11A, 7C, 9A /2009G619

XAFS studies for Al dopants in 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, 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 Al dopants 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

Under suitable doping of Al at Al sputtering voltage of 250 V, lowering O_2 flow rate to 1.70 sccm enhanced carrier generation efficiency and near-infrared reflectance.

Despite the small amount of Al dopants in the ZnO films less than 2 at.%, the XANES spectra for the Al K-edge were able to be observed as shown in Fig.1. 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%. Therefore, this result indicated that the Al dopants with higher carrier generation efficiency were found to have the Al K-edge absorption at higher energy level resulting from low electron density around the doped-Al. 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 spectral profiles preserved similar shape, implying that the low electron density around the doped-Al is attributed to more effective generation of free electrons rather than oxidization of Al.

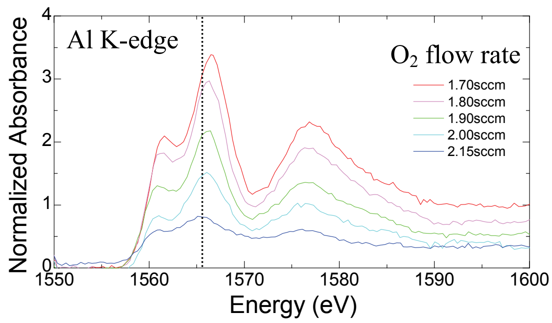

Fig.1 XANES spectra of the Al K-edge for the ZnO:Al films. These films were prepared by applying Zn sputtering power of 60W and Al sputtering voltage of 250V under various O_2 flow rates.

The Al K-edge features broadened with increasing O_2 flow rate. This behavior is attributed to deterioration of local structure around the Al dopants. In contrast, XANES spectrum of Zn K-edge had no broadening even at high O_2 flow rate, suggesting that the deterioration of local structure occurred only around the Al dopants.

In summary, optimization of ambient oxygen content to the lower limit provided successful substitution of Al for Zn sites. The efficient generation of electrons and the conservation of local structure around the appropriately doped Al were revealed by the XANES spectra in Fig.1.

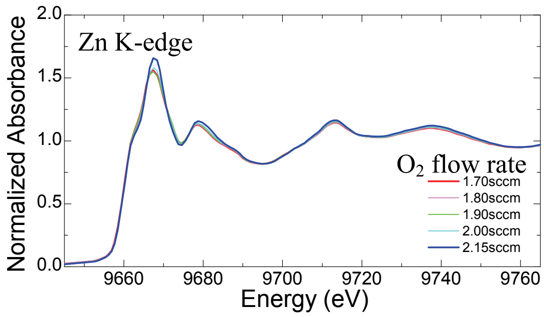

Fig.2 XANES spectra of the Zn K-edge for the same ZnO:Al films.

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References

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