Magnetic and X-ray absorption investigations of Co-doped ZnO films

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Abstract. We present an investigation of magnetic and structural properties of Co-doped ZnO (ZCO) film grown by pulsed laser deposition at different dopant concentrations ($c_{\text{Co}}$). X-ray diffraction patterns show that the films are single phase and exhibit ferromagnetism (FM) above room temperature (RT) with coercive fields up to 700 Oe. X-ray absorption fine-structure spectroscopy (XAFS) at the Co edge suggests that in films grown below 600°C dopant clustering involve less than 10% of the Co atoms in the alloy. In samples grown at higher temperature a larger fraction of Co atoms is involved in the formation of small metallic clusters. The experimental work has been accompanied by preliminary first-principles Density Functional Theory calculations.

1. Introduction

ZnO is expected to play an important role for many optoelectronic applications, such as ultraviolet (UV) lasers, light emitting diodes, thin film transistors. In fact ZnO is transparent in the visible region and the recent discovery of RT FM, after the Dietl’s theoretical predictions, makes transparent ferromagnets possible.

There are several reports where RT FM has been observed either in bulk materials or thin films. In Mn-doped ZnO FM has been attributed to the coexistence of different oxidation states of dopant ions (3+ and 4+) and the formation of the ZnxMn1-xO4 spinel (0 ≤ x ≤ 1) as well as to an oxygen vacancy-stabilized metastable phase. ZnMn2+O3−δ. On the other hand, recent papers reported that in ZnO films doped with transition metal ions RT ferromagnetism can be due to intrinsic point defects of the lattice or to the carrier concentration rather than to the doping with magnetic ions.

In this paper we investigated the effects of the growth parameters, such as substrate temperature ($T_s$), oxygen pressure ($pO_2$), and $c_{\text{Co}}$ on the structural and magnetic properties of c-axis oriented ZCO thin films. A preliminary theoretical investigation of structural and electronic properties of oxygen vacancy and Co impurity in ZnO has been also performed, in order to set up the theoretical framework to be employed for a more quantitative analysis of experimental data.

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2. Experimental and theoretical methods

Targets with nominal compositions of 2 at.%, 4 at.% and 6 at.% were sintered to deposit ZCO thin films by PLD on Al₂O₃ (0001) substrates, using a Nd-YAG laser operating at 355 nm. Hysteresis cycles have been measured at RT by means of a commercial vibrating sample magnetometer (ADE mod 10 VSM). X-ray Absorption Fine-structure Spectroscopy (XAFS) at the Co K-edge has been performed on some of the samples at the Samba beamline of SOLEIL synchrotron radiation facility (Saint-Aubin, France) by using a double-crystal monochromator equipped with Si (111) crystals and fluorescence mode with a single-element silicon drift detector.

First-principles calculations have been performed with the VASP (Vienna Ab Initio Simulation Package) code. Exchange and correlation effects are treated in Generalized Gradient Approximation, in Perdew-Wang formalism. The positions of defect or impurity electronic levels in the ZnO energy gap have been estimated by calculating transition energy levels.

3. Results and discussions

The XRD patterns (Fig.1) show mainly the presence of the wurtzite phase; all the spectra mainly exhibit the (002) peak, so that a fully c-axis orientation results. However, small quantities of Co-rich phases (CoO, ZnCoO₃), appear in the spectra at high c₃ values.

![XRD spectra of films with different c₃ values.](image)

![Hysteresis cycles of films grown with different dopant concentration.](image)

Magnetization (M) versus field (H) measurements showed a clear ferromagnetic behaviour in our samples, with saturation magnetization (Mₛ) values up to ~1 emu/g, depending on Tₛ, pO₂ and c₃ values. The optimal pO₂ value (~2x10⁻⁵ mbar) is lower than ones found for Mn-doped films, whereas the Tₛ value for which films with highest Mₛ result, depends on dopant concentration. For films with c₃ = 4 at.% the highest Mₛ value (~1 emu/g) is measured for the film deposited at Tₛ = 600 °C (pO₂ = 2x10⁻⁵ mbar). The influence of c₃ on the magnetic properties of the films is clearly visible in fig. 2. On increasing c₃, Mₛ is found to increase up to ~1 emu/g (c₃ = 4 at.%) and then it decreases.

![FT amplitude of EXAFS Co K-edge](image)
In Fig. 3 we show the Fourier Transform (FT) of the EXAFS spectra taken at the Co K-edge for two ZCO samples, with \( c_{Co} \) values of 4 at.% and 6 at.%. These FTs are compared to the spectrum recorded on a Co foil in transmission mode. To obtain the FTs, the raw absorption spectra were background subtracted, weighed by a \( k^2 \), and the \([2.5–13.5 \text{ Å}^{-1}]\) \( k \)-range was selected before transformation to \( R \) space. Phase shift correction was applied to the data, hence the peak positions of the FTs roughly correspond to the different interatomic distance between an “average” Co absorber and its neighbours. In the spectrum of the sample with \( c_{Co} = 6 \) at.% (grown at lower temperature) we can clearly distinguish two main peaks, the first at about 1.9 Å and the second at 3.12 Å (red spectrum). These values are within 0.1 Å from the Zn-O first shell and Zn-Zn second shell distances extracted in wurtzite ZnO by neutron diffraction using Rietveld method9 and close to the results of EXAFS experiments on similar samples10,11. Considering the approximation for the calculated phase shift in Fig. 3 and the very close atomic number and X-ray backscattering factors of Co and Zn atoms, it turns out that in this sample Co impurities substitute for Zn atoms in the wurtzite structure. The FT of the Co foil spectrum (blue line) shows a dominant peak at about 2.45 Å that corresponds to the Co-Co first shell coordination in the metal. The intensity of such peak is weak in the spectrum of the ZCO sample with \( c_{Co} = 6 \) at.% suggesting that Co metallic clusters, if present, have rather low concentration. A more quantitative analysis of these EXAFS data is in progress and detailed results (including precise determination of the bond lengths, substitutional and metallic fraction) will be published in a forthcoming paper; nevertheless, preliminary considerations based on the examination of Fig. 3 lead us to believe that the percentage of Co atoms involved in the formation of metallic clusters should be smaller than 10% of the total number of Co atoms in the sample. As for the sample grown at higher temperature with \( c_{Co} = 4 \) at.% Co, the relative FT (black line) shows a main broad peak which reaches its maximum at a distance close to the one of the Co-Co first shell in the metal; however its FT seems to arise from a mixed contribution of substitutional, metallic (around 50 %) and, probably, other minority signals. This result indicates that changing the growth parameters, and in particular the growth temperature, can have large effects on the Co local structure. It should be noted that, since Co clusters in the sample with \( c_{Co} = 4 \) at.% do not give any signature in XRD rocking curves, their size has to be very low and possibly nanometric. Anyway, EXAFS can seek out the formation of nanoclusters thanks to its strong local and chemical sensitivity.

Regarding the theoretical investigations, standard DFT formalism fails to reproduce the electronic properties of ZnO, underestimating its band gap and underbinding Zn-d bands7. The description of native defects (\( V_{O} \)) and transition metal impurities in ZnO is also inaccurate. Ad-hoc correction schemes have been applied, as the use of Hubbard-U corrections for Zn-3d and Zn-4s orbitals7, as well as the application of hybrid DFT functionals or self-interaction schemes12. While curing the ZnO band gap problem, there is still some uncertainty on the positions of the electronic levels induced by native defects and Co impurities. Thus, we have started our investigation on Co:ZnO applying the Hubbard-U correction scheme to different orbitals (3d orbital of Zn and Co, and O-2p orbitals), studying their effects on ZnO lattice parameters and band gap and on structural and electronic properties of \( V_{O} \) and substitutional Co (\( Co_{Zn} \)) atom in ZnO. Results are summarized in Table I. Increasing values of \( U_{Zn,d} \) open up the gap toward the experimental value: they push occupied Zn-d states down in energy and reduce the \( p-d \) hybridization in the valence band. At the same time, large values of \( U_{Zn,d} \) lead to smaller lattice parameters, that contract up to 6% for \( U_{Zn,d} = 12 \text{ eV} \) with respect to experiments. As regard \( V_{O} \), its negative-U behavior (i.e., +1-charged \( V_{O} \) unstable with respect to neutral and +2-charged) is correctly reproduced with all values of \( U \) employed, as well as the sign of atomic relaxations: Zn atoms surrounding the vacancy relax outward in the neutral state, inward in the +2-charge state. Vacancy transition levels are almost unaffected by \( U_{O,p} \), while showing more pronounced dependence on \( U_{Zn,d} \). In general, the use of \( U_{O,p} \) has small effects on bulk and defect properties. Moreover, considering the large shrinking of lattice constants obtained with \( U_{Zn,d} = 12 \text{ eV} \), and the fact that the distance of Zn-d states from valence band maximum results ~9 eV (while experimental spectra locate them at ~7-8 eV), the use of \( U_{Zn,d} = 7.5 \text{ eV} \) alone results to be the best choice to reproduce structural and electronic properties of ZnO. Zn atoms surrounding substitutional
Table 1. Values of U-correction terms (in eV) are reported, together with the calculated ZnO wurtzite lattice parameters, \( a \) and \( c/a \), and band gap, \( E_g \), to be compared to the experimental values of \( a = 3.25\text{Å}, \ c/a = 1.602, \ E_g = 3.5 \text{ eV} \), respectively. For the two defects investigated, \( \text{V}_\text{O} \) and \( \text{Co}_\text{Zn} \), we report the transition levels, \( \varepsilon_{\text{q/q'}}(\text{eV}) \), corresponding to the electronic levels induced by the defects.

| \( U_{\text{Zn-}d} \) | \( U_{\text{O-}p} \) | \( U_{\text{Co-}d} \) | \( a \) | \( c/a \) | \( E_g \) | \( \text{V}_\text{O}: \varepsilon_{0/2^+} \) | \( \text{Co}_\text{Zn}: \varepsilon_{+/-0} \) | \( \text{Co}_\text{Zn}: \varepsilon_{0/-} \) |
|---|---|---|---|---|---|---|---|---|
| 0 | 0 | 0 | 3.29 | 1.605 | 0.8 | 0.6\(^{15}\) | 0.9 | 3.0 |
| 7.5 | 0 | 2.2 | 3.17 | 1.58 | 2.0 | 1.06 | 0.46 | 3.52 |
| 7.5 | 0 | 4.4 | ~ 0 | 4.1 |
| 12 | 0 | ~ | 3.07 | 1.55 | 3.0 | 1.47 |
| 7.5 | 3 | 2.2 | 3.16 | 1.54 | 2.2 | 1.1 | 0.54 | 3.53 |

Co relax slightly outward in all cases considered. Adopting different \( U_{\text{Zn-}d} \) or \( U_{\text{O-}p} \) correction terms have negligible effects on the electronic properties of \( \text{Co}_\text{Zn} \), whereas the position of transition levels \( \varepsilon_{\text{q/q'}} \) (corresponding to the occupied \( e^- \) and unoccupied \( t^- \) minority-spin states) are strongly dependent from \( U_{\text{Co-}d} \) values. In particular, the \( U_{\text{Co-}d} = 2.2 \text{ eV} \) lowers the positions of both DFT \( e^- \) and \( t^- \) states, giving a transition level \( \varepsilon_{+/-0} \) in good agreement with experiments (0.3 eV) and unoccupied \( t^- \) within the conduction band. On the other hand, a larger \( U_{\text{Co-}d} \) (4.4 eV) erroneously increases the distance between occupied and unoccupied states, pushing \( t^- \)-states too high in energy while \( e^- \)-states result almost resonant with valence band.

In conclusion our results point out the role of growth parameters (\( T_s \) and \( pO_2 \)) and dopant concentration in the tailoring of the magnetic properties of the Co-doped ZnO thin films. Although the origin of the FM interaction is still to be clarified, we can rule out that double exchange mechanism, from the secondary phases, is the main responsible for the observed FM. In fact the estimated contribution of the total \( M_s \) value due to the Co clustering is about 60% for the 6 at.% Co-doped film. The remaining fraction of \( M_s \) (40%) is not due to secondary phases because XRD spectra gave no evidence of any RT ferromagnetic phases. Moreover, the secondary phases detected in the XRD spectra increase with \( c_{\text{Co}} \) so that, even if they could be responsible for the RT FM, the decrease of \( M_s \) for \( c_{\text{Co}} > 4 \text{ at.\%} \) cannot be accounted for. On the other hand, defects (oxygen and/or Zn vacancies in the ZnO lattice) should play a very important role. Their role has been recently discussed in the RT ferromagnetism observed in undoped ZnO films\(^{7,8}\) as well as in Co-doped ones, where Co atoms exhibit a paramagnetic behaviour\(^{13}\). The role of defects and the mechanisms of magnetic coupling will be the object of future combined experimental and theoretical investigations.

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