X-ray absorption spectroscopy study of copper-doped zinc oxide: a high *T*c diluted magnetic semiconductor

Q. Ma[1], L.-H. Ye[2], D.B. Buchholz[3], J.-H. Song[3], A.J. Freeman[2], J.B. Ketterson[2], R.P.H. Chang[3]

[1]*Northwestern Synchrotron Radiation Center at Advanced Photon Source, Argonne, IL 60439;*
[2]*Department of Physics and Astronomy, and Materials Research Center, Northwestern University, Evanston IL 60208*
[3]*Materials Science and Engineering Department, Northwestern University, Evanston IL 60208*

Introduction

Although neither copper (nor its oxides) or zinc (and its oxides) are ferromagnetic, spin polarized density functional calculations predict that certain copper-doped zinc oxide (ZnO:Cu) structures should be ferromagnetic [1]. Further, since there are no known ferromagnetic copper compounds, ZnO:Cu appears to be an unambiguous DMS material. A series of ZnO:Cu films were grown by pulsed-laser deposition (PLD). When deposited under the appropriate growth conditions the ZnO:Cu films show evidence of ferromagnetism; the *M-H* curve shows hysteresis and coercivity. To gain an understanding as to why some films were ferromagnetic and others were not, the films were examined by x-ray absorption spectroscopy.

Methods and Materials

Three PLD growth conditions were examined: N_2O ambient with an 8 cm target-to-substrate separation (8 cm t-s); O_2 ambient with an 8 cm t-s; and N_2O ambient with a 10 cm target-to-substrate separation (10 cm t-s). The details of the growth technique can be found in ref. [2]. X-ray absorption spectroscopy (XAS) was performed at the 5-BM-D bending magnet x-ray beam line at DND-CAT at the Advanced Photon Source. All the films in this study were determined by x-ray diffraction to grow with the ZnO *c*-axis normal to the plane of the substrate (i.e. the *ab*-plane parallel to the plane of the substrate). The films were examined both with the x-ray electric **E** vector parallel and perpendicular to the plane of the film.

Results

Only the films grown in an N_2O ambient with 8 cm t-s are ferromagnetic. Films grown with an 8 cm t-s in both the N_2O and O_2 ambient show evidence of copper substitution on zinc lattice sites (Cu_{Zn}) whereas films grown with a 10 cm t-s show evidence of copper-oxide clusters. Fig. 1 shows the Zn-edge data for all three growth conditions and a ZnO film reference spectrum. For the film grown with a 10 cm t-s, the spectrum is very similar to that of the ZnO reference whereas for films grown with an 8 cm t-s the ZnO features are altered significantly even at 1% Cu. The most probable explanation for this change is Cu_{Zn}. Fig. 2 shows the Cu-edge data for these samples compared to powder CuO and Cu_2O spectra. The spectra bear predominately the Cu^{2+} character. For the 10 cm t-s film, the bulk CuO features dominate the spectrum, indicating the existence of large CuO clusters; hence the reason why the Zn-edge data for the 10 cm t-s film, Fig. 1, is similar to that of ZnO. For both 8 cm t-s films, the Cu-edge spectra, Fig. 2, cannot be simply simulated by that of CuO. The *d*-state prepeaks are shifted downward by ~1 eV. Therefore, the band structures depart significantly from that of pure CuO. Also evident from Fig. 2 is that the films grown in an N_2O ambient show evidence of the Cu^{1+} state, which is seldom detected in the film grown in O_2.

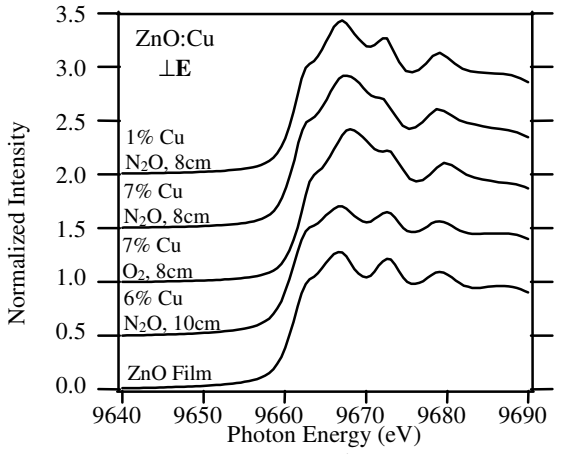

Fig. 1.

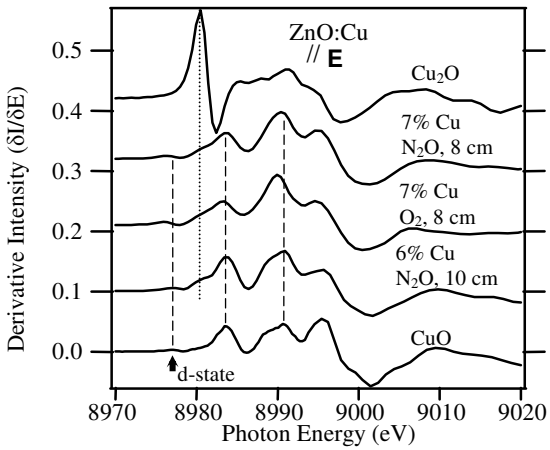

Fig. 2.

Discussion

The XAS study revealed that the ferromagnetism is observed only when the following conditions are met: 1) no clustering of copper and/or copper oxides occur, and 2) the sample contains a significant amount of Cu^{1+}.

Acknowledgments

Work at Northwestern is supported by the NSF (via its MRSEC program under Grant DMR-0076097), DARPA via Grant #N00014-02-1-0887 and NASA via Award No. 521-0077-05-A14/NCC2-1363. DND-CAT is supported by the E.I. DuPont de Nemours & Co., The Dow Chemical Co., the NSF via Grant DMR-9304725 and the State of Illinois via Grant IBHE HECA NWU 96. The APS is supported by the DOE via Contract No. W-31-109-Eng-38.

[1]L.-H. Ye, A.J.Freeman, Phys. Rev. B 73, 033203 (2006).
[2] D. B. Buchholz, R. P. H. Chang, J. H. Song, J. B. Ketterson, Appl. Phys. Lett. 87, 082504 (2005).