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## Synchrotron photoemission study of (Zn,Co)O films with uniform Co distribution

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### ABSTRACT

We present results of a resonant photoemission study of (Zn,Co)O films with Co content between 2% and 7%. The films were grown by Atomic Layer Deposition (ALD) at low temperature of 160 °C, and show fully paramagnetic behavior. The Co ions are uniformly distributed in the ZnO matrix and are free of foreign phases and metal accumulations as indicated by TEM data. The electronic structure of (Zn,Co)O films was studied by Resonant Photoemission Spectroscopy across the Co3p–Co3d photoionization threshold. We have observed that the resonant enhancement of the photoemission intensity from the Co3d shell is not the same for samples with different cobalt content. We suggest that the Co3d contribution to the valence band depends on both Co and H content.

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### 1. Introduction

Diluted magnetic semiconductors (DMS) have been recently intensively studied for spintronic applications (Bonanni and Dietl, 2010; Ueda et al., 2001) and ZnCoO focuses a great part of attention here (Khare et al., 2006; Assadi et al., 2009; De Carvalho et al., 2010; Zhang et al., 2009; Gilliland et al., 2010). This is possible because high cobalt concentration in ZnO is expected due to the nearly identical Co<sup>2+</sup> and Zn<sup>2+</sup> ionic radii. Ferromagnetic ordering in (Zn,Co)O has been found and reported by several groups, but the origin of the ferromagnetism is still not clear. It has been related to defects in the ZnO lattice (Coey et al., 2008), formation of foreign phases like CoO (Behan et al., 2008) and metal accumulations of the nanometers scale (Park et al., 2004) or uncompensated spins at the ZnCoO surface with higher Co content. Dimensions of inclusions that contribute to room temperature ferromagnetism can be at the level of only few nm, and so very difficult to detect. Ferromagnetism of these composite systems strongly depends on the growth conditions and co-doping with shallow impurities.

In our previous studies of a (Zn,Mn)O material we have demonstrated that low temperature growth, below 300 °C, leads to paramagnetic films with the uniform manganese distribution. These (Zn,Mn)O layers are free of manganese accumulations and

foreign phases (Wójcik et al., 2006, 2007). In the present work we focus on (Zn,Co)O films that were grown at 160 °C by the ALD method. The purpose of the study was to use resonant photoemission (RPES) to investigate the contribution of the Co3d electron shell to the (Zn,Co)O electronic structure and relate it to the uniformity of cobalt distribution and magnetic properties. We show that such information can shed a new light on the origin of magnetic ordering in this class of compounds.

There are only few RPES results on a (Zn, Co)O system reported to date (Wi et al., 2004; Kobayashi et al., 2005). In each of these papers, experimental photoemission data were obtained for only one (Zn, Co)O sample and none of them related the electronic structure with the Co content and distribution. The aim of the presented work is to partially fill this gap.

### 2. Experimental

The investigated (Zn,Co)O films were grown by the Atomic Layer Deposition (ALD) method at the same temperature of 160 °C and using the same zinc, cobalt and water precursors (dimethylzinc, Co(acac)<sub>2</sub> and water, respectively). The growth method as well as the growth conditions are described elsewhere (Łukasiewicz et al., 2009, 2010; Guziewicz et al., 2009). Different parameters of the ALD process (precursors' doses, purging time and proportion between zinc and cobalt precursors' pulses) resulted in different Co contents that varied between 0.1% and 7%. For further studies we chose three samples with the Co

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contents of 2%, 3.5% and 7%. All the samples were polycrystalline with the wurzite structure as proved by XRD.

The microstructure of the surface of the (Zn,Co)O films was characterized by Scanning Electron Microscopy (SEM). Structural characterization and chemical analysis were carried out on the cross-sectional transmission electron microscopy (TEM) specimens prepared using conventional mechanical polishing and Ar ion milling. The TEM specimens were finished at low ion energies ( $< 1$  keV) in order to minimize ion beam induced sample preparation artifacts. TEM studies were carried out using FEI Tecnai and Titan microscopes operated at 200 and 300 kV, respectively. The cobalt content was measured by both Energy Dispersive X-Ray Spectroscopy (EDX) and Secondary Ion Mass Spectroscopy (SIMS). The last method was also used to determine the hydrogen concentration. Accuracy of composition evaluation was established to be 10% of the measured Co content.

The electronic structure of the (Zn,Co)O films was studied by photoemission spectroscopy (PES). Before the PES experiment each (Zn,Co)O/Si film was prepared in an ultra-high vacuum system ( $p \approx 4 \times 10^{-10}$  Torr) using argon ion bombardment ( $U=600$  V,  $t=40$  min) and annealing to 200 °C (2 h).

PES spectra were taken in the binding energy (BE) range between the Fermi level and below 14 eV. This BE region covers the (Zn,Co)O valence band together with the Zn3d core level. We used resonant photoemission (RESPES), which is an effective tool for identification of the Co3d states in the valence band electronic structure of the (Zn,Co)O material. The experiment was performed at the 41 beamline at the MAX I storage ring at MAXLAB, Sweden. Photoemission spectra were recorded with the overall resolution of 200 meV at 50 eV photon energy.

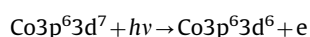
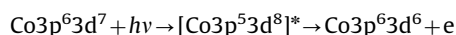
### 3. Results and discussion

SEM images of the surface of three investigated films are presented in Fig. 1. All the films were uniform and the EDX signals show a homogeneous Co and Zn distribution in the 200 nm  $\times$  200 nm scale. The films with 2% and 3.5% of cobalt have a granular microstructure while the surface of the films with 7% of Co reveals a more developed morphology.

Fig. 2a shows a cross-sectional low-magnification dark-field TEM image of the columnar structure of the (Zn,Co)O films with Co content of 3.5%. The selected area electron diffraction (SAED) pattern shows the (0 0 1) texture formation in the layers (Fig. 2b). The lattice parameters determined from the SAED pattern show good agreement with the bulk ZnO structure. Fig. 2c and d shows representative high-resolution TEM images from the (Zn,Co)O layers with (c) 3.5% and (d) 2% of Co content. The Co distribution in the layers was mapped using energy-filtered TEM (not shown). No hint for secondary or grain boundary phase formation was found in the three studied samples; however, it should be mentioned that Co-rich clusters smaller than  $\sim 1$  nm could be present in the samples but remained undetected by the techniques used in this work.

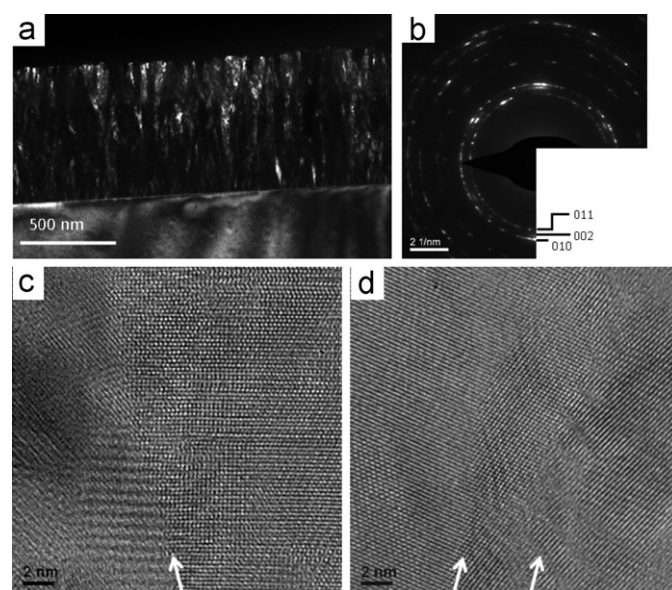
In Fig. 3 SIMS results show cobalt and hydrogen distribution along the growth direction.

We investigated the electronic structure of (Zn, Co)O films by resonant photoemission. RESPES is based on the Fano effect (Fano, 1961). This kind of phenomenon occurs in photoemission when the energy of incident photons is close to the energy difference between a fully occupied core level and a partially occupied shell as 3d shell in transition metals (TM), 4f shell in rare earths (RE) or 5f shell in actinides. Fano effect was for the first time observed in photoemission by Guillot et al. (1977) in a study of the electronic band structure of nickel and from that time it has been successfully used to investigate the electronic structure of materials that contain 3d, 4d or 5f electrons. The resonant photoemission process is the result of interference between two photoemission paths that, in the case of cobalt, can be described as follows:

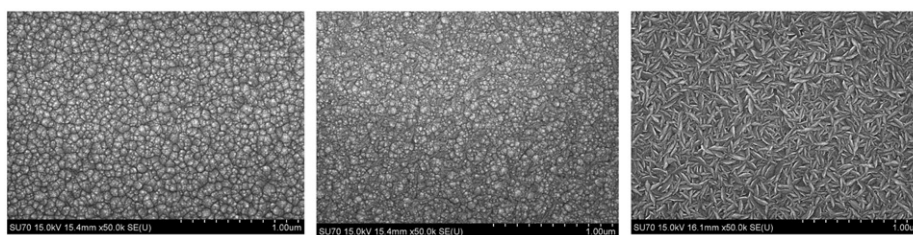


As a result, we observe an increase of the Co3d related features in photoemission spectra when photon energy is tuned to the Co3p  $\rightarrow$  Co3d photoionization threshold.

In Fig. 4 we show the set of Energy Distribution Curves (EDCs) for (Zn,Co)O film with 3.5% of Co. EDCs were taken for photon energies between 47 and 66 eV, e.g. across the Co3p  $\rightarrow$  Co3d transition, which is usually found at 62–63 eV. The spectra taken below the resonance are similar to the photoemission spectra of pure zinc oxide reported in the literature (Girard et al., 1997). As all the samples were polycrystalline, the changes observed in the



**Fig. 2.** (a) Cross-sectional dark-field TEM image shows the columnar structure of the (Zn,Co)O films grown by ALD at 160 °C with Co content of 3.5%. (b) Selected area electron diffraction pattern indicates (0 0 1) texture of the growth of the sample with 3.5% of Co. Representative high-resolution images of samples with (c) 3.5% and (d) 2% of Co indicate clean grain boundaries (marked with white arrows).



**Fig. 1.** SEM images for (Zn,Co)O films grown by ALD at 160 °C. The Co contents are 2% (left), 3.5% (middle) and 7% (right).

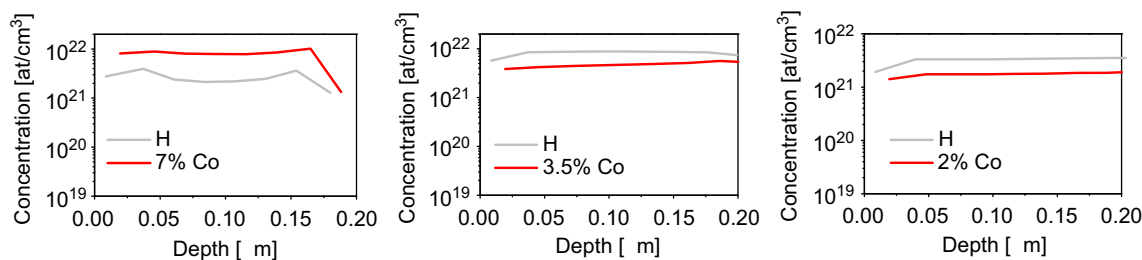


Fig. 3. Depth profiles of the (Zn,Co)O/Si films made by SIMS.

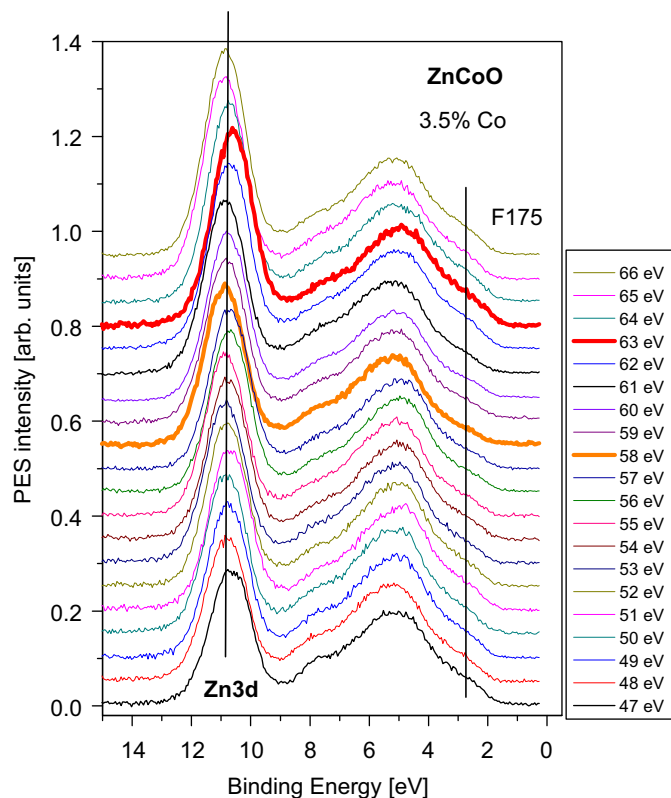


Fig. 4. EDC spectra of the (Zn,Co)O film with 3.5% Co measured across the Co3p→Co3d resonance. Thicker lines show resonant (63 eV, red online) and anti-resonant (58 eV, orange online) spectra. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

photoemission spectra taken with different photon energies are not influenced by the matrix element effects and can be interpreted in terms of resonant photoemission.

For all three investigated films the maximum of the Fano resonance was observed at photon energy 63 eV and the minimum at 58 eV. In Fig. 5 we present resonant and anti-resonant EDC spectra for films containing (a) 2%, (b) 3.5% and (c) 7% Co. We also show the difference spectra ( $\Delta\text{EDC} = \text{EDC}_{\text{rez}} - \text{EDC}_{\text{arez}}$ ) that is related to the Co3d contribution to the valence band of the (Zn,Co)O system. The difference curves are not shown over the Zn3d peak because the photoionization cross-section of the Zn3d states is very different for photon energies 58 and 63 eV, which would lead to artifacts in the calculated  $\Delta\text{EDC}$  spectra.

The surprising result is that resonant enhancement of the photoemission intensity from the Co3d electron shell is not the same for films with different cobalt contents. The resonant photoemission signal from the Co3d states for (Zn,Co)O films with 7% of Co was similar to that obtained for the film with 2% of cobalt. In Fig. 6 we have gathered the three  $\Delta\text{EDC}$  spectra for

easier comparison. Intensities of  $\Delta\text{EDC}$  presented there are normalized to the intensity of the respective Zn3d core level intensity taken at resonant photon energy (63 eV). It can be seen that films with different contents of cobalt give different Co3d contributions to the valence band electronic structure. For films containing 3.5% of Co we observe only one Co3d contribution, which is near the valence band edge (e.g. between 2 and 4 eV below the Fermi level) with the maximum at 3 eV (see Fig. 6). For two remaining (Zn,Co)O films (with 2% and 7% of Co) the additional Co3d contribution at 7 eV binding energy is also present. Moreover, the Co3d contribution of two latter films is shifted to higher binding energy with the maximum observed at about 4 eV below the Fermi level.

This result contests the existing opinion that there is no significant qualitative difference between photoemission results obtained for diverse (Zn,Co)O systems, even if they show distinct magnetic behavior (Hu et al., 2006). The point is that the observed differences are rather subtle; therefore a set of (Zn,Co)O samples should be compared in the same resonant photoemission experiment.

The  $\Delta\text{EDC}$  spectra presented above show that the Co3d photoemission feature at 7 eV below the Fermi level is not observed for all measured (Zn,Co)O systems. According to Kobayashi et al. (2005) this feature was assigned to the Co3d satellite structure. The lack of the satellite structure observed for the sample with 3.5% of Co (and the highest hydrogen content) means that in that case the Co3d states are coupled with the ligand electron states.

Probably the most interesting problem is to explain the physical origin of the differences in  $\Delta\text{EDC}$  spectra shown in Fig. 6. TEM images presented in Fig. 2 prove that the films are uniform and without any traces of secondary crystallographic phases; so this effect cannot influence the shape of the Fano resonance. On the other hand, XPS measurements (not shown here) suggest that redistribution of photoemission intensity from the Co3d states might be caused by cobalt–hydrogen bonds. We have measured the core level Co2p XPS spectrum of the sample with 3.5% of Co and apart from the contribution at binding energy of 780.2 eV that corresponds to cobalt oxides, we also observed another one at 781.9 eV that is assigned to Co surrounded by OH groups. The SIMS spectra presented in Fig. 3 confirm increased hydrogen content in this sample.

Hydrogen was found to be a common impurity in zinc oxide that plays a role of a shallow donor that strongly contributes to the high n-type conductivity in this material. Electrical measurements of the (Zn,Co)O sample with 3.5% of Co and high hydrogen content show that this sample is highly resistive (resistivity  $1.5 \times 10^3 \Omega \text{ cm}$ ). The XPS, SIMS and electrical results mentioned above suggest that hydrogen can be incorporated into the (Zn,Co)O matrix in a way described by Park and Chadi (2005). According to their investigations the most stable geometry of hydrogen in (Zn,Co)O is the interstitial position between two neighboring Co atoms (see Fig. 1b in Park and Chadi (2005)).

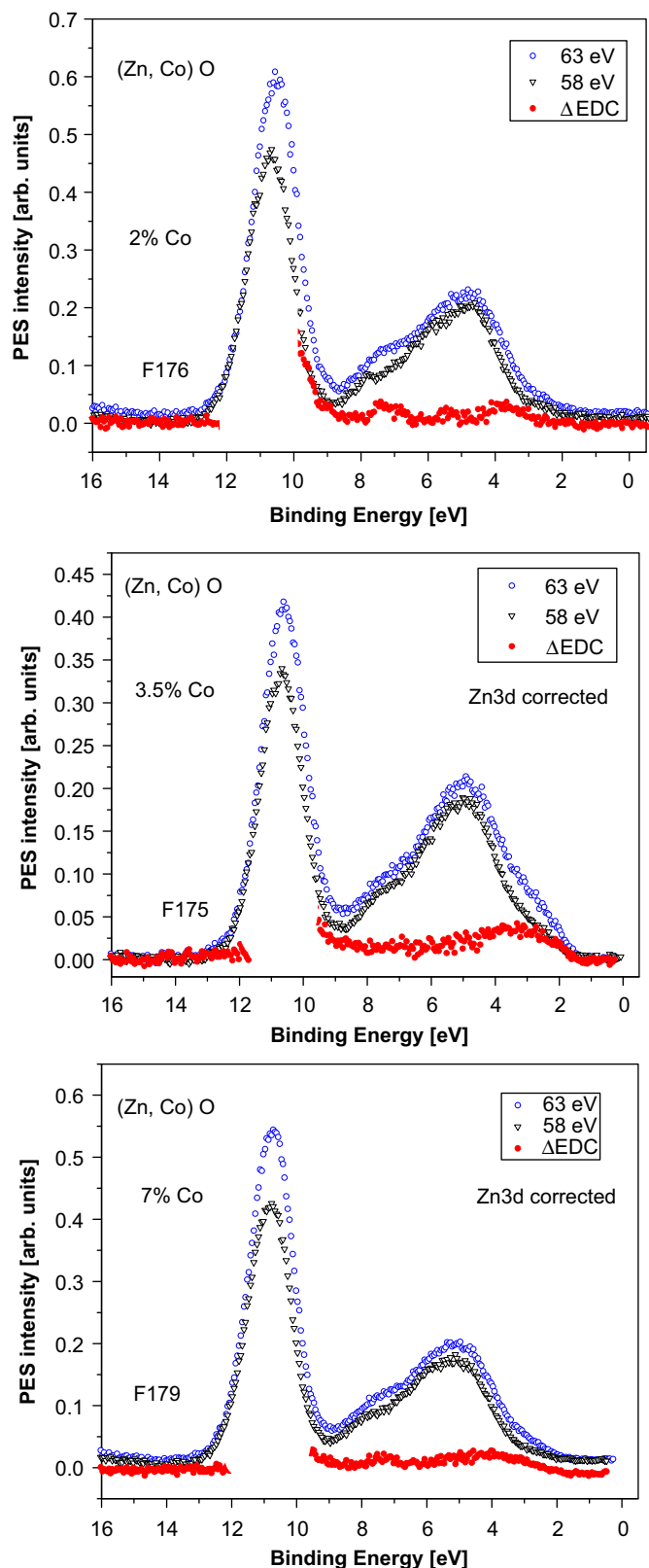


Fig. 5. EDC spectra taken at resonance (63 eV, solid circles, blue online) and anti-resonance (58 eV, open triangles, black online) photon energy along with the calculated difference curve ( $\Delta$ EDC, solid circles, red online). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

In this situation we will observe the XPS binding energies characteristic of Co(OH) bonds, because cobalt is surrounded by both hydrogen and oxygen atoms.

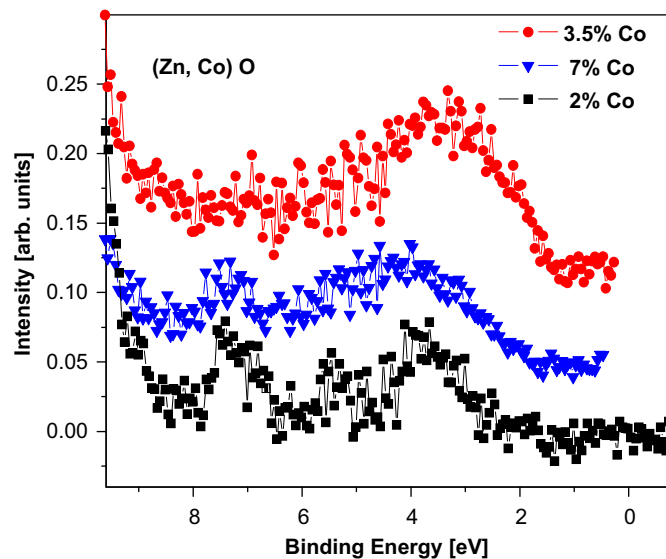


Fig. 6. Comparison of  $\Delta$ EDC curves obtained for (Zn,Co)O films with different Co contents (2% circles, black online, 3.5% squares, red online, 7% triangles, blue online). The intensity of each  $\Delta$ EDC curve was normalized to the intensity of the appropriate Zn3d photoemission peak. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

According to Park and Chadi, H forms bridge-like structure with Co ions that occupy the nearest lattice sites and strongly binds to these dimers. The H atom combines with two Co3d- $t_{2g}$  orbitals forming a bridge bond, which is stable if the spins of the two Co ions are parallel. Therefore hydrogen can directly mediate a short range spin-spin interaction in ZnCoO as was already observed (see for example Lee et al., 2006; Assadi et al., 2010; Singhal et al., 2010). On the other hand, since the hydrogenic level of the Co-H-Co complex is deep, hydrogen does not contribute in this case to electrical conductivity. Indeed, we do observe that a high hydrogen content was accompanied by a high resistivity.

Our latest magnetic studies on ferromagnetic (Zn,Co)O films show that the measured magnetic moment correlates with the hydrogen content (Godlewski et al., unpublished). However, there are additional factors like defects and interfaces that also play a role in the magnetic response of (Zn,Co)O systems. Therefore the role of hydrogen will be carefully clarified in a series of incoming experiments.

#### 4. Conclusions

In conclusion, we have investigated a set of paramagnetic (Zn,Co)O films with fully uniform Co distribution as was proved by high-resolution TEM images. Resonant photoemission study shows that the contribution of the Co3d electron states to the valence band electronic structure is not the same for different (Zn,Co)O films. The RPES signal observed for the sample with 3.5% of Co and a high hydrogen content was more intensive in the range of 2–4 eV below the Fermi level and does not show the satellite structure at 7 eV, which indicates that the Co3d states are strongly coupled with the ligand electron states. Also the Co3d electron states in this case are located closer to the valence band edge than that for samples with 2% and 7% of Co. We suggest that observed differences can be ascribed to different content of hydrogen, which promotes correlation of the Co3d electrons in a way described by Park and Chadi (2005).

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