Soft x-ray absorption spectroscopy on Co doped ZnO: structural distortions and electronic structure

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Abstract. We present soft x-ray absorption spectra from a series of Co doped ZnO films. We discuss systematic variations of the Co L-edge white line intensity and multiplet features for this series of samples. We document sizeable differences in the electronic state of the Co ionic cores, as well as in the local environment of the host lattice atoms, characterised by means of x-ray absorption spectra at the O K-edge and Zn L-edges. Model calculations allow to correlate the observed effects to small structural distortions of the ZnO lattice.

1. Introduction

Within the area of magnetism applications, ZnO:Co is an important model material for spintronics applications [1]. A series of ZnO:Co thin film samples, with Co diluted in the 10% range, are grown by means of the Atomic Layer Deposition (ALD) technique on Si substrates at temperatures $160 - 300\,^\circ$C. Table 1 summarises some of the growth parameters. The samples are characterised by means of Atomic Force Microscopy (AFM), Scanning Electron Microscopy (SEM), X-Ray Diffraction (XRD), Secondary Ion Mass Spectrometry (SIMS), X-ray Photoelectron Spectroscopy (XPS) and SQUID magnetometry [2, 3]. The absence of stable ferromagnetism in the case of ZnO:Co has been linked in the literature with the possible existence of Co rich clusters within the ZnO matrix [4]. Given previous work documenting strong intensity variations in the Ni L-edge white line intensity and in the O K-edge spectral features, upon the controlled oxidation of ultra thin Ni films [5], it appears appropriate to study the XAS of the Co L-edges, O K-edge, Zn L-edges to correlate the absence of ferromagnetism in ZnO:Co samples with the electronic state and local environment of the Co, O and Zn atoms. The existence of small Co rich clusters, can lead to local strain within the ZnO lattice.

2. Experimental

We discuss XAS measurements taken at the I1011 beam line at the MAX IV synchrotron radiation facility in Lund, Sweden [6, 7]. We focus here on measurements performed in the Total Electron Yield (TEY) and characterise the near surface region of the samples. In figure 1, and figure 2 TEY results using linearly polarised x-rays are shown at normal x-ray incidence. All XAS spectra are normalised to the atomic continuum on a *per atom* basis to allow for a meaningful comparison. No measurable X-ray Magnetic Circular Dichroism (XMCD) was found in the TEY mode, for magnetic fields up to 0.5 T at 300K. The absence of ferromagnetism at 300K for the near surface region is in agreement with previous observations [3, 8]. To allow for

Sample	T_g [°C]	ZnO:CoO $m{:}n$	t [nm]	x_{Co} [%]
F213	300	8:1	130	8.8
F254	160	8:1	70	18-36
F279	300	8:1	1280	5.9
F307	200	2:1	250	8
F328	200	2:1	60	11.4

Table 1: List of the samples investigated in this study. We indicate the growth temperature, the ZnO to CoO cycles' ratio, thicknesses, and the Co concentrations obtained from SIMS.
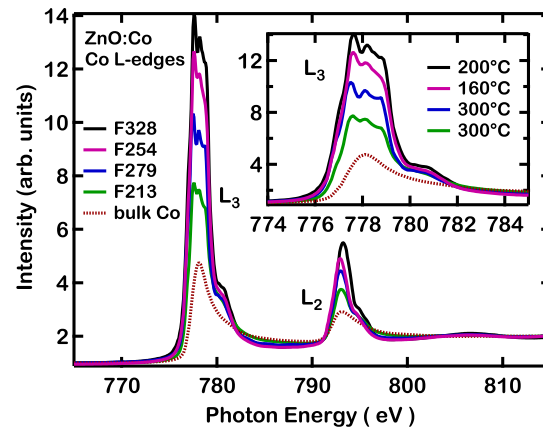

Figure 1: Co L-edge XAS spectra. White line intensity variations are found as a function of the growth parameters. A correlation with the growth temperature (see insert) is found.

a determination of the electronic state of the Co atoms, spectra were taken also for a reference metallic Co sample using a thin film grown and characterised *in situ* [7].

3. Results

The Co L-edges of the ZnO:Co films do indeed exhibit the typical multiplet shapes observed earlier on ZnO:Co magnetically dilute samples [8, 10]. We denominate the samples using a growth sequence number, such as F328 (Table 1, Fig. 1). We observe in the data presented in figure 1 a strong increase of the white lines intensity, versus the Co bulk. The white line area is proportional to the number of empty Co(3d) final states. We observe also a decrease of intensity in the spectral regions following the white lines (782-790 eV and 796-802 eV). These spectral areas correspond to Co(4s) final states. The data of Table 1 indicate that the spectral area variations correlate best with the growth temperature. Growth at low temperatures leads to higher white line intensities. Furthermore, in the data of figure 1, it can be observed that small relative intensity variations within the multiplet fine structure components take place. Interestingly, even in cases where the Co L-edges indicate only small variations in the few percent range in terms of overall intensity, clear variations in the O K-edge and Zn L-edges can be observed, as shown in the TEY data of figure 2. The variations observed at the Co L-edge are of the order of several 10% of the XAS intensity, at the Zn L-edge they are of order few %, in particular in the region close to the edge. Even if in terms of absolute intensity these can be considered small, their relative intensity variation cannot be neglected. The data of figure 2 indicate that intensity variations at the O K-edge can be very strong close to the edge, comparable in strength to the intensity variations of the Co data (around 530 eV).

4. Discussion

In figure 1 the XAS intensity variations at the Co L-edges traces the existence of more empty Co(3d) states and of less Co(4s) empty states, versus metallic Co. A similar result is found for the case of controlled oxidation of ultra thin Ni films for the Ni(3d) and Ni(4s) states [5]. For the Ni films these intensity variations correlate with the decrease of the ferromagnetic response [5]. As each Ni atom is losing first neighbour Ni atoms and acquiring as first neighbour O atoms, the alignment of the magnetic moment of the Ni atoms tends to switch from parallel to antiparallel

versus the closest Ni neighbour atoms. A similar effect can be expected here with the Co atoms. The strong variations of spectral intensities for the Co atoms can be understood assuming the existence of Co rich clusters within the ZnO lattice, as suggested earlier [4]. Stronger L-edge white lines allow to conclude, assuming Co clusters are present within the ZnO lattice, either that they are less numerous leading to more substitutional Co, or smaller in size, or possibly incorporating more O atoms. Given the fact that Co is diluted in the ZnO lattice in the 10% range, the variations in intensity at the Zn and O edges link the stronger variations observed at the Co-edges, to small structural distortions relating with the ZnO lattice. Strain is indeed expected within the ZnO lattice if Co clusters are present, with Co not fully substituting the Zn atoms. It can be seen from the data of figure 1, and figure 2 that in cases where the Co white lines are strongest such as in the case of samples F254 and F328, still sizeable intensity variations are observed at the Zn L-edge and O K-edge. It is furthermore observed that the multiplet fine structure at the Co L-edge presents small differences in energy and relative intensities of the features observed, indicating that the Co atoms are at least partly located in an environment of different crystal symmetry. To elucidate the origin of the spectral variations we observe to structural distortions in the ZnO lattice, we perform model calculations at the O K-edge and Zn L_3-edge using the FEFF code, and compare model spectra with our experimental results.
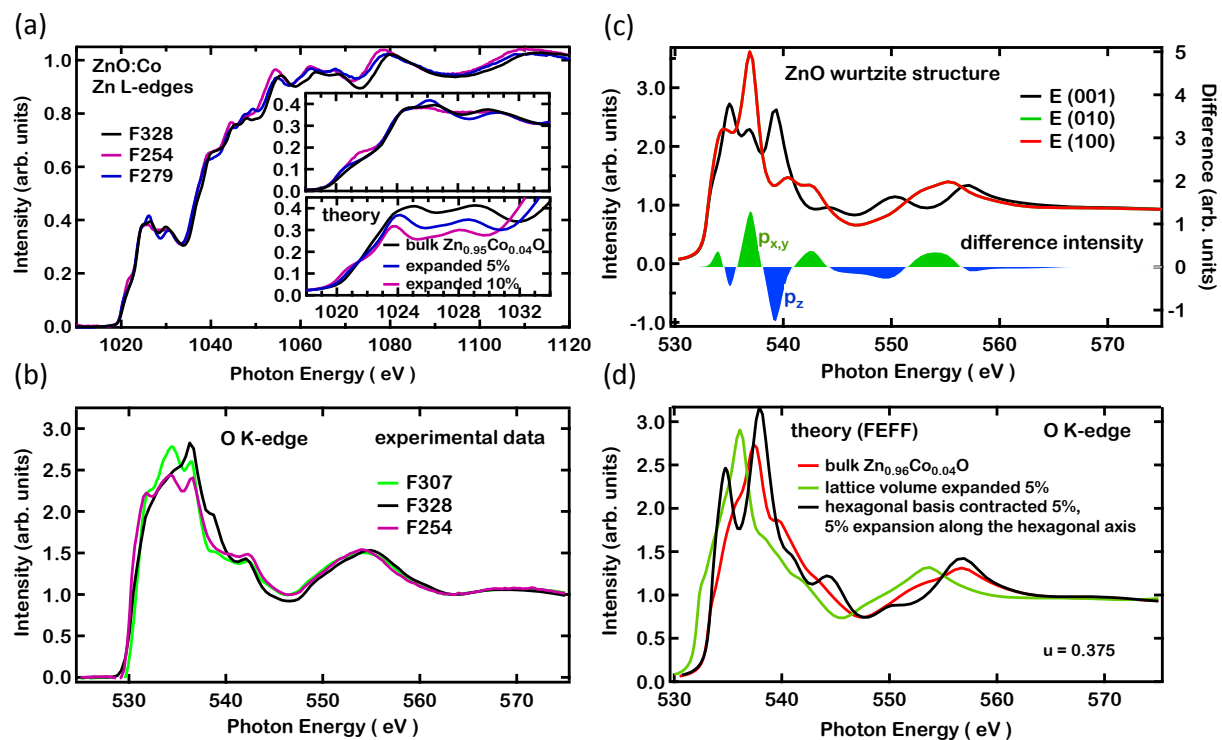

Figure 2: (a) XAS spectra for the Zn L-edges. In the insert the experimental spectra are shown, as well as two model calculations. (b) XAS O K-edge experimental spectra. (c) and (d) theoretical spectra for ZnO:Co thin film samples. For theory the Co content is 4%.

To calculate the XAS spectra we use the FEFF9 version of the *ab initio* FEFF code [11, 12]. We have used earlier the FEFF code to calculate the N K-edge XAS of GaN, and our results for GaN are consistent with earlier FEFF calculations and experimental data of c-axis oriented GaN films [13]. For the present calculations a ZnO cluster with a radius of $12\mathring{A}$ (608 atoms) is used, around the photo-excited O atom, in the wurtzite crystal structure, with lattice constants of $3.249\mathring{A}$ (x,y axis of the hexagonal unit cell in the hexagonal plane), $5.207\mathring{A}$ (z axis along the

hexagonal axis) and the parameter $u = 0.375 \mathring{A}$. A Hedin-Lundqvist energy dependent exchange correlation potential with a constant imaginary part of 0.25 eV is used here. The calculations of figure 2 are performed with unpolarized light given the random granular growth. Linearly polarized light is used for calculations shown in figure 2, to explore the angle dependence in the wurtzite structure and assign the various spectral features. The Co atoms occupy Zn sites and are randomly distributed. Several different Co atom configurations have been considered, the results being similar to better than 2%. We use a $8 \mathring{A}$ radius for self-consistency and full multiple scattering. This value is sufficient to assure the convergence of the results versus cluster size.

It is found that it is possible to reproduce the order of magnitude of the difference of spectral shapes of samples F307 and F254 versus F328 by considering small structural distortions of order of 5% of the lattice constant. We are able to reproduce in particular the strong variations at the edge, around 530 eV in the experimental data. The samples exhibit granular growth, with a typical grain size of order 4-5 nm and it is probable that a broadening of the absorption edge should be observed, as can be reproduced by the calculations, due to small structural distortions for each grain as presented in figure 2. figure 2 shows the symmetry assignment of the various spectral features at the O K-edge. The hexagonal z-axis is probed by orienting the electric field along the (001) direction. Focusing on the Zn L_3-edge data of figure 2, we also find that it is possible to reproduce the observed intensity variations with a ZnO lattice expansion of the 5-10% range. The existence of structural distortions for ZnO:Co constitutes an important result for magnetism applications. It has been proposed that structural distortions in ZnO:Co affect the magnetic properties. A decrease in the lattice constant of the order of 5% contribute to an increase in the Curie temperature of the order of 100 K in theoretical models [1].

5. Conclusions

We document intensity variations at the core level edges of all constituent atoms for ALD grown ZnO:Co samples, correlating with the sample growth temperature. The observed effects at the Co L-edges support that small Co rich clusters exist within the ZnO lattice. Co clusters are expected to induce local strain within the host lattice. Modelling of the O K-edge and Zn L-edges, using the FEFF *ab initio* code supports that small structural variations of the ZnO lattice constitute a possible explanation for the observed spectral intensity variations. We conclude that it is possible to use ALD growth, in particular focusing on the growth temperature in combination with XAS, to establish specific properties of the samples, such as the ferromagnetism of ZnO:Co.

6. Acknowledgements

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