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XAFS studies for the elements in the transparent conductive ZnO thin films

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Introduction

Transparent conductive oxide films have been widely utilized as transparent electrodes for flat panel displays and photo-voltaic solar cells and so on. The authors have developed aluminum-doped zinc oxide (ZnO:Al) films as solar heat shielding coatings [1, 2]. Suitable substitution of doped-Al^{3+} for Zn^{2+} sites generates free electrons, which make the films conductive and near-infrared reflective. This study aimed to investigate the influence of the local structure of the doped-Al ions on carrier generation efficiency.

Experimental

Thin films of ZnO:Al were prepared on SiO_2 substrates by reactive sputtering process using metallic Zn and Al targets under Ar+O_2 atmosphere. The sputtering voltage of the Al target and the oxygen flow rate during sputtering affected not only the Al content but also the carrier generation efficiency.

Zn K-edge XAFS spectra for the ZnO:Al films were measured at the BL-9A and 7C station of the KEK PF rings in fluorescence yield mode using a Lytle detector. Al and oxygen K-edge XANES spectra were acquired at the BL-11A station in total electron yield mode in vacuum ambient (<10^{-5} Pa).

Results and Discussions

Although the doped Al ions were dilute (<4 at.%) in the highly conductive ZnO films, the XANES spectra for the Al K-edge were able to be observed. The Al K-edge XANES spectra (1550~1670eV) were similar in shape to the spectra for the Zn K-edge (9650~9670eV) as shown in Fig.1. This result shows the local structure around the doped-Al was analogous to the Zn site, suggesting most of the doped Al substituted in the Zn sites.

The ZnO:Al films with higher carrier generation efficiency was found to have the Al K-edge absorption at higher energy level. Figure 2 indicates a typical result showing the shift in the XANES spectra. The energy resolution for these spectra was improved by narrowing the slit width to 50 μm. The ZnO:Al film prepared under high O_2 flow rate of 2.15 sccm had the carrier generation efficiency of 4%, while low O_2 flow rate of 1.70 sccm caused drastic enhancement of the efficiency to 66%. Figure 2 shows that the Al ions generating more free electrons provided the Al K-edge absorption at higher energy level. The shift in absorption energy is not due to a band gap widening because there was no shift in absorption energy for the oxygen K-edge XANES spectra. The shift in the Al K-edge absorption energy preserved similar spectrum shape, implying that the low electron density around the doped-Al ions is attributed to more effective generation of free electrons rather than oxidization of Al.

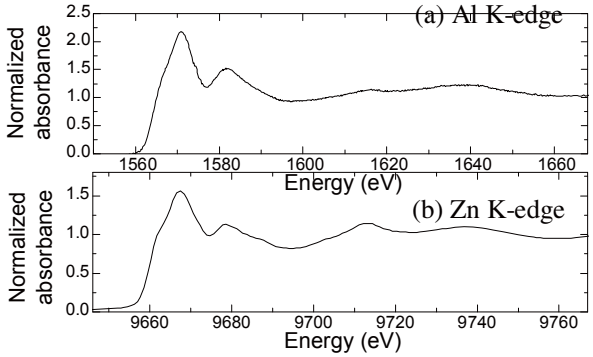

Fig.1 Typical XANES spectra of (a) the Al K-edge and (b) Zn K-edge for the ZnO:Al films.

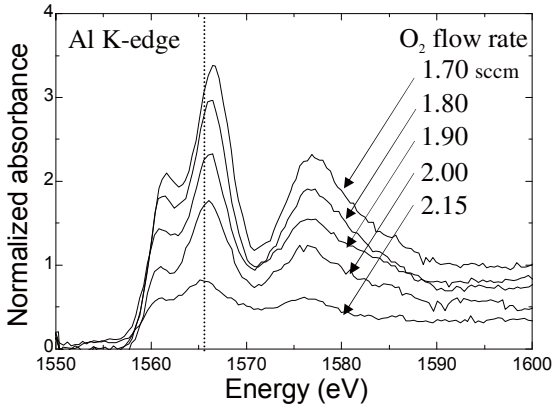

Fig.2 XANES spectra of the Al K-edge for the ZnO:Al films. These films were prepared by applying Zn sputtering power of 60W and Al sputtering voltage of 250V under various O_2 flow rates.

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