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Effect of annealing on $Zn_{1-x}Co_xO$ thin films prepared by electrodeposition

A. El Manouni^{a,b}, M. Tortosa^a, F.J. Manjón^a, M. Mollar^a, B. Marí^{a,*}, J.F. Sánchez-Royo^c

^a *Departament de Física Aplicada—ETSED, Universitat Politècnica de València, Camí de Vera, s/n, 46022 València, Spain*

^b *Departament de Physique, Faculté des Sciences et Techniques, Université Hassan II, Mohammedia, Morocco*

^c *Departament de Física Aplicada—ICMUV, Universitat de València, C/Dr. Moliner 50, 46100 Burjassot, València, Spain*

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ABSTRACT

Polycrystalline thin films of $Zn_{1-x}Co_xO$ with different cobalt (Co) content were grown on indium tin oxide (ITO) substrates by cathodic electrodeposition technique and subsequently annealed in air at 400 °C. The effect of annealing in their structural, optical and chemical properties has been characterized by X-ray diffraction (XRD), energy-dispersive spectroscopy (EDS), X-ray photoelectron spectroscopy (XPS), Raman scattering and optical spectroscopy. Our measurements indicate that moderate annealing increases the crystal quality of the films. The films are highly transparent in the visible range and evidence an increase of the band gap and of the intensity of three typical Co absorption bands in the visible with the amount of Co. Thermal annealing produces an increase of the intensity of the Co^{2+} -related absorption bands revealing that higher amount of Co atoms are occupying Zn sites.

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1. Introduction

Diluted magnetic semiconductors (DMSs) have attracted much interest in recent years due to combining semiconductors physics and magnetic material properties. Offering the possibility to manipulate both the spin and charge degrees of freedom, DMSs are potential candidates for technological applications in the field of spin-dependent semiconductor electronics called spintronics including, spin transistors, microwave devices and ultra dense nonvolatile semiconductor memories [1–3]. Recent theoretical and practical investigations suggest that wide band gap semiconductors, such as II–VI compounds, are the most promising candidates for developing DMSs with high Curie temperatures [2,4]. Therefore, numerous experimental groups have made a considerable effort in trying to grow ZnO doped with suitable 3d magnetic transition metals (TM), such as Co^{2+} , Mn^{2+} , Fe^{2+} , Ni^{2+} , etc., substituting a Zn cation site in the ZnO lattice [5,6]. The coupling of localised d electrons of the TM with the semiconducting band gap leads to a number of exciting properties as magneto-optical and magneto-electrical effects [7,8]. These properties are very sensitive to the shape of the samples and to the preparation method.

Numerous techniques are actually performed to prepare ternary $Zn_{1-x}Co_xO$ thin films: molecular beam epitaxy [9], radio-frequency magnetron sputtering [10], sol–gel process [11], pulsed laser deposition [12] and cathodic electrodeposition [13]. Among

these techniques, the last one presents many advantages: (i) the deposition is realized at low temperature and at atmospheric pressure; (ii) it requires a simple low cost apparatus; and (iii) the film thickness can be controlled by the charge consumed during the deposition process. Besides ZnCoO, the electrodeposition technique is suitable for synthesizing other ZnO-related compounds such as ZnCdO [14] and ZnMnO [15].

In this paper, we report on the effect of annealing in air atmosphere at 400 °C on the structural and optical properties of $Zn_{1-x}Co_xO$ thin films prepared by means of cathodic electrodeposition technique on glass covered with ITO as a substrate. X-ray diffraction (XRD), energy dispersive spectroscopy (EDS), X-ray photoelectron spectroscopy (XPS), Raman scattering and optical transmittance have been used in order to characterize the electrodeposited $Zn_{1-x}Co_xO$ thin films at room temperature after the corresponding annealing process.

2. Experimental

The experimental setup used to prepare $Zn_{1-x}Co_xO$ thin films with thicknesses ranging from 520 to 850 nm by cathodic electrodeposition technique consists of a computer-controlled potentiostat/galvanostat and a classical three-electrode electrochemical cell filled with a solution containing 0.1 M $KClO_4$ as supporting electrolyte and dissolved oxygen in a DMSO solution. Zn and Co chlorides were used as precursors: $ZnCl_2$ 25 mM and $CoCl_2$ in different concentrations. A glass coated with indium tin oxide (ITO) substrate with sheet resistance of 10 Ω /square,

* Corresponding author.

E-mail address: bmari@fis.upv.es (B. Marí).

previously cleaned in an ultrasonic acetone bath during 15 min and then rinsed in distilled water and dried, was the working electrode. Pt and Ag/AgCl electrodes were used as counter electrode and reference electrode, respectively. The deposition potential was fixed at -0.9 V and the solution temperature was maintained at 90°C by a thermostat. Transparent thin films with smooth surfaces are obtained when using DMSO in contrast with the nanocolumnar structure appearing when water is used as solvent [16]. After deposition, the films were rinsed with DMSO and distilled water and subsequently annealed at 400°C in air during 1 h.

The structural characterization was done by high-resolution XRD using a Bruker diffractometer through $\theta-2\theta$ scans with copper anticathode ($\text{CuK}\alpha$, 1.54 \AA). The chemical composition was determined by EDS and XPS. XPS measurements were performed in an Escalab 210 using the $\text{Mg K}\alpha$ line. All the spectra have been referred to the Fermi level. Previous to XPS measurements, samples were introduced in the analysis chamber and sputtered by using an Ar^+ gun for 15 min, in order to clean the surface. Additional structural and chemical characterization is provided by Raman scattering measurements performed with a Jobin Yvon T64000 triple spectrometer coupled to a liquid N_2 cooled CCD camera. Finally, optical transmittance measurements were performed by means of a coupled deuterium-halogen lamp in association with a 500 mm Jobin Yvon HR-460 spectrometer coupled to a back-thinned CCD detector optimised for the UV-vis range.

3. Results and discussion

The initial cation $[\text{Co}]/[\text{Zn}]$ ratio present in the starting solution and the final Co content in the solid $\text{Zn}_{1-x}\text{Co}_x\text{O}$ films as obtained

Table 1
Initial cations ratio $[\text{Co}]/[\text{Zn}]$ present in the starting electrolyte and final Co content in the solid ZnCoO film as measured by EDS

Initial ratio $[\text{Co}]/[\text{Zn}]$ in the starting liquid solution	Final Co content (x in $\text{Zn}_{1-x}\text{Co}_x\text{O}$)
0.00	0.00
0.04	0.01
0.10	0.07
0.12	0.08
0.20	0.17

from EDS are summarized in Table 1. According to EDS the Co amount in the solid films ranges from 0% to 17%.

The XRD pattern of electrodeposited $\text{Zn}_{1-x}\text{Co}_x\text{O}$ films keeps the typical ZnO wurtzite structure mainly oriented in the 002 direction. Increasing the Co content produces a gradual deformation of the wurtzite structure as already reported [13]. No changes in the XRD spectra are observed after thermal annealing at 400°C .

The XPS spectra of Co 2p and O 1s levels of the $\text{Zn}_{1-x}\text{Co}_x\text{O}$ thin films annealed at 400°C with different Co concentrations are shown in Fig. 1. The Co $2p_{3/2}$ and Co $2p_{1/2}$ peaks are localised at binding energies 781 and 797 eV, respectively, and correspond to oxidized Co (see Fig. 1(a)). No feature is observed at 779 and 794 eV, where the metallic Co peaks were located in as-grown samples [13,17]. Metallic Co has been also observed in $\text{Zn}_{1-x}\text{Co}_x\text{O}$ films prepared under reducing atmosphere [18]. When Co exists as a metal cluster the energy difference between Co $2p_{3/2}$ and Co $2p_{1/2}$ peaks is 15.05 eV [19], however, in our samples this difference is varying from 15.84 to 15.11 eV for x values going from 0.009 to 0.17. This result excludes the formation of a Co metal cluster in our annealed $\text{Zn}_{1-x}\text{Co}_x\text{O}$ thin films despite the existence of Co in a Co^{2+} oxidation state as reported in different works [20,21]. Satellite peaks also appear at about 787 and 803 eV (see Fig. 1(a)) and it originate from the charge-transfer band structure characteristic of the 3d TM monoxides [22]. The calculated differences between the main peaks and the corresponding satellites further lead to conclude that Co ions are in a tetrahedral crystal field surrounded by oxygen atoms and have a chemical valence of the 2^+ state [23]. Fig. 1(b) shows the signal of electrons from the O 1s level. The spectra are asymmetric and it can be deconvoluted into two mean peaks O1 and O2 localised at about 530.8 and 533 eV, respectively. O2 peak is attributed to the presence of hydrated oxide species like OH [24], while O1 peak is due to the ZnO crystal lattice oxygen [25]. The hydrophilic character of zinc oxide might be at the origin of the O2 peak.

It can also seen in Fig. 1(a) and (b) that, as Co content increases, the Co 2p and the O1 peak rigidly shift towards lower binding energy values by 0.4 eV. This shift has been also observed for the Zn 2p peak (not shown). These facts indicate that films tend to be more intrinsic with doping, which would suggest that Co doping introduces energy levels into the ZnO band gap that captures free carriers. This is in agreement with the low conductivity exhibited by ternary ZnCoO.

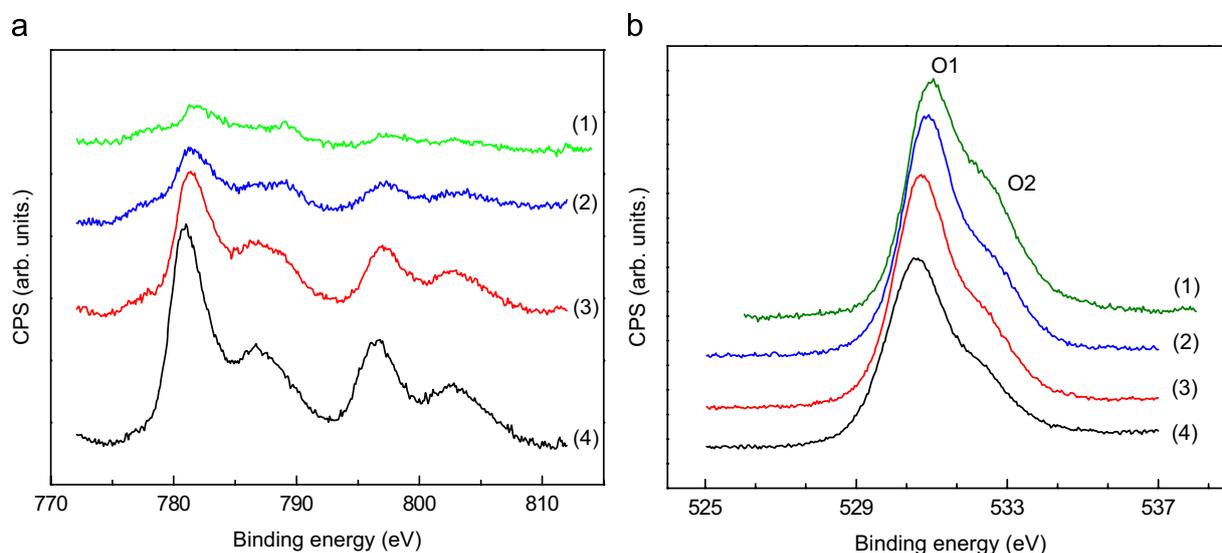


Fig. 1. XPS spectra of $\text{Zn}_{1-x}\text{Co}_x\text{O}$ films annealed at 400°C for different Co contents: (a) Co 2p region, (b) O 1s region. (1) $x = 0.01$; (2) $x = 0.07$; (3) $x = 0.08$; (4) $x = 0.17$.

Fig. 2 shows the Raman spectra measured in backscattering geometry in the annealed $\text{Zn}_{1-x}\text{Co}_x\text{O}$ thin films with different Co concentrations ($x = 0.01, 0.08$ and 0.17). For the sample doped with Co concentration $x = 0.01$, the Raman spectrum shows a resolved peak centred around 436 cm^{-1} corresponding to $E_2(\text{high})$ mode in ZnO and some broad bands near $245, 320, 540, 570$ and 630 cm^{-1} which correspond to LA band, TO–TA mode, TA+TO mode, LO band, and TA+LO mode in ZnO, respectively [26]. The observation of the $E_2(\text{high})$ mode, previously not observed in as-grown samples indicates that the crystalline quality of the ZnO film is increasing with annealing. As the Co content in $\text{Zn}_{1-x}\text{Co}_x\text{O}$ increases, the $E_2(\text{high})$ peak intensity decreases quickly what indicates that the wurtzite lattice is not properly crystallized even under thermal annealing for the larger Co concentrations. When x increases to 0.17 , the Raman spectrum is completely different and exhibits no signal of the wurtzite structure of ZnO due to the strong deformation of the wurtzite lattice due to Co

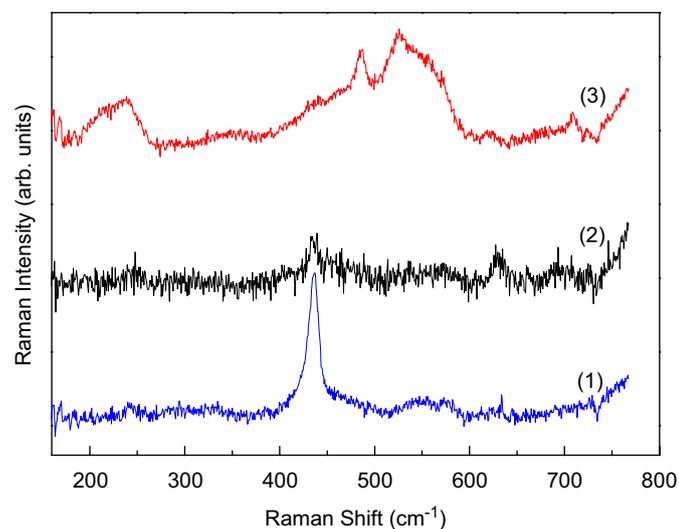


Fig. 2. Raman spectra for several $\text{Zn}_{1-x}\text{Co}_x\text{O}$ samples annealed at $400\text{ }^\circ\text{C}$ with different Co content. (1) $x = 0.01$; (2) $x = 0.08$; (3) $x = 0.17$.

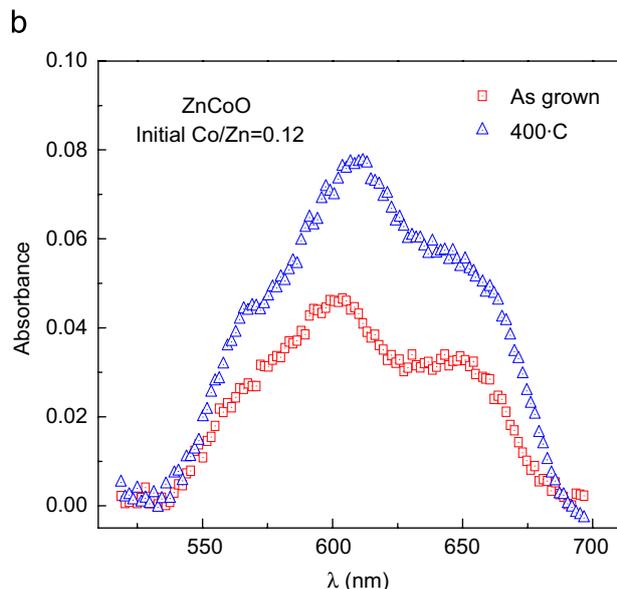
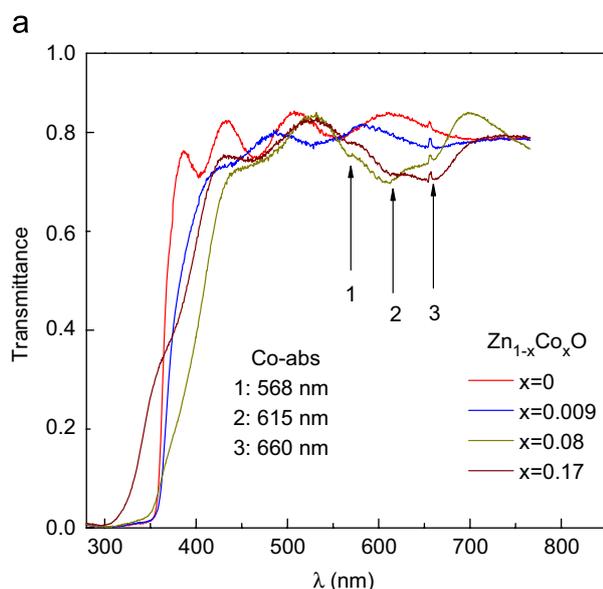


Fig. 3. Optical transmittance spectra of $\text{Zn}_{1-x}\text{Co}_x\text{O}$ thin films for different Co concentrations, (a) annealed at $400\text{ }^\circ\text{C}$, (b) details of the absorption bands due to tetrahedrally coordinated Co^{2+} .

doping. This result is coherent with the lack of any wurtzite diffraction peaks in samples with high Co content [13].

Fig. 3 (a) shows optical transmittance spectra of $\text{Zn}_{1-x}\text{Co}_x\text{O}$ thin films with different Co concentrations annealed in air at $400\text{ }^\circ\text{C}$. The optical transmittance spectra of an undoped and annealed ZnO thin film are shown for comparison. All films exhibit a high transparency in the visible range. It can be seen that the spectrum of ZnO sample is characteristic of pure ZnO phase with an absorption edge observed at 3.43 eV that corresponds to the band gap edge E_g for crystalline ZnO. As the Co concentration increases the fundamental absorption edge becomes deformed. A similar trend with increasing Co concentration in $\text{Zn}_{1-x}\text{Co}_x\text{O}$ synthesized by PLD has already been reported [27] and explained as due to $sp-d$ exchange interactions between band electrons and the localised d electrons of the Co^{2+} ions substituting Zn^{2+} [28,29]. Three characteristic optical absorption peaks in the visible range labelled as (1), (2) and (3) in Fig. 3(a) can also be observed. These peaks are assigned as due to $d-d$ electronic transitions of high spin state of Co^{2+} involving crystal-field split $3d^7$ levels in tetrahedrally-coordinated Co^{2+} ions substituting Zn^{2+} ions. The internal transitions around $568, 615$ and 660 nm are attributed to ${}^4A_2(F) \rightarrow {}^2A_1(G)$, ${}^4A_2(F) \rightarrow {}^4T_1(P)$ and ${}^4A_2(F) \rightarrow {}^2E(G)$ transitions, respectively [28,30,31].

Comparing with the transmission spectra of the as-grown samples the main difference observed in the annealed samples is an increase of the intensity of the three absorption bands located in the visible. Fig. 3(b) shows a detail of the absorbance of the Co-related absorption bands for a typical $\text{Zn}_{1-x}\text{Co}_x\text{O}$ sample before and after annealing. The intensity of these Co-related absorption bands increasing with the annealing provides evidence that the excess of metallic Co detected by XPS in the surface of the as-grown $\text{Zn}_{1-x}\text{Co}_x\text{O}$ films is now occupying a Zn site in the ZnO wurtzite structure.

4. Conclusion

Ternary $\text{Zn}_{1-x}\text{Co}_x\text{O}$ thin films with Co concentrations from 1% to 17% have been grown by cathodic electrodeposition technique at low temperature and atmospheric pressure on ITO/glass substrate. EDS confirms the presence of Zn, Co and O in both

as-grown and annealed samples. In general, the films annealed in air atmosphere at 400 °C show an improvement of the crystal quality as shown by Raman measurements. In these samples, XPS and optical transmission spectroscopies confirm the incorporation of Co²⁺ cations in substitution sites of Zn²⁺ in wurtzite structure of ZnO. For films with Co concentration above 10%, the XPS spectra prove that metallic Co and O adsorbed in the surface of the as-grown films disappear with moderate annealing. Finally, the increase of the intensity of the absorption bands related to tetrahedrally-coordinated Co²⁺ in Zn_{1-x}Co_xO films reveal that the metallic Co detected in the surface of the films before the annealing are now occupying Zn sites.

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