

Amorphization and Ir valence states in the zinc-iridium oxide-peroxide thin films

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Recently we have demonstrated that nanocrystalline ZnO-IrO₂ thin films becomes amorphous and undergoes a transition from n- to p-type conductivity with increasing iridium concentration. In this study, the Zn K-edge and Ir L₃-edge XAFS spectra were measured in transmission mode at the SOLEIL Samba beamline. Zinc-iridium oxide-peroxide thin films were deposited on polyimide tape substrates by reactive magnetron co-sputtering of Zn and Ir metallic targets in an Ar and O₂ atmosphere. The XRD, Raman and XRF elemental analysis of the films was also carried out.

The contributions from the first and second coordination shells to EXAFS were extracted and analyzed within Gaussian/cumulant multiple scattering approximation. After Ir incorporation, nanocrystalline ZnO:Ir thin films gradually become amorphous (7.0–16.0 Ir at. %). The next-neighbours Zn-Zn₂ EXAFS signal gradually disappears, while the XANES and the FT EXAFS signal (Zn-O₁) demonstrate structural broadening of the typical ZnO₄ tetrahedral network. With increasing Ir, the incorporation of unusual planar ZnO₄ units appears. In addition, the intense Raman band at 720 cm⁻¹ appears attributed to the peroxide O₂²⁻ ions.

The XANES shift of the Ir-L₃ white line and EXAFS analysis demonstrate the change of the octahedral Ir⁴⁺ network environment as in nanocrystalline IrO₂ films to the isolated octahedral Ir⁵⁺ environment in the low concentrated amorphous ZnO:Ir films.