SYNCHROTRON PHOTOEMISSION STUDY OF (Zn,Co)O FILMS WITH UNIFORM Co DISTRIBUTION

E. Guziewicz [1*], M. Lukasiewicz [1], L. Wachnicki [1], K. Kopalko [1], B.S. Witkowski [1], J. Sadowski [2], and M. Godlewski [1,3]

[1] *Institute of Physics, Polish Academy of Sciences, Al. Lotników 32/46, 02-668 Warsaw, Poland*

[2] *MAX-lab, Lund University, Box 118, SE-22100 Lund, Sweden*

[3] *Department of Mathematics and Natural Sciences, College of Science, Cardinal Wyszyński University, ul. Dewajtis 5, 01-815 Warsaw, Poland*

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**) e-mail: guzel@ifpan.edu.pl*

Zinc oxide containing transition metal (TM) elements is intensively studied because of prospective application in spintronics [1,2]. 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 is often related to to formation of foreign phases and metal accumulations in the nm scale. The ferromagnetism of these composite systems strongly depend on the growth conditions and co-doping with shallow impurities [1].

In our previous studies on (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 [3-4].

The presented photoemission studies are focused on (Zn,Co)O material grown at low temperature. We have shown that in order to avoid the presence of foreign phases and metal accumulations (Zn,Co)O films should be grown at temperature below 200°C [5-6]. These films are paramagnetic and, as shown by SIMS and TEM studies, free of foreign phases and accumulations of metallic cobalt. The subject of the present study was to investigate the electronic structure of uniform (Zn,Co)O films with different cobalt content.

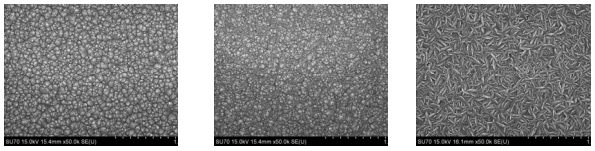

Figure1. SEM images for (Zn,Co)O films grown by ALD at 160°C. The Co content is: 2% (left), 3.5% (middle) and 7% (right).

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, $Co(acac)_2$ and water, respectively). The growth method as well as properties of obtained films are described elsewhere [7]. Different parameters of the ALD process (precursors' doses, purging time and proportion between zinc and cobalt precursors' pulses) resulted in different Co content that varied between 0.1% and 7%. For photoemission studies we prepared three samples with Co content 2%, 3.5% and 7%. SEM images of the surface of these films are presented in Fig. 1.

We investigated the electronic structure of these films in the energy range between the Fermi level and 14 eV below. This binding energy region covers the (Zn,Co)O valence band together with the Zn3*d* core level. We used the resonant photoemission spectroscopy, which is as an effective tool for identification of the Co3*d* ion charge states in the valence band electronic structure of the (Zn,Co)O material.

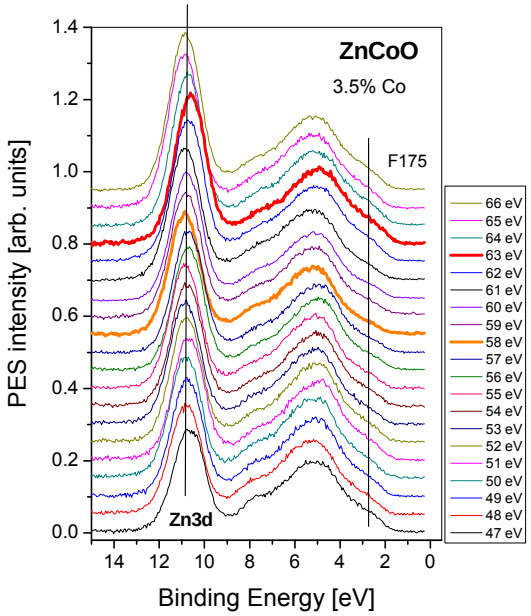

Figure 2. EDC spectra of the (Zn,Co)O film with 3.5% Co measured across the Co3*p*→Co3*d* resonance. Thicker lines shows resonant (63 eV, red on-line) and anti-resonant (58 eV, orange on-line) spectra.

The resonant photoemission process is the result of intererence between two photoemission paths that, in the case of cobalt, can be described as follows:

$$Co3p^6 3d^7 + h\nu \rightarrow [Co3p^5 3d^8]^* \rightarrow Co3p^6 3d^6 + e$$
$$Co3p^6 3d^7 + h\nu \rightarrow Co3p^6 3d^6 + e$$

As a result, we observe an increase of Co3*d* related features in photoemission spectra when photon energy is tunned to the Co3*p*→Co3*d* energy difference.

In Fig. 2, we show the set of Energy Distribution Curves (EDC's) for all measured (Zn,Co)O films. EDC's were taken for photon energies between 47 eV and 66 eV, *e.g.* across the Co3*p*→Co3*d* transition.

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. 3, we present resonant and anti-resonant EDC spectra for films containing a) 2% Co, b) 3.5% Co, and c) 7% Co. We also show the difference spectra (ΔEDC) that is related to the Co3*d* contribution to the valence band of the (Zn,Co)O system.

We noticed that resonant enhancement of the photoemission intensity from the Co3*d* shell does not scale with the cobalt content. The strongest photoemission response from the Co3*d* electron shell was observed for (Zn,Co)O film with 3.5% of cobalt. The resonant photoemission signal from the Co3d states for (Zn,Co)O films with 7% of Co was similar to that which was obtained for (Zn,Co)O film with 2% of cobalt.

Moreover, we also noticed that films with different content of cobalt give different Co3*d* contributions to the valence band electronic structure. For films containing 3.5% of Co we observe only one Co3*d* contribution, which is located between 2 eV and 4 eV below the Fermi level with the maximum at 3 eV (see Fig. 3b). For two remaining (Zn,Co)O films the additional Co3*d* contribution at higher binding energy is also present. In case of film with 2% of Co it is located 9 eV below the Fermi level (see Fig. 3a), while for (Zn,Co)O film with 7% of Co it is observed at 7.4 eV below the Fermi level (see Fig. 3c).

We expect that photoemission investigation of the Co3*p* core level may shed some light on the Co states in the measured (Zn,Co)O films.

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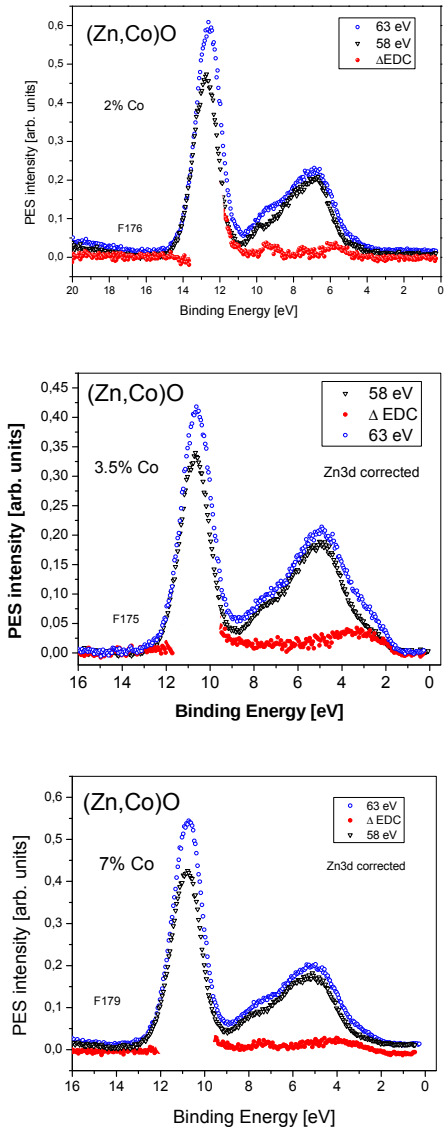

Figure 3. EDC spectra taken at resonance (63 eV, blue solid circles) and anti-resonance (58 eV, black open triangles) photon energy along with the calculate difference curve (ΔEDC, red open circles).