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Advantageous use of metallic cobalt in the target for Pulsed Laser Deposition of cobalt-doped ZnO films

Minju Ying[1,2*], Harry J. Blythe[1], Wala Dizayee[1,3], Steve M. Heald[4], Fatma M. Gerriu[1], A. Mark Fox[1], and Gillian A. Gehring[1*]

[1]Department of Physics and Astronomy, University of Sheffield, Sheffield S3 7RH, UK

[2]Key Laboratory of Beam Technology and Material Modification of Ministry of Education, College of Nuclear Science and Technology, Beijing Normal University, Beijing 100875, P.R. China

[3]Department of Science, Salahaddin University, Erbil, Iraq

[4]Advanced Photon Source, Argonne National Laboratory, Argonne, IL 60439, USA

[*]Contact authors:英敏菊 mjying@bnu.edu.cn; g.gehring@sheffield.ac.uk

Abstract

We investigate the magnetic properties of ZnCoO thin films grown by pulsed laser deposition (PLD) from targets made containing metallic Co or CoO precursors instead of the usual Co_3O_4. We find that the films grown from metallic Co precursors in an oxygen rich environment contain negligible amounts of Co metal, and have a large magnetization at room temperature. Structural analysis by X-ray diffraction and magneto-optical measurements indicate that the enhanced magnetism is due, in part, from Zn vacancies that partially compensate the naturally occurring n-type defects. We conclude that strongly magnetic films of $Zn_{0.95}Co_{0.05}O$ that do not contain metallic cobalt can be grown by PLD from Co-metal-precursor targets if the films are grown in an oxygen atmosphere.

Cobalt-doped ZnO (ZnCoO) is a promising magnetic semiconductor that combines room temperature ferromagnetism with a wide direct bandgap.[1-3] Despite the large body of work, the origin of the room-temperature ferromagnetism still remains controversial. The most common growth method is pulsed laser deposition (PLD); which has several desirable characteristics for the growth of complex oxide thin films compared to other film growth techniques. These include the stoichiometric transfer of material from the target to the film and the control of oxygenation during the film growth. A general trend for Co-doped ZnO has been to find that a deficiency of oxygen in the growth chamber enhances the ferromagnetism through the formation of donor states[4-7] and that annealing films in air or oxygen quenches any magnetization[8-10] although there are also a few conflicting results in which magnetism is observed in ZnO oxygenated films with and without doping with Co.[11,12] The role of metallic Co precipitates is less clear, with some authors claiming that they are responsible for all of the observed magnetic properties[13-15]; however, other authors have identified ferromagnetic phases in ZnCoO films that lack any metallic component.[16,17]

The PLD growth of ZnCoO starts from a target that has been made to the desired composition by a solid-state reaction of a Co-containing compound and zinc oxide. The oxygen content of the films is normally controlled by varying the oxygen pressure in the PLD chamber during the growth. However, the choice of the Co target precursor compound provides an alternative method to influence the oxygen content of the films.

In the present work we investigate the properties of Zn0.95Co0.05O thin films grown from targets made by mixing ZnO powder with powders of either metallic Co or CoO and compare them to films grown from the more standard targets made by mixing ZnO and Co3O4 powders.[14,18] In all cases, the targets were made from the powders by a process of sequential grinding for 30 minutes, using a pestle and mortar, and then sintering at 400 °C, 600 °C, 800 °C and 1000 °C in air for 12 hours. We find that films grown with metallic Co in the target, plus some oxygen in the PLD chamber, are ferromagnetic but contain no detectable fraction of metallic cobalt. Both structural analysis and magneto-optical measurements point to the presence of Zn vacancies in the oxygenated films, and we conclude that the observed magnetism is related to the partial compensation of the donor states. The most important feature of this work is that we have identified a method to grow by

PLD ferromagnetic films of ZnCoO that do not contain metallic Co, namely, to use metallic Co in the process of making the target and to compensate for the lack of oxygen by including oxygen gas in the growth chamber. Such films should find applications in spintronics as the magnetism is due to polarized electrons in extended defect states, so that they can act as sources of polarized carriers.

Three different PLD targets all with the same nominal composition of $Zn_{0.95}Co_{0.05}O$were prepared by the solid-state reaction technique in which high-quality ZnO was mixed with either Co metal, CoO or Co_3O_4 powders. The powders purchased from Alfa Aesar had purities of 99.9995% for ZnO, 99.998% for Co metal, 99.995% for CoO and 99.9985%for Co_3O_4. Five films were ablated at a substrate temperature of 450 °C for the same deposition time of 40 minute. The substrates were double-sided-polished, single-crystal, C-cut sapphire with dimensions 5mm×5mm from Pi-Kem. A Lambda Physik LEXTRA 200 XeCl excimer laser with an operating wavelength of 308 nm and a 10 Hz repetition rate was used for the ablation of the target. The key properties of the films are summarized in Table I. Films A, B, and C were grown from the Co-metal precursor target at three different oxygen pressures, starting at base pressure (3×10^{-2} mTorr). For films grown in oxygen pressure, the pressure is set at 10 mTorr or 100 mTorr by a gas flow controller during the growth process. These films enable us to study the influence of off-setting the oxygen deficiency in the target by including oxygen during the PLD growth. Films D and E, which were grown from the CoO or Co_3O_4precursor targets, respectively, enable us to compare the effects of the Co chemistry of the precursor on the properties of the films grown at base pressure. We only grew films at base pressure because of the extensive results on oxygenating ablated films made from targets containing Co_3O_4.[4,8-10]

The concentrations of Co in the films were evaluated by Energy Dispersive X-Ray spectroscopy (EDX), and are given in Table I. With the exception of film C, the values are higher than the target by a factor of ~1.5, which is typical for PLD films.[19] The lower Co concentration for film C may be due to the oxygen gas in the PLD chamber slowing the Zn ions sufficiently to enhance their probability of sticking to the film.

Table I. Key parameters of the films: the precursor, the pressure in PLD chamber during film deposition, the films thickness as measured using a Dektak surface profiler,

the concentrations of Co in the films as determined by EDX, the c lattice parameters and grain sizes deduced from XRD, fraction of Co atoms present as Co metal given by x-ray absorption, saturation magnetization M_s at 5K and 300K, and saturation magnetization expected from the metallic Co contribution.

	Precursor (5%)	Pressure (mTorr)	Thickness (nm)	% Co in films	c lattice (Å)	Grain size (nm)	Fraction of Co in form of Co metal	Ms(emu/cm^3) 5K, 300K		Magnetization from metallic Co (emu/cm^3)
A	Co	3×10^{-2}	730	8±1	5.249	35.0	0.24±0.02	13.5	~2	12.7
B	Co	10	300	8±0.5	5.218	42.2	0.0±0.02	7.6	6.7	~0
C	Co	100	100	4±1	5.209	50.6	0.0±0.02	12.5	9.1	~0
D	CoO	3×10^{-2}	580	7±0.3	5.258	42.2	0.09±0.02	6.4	~0	4.1
E	Co_3O_4	3×10^{-2}	640	7±0.3	5.260	36.2	0.10±0.02	10.2	~0	4.6

The lattice constants and grain sizes were measured by x-ray diffraction (XRD) using an X'Pert PRO MPD diffractometer using a $\theta - 2\theta$ scan [20]. The grain sizes were deduced from the line widths using the Scherrer equation; the largest grains occurred for the film grown at higher oxygen pressure. The c lattice constants of films A, D and E are all larger than the accepted range for pure ZnO, which is between 5.2042 and 5.2075Å.[21] Our results appear to indicate that the films grown at base pressure contain Zn interstitials and the reduction in the lattice constant seen for the films grown at higher oxygen pressures indicates a reduction in the number of Zn interstitials, coupled with an increasing number of Zn vacancies as the level of oxygen was increased.[22]

The relative amounts of Co^{2+} and metallic Co in the films were studied by x-ray absorption and extra-fine-structure-absorption spectroscopy (XAS and EXAFS) using the beamline 20-BM at the Advanced Photon Source at the Argonne National Laboratory. The samples were measured at an incident angle of 6° with the x-ray polarization perpendicular to the plane of the films (along the c-axis). Figure 1(a) compares the near-edge spectra with a previously measured sample that had all of the Co in substitutional Zn^{2+} sites.[23] A spectrum for pure Co is also included for reference. All of the samples showed a dominant signal from substitutional Co, but some had a small metallic Co contribution, as indicated by an increased signal in the region indicated by the arrow. To quantify the amount of metal, linear combination fits were carried out using the Athena program.[24] The results are listed in Table I. The striking finding is that all of the films grown at base pressure contained significant amounts of metallic Co, but not the films grown at higher oxygen pressure, even though they were both made from targets based on metallic Co.

The environment of the Co ions was checked using EXAFS. The near-edge spectra of these films were compared with two standards: a film of ZnCoO which was known to be fully substitutional and with metallic Co; these results were analyzed to give the percentages of metallic Co in the samples as given in Table I. The data from sample B was transformed to give the electronic density around the Co ions and the result compared to that expected if all the Co ions were on Zn sites as shown in Fig. 2(b); the comparison indicates that the Co was substituting on the Zn sites. The near-edge data for films E and D, shown in figures 1(c) and (d), were compared with metallic Co, Co_3O_4 and CoO. No signal from the precursors, Co_3O_4 or CoO, was detected.

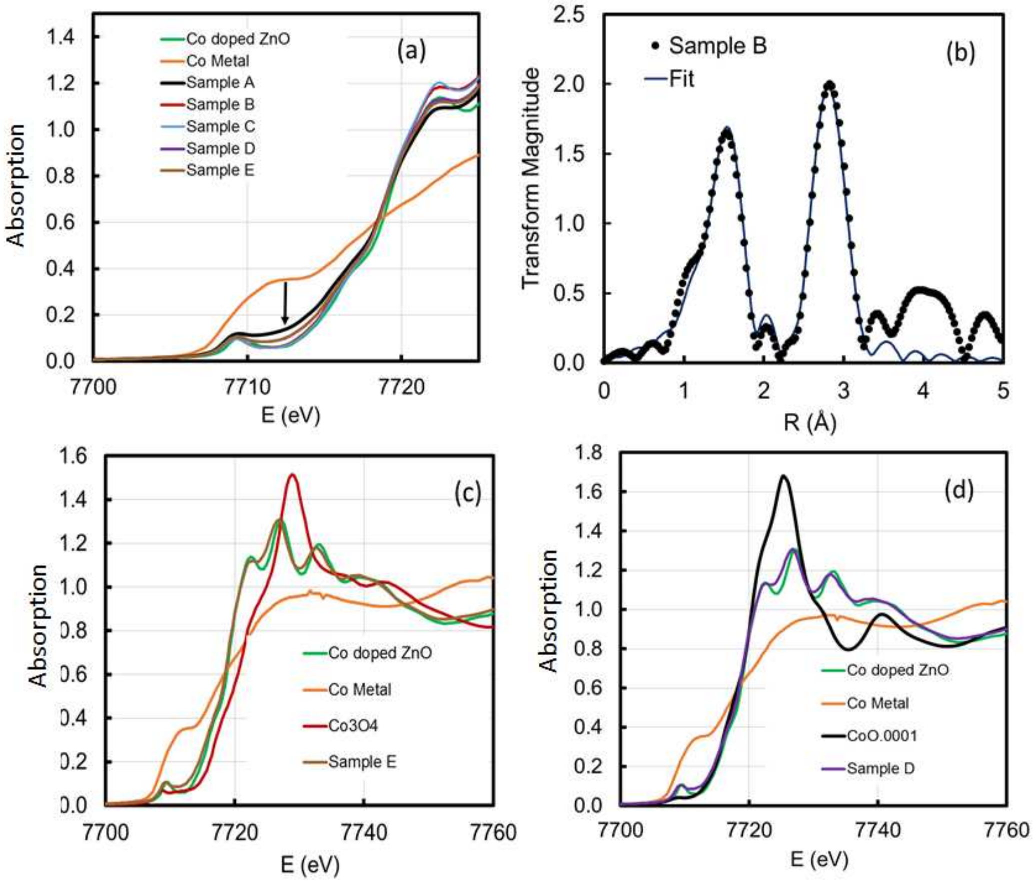

Fig. 1(Color online)(a)X-ray near edge spectrafor films A – E. For comparison, the edge

step height has been normalized to 1, and results are also shown for a sample that had all of the Co substituting for Zn on Zn sites (shown in green) and also a pure Co sample (shown in orange). (b) Comparison of the EXAFS transform data for sample B fitted to the expected function for fully substitutional Co^{2+} (c) A comparison of the X-ray near edge spectra for sample E with that expected for metallic Co and for Co_3O_4(d). An equivalent plot for sample D comparing it with metallic Co and CoO.

Magnetization measurements taken with a SQUID magnetometer are presented in Figure 2. Hysteresis loops for the three films grown from the metallic precursor are shown in Fig.2(a) while Fig. 2(b) shows the magnetization loops for the three films grown at base pressure. The values of the saturation magnetization, M_s, at 5 K and 300 K are summarized in Table I. The most striking feature of the data is that M_s remains high at room temperature only for films B and C, i.e. the films grown from the Co precursors in an oxygen environment. This is interesting because up until the present time Co_3O_4 has been the most commonly used precursor for the production of ZnCoO targets for PLD.

The structural data in Table I indicate the presence of metallic Co nanoparticles in the films grown at base pressure (films A, D and E). It is therefore important to separate out any ferromagnetic contribution from metallic clusters from the total magnetization of the samples. The contribution of the metallic clusters at 5 K can be estimated by assuming that at 1T the Co atoms carry the usual moment of 1.78 μ_B. The values listed in the final column of Table I were deduced from the measured concentration of Co in the films and the fraction of Co atoms that are in the metallic state. This analysis indicates the magnetism of film A could be entirely due to the metallic Co, while the other films show an additional component due to the Co^{2+} in ZnO. The very small magnetization observed at 300K indicates that only a small fraction of the metallic Co nanoparticles in film A are saturated in 1T ($m_{nano}B < 300k_B$) implying that the particles are very small <2nm. The larger additional magnetization of film E, due to the intrinsic magnetization of the Co-doped ZnO, compared to D may be due to magnetism arising from the grain boundaries,[25] as this film has smaller grains. (See Table I.)

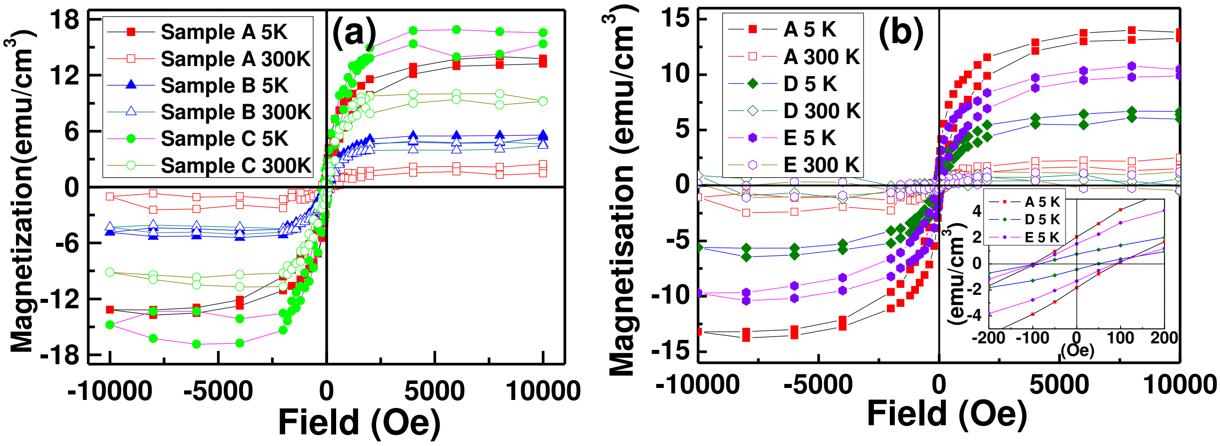

Fig. 2(Color online)The ferromagnetic component at 5K and 300K for (a) films A, B and C, and (b) films A, D, and E (the diamagnetic contribution from the substrate and temperature dependent paramagnetic contributions from the films have been subtracted from the raw data).

Magnetic circular dichroism (MCD) spectra were taken in order to determine the energies of the spin-polarized electron states using the system based on a photo-elastic modulator.[26] The MCD spectrum measures the fractional difference of the absorption for left and right polarization, which is determined by the orbital polarization of the states that are involved in the electronic transitions, and is zero in the absence of magnetism. The observed magnetization is dominated by the electron spins and hence the MCD measures the product of the spin polarization and a factor that depends on the spin-orbit coupling. We focus our attention here especially on the spectral region at and below the band gap at 3.4 eV, since this is where the magnetically polarizable defect states occur.

The spectra taken in a field of 1.2T at room temperature for films A, D and E are shown in Fig. 3(a), and those for films A, B and C in Fig. 3(b). These MCD signals include the following features:

(1)the dispersive feature due to the d-d transition from Co^{2+} ions at around 2eV.

(2) a broad negative signal crossing the axis at ~3eV indicating metallic Co cobalt[27-29]

(3) a broad positive signal indicating the presence of Zn vacancies[30]

(4) a sharp negative dip at E>3.3V indicating a spin-polarized band[31,32]

All the samples show the d-d transition (feature 1). This is expected, as the XAS indicates that at least 76% of the Co in each sample was in the form of Co^{2+}. The three films made at base pressure, A, D, E, show a signal from the metallic Co cobalt (feature 2). This is largest for film A, which had the largest concentration of metallic Co cobalt (See table I). Films A, D and E also show a strong negative signal at the band gap (feature 4) which is characteristic of films that have been grown at base pressure and arises from a spin split conduction band.[29]

The most striking feature of the MCD spectra in Fig. 3(b) for the three films prepared from metallic Co is the replacement of the negative signal from metallic Co by a positive signal in the range 2.3-3.0eV (feature 3). This feature first appears in film B (growth pressure 10mTorr) and grows in strength in film C, grown at 100mTorr. The positive MCD signal for 2<E< 3eV occurs as the spin polarized single electron trapped at the Zn vacancy site is excited to the conduction band.[12,18]

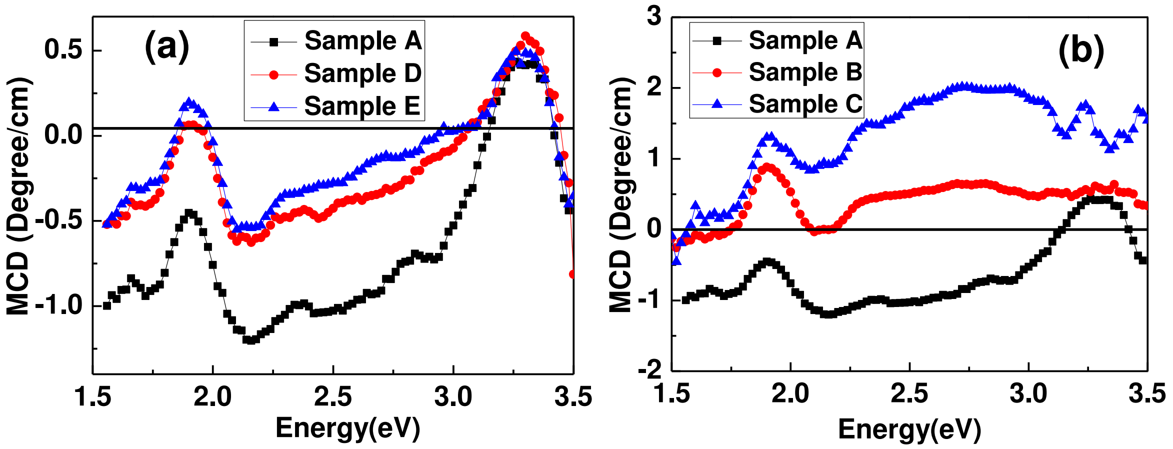

Fig. 3(Color online)MCD spectra for Zn$_{0.95}$Co$_{0.5}$O films prepared at base pressure with different precursors (a) and for Zn$_{0.95}$Co$_{0.5}$O films prepared at different oxygen pressure with Co metal as the target precursor (b).

The combination of structural, magnetic and MCD data presented above enables us to draw conclusions about the origin of the magnetism in the samples. The three films grown at base pressure from different targets all contain small superparamagnetic clusters of metallic Co that dominated the magnetism at low temperatures but had almost vanished in 1T at 300K. The film grown from the Co$_3$O$_4$ target had the largest contribution due neither to Co metal nor residual Co$_3$O$_4$ at low temperature, but this had also vanished by 300K.

The results for films B and C that were both grown from the Co-metal precursor in an oxygen atmosphere are particularly significant. Film C had the largest magnetization at room temperature and a sizeable coercive field of 185Oe at 5K. The origin of its magnetism is made clear from the XRD and MCD data that point to the presence of vacancies on the Zn sublattice that can partially compensate for the naturally occurring n-type oxygen vacancies and Zn interstitials. The magnetization is due to a cooperative interaction between the electrons moving between the sites of the Zn vacancies; a theoretical cluster model for ZnO supports this view.[33] In film C, grown at the highest oxygen pressure, this magnetism is strong enough to also produce a small spin-splitting of the hole states in the valance bands that is observed in MCD.

This study differentiates these films made with metallic cobalt as the Co precursor from the other samples made with Co_3O_4 which are magnetic only when they are oxygen deficient due to Zn interstitials and oxygen vacancies. In these n-type samples, the magnetization decreases sharply as oxygen is added.[4,8-10]

An undoped ZnO film has Zn interstitials and O vacancies when oxygen deficient and Zn vacancies and O interstitials when grown with excess oxygen. The magnetism in the films with excess oxygen is due to Zn vacancies.[12] The addition of Co in the films may prevent the formation of Zn vacancies because the excess oxygen is compensated by the inclusion of Co^{3+}, this is seen by the quenching of the PL signal from the Zn vacancies.[34,35] We postulate that films grown with Co_3O_4 as the precursor are more likely to develop Co^{3+} ions than films grown with metallic Co. Hence the Zn vacancy magnetism occurs preferentially in the films of ZnCoO made with the metallic precursor.

We conclude that films made with metallic Co as a precursor and grown in an oxygen atmosphere are different from the majority of films of $Zn_{0.95}Co_{0.5}O$ that have been studied so far. The choice of precursor in the target is important, even though neither of the oxide precursors was found to be present in the film. In samples that are dominated by n-type Zn interstitials and oxygen vacancies the magnetization decreases sharply as oxygen is added.[4] In contrast, in the films grown from Co metal precursors that have Zn vacancies, we found the largest RT magnetization in films grown at the highest pressure, which also had the largest grain sizes. The results indicate that the use of Co-metal as the precursor for the target is beneficial for the growth of films that do not contain metallic Co but are strongly magnetic.

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