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Transport properties and chemical state of fluorine in anatase $TiO_{2-x}F_x$ epitaxial thin films

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Introduction

It is reported that anatase TiO_2 shows high conductivity and good transparency by the substitution of pentavalent cations such as Nb^{5+} or Ta^{5+} for tetravalent Ti^{4+} ions [1, 2]. In this study, we focused on monovalent fluorine anion, F^-, as a new electron donor. F^- is known to work as a good electron donor in conventional transparent oxides such as ZnO or SnO_2 by substituting O^{2-} site. On the other hand, there is no report on the electrical properties of F-doped TiO_2. Therefore, we fabricated anatase $TiO_{2-x}F_x$ epitaxial films and clarify its transport property and chemical state of fluorine in detail.

Experiments

Anatase $TiO_{2-x}F_x$ thin epitaxial films were grown by using reactive pulsed laser deposition method. A pellet of TiF_3 was ablated by Kr:F excimer laser under oxygen atmosphere. $LaSrAlO_4$ (LSAO) (001) single crystals were used as substrates. Thin undoped anatase TiO_2 films were epitaxially grown on the substrates as buffer layers before the ablation of TiF_3 targets. Oxygen partial pressure (P_{O2}) and substrate temperature (Ts) during the deposition were optimized as growth parameters.

The crystal structures of the films were determined by X-ray diffraction (XRD) measurements. The transport properties of the $TiO_{2-x}F_x$ films were evaluated by 4-probe resistance and Hall measurements. We also conducted XPS measurements at BL-2C of the Photon Factory, KEK.

Results and Discussion

The XRD spectra of the films showed that under the optimized condition of P_{O2} = 1 x 10^{-5} Torr and T_S = 400 - 500 °C, (001)-oriented anatase $TiO_{2-x}F_x$ grew epitaxially without any impurity phases.

In addition, the resistivity of the film at room temperature reached as low as 1.6 × 10^{-3} Ω cm under the growth condition of T_S = 400°C. The Hall effect measurements revealed that electron density of the film was 5 x 10^{20} cm^{-3}, which is an order of magnitude higher than the value of undoped anatase TiO_2 films. This high density of electron strongly indicates that F^- ions are successfully doped at O^{2-} sites in anatase TiO_2 and release carrier electrons.

On the other hand, fluorine doped in oxides is volatile at high temperature. Therefore, it should be checked whether F^- ions really exists in our films. In order to confirm the existence of fluorine, we conducted XPS measurements. Figure 1 shows the F 1*s* core level spectrum of the $TiO_{2-x}F_x$ thin film grown under optimized condition. A clear F 1*s* peak was observed in the spectrum, which definitely indicates that F is doped in the film.

We also discussed about chemical shift of the F 1*s* peak. It is reported that F^- ions which substitute O^{2-} sites and those which compose minute secondary phases, such as $TiOF_2$, shows different values of chemical shifts [3]. The observed F 1*s* spectrum consists of single peak. Therefore, we concluded that the fluorine ions of our films have only one chemical state at least at the surface of the film.

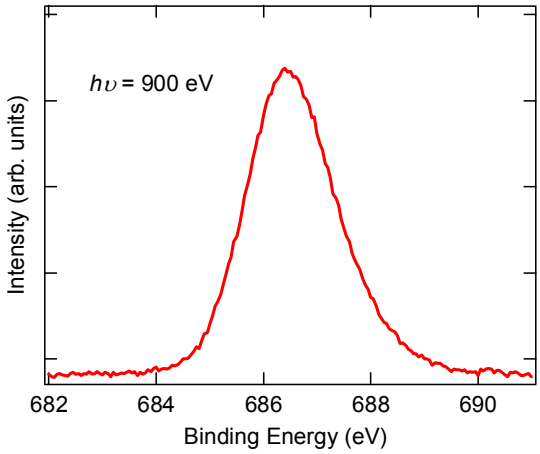

Fig. 1: F 1*s* core level spectrum of $TiO_{2-x}F_x$ film

References

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