	Experiment title: Structural studies of indium-tin oxide thin films doped with Co using x-ray absorption spectroscopy	Experiment number: MA-441
Beamline: BM29	Date of experiment: from: 12-Feb-08 to: 16-Feb-08	Date of report: 1-03-09
Shifts: 9	Local contact(s): Angela Trapananti	<i>Received at ESRF:</i>
Names and affiliations of applicants (* indicates experimentalists): J. Stankiewicz*, G. Subías*, J. García* Instituto de Ciencia de Materiales de Aragón, CSIC- Universidad de Zaragoza, Departamento de Física de la Materia Condensada, C/ Pedro Cerbuna 12, 50009 Zaragoza.		

Report:

Diluted magnetic semiconductors (DMS) that are ferromagnetic (FM) at room or higher temperatures attract much attention because of their potential applicability in spin-based devices. Currently, there is no consensus on the origin of ferromagnetism in oxide DMS. The present work [1] was undertaken to investigate the local structural environment of Co atoms in Co-doped indium oxide (IO) and indium-tin oxide (ITO) films using x-ray absorption spectroscopy (XANES and EXAFS) at the Co K-edge. These results will permit us to discern whether the Co ion is substituted for the In site or it forms aggregates. In this way, we may judge whether the observed ferromagnetism in our films is of intrinsic or extrinsic origin.

XANES and EXAFS spectra at room temperature were recorded at the BM29 beam line in fluorescence mode (3-element solid-state germanium detector) in thin films, obtained by magnetron sputtering under various deposition conditions and with different Co concentrations. The beam was monochromatized by a fixed-exit Si(111) double-crystal and the energy resolution, $\delta E/E$, was estimated to be about 1×10^{-4} at the Co K-edge.

Normalized Co K-edge XANES data for Co-doped ITO thin films from 3 at.% up to 12 at.% and for Co-doped IO thin films from 2 at.% up to 18 at.% are plotted in Fig. 1(a) and Fig. 1(b), respectively. Typical XANES spectra for Co metal foil (Co^0) and for CoO powder (Co^{2+}) are also shown for reference purpose. Spectra for ITO films with Co contents less or equal to 4 at.% are alike. The position of the absorption edge coincides with that for divalent CoO. In addition, a weak pre-edge peak around 7709 eV and a strong white line, around 4 eV above the absorption edge, typical of Co^{2+} in octahedral coordination of oxygen atoms, are observed. However, in the near-edge region (up to 60 eV above the absorption edge) these spectra are quite

different from that of CoO. This indicates that all Co atoms seem to be substituted for In atoms. XANES spectra of IO films with Co contents less or equal to 4 at.% have also a similar shape as ITO:Co films corresponding to the most of Co atoms in the 2+ state. As Co content increases, the intensity of the pre-edge feature in these spectra is enhanced whereas the white line and the structures above the edge are considerably reduced indicating more disorder in the local structure. For films with higher Co content, a fraction of Co metallic inclusions are quite likely and the local structure disorder increases as the Co content does.

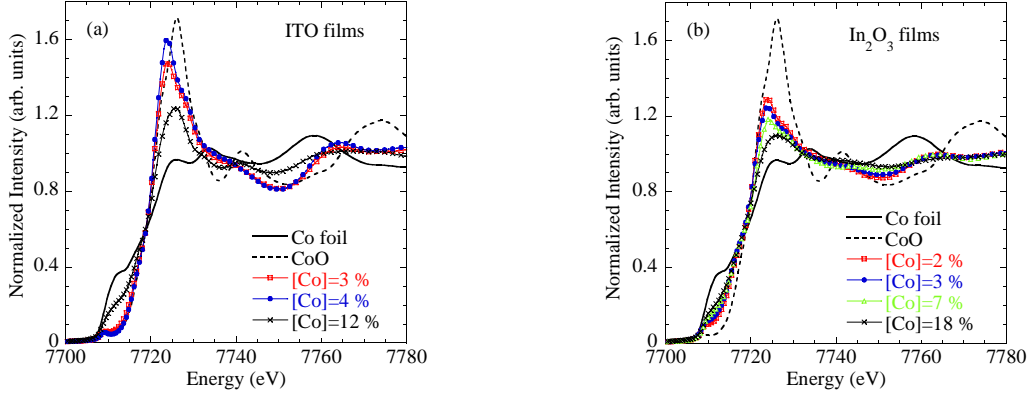


Fig. 1. Normalized x-ray absorption spectra at the Co K-edge for (a) ITO:Co and (b) IO:Co thin films with different Co content. Co K-edge EXAFS analysis follows the same lines (Fig. 2). The quality of fittings ensures that Co atoms substitute for the In in low Co-content ITO and IO films. However, in IO:Co films we have larger static local disorder than in ITO:Co films, estimated from the Debye-Waller factor. On the other hand, in the high Co-content films, metallic Co^0 clusters contribute significantly to spectra. For the ITO film with 12 at.% of Co, we fitted it assuming two different phases: metallic Co^0 and CoO.

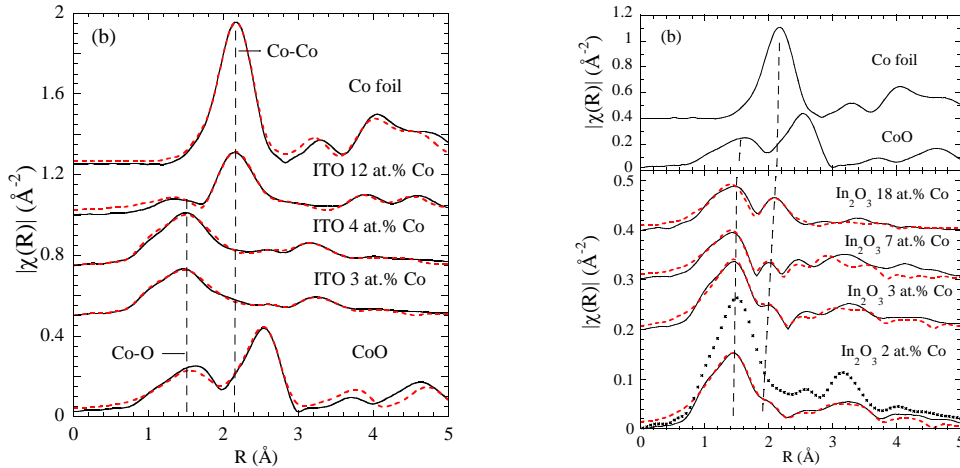


Fig. 2. Fourier Transform of $k\chi(k)$ (solid lines) for ITO:Co and IO:Co thin films. The dashed lines correspond to the best fits. Our studies show that Co atoms substitute homogeneously for In atoms in ITO films, obtained by direct deposition and in IO films, obtained by sequential deposition, with less than 7 at.% of Co. These films show very weak FM at room temperature. We suggest that it is intrinsic caused by exchange coupling between the spin of the carriers and the local magnetic moments. However, we cannot completely exclude non-carrier mediated mechanisms, such as magnetic impurity clusters. Increase of the Co content leads to the formation of metallic Co^0 clusters, which are mainly responsible for the observed ferromagnetism.