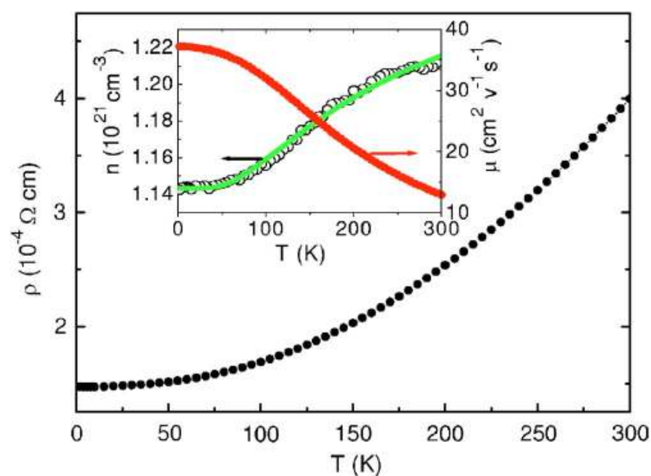


FIG. 2. (Color online) Resitivity as a function of temperature for the NTO/LAO film grown at 850 °C and $10^{-5}$ Torr. Inset shows $n$ (black circles are experiment data and green curve is the theoretical data) and $\mu$ as a function of temperature.

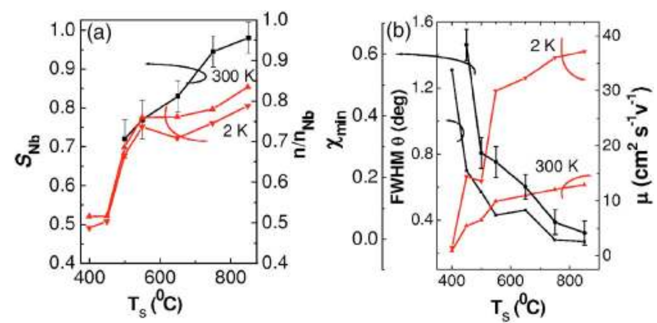


FIG. 3. (Color online) (a) Carrier concentration (at 300 and 2 K) and $S_{Nb}$ of NTO/LAO films as a function of $T_S$. (b) $\mu$ (at 300 and 2 K), FWHM, and minimum channeling yield of titanium in NTO/LAO films as a function of $T_S$.

$10^{-5}$ Torr. This sample shows metallic behavior with the room temperature (RT) resistivity of $\sim 3.99 \times 10^{-4}$ Ω cm. The temperature dependence of carrier concentration $n$ and mobility $\mu$ is shown in the inset of Fig. 2. The room temperature $n$ is $\sim 1.21 \times 10^{21}$ cm$^{-3}$ and it decreases slightly as the temperature decreases (from $1.21 \times 10^{21}$ cm$^{-3}$ at RT to $1.14 \times 10^{21}$ cm$^{-3}$ at 2 K, the difference is $\sim 7 \times 10^{18}$ cm$^{-3}$). Such small decrease of $n$ with temperature indicates that the niobium impurity level expands into a substantial impurity band and may overlap with the conduction band forming a degenerate semiconductor. However, there could be a small amount of conduction carriers from thermal activation of other native defect levels (i.e., $Ti_i$ and $V_O$ in the oxygen poor regime),[14] which lead to the slight decrease of carrier density with cooling. We fitted the carrier concentration data by the simplified formula of $n = n_0 + \{n_1 \exp[-E_d/(k_B T)]\}/2$ in the inset of Fig. 2, where $n_0$ corresponds to the carrier from niobium, $n_1$ corresponds to the native defects, $k_B$ is the Boltzmann constant, and $E_d$ is the activation energy of the native donors. We obtained the values as $n_0 = 1.14 \times 10^{21}$ cm$^{-3}$, $n_1 = 3.1 \times 10^{20}$ cm$^{-3}$, and $E_d = 0.02$ eV.

Figure 3(a) shows the substrate temperature dependence of niobium substitutional fraction ($S_{Nb}$) and carrier activation efficiency $n/n_{Nb}$ (at 2 and 300 K), where $n_{Nb} = 1.45 \times 10^{21}$ cm$^{-3}$ is the niobium doping concentration. It is noted from the above discussion that the low temperature carrier concentration is more likely to be from niobium donors only. Indeed, with increasing the growth temperature, both the carrier density at 2 K and niobium substitutional fraction show a clear increase. The carrier activation efficiency ($n/n_{Nb}$) at each growth temperature is slightly lower than the niobium substitutional fraction. Figure 3(b) shows the growth temperature dependence of mobility, minimum channeling yield of titanium, and full width at half maximum (FWHM) of the anatase (004) peak. Apparently, the mobility shows a great enhancement with the increase of substrate temperature due to the improvement of crystalline structural quality.

Figure 4(a) shows the oxygen pressure dependence of carrier density and niobium substitutional fraction of the films grown at 850 °C. With the increase in the oxygen pressure ($P_{O_2}$) from $10^{-5}$ to $5 \times 10^{-4}$ Torr, the carrier concentration decreases by several orders though the niobium substitutional fraction that only decreases from 98% to 84%. There have been some suggestions that the decrease of carrier concentration might be due to the decrease of oxygen vacancies while the film being grown at high $P_{O_2}$. However, as discussed above, most of the carriers are from niobium donors

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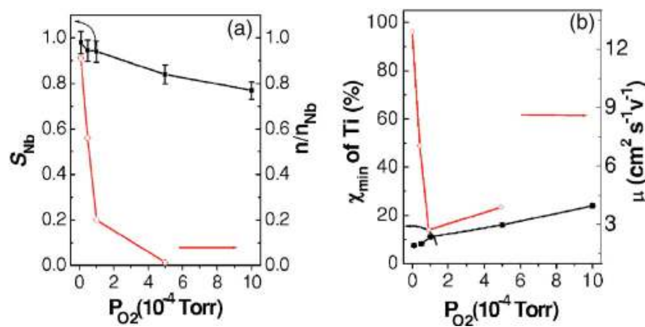


FIG. 4. (Color online) (a) Carrier concentration at 300 K and $S_{Nb}$ of NTO/LAO films as a function of $P_{O_2}$. (b) $\mu$ at 300 K and $\chi_{min}$ of titanium in NTO/LAO films as a function of $P_{O_2}$. (Due to the high resistivity of the film grown at $5\times10^{-4}$ Torr, a thick film ~250 nm was used for electric measurement. The resistivity of the one grown at $10^{-3}$ Torr is too high to be measured.)

instead of oxygen vacancies. Since the niobium substitutional fraction does not change considerably, the decrease of carrier concentration may indicate that a large number of "electron killers," i.e., $V_{Ti}$ and $O_i$, form due to their low formation energy[15] and hence compensate for the electrons provided by Nb. Therefore, our result supports one of the practical doping principles[16] that *p*-type native defects are easy to form at host anion rich growth condition. Figure 4(b) shows the RT mobility and $\chi_{min}$ of titanium in NTO films as a function of oxygen partial pressure. As $P_{O_2}$ increases, the mobility decreases, which is believed to be due to the increase of disorder as evidenced by the increase of $\chi_{min}$.

We have to point out that the good conductivity of NTO is mainly due to its large carrier concentration rather than high mobility. The large carrier concentration (almost equal to doping concentration) of NTO when grown at $10^{-5}$ Torr is due to the following. (1) In this host, under anion poor (equal to host cation rich) growth condition, the *p*-type native defects are not easy to form according to the doping rules.[16] (2) Niobium, acting as shallow donor, is extremely soluble in $TiO_2$ even at this growth condition unfavorable for cation substitution.

In summary, the structural and electric properties of niobium doped $TiO_2$ thin films grown at various conditions were studied via x-ray diffraction, Rutherford backscattering channeling, and transport measurements. Niobium was found to easily incorporate substitutionally into titanium lattice site with low activation energy (~0.068 eV/atom for anatase and ~0.074 eV/atom for rutile). By increasing $T_S$, the carrier concentration increases linearly with niobium substitution fraction, and the mobility also improves as the structural quality is enhanced. With increasing $P_{O_2}$, the carrier concentration decreases dramatically though the niobium substitution fraction does not change significantly. This may indicate that a large number ($\sim10^{20}$ $cm^{-3}$) of *p*-type native defects (such as $V_{Ti}$, $O_i$, etc.) form and "kill" the electrons produced by Nb donor. The excellent conductivity of epitaxial NTO thin film grown at $10^{-5}$ Torr is due to the high solubility of niobium in $TiO_2$ even at the growth condition unfavorable for cation substitution.

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