

X-Ray Absorption Spectroscopy Study of Copper Doped ZnO Thin Films

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Abstract. X-ray absorption spectroscopy technique is used to study copper-doped ZnO thin films, prepared by pulsed-laser deposition. The samples with various doping levels are examined. It is found that the samples contain metallic clusters with the sizes ≤ 2 nm as well as Cu^{1+} and Cu^{2+} states. The Cu^{1+} states exist as stable oxide clusters, while the Cu^{2+} ones participate in the ZnO lattice some of which may be pertaining to the surfaces of the Cu clusters as well. The copper clusters of ~ 1 nm are unstable and fragment under monochromatic x-ray beam illumination.

Keywords: X-ray absorption, XANES, EXAFS, Copper-doped ZnO, Cluster

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INTRODUCTION

Copper-doped zinc oxide (ZnO:Cu) is used in a variety of applications including sensors [1] and catalysts [2]. Spin polarized density functional calculations also predict certain ZnO:Cu structures should be ferromagnetic [3]. When deposited under the appropriate growth conditions, ZnO:Cu films grown by pulsed-laser deposition (PLD) show evidence of ferromagnetism [4]. To gain an understanding as to why only specific growth conditions yield films that are ferromagnetic, the films were examined by x-ray absorption spectroscopy (XAS). In this paper, we present part of this study that focuses on a series of samples that exhibited clustering of the copper species due to specific PLD growth parameters [5]. Although these samples were not ferromagnetic, the results of the XAS measurements proved interesting in their own right, adding insight to the chemical and structural properties of copper clusters in ZnO as well as the interaction of these clusters with x-ray illumination.

EXPERIMENTAL

The ZnO:Cu films were grown by PLD using a ZnO target and a Cu target. A computer-controlled shutter was used to alternate ablation between the two targets; the number of laser pulses on each target was adjusted to obtain the desired Cu doping levels. Less than one monolayer of film was deposited in a typical ZnO-Cu cycle to help insure a uniform distribution of Cu in the ZnO film. The films were grown on $\hat{c}$ -plane sapphire-substrates to a thickness of ~ 270 nm. The

target-substrate separation was fixed at 10 cm. The films were grown in a N_2O ambient at a pressure of 5×10^{-2} Torr. The details can be found in reference 4.

X-ray absorption spectroscopy measurements are carried out at the 5BM-D bending magnet beamline of the DND-CAT located at the Sector 5 of the Advanced Photon Source (APS), Argonne National Laboratory. A Si(111) monochromator is used to select the x-ray energies. A pair of the Rh-coated mirrors is used to collimate and then focus the beam vertically down to 0.2 mm at the FWHM at the sample 25-meter away. The incident beam size is defined by two pairs of Huber slits to $0.2 \times 10 \text{ mm}^2$. The x-ray absorption spectra around the Cu and Zn-K edges are measured at a grazing angle using a 13-element Ge detector at 90° to the x-ray beam path. Three ion chambers are used along the beam path: the first measures the incident beam intensity, the second measures the reflected beam, and the third measures the beam transmitted through a copper foil for energy calibration. Each sample is oriented in a way to avoid the Bragg conditions. Self absorption effect is not observed in the spectra presented here most due likely to the low Cu doping level.

RESULTS AND DISCUSSION

Figure 1 displays the Fourier transforms of the EXAFS spectra of the ZnO:Cu samples compared with that of the Cu foil. There exist features consistent with both Cu-O interactions and metallic Cu clusters in all the samples. Of particular interest are the results for the Cu 1% sample. Under the monochromatic x-ray

beam, a dramatic change occurs in this sample during 13 hours of illumination. This is not the case for the Cu 2% and 6% samples, for which no changes in the spectra occur in the x-ray beam. The metallic peak decreases and the oxide peak increases with lowering the doping level [spectrum (c) to (a)], and even further so in the x-ray beam [from (a) to (a')]. The copper oxides may exist as oxide clusters, in the ZnO lattice as $\text{Cu}_{\text{Zn}}\text{O}$, and/or oxides on the surfaces of metallic clusters, with either of two possible oxidation states, i.e., Cu^{1+} and/or Cu^{2+} .

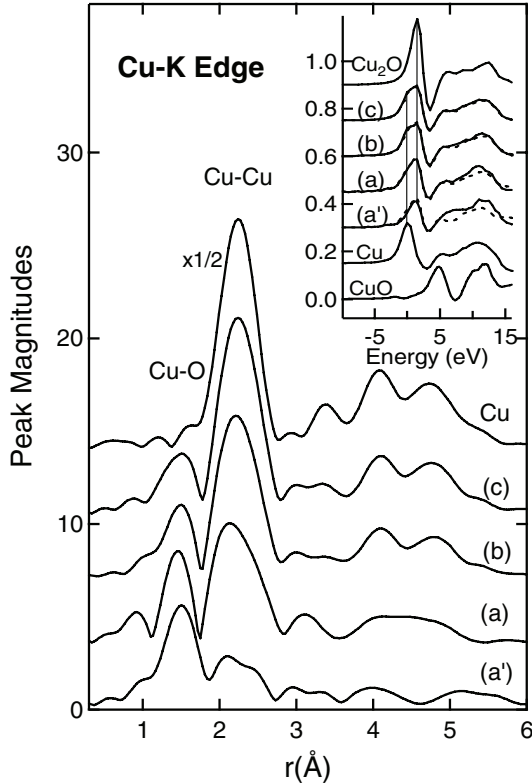


FIGURE 1. The main panel displays the Fourier transforms of the EXAFS spectra and the insert the first derivatives of the XANES spectra, for ZnO:Cu (a) Cu 1%, (a') Same Cu 1% sample after 13-h x-ray exposure, (b) Cu 2%, (c) Cu 6%, and the reference materials (metal Cu, powder CuO, and powder Cu_2O). The dashed curves in the insert are the results obtained from the linear combination fitting.

The insert shows the derivatives of the XANES data. The energy zero is set at the metal Cu-K edge. These data clearly identify the Cu^{1+} state, while the presence of any Cu^{2+} states is less obvious. In order to appreciate the contributions by each component to the XANES, a linear combination fitting (LCF) is carried out using the reference spectra from -20 eV to 30 eV. It is found that all the XANES spectra can best be simulated only when a Cu^{2+} component is included. In this analysis, both the relative weights and absorption edge energies are allowed to vary. The energy shifts are within ± 0.5 eV.

TABLE 1. The results obtained by the LCF fittings.

Sample	Cu^0	Cu^{1+}	Cu^{2+}	R-factor
(c) Cu 6%	0.411	0.462	0.127	3.7×10^{-3}
(b) Cu 2%	0.370	0.460	0.170	7.5×10^{-3}
(a) Cu 1%	0.301	0.455	0.244	3.2×10^{-2}
(a') Cu 1% [†]	0.186	0.411	0.403	1.0×10^{-1}

[†]The Cu 1% sample after 13-h x-ray exposure.

Table 1 shows the LCF analysis results. In (c) the Cu^0 state weights about equally as Cu^{1+} . With lowering the doping level, it decreases while Cu^{2+} increases. For Cu 1% the x-ray beam decreases Cu^0 and increases Cu^{2+} significantly. The Cu^{1+} weight changes only slightly. To illustrate the changes from (a) to (a'), Figure 2 displays the weights against the x-ray exposure time. It is clear that the Cu clusters disintegrate in the x-ray beam from which more Cu^{2+} is created. The increase in Cu^{2+} with both the doping level and the x-ray exposure may account for the Cu-O peak increases (see Fig.1) since it normally bonds to more oxygen. The Cu^{1+} oxide appears to be stable. Note that the fit quality is worsening starting from the CuO edge (~ 5 eV) with increasing the Cu^{2+} content. It may suggest that the use of the bulk CuO spectrum may not be as adequate as the use of the bulk Cu and Cu_2O spectra.

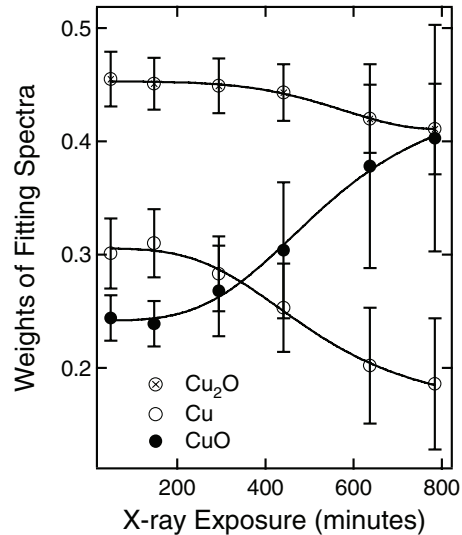


FIGURE 2. Results of the linear combination fittings vs. x-ray exposure time for the ZnO:Cu 1% sample.

To understand the origin of the differences seen in the LCF fittings, difference spectra, in which the weighted sum of bulk Cu and Cu_2O spectra are subtracted from the sample spectra, were calculated. Figure 3 compares such calculated Cu-K edge spectra with bulk CuO. Also shown is the Zn-K edge spectrum

measured on the ZnO:Cu 6% sample. Although noisier due to the difference in operation, the data show with a good certainty an edge structure with few features, compared to that of bulk CuO. Notably absent in these spectra is the “shakedown” feature that is associated to bulk CuO. The theoretical work reported by Špir [6] reproduces such an edge profile for tiny CuO_x clusters too. Starting from 50 eV the EXAFS oscillations resemble the Zn-K edge spectrum, and the resemblance increases with lowering the doping level and with the x-ray exposure. The detailed analysis of these data is underway and will be reported in the near future. These results indicate convincingly that the Cu^{2+} states in these samples are incorporated in the ZnO lattice. For the Cu 1% sample, it may be readily concluded that the Cu^{2+} states created in the x-ray beam are mostly at the interfaces between the ZnO lattice and the surfaces of metallic Cu clusters, which is supported both by the ZnO-lattice-like, Cu-K edge EXAFS oscillations and by the clear dependence on the sizes of the metallic Cu clusters.

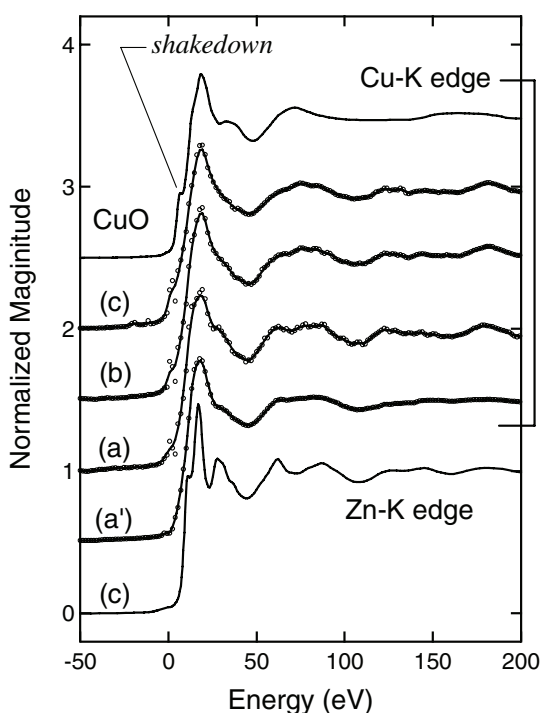


FIGURE 3. The difference spectra (open circles) of the ZnO:Cu samples obtained from the Cu-K edge data: (a) Cu 1%, (a') same Cu 1% sample after 13-h x-ray exposure, (b) Cu 2%, and (c) Cu 6%. Also shown are the bulk CuO spectrum and the Zn-K edge spectrum measured on (c).

To appreciate the sizes of the metallic Cu clusters in these samples is not trivial, since the samples are segregated with regard to the copper species. However, it is possible in the cases of the Cu 6% and 2% samples to isolate the dominating signals of the Cu clusters

using the Fourier transform technique. The phases of the Cu-Cu peaks match very well those of the Cu metal in k space, suggesting that the contributions from the oxides are at minimum. Therefore, by comparing with the Cu metal and assuming other things equal, the relative changes in the peak heights give an estimate of the cluster sizes [7]. By assuming a globular shape for these clusters, it is found that the cluster size is ~ 2 nm in the Cu 6% sample, ~ 1.7 nm in the Cu 2% sample, and crudely, ~ 1 nm in the Cu 1% sample, which yields surface-to-volume ratios of 30%, 35%, and 60%. The increase in the Cu^{2+} content with the surface area may suggest that most of the Cu^{2+} states are pertaining to the surfaces of the Cu clusters in all the samples as well.

The reason for the x-ray induced fragmentation of the Cu clusters in the Cu 1% sample is unclear, except for the smaller size. Given the low photon flux density from a bending magnet beamline, the damage is likely induced by the electronic excitations by x-rays.

CONCLUSION

X-ray absorption measurements reveal that all the samples contain metallic Cu clusters with the sizes ≤ 2 nm as well as the Cu^{1+} and Cu^{2+} states. The Cu^{1+} states exist as stable oxide clusters, while the Cu^{2+} ones are incorporated in the ZnO lattice some of which may be pertaining to the surfaces of the metallic clusters as well. The copper clusters of ~ 1 nm fragment under monochromatic x-ray beam illumination.

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