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X-ray absorption study of ZnO and Al-doped ZnO films

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Introduction

Zinc oxide(ZnO), a representative wide gap II-VI semiconductor, has been widely studied recently because of its potential application such as low-cost transparent electrode material and light-emitting devices. It is also a possible candidate for the cathode material for organic EL devices[1]. For such applications, it is highly desirable to be able to tune the electronic properties in controllable way. Undoped ZnO is an n-type semiconductor with the direct band gap of 3.37 eV at room temperature. Its crystal structure(wurtzite structure) is shown in Fig. 1. The valence band of ZnO is mainly of O 2*p* character and the conduction band Zn 4*s* character. This allows for relatively high carrier mobility and rapid shift of the Fermi level by electron doping. Among possible n-type dopants, Al, with its small ionization energy and high solubility in ZnO, gives possibility to control the electronic properties in a fairly wide range. However, detailed understanding of doping mechanism including the dopant site and the electronic structure near the Fermi level in Al doped ZnO is still lacking. We here studied the geometrical and electronic structure of heavily Al-doped ZnO thin films where the Mott critical density is exceeded by means of Zn 2*p*, O 1*s*, and Al 1*s* X-ray absorption spectroscopy(XAS).

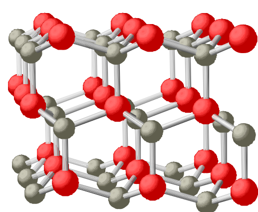

Fig. 1 Crystal structure of ZnO

Experimental

Samples with thickness of about 30nm were prepared by RF magnetron sputtering on glass substrate. An ITO layer was first deposited on the glass substrate below ZnO in order to assure electrical contact that was necessary for electron yield measurements. A powder mixture of ZnO with a purity of 99.99 % and Al_2O_3 with a purity of 99.99 % as the dopant was used as the target. The content of the dopant was varied from 0 to 23 at. %. The films have preferential c-axis orientation perpendicular to the substrate as confirmed by XRD, except for the films with the highest dopant concentrations. No other phases than wurtzite ZnO were detected by XRD. We also prepared ZnO films sputtered at different Ar/O_2 flow ratio. Temperature and angular dependent XAS measurements were performed at BL-11A in the total electron yield mode and in the case of Al 1*s* also in the fluorescence mode.

Results

Out of the results, doping and angular dependence of Zn $2p_{3/2}$ XAS spectra at room temprature are shown in Fig. 2. In the region $h\nu$ =1020~1023eV(shaded in the upper panel of Fig. 2), the spectra have little angular dependence in contrast to the higher energy part and therefore can be attributed to Zn 2*p*–4*s* transition, that reflects the electronic structure of the bottom of the conduction band. Smearing of the spectral feature in the higher energy region may be attributed to increasing structural disorder upon doping. Shift of the absorption threshold to higher energy with increasing Al concentration is clearly seen. The size of this shift is roughly in agreement with the optical measurements and the rigid-band model based on a band structure calculation, and can be interpreted as filling of the conduction band. Interestingly however, a distinct peak appeared just above the threshold for doped samples, suggesting that the rigid band picture is not appropriate in describing the electronic structure of Al-doped ZnO. Detailed analysis including the temperature and core-hole effect is under way.

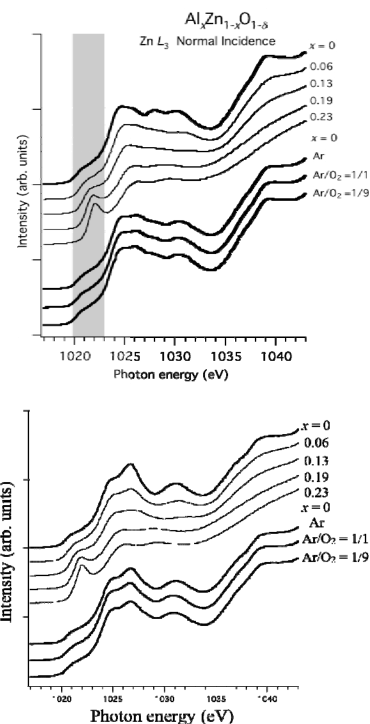

Fig. 2 Zn $2p_{3/2}$ XAS spectra at room temperature. Upper(lower) panel shows spectra taken at normal(grazing; 60°) incidence.

References

[1] H. Yamauchi et al., Extended Abstracts of the 2006 Int. Conf. on Solid State Devices and Materials, pp.778-779

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