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We report on the characterization of ternary $Zn_{1-x}Co_xO$ alloy crystalline films grown by electrodeposition onto FTO-coated substrates. The $Zn_{1-x}Co_xO$ films have hexagonal wurtzite structure as shown by X-ray diffraction measurements. The Co incorporation into the ZnO lattice is confirmed by the presence of absorption peaks assigned to Co in trigonal crystal field. X-ray photoemission spectroscopy indicates that as-grown films have a considerable concentration of not-fully oxidized metallic Co in the surface that correlates with the O concentration in the surface. Finally, Raman measurements of as-grown films indicate that they are polycrystalline with grains of nanometric size showing short-range order but no long-range order. The Raman spectra show no trace of first-order phonons and resemble the one-and two-phonon density of states of ZnO

1 Introduction Diluted magnetic semiconductors (DMS) have recently received considerable attention due to the complementary properties of semiconductor and ferromagnetic materials. DMS provide both charge and spin degrees of freedom which are promising for spintronic devices. In these devices, both magnetic and transport properties should be coupled to exploit the permanent magnetization for information storage and the high speed of reading of electronic devices in a single device. $Zn_{1-x}Co_xO$ films offer a special interest in advanced spintronic devices because of their magnetic and optical properties [1, 2].

Cathodic electrodeposition has recently emerged as an alternative method for ternary oxide thin film deposition [3-5]. This technique presents some interesting advantages: a) deposition occurs at temperature lower than 100 ºC and at atmospheric pressure, b) the film thickness can be directly monitored by the charge consumed during the deposition process, and c) it is a low-cost method. The main drawback is that only conducting substrates can be used.

In this work, we report the characterization of as-grown $Zn_{1-x}Co_xO$ films by X-ray diffraction (XRD), scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS) and Raman scattering spectroscopy (RSS).

2 Experimental details Ternary $Zn_{1-x}Co_xO$ alloy crystalline films have been grown by electrodeposition onto Fluordoped Tin Oxide (FTO)-coated substrates. The electrodeposition procedure consists of a classical three electrode electrochemical cell and a solution containing $ZnCl_2$ and $CoCl_2$, in different concentrations, $KClO_4$ as supporting electrolyte and dissolved oxygen in a Dimethylsulfoxide (DMSO) solution. A potentio/galvanostat was used to keep a constant potential. The film widths can be precisely controlled through the amount of deposited electrical charge. Growth variables have been fixed during the electrodeposition process, potential at -0.9V and temperature at 90 ºC.

SEM images were obtained by using a Jeol scanning electron microscope JSM 6300. High-resolution XRD patterns in the θ–2θ configuration were taken using the radiation of a copper anticathode (CuKα, 1.54 Å). The samples prepared were introduced in the analysis XPS chamber for the photoemission measurements. Before the measurements, all samples were cleaned by Ar sputtering. The XPS measurements showed in this work were carried out in an Escalab 210 from VG Scientific by exciting with the Mg-Kα line (1253.6 eV). All spectra have been referred, in energy, to the Fermi level. RSS measurements were per-

formed in backscattering geometry with a micro-Raman equipment of WITEC GmbH consisting in a confocal microscope attached via optical fibers to a laser working at 532 nm and to a spectrometer with 300 mm focal length coupled to an Andor CCD camera. The resolution of Raman spectra is 4 cm^{-1}. The Raman spectra were collected from the optimum focal plane which was found by sweeping the z with nanometric positioning system placed under the confocal microscope. The excitation laser intensity was kept below 2 mW in order to avoid thermal damage to the samples.

3 Results and discussion Figure 1 shows the XRD pattern of the as-grown $Zn_{1-x}Co_xO$ films for different nominal Co concentrations. It can be observed that the films with low Co concentration up to 10% grow with a strong orientation along the (002) direction. Above 10% Co concentration the growth along the (101), (102) and (103) directions is observed and for samples with 20% Co preferential orientation of the films is found along the (101) direction. No signal of diffracted X-rays from ZnO was found for films with nominal Co concentration above 30%.

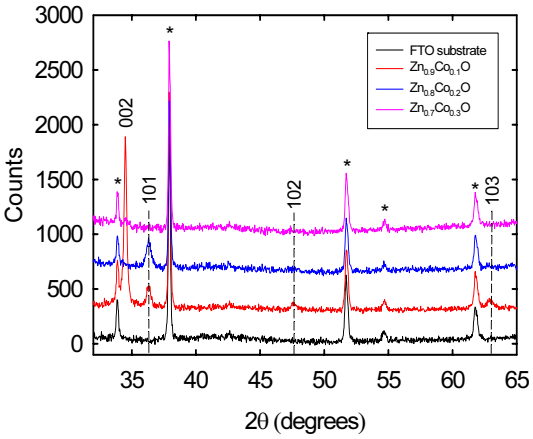

Figure 1 XRD θ –2θ scan diagram of $Zn_{1-x}Co_xO$ films for different nominal Co concentrations. Peaks belonging to the FTO are marked with an asterisk.

Figure 2 shows a SEM micrograph of one of the $Zn_{1-x}Co_xO$ films. It can be observed that the image shows a rather uniform and homogeneous surface similar to other samples obtained by electrodeposition from DMSO solutions [4]. This result is in agreement with the good transparency of the films found by optical absorption measurements observing transmittances higher than 90% [5].

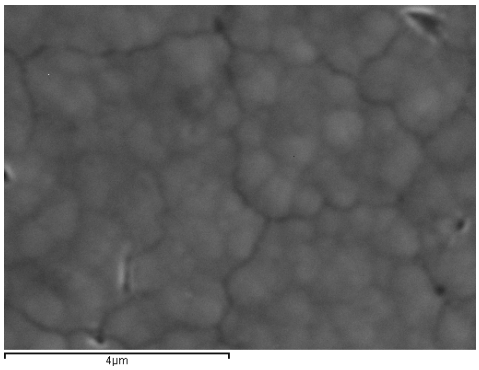

Figure 2 SEM image of a $Zn_{1-x}Co_xO$ film.

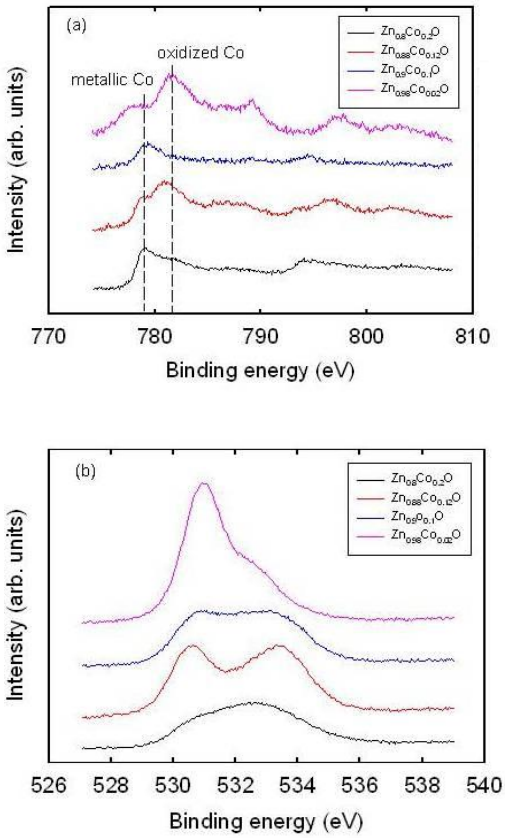

Figure 3 XPS spectra of $Zn_{1-x}Co_xO$ films for several nominal Co concentrations: (a) Co 2p zone; (b) O 1s zone.

Figure 3 shows the XPS spectra the as-grown $Zn_{1-x}Co_xO$ films for different Co concentrations. In Fig. 3(a) we show the signal of electrons from the Co 2p level of the different samples studied. We find that the spin-orbit doublet structure of Co at 781 and 797 eV is accompanied by two satellite bands at slightly higher binding energies. Besides, there is a band at lower binding energy (779 eV). The doublet structure and its sidebands are commonly attributed to oxidized Co incorporated into the ZnO structure in a Co^{2+} configuration [6]. However, the band at 779 eV

can be attributed to metallic Co present in the surface that it is not oxidized and therefore not incorporated into the ZnO structure. Figure 3(b) shows the signal of electrons from the O 1s level of the different samples studied. It can be observed that there are two overlapping bands. The band at 530.5 eV is attributed to O incorporated in the ZnO lattice while the band at 533 eV can be attributed to O adsorbed in the sample surface. It can be observed that the peak with 530.5 eV binding energy has a higher intensity in the samples with 2.5 and 12% Co concentration, which correspond to these showing the higher concentration of oxidized Co in the surface. Therefore, we can conclude that the presence of metallic Co in the surface of the as-grown $Zn_{1-x}Co_xO$ films is likely due to the smaller supply of O or the smaller incorporation of O during the film deposition procedure.

Figure 4 shows the Raman spectrum measured in back-scattering geometry in as-grown $Zn_{1-x}Co_xO$ film with a nominal 12% Co concentration. The Raman spectrum of a ZnO single crystal and the *ab initio* calculated one-phonon density of states of ZnO [7] are also plotted for comparison. One can observe that he Raman spectrum of the film show broad bands that do not correspond to those of the main first-order phonons observed in the single crystal. Note that even the E_2(high) mode near 440 cm^{-1}, which has the highest intensity, is absent in the Raman spectrum of the film. However, the experimental spectrum shows bands that are very similar to those presented in the calculated one-phonon density of states. Furthermore, other bands observed in the experimental spectrum of the film can be attributed to multiphonon bands that correspond mainly to the two-phonon density of states [7]. This result indicates that our $Zn_{1-x}Co_xO$ films are either composed of wurtzite nanocrystalline islands that grow mainly along the wurtzite c axis showing short-range order inside the island but not having long-range order, or they have so many defects that the long-range order is completely lost. The absence of long-range order prevents that the Raman selection rules are obeyed and so there is a lack of first-order phonons in the experimental Raman spectrum. Furthermore, the lack of selection rules for Raman scattering allows that the full spectrum of phonons is observed and this explains the similarity of some observed bands with those present in the calculated one-phonon density of states.

4 Conclusions We have succeeded in preparing ternary $Zn_{1-x}Co_xO$ DMS films by cathodic electrodeposition at low temperature and at atmospheric pressure. The films exhibit wurtzite structure with a preferred orientation along the (002) direction for small Co concentration and along the (101) direction for Co concentration above 10%. All films have blue-green color with a transmittance above 90% in the visible spectral range. EDX measurements show that the samples have a real Co concentration that increases linearly with the nominal Co concentration but slightly below the nominal one. SEM measurements indicate that the surface of the films is relatively flat with no appreciable structures. XPS measurements show that the films have considerable amount of non-oxidized metallic Co at the surface and that this is related to the defect of O at the surface. Raman measurements show that the films either have a lot of defects or are formed by nanometer-sized unconnected islands that exhibit short-range order but no long-range order. Both explanations are consistent with the high resistivity of the as-grown DMS films.

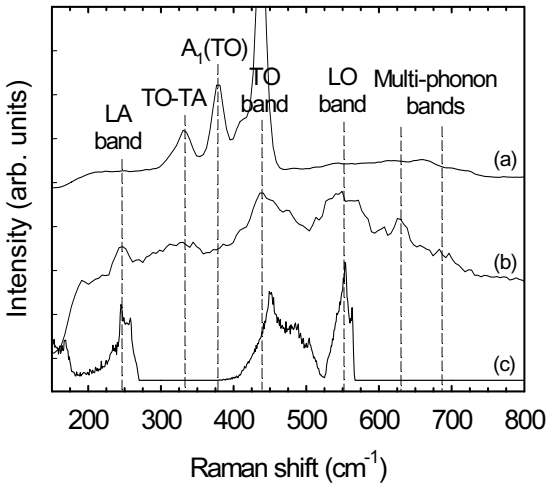

Figure 4 (a) Raman spectrum of a single crystal, (b) Raman spectrum of the $Zn_{1-x}Co_xO$ film with nominal 12% Co concentration, and (c) *ab initio* calculated one-phonon density of states.

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