X-ray absorption spectroscopy study of copper-doped zinc oxide: a high 7c diluted magnetic semiconductor

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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: N₂O ambient with an 8 cm target-to-substrate separation (8 cm t-s); O₂ ambient with an 8 cm t-s; and N₂O 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-electric 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 N₂O ambient with 8 cm t-s are ferromagnetic. Films grown with an 8 cm t-s in both the N₂O and O₂ ambient show evidence of copper substitution on zinc lattice sites (Cu₂O) 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 Cu₂O. Fig. 2 shows the Cu-edge data for these samples compared to powder CuO and Cu₂O spectra. The spectra bear predominately the Cu²⁺ 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 N₂O ambient show evidence of the Cu¹⁺ state, which is seldom detected in the film grown in O₂.

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 Cu¹⁺.

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