

論文内容の要旨

論文題目 Elucidation of carrier generation mechanism in TiO₂-based
transparent conducting oxides

(二酸化チタン系透明導電体におけるキャリア生成機構の解明)

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[Introduction]

Transparent conducting oxides (TCOs) have been recognized as one of key-materials which sustain rapid advance in opto-electronics. Although Sn-doped In₂O₃ (ITO) is most widely used as a practical TCO, it is still a challenging issue to widen the material variety of TCOs, based on requirements for adding novel electronic properties to TCOs.

Recently, it has been reported anatase Ti_{0.94}Nb_{0.06}O₂ (TNO) epitaxial thin films grown by pulsed laser deposition (PLD) exhibit excellent transparent conducting properties, i.e., low resistivity (ρ) of $2.1 \times 10^{-4} \Omega \text{ cm}$ and high internal transmittance of ~95% in the visible region, which are comparable to those ITO¹⁾. It is expected that Nb doping generates n-type carriers into Ti 3d nature conduction band. However, d-electron-based compounds are, in general, disadvantageous for electrical conduction because of anisotropy in chemical bonds. Indeed, conventional TCOs, such as ITO and ZnO, are known to be based on s-electrons. The mechanism of high electrical conduction in TNO is interesting from both fundamental and practical viewpoints, but such investigations have been scarcely attempted so far.

In this study, I studied the electrical properties and electronic stases of TNO epitaxial films with the aid of transport and spectroscopic measurements, focusing on the role of excess oxygen, which is anticipated to kill carriers, and thus to significantly affect the electric properties of TNO.

[Experimental Method]

$\text{Ti}_{1-x}\text{Nb}_x\text{O}_2$ ($x = 0, 0.06, 0.1, 0.2, 0.3$) thin films were grown on LaAlO_3 (100) substrates by PLD at a substrate temperature of 650°C and an oxygen pressure of $7 \times 10^{-6} - 1 \times 10^{-4}$ Torr. The as-grown films ($x = 0.06$) were further subjected to post-deposition annealing at 400°C in an oxygen atmosphere with an oxygen partial pressure ($P_{\text{O}_2}^{\text{anneal}}$) of $3.5 \times 10^{-1} - 3.5 \times 10^2$ Torr in a rapid thermal annealing furnace. X-ray diffraction (XRD) measurements confirmed epitaxial growth of (001) oriented anatase TiO_2 phase, without any impurity phases (Fig. 1). Transport properties, including resistivity (ρ) and carrier concentration (n_e), were characterized by a standard Hall-bar technique. X-ray photoemission spectroscopy (XPS) measurements were carried out at beam-line 2C of the synchrotron radiation source at Photon Factory (PF) in Tsukuba.

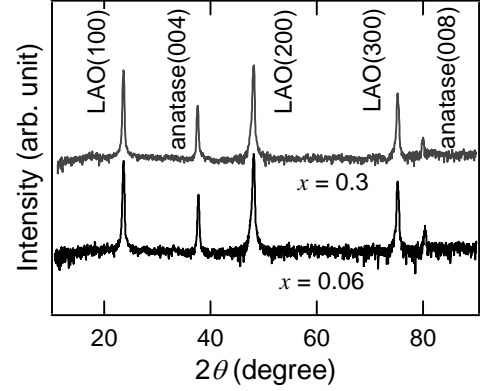


Figure 1: Typical XRD patterns of TNO films ($x = 0.06, 0.3$)

[Carrier Compensation by Excess Oxygen in Anatase $\text{Ti}_{0.94}\text{Nb}_{0.06}\text{O}_{2+\delta}$ Epitaxial Thin Films]

During my master course, I have found that post-deposition annealing gives significant influence on the electrical transport properties of anatase $\text{Ti}_{0.94}\text{Nb}_{0.06}\text{O}_2$ (TNO) epitaxial thin films. That is, annealing TNO films in pure oxygen drastically reduced the carrier density (n_e) and the resistivity, but oxygen annealed films recover high conductivity by annealing in reducing atmosphere (pure H_2). Core-level X-ray photoemission spectroscopy revealed that Ti and Nb respectively exist as tetravalent and pentavalent ions in fully oxidized samples. The concentration of Nb^{5+} relative to that of Nb^{4+} tends to increase with O_2 annealing. These results suggest that carriers released by Nb donors are compensated by excess oxygen atoms incorporated by O_2 annealing.

Based on these results, in order to directly observe these impurity states associated with excess oxygen, I performed resonant photoemission spectroscopy.

Figures 2(a) show Ti $2p$ - $3d$ resonant ($h\nu = 461.2$ eV) valence band spectra respectively, of as-grown and annealed ($P_{\text{O}_2} = 3.5 \times 10^2$ Torr) films. Figure 2(b) compares expansions of resonant and off-resonant spectra near the band gap. The resonant spectrum of the as-grown film clearly exhibits a peak at the Fermi level, corresponding to the bottom of the Ti $3d$ -nature conduction band. In the O_2 -annealed sample, the peak intensity is substantially suppressed,

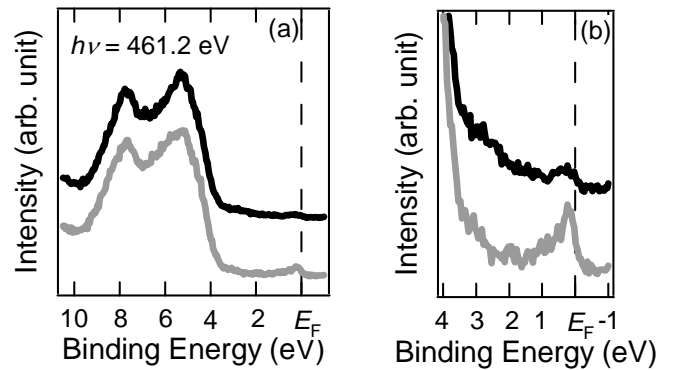


Figure 2: Valence-band spectra of as-grown (gray line) and oxygen-annealed (black line) TNO ($x = 0.06$) films. (a) Ti $2p$ - $3d$ resonant ($h\nu = 461.2$ eV), and (b) Close-up view of Ti $2p$ - $3d$ resonant spectra near the Fermi energy.

reflecting the abrupt reduction in n_e , and a characteristic shoulder-like in-gap state appears at ~ 3.0 eV just above the top of the valence band. The location of the in-gap state relative to the valence band is consistent with that of impurity states originating from interstitial oxygen, as predicted by band calculations.²⁾ As a consequence, I proposed a carrier compensation model in which p-type acceptor states originating from interstitial excess oxygen kill electron carriers generated by Nb doping.

[Suppression of carrier activation in heavily Nb-doped $\text{Ti}_{1-x}\text{Nb}_x\text{O}_{2+\delta}$]

Early studies on TNO have showed that Nb dopants in lightly doped TNO are almost completely ionized with an efficiency of $>90\%$ but in heavily Nb doped region the ionized efficiency decreases with increasing Nb concentration. In order to elucidate the origin of abrupt suppression in carrier activation at higher Nb region, I have investigated the electronic properties of TNO thin films as a function of Nb concentration by using synchrotron-radiation photoemission spectroscopy.

Figure 3 shows Nb $3d$ core level spectra of TNO films with different Nb concentration x . Each spectra in Fig. 3 exhibits a major Nb^{5+} peak together with a minor Nb^{4+} peak at lower binding energy. Notably, the peak intensity of the Nb^{5+} maintained constant $\sim 80\%$ against increasing x doping.

Figures 4(a) show carrier density n_e at room temperature plotted against Nb concentration x . As seen from the figure, n_e starts deviating downward from an ideal $n_e = n_{\text{Nb}}$ line at $x > 0.06$, corresponding to the suppression of ionization efficiency.

Figures 4(b) plot relative intensity ratio of Nb^{5+} and carrier activation ratio n_e/n_{Nb} as functions of x . The relative intensity ratio of Nb^{5+} maintains constant $\sim 80\%$ up to $x = 0.03$, while n_e/n_{Nb} decreases from 0.9 to 0.45 with increasing x from 0.06 to 0.3. These imply that electron carriers generated by Nb doping were compensated by excess interstitial oxygen incorporated during film deposition, similar to the oxygen annealed samples mentioned above. However, the conductivity of heavily Nb doped films no longer changed by further annealing under reducing conditions. This suggests that there are two kinds of excess oxygen atoms: one is introduced into or released from TNO by annealing in oxidizing and reducing conditions, respectively, in a reversible way. The other is strongly incorporated into TNO crystal so that it cannot be released by post-deposition annealing.

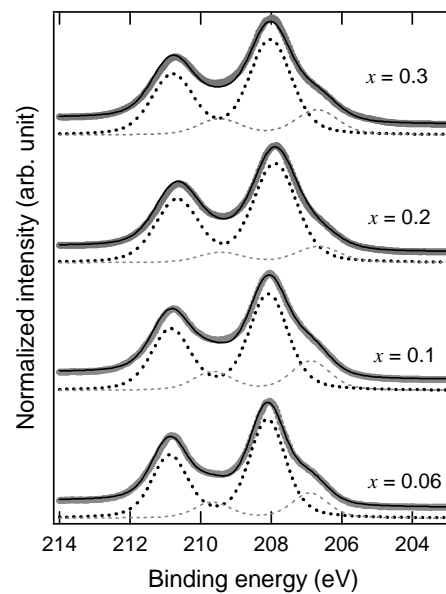


Figure 3: Nb $3d$ core-level XPS spectra of TNO films. Gray dots indicate experimental data. black dash curves represent the components of Nb^{5+} $3d$ obtained by least-squares fitting. Gray dash curves represent the components of Nb^{4+} $3d$ obtained by least-squares fitting. The thin curve represents the total fitting result.

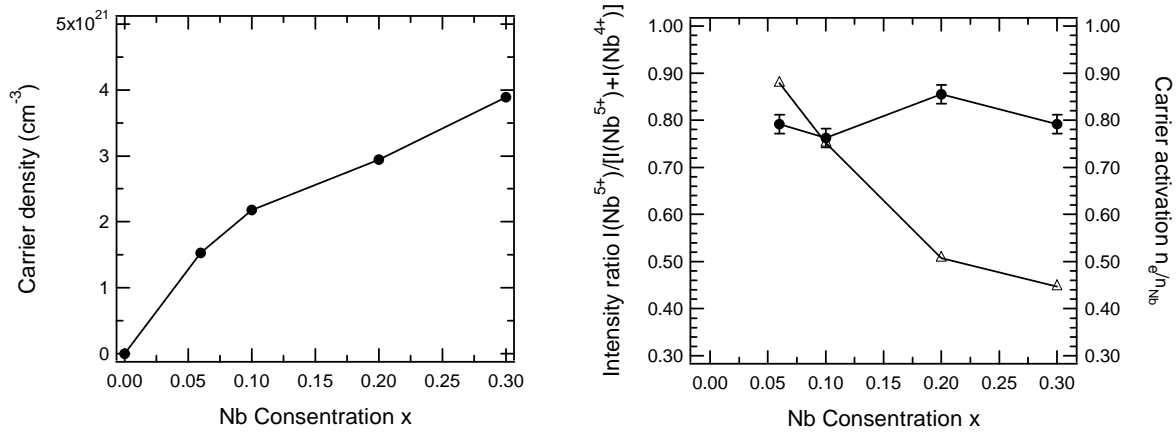


Figure 4: (a) carrier density of TNO films as functions of Nb concentration x .
 (b) Intensity ratio $I(\text{Nb}^{5+}) / [I(\text{Nb}^{5+}) + I(\text{Nb}^{4+})]$ and carrier activation as functions of x .

[Summary]

I studied the electrical properties and electronic stases of TNO epitaxial films with different oxygen or Nb contents. Valence-band photoemission spectroscopic measurements showed that an in-gap state evolved just above the O 2p valence band accompanied with O₂ annealing. The location of the in-gap state relative to the valence band is consistent with that of impurity states originating from interstitial oxygen, as predicted by band calculations. As a consequence, I proposed a model in which excess oxygen atoms located adjacent to Nb behave as p-type defects, which compensate electron carriers generated by Nb doping. In highly doped TNO, it is suggested that electron carrier released by Nb dopants were compensated by another kind of excess oxygen incorporated during film growth.

- 1) Y. Furubayashi *et al.*, Appl. Phys. Lett. **86**, 252101 (2005).
- 2) H. Kamisaka *et al.*, J. Chem. Phys. **131**, 034702 (2009).