

Tunable Magnetic and Transport Properties of Single Crystalline (Co, Ga)-codoped ZnO Films

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High-resolution x-ray measurements confirm that the films exhibit a strong *c*-axis texture without any second phase. The typical ϕ scan from a (10-11) plane of the ZnCoGaO thin film was also performed to verify its single crystalline characteristics, as shown in Fig. 1. The sixfold symmetry of the ZnO hexagonal structure crystal basal plane is clearly revealed by the six peaks separated by 60°. The full width at half maximum of the peaks is about 1.5°, revealing very good epitaxy.

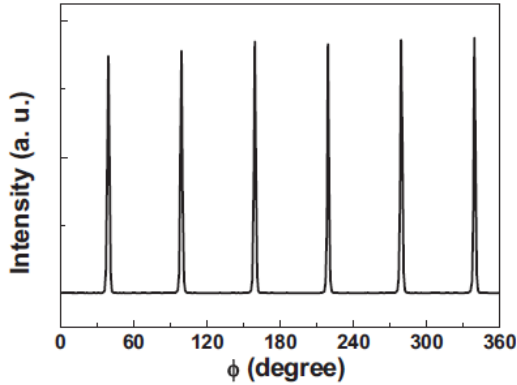


Fig. 1: A typical ϕ scan from a (10-11) plane of the ZnCoGaO thin film.

The x-ray absorption near-edge structure (XANES) is highly sensitive to the presence of TM clusters in host oxides. Figure 2(a) shows the Co K-edge XANES spectra of the samples as well as those of the standard Co metal and the oxide for comparison. In contrast to the marked shoulder around 7712 eV for the Co metal, the Co K-edge spectra of all the samples show clear 1s to 3d preedge features around 7709 eV, which are characteristic of Co²⁺ substitution for Zn²⁺ in ZnO. Extended x-ray absorption fine structure (EXAFS) is also adopted to clarify the local structures around the Co atoms. Figure 2(b) plots the radial distribution function (RDF), the Fourier transform amplitude of EXAFS, at the Zn and Co K-edge for the CoGa:ZnO samples. For the Zn RDF, the first and second peaks observed can be identified as Zn–O and Zn–Zn bonding, respectively. The RDFs for all samples at the Co K-edge are very similar to those of the Zn K-edge spectra, implying that Co ions have similar local structures, as do the Zn ions in ZnO. The results suggest that most Co actually substitutes for Zn without the

formation of any detectable metallic Co or other secondary phase. The Ga K-edge XANES spectra of the samples were also obtained and shown in Fig. 2(c). XANES simulations that correspond to Ga with tetrahedral (corresponding to the wurtzite structure in which Ga replaces Zn in ZnO) and octahedral coordination (corresponding to the spinel ZnGa₂O₄ phase) are also presented for comparison. Clearly, in the films with a low Ga concentration (about 1% or 2%) Ga is basically tetrahedrally coordinated by oxygen. However, when the Ga concentration increases to 4%, the increase in the intensity of peak A and the flattening of doublet B indicate that a certain amount of Ga atoms are octahedrally coordinated, indicating that only a portion of Ga atoms are doped into the ZnCoO lattice and the others may precipitate with ZnGa₂O₄, which is the only equilibrium compound in the ZnO–Ga₂O₃ phase diagram. All of these findings can also be confirmed by RDF from Ga K-edge EXAFS for the CoGa:ZnO thin films, as shown in Fig. 2(d). Therefore, most of the Ga can replace Zn in the ZnCoO lattice when the Ga concentration does not exceed 2%, while as the Ga concentration increases to 4%, some of the Ga atoms aggregate or precipitate out.

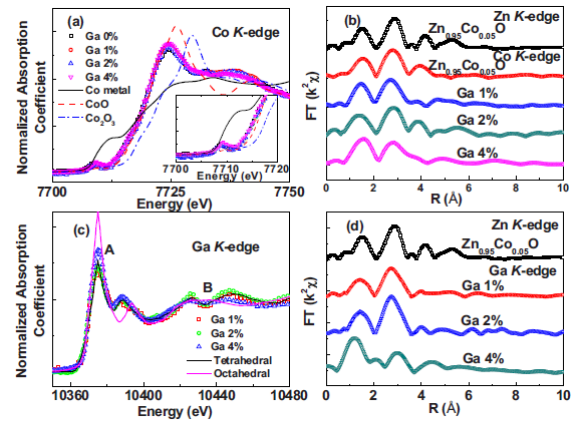


Fig. 2: Normalized absorption spectra of the CoGa:ZnO thin films on (a) Co and (c) Ga K-edges, and the radial distribution functions of (b) Co and (d) Ga from Fourier transform magnitude of EXAFS of Co and Ga K-edges, respectively.