

Nanometer scale mapping of cobalt in Al-doped ferromagnetic $\text{Zn}_{0.7}\text{Co}_{0.3}\text{O}$ thin film

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Abstract. There has been a renewed interest in zinc oxide in the materials science community after it was shown to be ferromagnetic when doped with cobalt. However, it has remained difficult to tell whether the origin of the phenomenon was intrinsic or due to secondary phases. Here, we examine with analytical transmission electron microscopy the distribution of cobalt in a thin film of ferromagnetic Al-doped $\text{Zn}_{0.7}\text{Co}_{0.3}\text{O}$ that we have grown by pulsed laser deposition on alumina. We show that precipitation of a secondary phase does occur, but that it concerns less than 10% of the cobalt atoms. The precipitates appear to be made of hexagonal metallic Co, and their average diameter is 4 nm. Their magnetism could be the reason for the low measured Curie temperature of the sample (50 K). On the other hand, the overall measured magnetization of $0.7 \mu_B$ per cobalt atom suggests that the Co atoms in solution are at the origin of most of the signal.

PACS. 68.37.Lp Transmission electron microscopy (TEM) (including STEM, HRTEM, etc.) – 75.50.Pp Magnetic semiconductors

1 Introduction

A breakthrough in the field of new materials for spintronics was the report in 2001 of room temperature ferromagnetism in Co-doped ZnO films [1]. Since then, intensive research has been carried out to assess the intrinsic nature of ferromagnetism in ZnCoO and assess the presence and the role of transition metal clustering [2]. Up to now, no definite conclusion has been drawn. During the last three years, we have carried out an extensive study of this system. We have thus grown $\text{Zn}_{1-x}\text{Co}_x\text{O}$ thin films by pulsed laser deposition (PLD) on Al_2O_3 (0001) and ZnO substrates. For $x \sim 0.3$, the low temperature magnetic moment, as measured by SQUID magnetometry, amounts on average to $1 \mu_B/\text{Co}$ atom with no significant reduction up to 400 K [3]. We investigated the Magneto-transport properties in tunnel junctions of the type ZnCoO/I/Co metal, I being an insulating tunnel barrier ($\text{I} = \text{ZnO}$, ZnMgO or SrTiO_3). We measured 3.5% tunnel magnetoresistance (TMR) at room temperature [4].

In order to better understand the ferromagnetism in this material, we carried out a set of experiments on a unique sample. The main growth parameters for this sample were a temperature of 360°C and an oxygen partial pressure lower than 10^{-6} torr (see Ref. [3] for details). The substrate was sapphire (0001) and the target

composition $\text{Zn}_{0.75}\text{Co}_{0.25}\text{O}$ with 1% alumina. Rutherford backscattering spectrometry (RBS) on test samples has shown that in those conditions such a target composition leads to a film containing 30% Co. The aluminium was added to provide n-type conductivity; it actually also modified the magnetic properties: the magnetic moment was $0.7 \mu_B/\text{Co}$ atom, not far from expectations, but contrary to undoped ZnCoO samples, there was no opening of the hysteresis cycle at room temperature. The temperature above which hysteresis cycles were no longer opened was 50 K. Undoped samples that are ferromagnetic at room temperature probably have a different microstructure. The studies we have carried out include investigations by X-ray diffraction (XRD), X-ray absorption spectroscopies (XANES, EXAFS, XMCD) [4], transmission electron microscopy (TEM) and electron spin resonance (ESR) [5]. While X-ray absorption clearly shows signals of Co^{2+} and a tetrahedral Zn-like environment [4], XRD exhibits low intensity peaks of hexagonal cobalt, the width of the XRD 0002 peak indicating an average size of 4 nm. Finally, an ESR signal can be interpreted as that of clusters [5].

The part of the study we present below concerns microstructure characterization by TEM and electron energy loss spectroscopy (EELS) in the scanning transmission electron microscope (STEM). These combined techniques allow one to measure the two populations of cobalt atoms: precipitated in metallic clusters, or dispersed in

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the matrix. One can discuss in turn the origin of the ferromagnetism in this material. As a matter of fact, we will see that the precipitates cannot by themselves account for all the measured magnetic properties: the cobalt atoms dissolved in the ZnO matrix must also play an essential role.

2 Experimental

Cross-sectional samples for TEM were thinned by mechanical polishing, using a tripod polisher to about 5 to 10 μm , then ion milled using a Gatan-PIPS ion miller (Ar, 2.5 keV, 8°) until electron transparent. Transmission electron microscopy was carried out using a Topcon EM002B electron microscope, operated at 200 kV (0.19 nm spatial resolution), equipped with a Tracor Noran energy dispersive X-ray spectroscopy (EDX) detector and a Gatan-US1000 digital camera. EELS experiments were performed in a VG HB 501 dedicated STEM, operated at 100 kV with a field emission gun and equipped with a Gatan-PEELS spectrometer coupled to a CCD detector by optical lenses. The spectrum image method [6] was employed to map the variations in concentration. The typical probe diameter was 0.7 nm, the spatial step 1.5 nm, and the recording time per pixel 0.5 s. In order to quantify the local amount of cobalt into the samples, we used ionization cross sections at the Co-L edges experimentally adjusted by comparison with EDX spectra recorded in the same area. From previous EDX measurements on Co and Al mixtures of known composition [7], we assume that the ratios of $K\alpha$ peak intensities from elements of this area of the periodic table, obtained in thin sample areas, give indeed, after applying the detector built-in correction factors, the concentration ratios of these elements with an error of the order of a percent. This ratio was in the present case equal to that expected (3 Co for 7 Zn) in all the areas analysed. We scaled the EELS cross sections so that the count ratio of the Zn-L and Co-L edges of a spectrum sum of all the 512 spectra of a 32×16 spectrum image gives this concentration. These adjustments were made using EEL spectra recorded with 1 eV per channel, which included oxygen K-edge and the L edges of all the metallic constituents of the matrix (Al, Co, Zn). In the spectra recorded at 0.5 eV per channel, such as those presented below, where only O-K and Co-L were present, the cross sections were assumed to be in the same ratio; in this case, we used the Co-L/O-K ratio as a measure of Co-L/Zn-L, assuming a constant O/(Zn+Co) ratio.

3 Electron diffraction

A first means to detect the presence of a secondary phase is diffraction, of X-rays or of electrons. We have detected small amounts of such a phase by X-ray diffraction (unpublished results). In the present section, we discuss in detail electron diffraction data. The $\text{Zn}_{0.70}\text{Co}_{0.30}\text{O}$ film appears to have a strong 0001 texture; the dimensions of

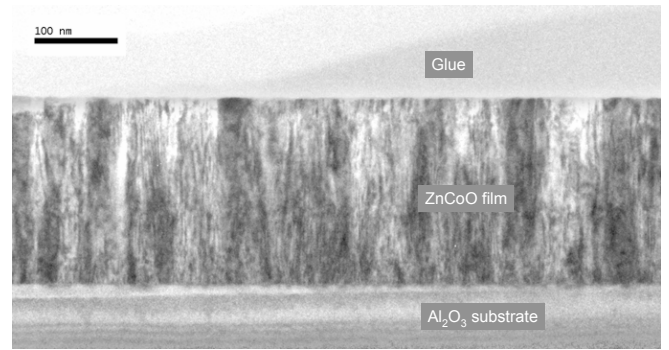


Fig. 1. TEM cross section of the sample in the $[1\bar{1}0]$ zone axis of the alumina substrate. Note the elongated shape of all grains.

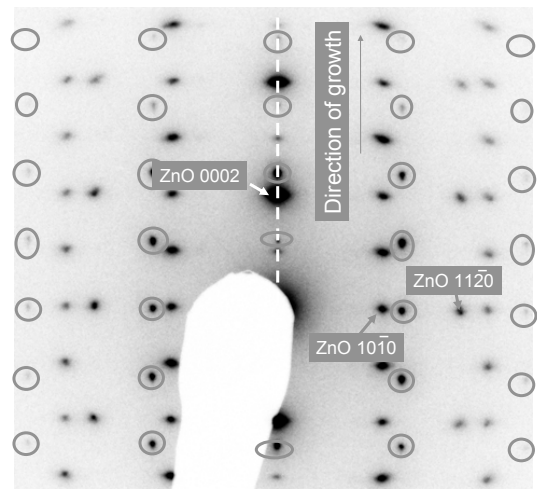


Fig. 2. Selected area electron diffraction pattern recorded in the region imaged in Figure 1, the diameter of the area selected is 500 nm. See the intensity profile along the dashed line in Figure 3. Circled spots come from the alumina substrate.

the grains are about the film thickness in length and between 10 and 50 nm in width (Fig. 1).

A selected area electron diffraction pattern of the region imaged in Figure 1 is presented in Figure 2. Quite remarkably given the large number of grains that contribute to the pattern, essentially only two orientation variants of the ZnCoO film occur in this region, both with their c axis aligned on the sapphire c axis. These orientations are that of the substrate on the one hand, and one that is rotated 90° with respect to the common c axis on the other hand. Therefore most of the grains appearing in Figure 1 are in a twin relationship with one another, which might give their grain boundaries specific properties. Using the substrate reflections as internal references, the crystal parameters of the film can be measured with an accuracy of a fraction of percent. The film spot positions give reticular distances very close to those of pure bulk ZnO: along the c axis, $d_{0002} = 2.62 \text{ \AA}$, which represents a 0.6% increase with respect to pure ZnO; in the basal plane, the d -values of the film are equal within error to those of ZnO.

Another remarkable point in this pattern is that all the spots that are visible without contrast enhancement

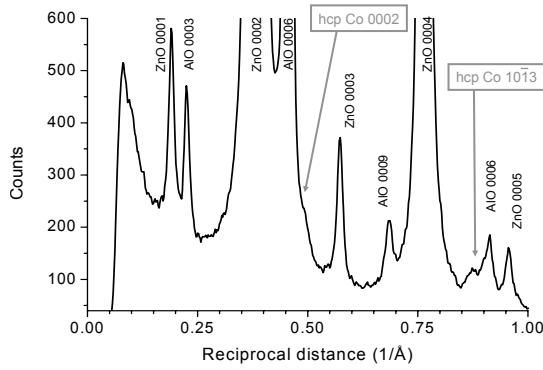


Fig. 3. Diffracted intensity along the line shown in Figure 2. Two peaks (arrowed) can be attributed to hcp cobalt.

can be identified as belonging to either the substrate or the ZnO phase of the films: given the linear response of the camera this already means that the contribution from a secondary phase is small. However, when recording a profile along the growth axis (see Fig. 2) and displaying it with an enlarged scale, such a phase clearly appears (Fig. 3). Two peaks that can be attributed to neither ZnO nor alumina can be discriminated from the background noise (arrows in Fig. 3). Given the intrinsic width of the peaks and their small amplitude, the d -values of the second phase can be evaluated with less precision than that of the ZnCoO matrix. The spots correspond to distances $d_1 = 2.015 \pm 0.02 \text{ \AA}$, and $d_2 = 1.14 \pm 0.02 \text{ \AA}$. We attribute them to metallic hcp cobalt ($d_{0002} = 2.023 \text{ \AA}$, and $d_{10\bar{1}3} = 1.149 \text{ \AA}$), probably distorted. Given the presence of these reflections along the reciprocal c axis, one would expect the presence of the $10\bar{1}0$ or $11\bar{2}0$ (for the parallel orientation), and $10\bar{1}1$ (for $10\bar{1}3$ orientation) reflections of hcp cobalt in the basal reciprocal plane. We have then made a profile similar to the previous one along the horizontal axis. Reflections indeed come out of the background at $d_3 = 2.17 \pm 0.02 \text{ \AA}$ ($d_{10\bar{1}0} = 2.17 \text{ \AA}$), $d_4 = 1.96 \pm 0.02 \text{ \AA}$ ($d_{10\bar{1}1} = 1.91 \text{ \AA}$). This gives a very strong clue of the presence of hcp cobalt in our samples. To quantify this presence is however delicate using such signals as they are very close to the noise level. We will rather make such an evaluation using direct imaging of the Co particles and EELS (see Sects. 4, 5). The fact that our d_4 value is larger than $d_{10\bar{1}1}$ of hcp Co by 2.6% would indicate that the precipitates considered (which belong to the $10\bar{1}3$ family) are either in tension in the plane or that they contain constituent other than cobalt, which in turn might modify their magnetic properties.

4 TEM images of Co precipitates

In carefully chosen orientations, cobalt precipitates can be visible in TEM through the moiré patterns (Fig. 4) that their crystallographic planes make with those of the matrix. The orientation relationships being rarely exact, these moirés can be found with a wide variety of periods and orientations. Assuming that in the zone orientation

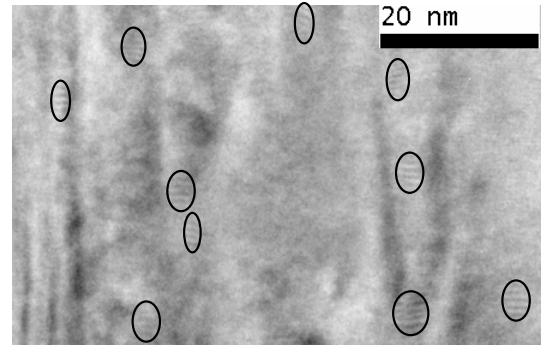


Fig. 4. TEM cross section in a thin part of the area shown in Figure 1, in the same zone axis, but at higher magnification. Note the presence of precipitates visible thanks to their moiré fringes (circled).

of Figure 4, most of the precipitates give moirés, and supposing a given thickness to the foil, one can estimate the absolute density of precipitates in the sample. Then, their average size being measurable, one can infer the absolute fraction of the cobalt atoms that are in the form of metal precipitates. As this procedure implies quite an amount of assumptions, it is necessary to analyse the matrix between the particles and check whether the concentration found there is compatible with the counting made here. We will see with EELS mapping (Sect. 5) that the evaluation which follows is reasonable.

In Figure 4, most of the precipitates visible exhibit moiré fringes perpendicular to the c axis, with a period of about $9 \text{ \AA}$, which indicates that they belong to the 0002 -oriented family. Supposing a sample thickness greater than 20 nm , their number in the image corresponds to a density $d_{\text{precipitates}} < 2 \times 10^{17} \text{ cm}^{-3}$. This makes the average distance between precipitates greater than 17 nm . Given an average size of 4 nm , each precipitate contains on average less than 4000 Co atoms . This indicates that the total cobalt density in the form of metallic precipitate is less than $8 \times 10^{20} \text{ cm}^{-3}$. As in principle, 30% of the Zn sites are occupied by Co atoms, the total density of these atoms is $0.3 \times 4.2 \times 10^{22} \text{ cm}^{-3} = 1.26 \times 10^{22} \text{ cm}^{-3}$. This indicates that less than 7% of the Co atoms are in precipitates such as those visible in Figure 4; or in other words, more than 93% of the Co atoms are in another form, perhaps in solution in the matrix. This can be checked accurately by EELS.

5 EELS mapping of Co atoms

In this section, we will spatially localise all the Co atoms using electron energy loss spectroscopy (EELS) in the ‘spectrum image’ mode. Comparison of the maps made with the O-K and Co-L edges (Fig. 5) allows one to locate without ambiguity a metallic cobalt precipitate. Moreover after properly scaling the signals, these maps provide the actual ratio of Co with respect to Zn at each nm-sized pixel: in Figure 6, it thus appears quite clear that most of the cobalt atoms are localised outside the precipitates,

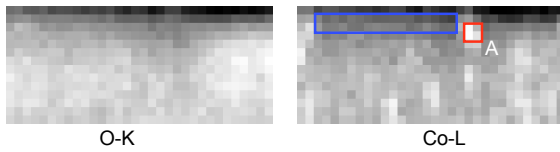


Fig. 5. Elemental maps deduced from the O-K and Co-L regions of an EELS spectrum image. The pixel size is 1.5 nm. The spectra corresponding to the pixels squared in the Co image are displayed in Figure 8. The black area on top is a hole in the thin foil.

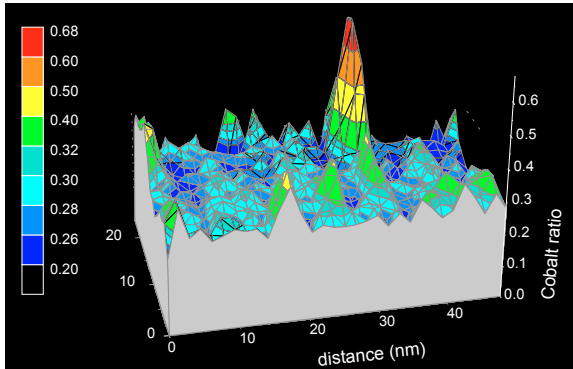


Fig. 6. Three-dimensional EELS map of the cobalt ratio $\text{Co}/(\text{Zn}+\text{Co})$ deduced from the maps in Figure 5. The value of the $\text{Co}/(\text{Zn}+\text{Co})$ ratio is coded in colour (grey-levels in the printed version) following the scale in inset.

and that their concentration is fairly constant at around 28%.

As this picture has been recorded in a very thin area of the sample next to the hole, this undoubtedly indicates that most of the cobalt atoms are not in the form of clusters.

As there is one spectrum per pixel, we can now compare a spectrum recorded on a cluster (A in Fig. 5), and the spectrum sum of all spectra, representing the matrix (Fig. 7). We can see that there is a significant signal from oxygen in the precipitate spectrum, which is related to the fact that, even in a very thin sample area, there must be a given thickness of matrix superimposed over this ~ 4 -nm cluster. Pure fine structure information from the precipitate cannot thus be obtained; however, there is a definite difference between the average of the four pixels where the precipitate modifies the signal and an average of 34 pixels taken at the same sample thickness in the matrix (Fig. 8). Most noticeably, the background between the Co-L_2 and L_3 lines is higher in the precipitate spectrum. If we now compare these spectra to reference spectra recorded in equivalent conditions on Co and CoO [8] (dotted lines in Fig. 8), we find indeed that a low background corresponds to an oxidised form, whilst a high background corresponds to metal. Although this is no surprise, these comparisons unambiguously show that the Co atoms that are in the matrix are in an oxidised form. This has been confirmed and detailed by X-ray absorption experiments [4].

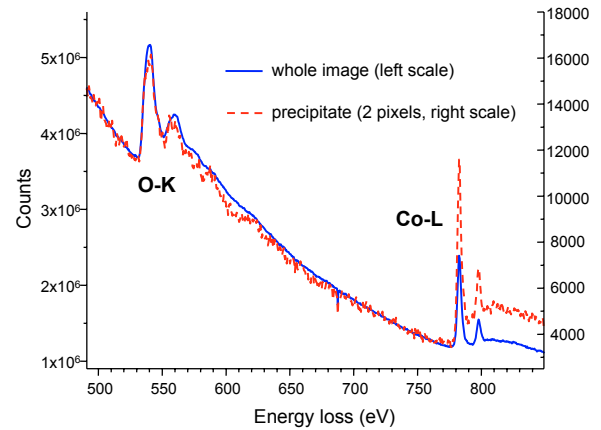


Fig. 7. Comparison between a spectrum recorded on the Co cluster 'A' in Figure 5 and a spectrum sum of all the spectra in Figure 5. (Colour in the electronic version.)

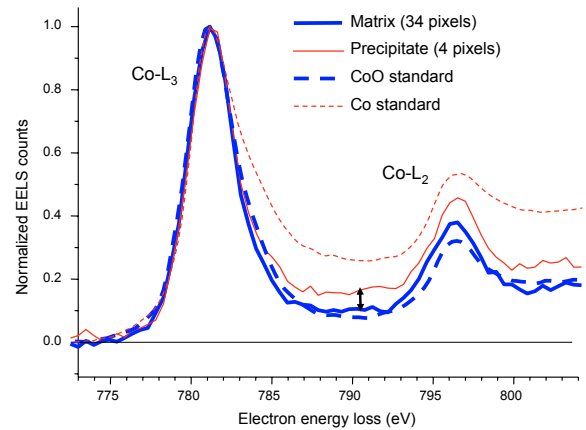


Fig. 8. Comparison of the $\text{Co-L}_{2,3}$ edges recorded on precipitate and matrix to Co and CoO references from the work of reference [8]. See Figure 5 for the definitions of 'precipitate' and 'matrix'. (Colour in the electronic version.)

6 Discussion and conclusion

The combination of electron diffraction (Fig. 2), TEM imaging (Fig. 4), and EELS quantitative mapping, shows that cobalt atoms are present in at least two types of sites in the sample analysed: in metallic hcp precipitates for less than 10%, and matrix sites for the rest. Comparison with the measured magnetic properties tends to indicate that both types of Co atoms are magnetically active. hcp cobalt particles should be super paramagnetic with a blocking temperature proportional, to first order, to their volume. A rough calculation indicates that this temperature, for hcp-Co spheres with a diameter of 4 nm, should be ~ 50 K, the temperature where we observe the closure of the hysteresis cycle. This tends to show that, although they represent a small fraction of the Co atoms, the metallic particles probably participate in the global magnetic properties of the film. In other respects, if all the magnetism originated in the particles, their magnetic moments would need to be as high as $\sim 10\mu_B$ per Co atom, which is not likely in metallic cobalt. We therefore conclude that

both types of cobalt atoms play a role in the measured magnetism: those in the metallic precipitates and those in the matrix. Future and more detailed experiments are under way to clarify these two roles.

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