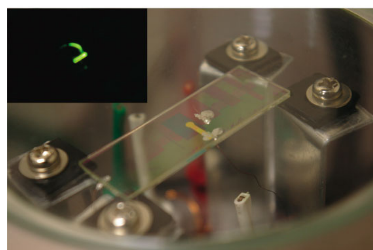
X-Ray Absorption Study of Al-Doped ZnO Films: An Alternative to Indium Tin Oxide as a Transparent Conducting Material

Zinc oxide (ZnO), well known for its use as zinc white in paints, is a transparent semiconductor that can be used as a transparent electrode material in light emitting devices. Being composed of commonly available elements, ZnO is expected to replace compounds which contain rare elements, such as indium tin oxide (ITO), widely used in flat panel displays. X-ray absorption spectroscopy, which probes unoccupied electronic states, provides information about the conduction band that will be useful in optimizing the electronic properties of the newly developed materials. It is found that localization of the electronic states due to structural disorder limits the electronic conductivity of heavily Al-doped ZnO.

Today indium tin oxide (ITO) is the most commonly used material for transparent electrodes in industrial applications. Because of the rarity and consequent high price of indium, materials with similar properties and higher availability are much sought-after. Among these materials, zinc oxide (ZnO), a representative wide gap II-VI semiconductor, has been widely studied recently. In particular, ZnO and Al-doped ZnO (AZO) are possible candidates for use in the transparent electron injection layers in organic devices such as field-effect transistors (FET) and light-emitting devices [1–4], which are the key elements for future technologies such as organic flexible sheet displays. Yamauchi *et al.* fabricated an active light-emitting device with a ZnO transparent FET and AZO electrode [5]. Figure 1 shows a photograph of the active light-emitting device and a schematic of the device structure. The inset photograph shows the emitting area of the device.

For actual applications, it is highly desirable to be able to tune the electronic properties of a material in a controllable way. In principle, it is possible to control the electronic properties of a semiconductor by adding proper impurities as carrier dopants. With Al doping, it is possible to obtain thin films with high conductivity and good crystallinity. Although it is expected that the doped Al atoms substitute zinc ions and supply one extra electron per Al atom in the conduction band, the details of the dopant structure and carrier doping mechanism are still not clear. Proper understanding of the mechanism is necessary to achieve better control of electronic properties such as the conductivity and the magnitude of the band gap [6]. Local structural and electronic information around the dopant atoms from X-ray absorption fine structure (XAFS) analysis will be useful in this regard.



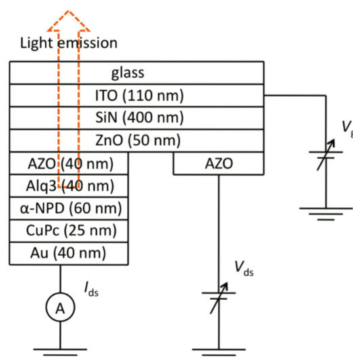


Figure 1
(left) Active light-emitting device driven by ZnO transparent field-effect transistor and its emitting area (inset) [5]. (right) The device structure and the electrical measurement circuit.

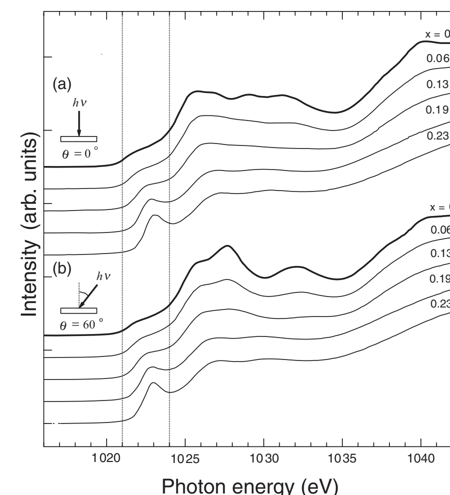


Figure 2
Zn L_3-edge XAFS spectra of Al-doped and undoped ZnO ($Al_xZn_{1-x}O$) films recorded at room temperature and (a) normal and (b) grazing incidence.

For the X-ray absorption measurements, samples 30 nm thick were prepared on glass or quartz glass substrates by RF magnetron sputtering. The content of the dopant was varied from 0 to 23 at.% (0, 6, 13, 19, and 23 at.%). We also prepared ZnO films sputtered at different Ar/O_2 flow ratios. XAFS measurements were performed at BL-11A, in the total electron yield mode at room temperature.

Figure 2 shows Zn L_3-edge XAFS spectra of Al-doped and undoped ZnO films recorded at room temperature. The spectral feature around 1020-1023 eV shows a change accompanying Al doping, and has little angular dependence compared to the higher energy part of the spectrum. The conduction band of ZnO is composed mainly of Zn 4s states, and is fairly isotropic. Therefore the feature between 1020 and 1023 eV can be attributed to the Zn 2*p* -> 4*s* transition, which reflects the electronic structure at the bottom of the conduction band. We can also see a shift of the absorption threshold to higher energies with increasing Al content. The size of the shift is roughly in agreement with optical measurements and the *rigid-band model* based on first principles calculations, and can be interpreted as the filling of the conduction band. However, a distinct peak appears just above threshold for the Al-doped films, suggesting that the rigid band picture is not appropriate in describing the electronic structure of Al-doped ZnO. On the other hand, the lineshape in the higher energy region becomes broader with increasing Al doping. These changes are related to structural disorder around the Zn atoms.

Further study of the decay channels of the Zn 2*p* core hole created by X-ray absorption, which reflect the dynamics of the doped electrons in the conduction band, shows that the spectral feature appearing at the Zn L_3-edge threshold for the heavily-doped samples is an indication of the localization of the doped electrons due to structural disorder [8]. This explains microscopically the observed lowering of the electronic conductivity at high Al concentrations and will be important in designing materials optimised for device applications.

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