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Structural and magnetic characterization of mixed valence Co(II, III)$_x$Zn$_{1-x}$O epitaxial thin films

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ABSTRACT

In this article, we report on the Co atom incorporation, secondary phase formation and composition-dependent magnetic and optical properties of mixed valence Co(II, III)$_x$Zn$_{1-x}$O epitaxial thin films grown by pulsed laser deposition. The intended total Co concentration is varied between ~6–60 at.% with relatively higher concentration of +3 over +2 charge state. Mixed valence Co(II, III) shows high solubility in ZnO (up to 38 at.%) and ferromagnetism is observed in samples with total Co incorporation of ~29 and 38 at.%. Electron diffraction pattern and high resolution transmission electron microscopy images reveal single crystalline nature of the thin films with wurtzite structure. Co oxide interlayer, with both rock salt and spinel structure, are observed to be formed between the substrate and wurtzite film for total Co concentration at ~17 at.% and above. Magnetization shows composition dependence with a saturation moment value of ~93 emu cm^{-3} and a coercive field of ~285 Oe observed for ~38 at.% Co:ZnO films. Ferromagnetism was not observed for films with Co concentration 17 and 9 at.%. The Co oxide interlayer does not show any ferromagnetism. All the films are *n*-type with carrier concentration ~10^{19} cm^{-3}. The observed magnetism is probably resulting from direct antiferromagntic exchange interaction between Co^{2+} and Co^{3+} ions favored by heavy Co alloying giving rise to ferrimagnetism in the system.

1. Introduction

Ferromagnetic semiconductors have attracted intense research activities due to their fascinating possibilities for novel spin electronic devices such as non-volatile transistors and spin LEDs as well as possibilities for integrating logic, storage and communication functionalities on a single platform [1,2]. In the context of relevant materials for spintronics, Dietl et al. had predicted within mean field approximation that ZnO might be a potential candidate for room temperature dilute magnetic semiconductors (DMS) [3,4]. This demands the material to have *p*-type carrier concentration ~10^{20} cm^{-3} and solubility of transition metal to few percentages in order to realize *p–d* exchange mediated DMS. However, *p*-type doping in ZnO remains elusive [5]. Nonetheless, in search for experimental room temperature ferromagnetism (RTFM), ZnO doped with different transition metals have been investigated extensively and contradictory reports exist in the literature on the observation of RTFM in ZnO with and without doping with transition metal impurities [6–8]. Among various proposals, metal cluster [9,10], oxygen point defect [11], unintentional hydrogen doping [12] and Zn interstitial [13] have been considered as sources of RTFM in ZnO. Point defects play an important role in controlling many physical properties in ZnO and in this context Coey et al. have put forward an oxygen point defect mediated bound magnetic polaron (BMP) model that has yet to be experimentally verified [14]. In another report, Coey et al. suggested that the doping of mixed valence TM could be an effective approach to enhance the magnetization in wide gap semiconductor (Fe doped TiO$_2$) through charge transfer to the defect band near Fermi level [15]. This charge transfer will cause the defect band to spin split according to Stoner criteria. Various crystallographic defects have been proposed, e.g., point defects, line defects, interfaces and boundary between phase separated regions, from which defect band might originate. In one report, antiferromagnetic Co$_3$O$_4$ doped with diamagnetic ZnO and TiO$_2$ powders was found to be ferromagnetic at room temperature attributed to octahedral reduction of Co^{3+} to Co^{2+} at the surface [16,17]. Besides this, to the best of our knowledge there are no detailed studies related to the effect of mixed valence Co:ZnO on the structure and magnetic properties particularly in the form of thin film single crystals. In the present report we have investigated the structure, secondary phase formation, optical emission and magnetism in ZnO doped with mixed valence Co(II, III) as a function of total Co

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concentration ($x=7$, 13, 27, 58 at.%, with relatively higher proportions of $+3$ charge state by mixing CoO and Co_3O_4 together with ZnO). Our results indicate the existence of ferro/ferri magnetism at relatively higher concentration of Co (for targeted 58 and 27 at.% of Co) as compared to our previous reports on CoO doped ZnO, where ferromagnetism was observed even at low Co concentrations [18]. Due to the high Co content, Co-rich CoO and Co_3O_4 cubic phases are observed to form between the wurtzite Co:ZnO film and sapphire substrate. These cubic phases do not exhibit any ferro/ferri magnetism as confirmed by magnetic measurement on thin film grown up to the interlayer formation stage.

2. Experimental techniques

Sintered pellets were prepared by mixing and grinding powders of Co_3O_4, CoO and ZnO obtained from Sigma Aldrich (99.9% purity). A higher concentration of Co(III) was taken than Co(II) to vary the total Co content in the films as 58, 27, 13 and 6 at.% (we refer to them as S1, S2, S3 and S4, respectively). We also have interrupted the growth of S1 sample to the first and second stage (sample S5 and S6) [19] in order to evaluate the structure and magnetism due to the Co rich interlayer phases. The relative amount of Co $+2$ and $+3$ charge states out of the total Co content is given in Table 1. Sintering was performed at 900 °C for 6 h under atmospheric pressure with slow ramping to allow sufficient time for calcinations of the binder. All the films were grown on *c*-plane sapphire (MTI corporation, USA) following our single crystal/epitaxial growth scheme employed in PLD under *n*-type growth condition (O_2 partial pressure 10^{-5} Torr) [19]. An excimer laser ($\sim$248 nm) with energy fluence $\sim$1.5 J cm^{-2} was used to ablate the target pellets. Energy dispersive spectroscopy was done both in SEM and TEM characterization to quantify the Co incorporation both in the pellets and thin films, respectively. Hall measurement was carried out in an ECOPIA Hall apparatus. Magnetic measurements were carried out in a superconducting quantum interference device (SQUID) magnetometer. Magnetization data is presented in terms of per unit volume of the film instead of per Co atom, with the thickness data obtained from cross sectional TEM images. Microstructure, secondary phase formation, high resolution imaging, dopant incorporation and charge state determination were performed through diffraction, imaging and electron energy loss spectroscopy techniques in a FEI TITAN^{3TM} 80–300 kV aberration corrected transmission electron microscope. Cross sectional TEM samples were prepared by conventional mechanical polishing followed by Ar ion milling to create large electron transparent areas. Cathodoluminescence (CL) spectra were collected using a Gatan mono CL (serial mode) in FEI quanta 3D FE-SEM with 20 keV electron beam energy. All spectra have been collected with Peltier cooled (-25 °C) photo multiplier tube (PMT) with a step of 1 nm and acquisition time of 0.6 s step. Entrance and exit slit for the spectrometer were set at 1 mm.

3. Results and discussion

3.1. Composition analysis

SEM-EDS has been used to quantify the Co content with respect to Zn both in the pellets (after sintering) and thin films (after PLD

Table 1
SEM and TEM EDS quantification from various areas of pellets and thin film samples.

Samples	Targeted Co concentrations (at.%)			SEM EDS (Pellets) Co (at.%)	SEM EDS (Film) Co (at.%)	TEM-EDS			
						Co:ZnO		IL	
	Co(III)	Co(II)	Total Co			Co	Zn	Co	Zn
S1	35	23	58	54	56	38	62	83	17
S2	16	11	27	28	41	29	71	67	33
S3	8	5	13	16	13	17	83	–	–
S4	4	3	7	9	10	9	91	–	–
S5 (one step)	–	–	–	–	–	26	74	29	71
S6 (two step)	–	–	–	–	–	48	52	86	14

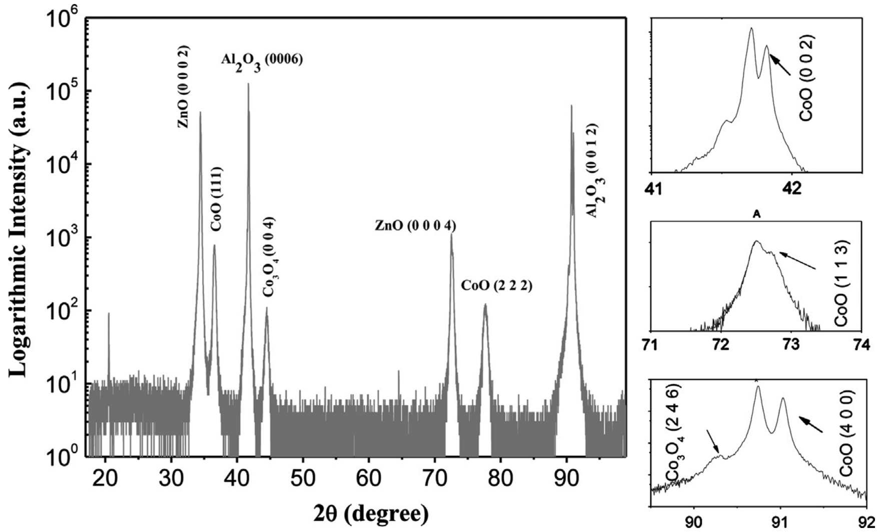

Fig. 1. X-ray diffraction data from sample S1. Considering the powder diffraction data as well as constraint of the thin film orientation on substrate (taking help from TEM), the peaks have been assigned to different phases. Inset displays the presence of other peaks at the relevant angular position.