Electronic Structure of Zn$_{1-x}$Cu$_x$O Films Studied by X-ray Absorption and Emission Spectroscopies

J. W. Chiou,$^{1,2}$ H. T. Cao,$^3$ K.V. Rao,$^3$ E. Arenholz,$^2$ C. L. Dong,$^{1,2,4}$ C. L. Chang,$^1$ Y. Y. Chen,$^4$ W. F. Pong,$^1$ J.-H. Guo$^2$

$^1$Department of Physics, Tamkang University, Tamsui, Taiwan 251, R.O.C.
$^2$Advanced Light Source, Lawrence Berkeley National Laboratory, Berkeley, CA 94720
$^3$Dept. of Materials Science, Royal Institute of Technology, SE-100 44 Stockholm, Sweden
$^4$Institute of Physics, Academia Sinica, Nankang, Taipei, Taiwan 11529, R.O.C.

Introduction
Zinc oxide (ZnO) II–VI semiconductor is an important material for optoelectronic applications. Nanostructured ZnO are particularly interesting because they can be used to tune electronic and optoelectronic devices that involve UV lasing action. Recently, dilute magnetic semiconductors (DMSs) have been intensively investigated because of their great potential in spintronics applications. Especially, the magnetic transition metal (TM) doped ZnO shows Curie temperature exceeding room temperature, which makes it possible to be used in practical devices. In this work, x-ray absorption (XAS) and x-ray emission (XES) spectroscopies were performed to gain insight into the electronic structure of Cu (non-magnetic element) doped ZnO films.

Methods and Materials
Zn$_{1-x}$Cu$_x$O films were grown on the glass substrates by ion-beam sputter deposition ($x=0.006, 0.027, 0.038$ and $0.063$). O $K$-edge XAS and XES measurements were carried out on undulator beamline 7.0 at the Advanced Light Source. The resolution of the monochromator was about $0.2$ eV for x-ray absorption and $0.35$ eV for the excitation of x-ray emission measurements. X-ray emission spectra were obtained using a fluorescence spectrometer [1] with a resolution of $0.35$ eV.

Results
Figure 1 (lower panel) shows x-ray absorption (top) and O $K\alpha$ emission spectra recorded at various excitation energies (bottom). The vertical arrows (top) indicate excitation energies at which resonant x-ray emission spectra were measured. By selecting different excitation energies, predominant contribution of the specific admixture of O 2p with Zn 3d, 4s, and 4p states is expected. There are three distinct structures can be observed in the XES spectra, labeled as A, B, and C, are mainly due to O 2p–Zn 4p states, the mixed states of O 2p–Zn 4s and O 2p hybridized with Zn 3d states, respectively [2].

Discussion
The O $K$-edge spectra in Fig. 1 (top) show that the intensities of near-edge features decreased with the increasing of Cu-doping, which expresses that the occupation of O 2p derived states is enhanced through O 2p–Zn 4p hybridization. Furthermore, two significantly shoulder observed on the pre-edge since Cu doping induces a small amount of empty states within bandgap region, which suggests hole doping. Besides (a), all spectra in Fig. 1 (bottom) show the similar spectral profile and intensities at different excitation energies and are similar to that of ZnO [2]. The most intense feature A is found to shift about $0.2$ eV towards higher energy in the spectrum (b) due to the oxygen atoms are on slightly inequivalent sites [3]. On the contrary, the spectrum (a) shifts to lower energy and show different spectral profile as compared to that of ZnO, indicating that the doped holes are localized to Cu impurity sites. The Cu doping induced holes may act as charge carriers that may play a role to induce ferromagnetic properties of Zn$_{1-x}$Cu$_x$O.