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Origin of abrupt decrease in carrier activation at heavily Nb-doped anatase $Ti_{1-x}Nb_xO_{2+\delta}$ epitaxial thin films

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Introduction

Anatase $Ti_{1-x}Nb_xO_{2+\delta}$ (TNO) x = 0.06 epitaxial thin films grown by pulsed laser deposition (PLD) are an excellent transparent conducting oxide characterized by a low resistivity of 2.1 $\times 10^{-4}$ Ωcm at 300 K and a high internal transmittance of ~95% in the visible region [1]. TNO have shown 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 [2]. However, the mechanism of this phenomenon has not been clarified. In this study, we have investigated the electronic structures of anatase TNO thin films as a function of Nb concentration x using PES to elucidate the origin of abrupt decrease in carrier activation in heavily Nb-doped regime.

Experiment

Anatase epitaxial thin films of TNO with different Nb contents (x = 0.06, 0.1, 0.2, and 0.3) were grown on $LaAlO_3$ (100) substrates by PLD at a substrate temperature of 650 °C and an oxygen pressure of 1 × 10^{-4} Torr. X-ray diffraction measurements confirmed epitaxial growth of (001) oriented anatase TiO_2 phase, without any impurity phases. PES measurements were carried out at BL-2C of the synchrotron radiation source at Photon Factory, KEK. The Fermi level of the samples was referred to that of a gold foil that was in electrical contact with the samples. Photon energies of Ti 2*p*-3*d* and O1*s*-2*p* resonance were determined from X-ray absorption spectra of Ti *L*-edge and O *K*-edge of TNO films, respectively.

Results and Discussion

The existing ratio of Nb^{5+} evaluated from Nb 3*d* core-level PES spectra maintained a constant value of ~0.8 at x = 0.06 - 0.3, implying that the electron carriers generated by Nb doping are compensated by *p*-type defects incorporated during film deposition. Because the conductivity of heavily Nb-doped films was no longer changed by further annealing under reducing conditions, the *p*-type defects are thought to be interstitial oxygen atoms strongly combined with multiple Nb atoms.

Ti 2*p*-3*d* and O1*s*-2*p* resonant PES measurements of x = 0.06 – 0.3 films revealed that the in-gap states positioned ~1 eV below the Fermi level (E_F) have a mixed character of Ti 3*d* and O 2*p* orbital, whereas the states at E_F mainly have Ti 3*d* nature. Figure 1 shows Ti 2*p*-3*d* on-resonant valence-band spectra of TNO x = 0.06, 0.2, and 0.3 thin films. The valence band is shifted to higher binding energy with increasing x, reflecting the chemical-potential shift of TNO with electron carrier doping. In addition, the spectral weight of peak *A* (the states at E_F) and peak *B* (the in-gap states positioned ~1 eV below E_F) increase with increasing x. The former is corresponding to the increase of carrier concentration, and the latter is corresponding to the decrease of carrier activation. Therefore, we concluded that the interstitial oxygen atoms strongly combined with surrounding Nb atoms produce in-gap states ~1 eV, and compensates carrier electrons in the heavily doped region.

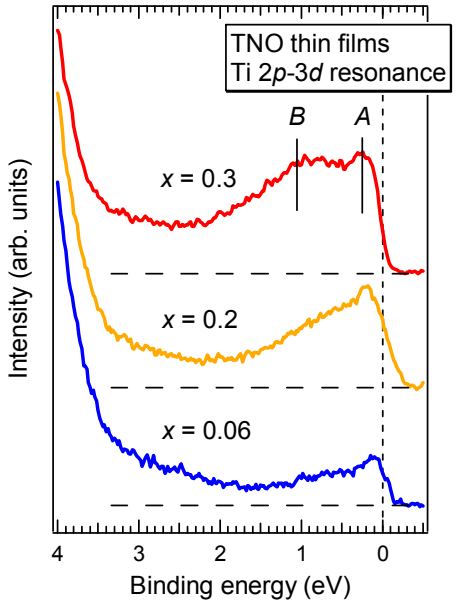

Fig.1: Ti 2*p*-3*d* on-resonant ($h\nu$ = 460.85 eV) valence-band spectra of TNO x = 0.06, 0.2, and 0.3 thin films.

References

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