STUDIES ON STRUCTURAL, SURFACE MORPHOLOGICAL, OPTICAL, LUMINESCENCE AND UV PHOTODETECTION PROPERTIES OF SOL GEL OXIDES THIN FILMS

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ZnO and ZnCoO thin films have been deposited onto glass substrates by sol–gel spin coating method. Zinc acetate dihydrate, cobalt acetate tetrahydrate, Isopropanol and monoethanolamine (MEA) were used as a precursor, doping source, solvent and stabilizer respectively. The molar ratio of MEA to ions metal was maintained at 1.0 and a concentration of metal ions is 0.6 mol.L^{-1}. The XRD results showed that both films crystallized under hexagonal wurtzite structure and presented a preferential orientation along the c-axis with the maximum crystallite size was found is 25nm. Atomic force microscope (AFM) images revealed the good uniformity for both films, an increase of surface roughness is observed with doping. The average transmittance in the visible region was higher than 85% for both films and the optical band gap of Zinc oxide films decreased with Co doping. Photoluminescence of the films showed a ultraviolet (UV) and defect related visible emissions like violet, blue and green, and indicated that cobalt doping resulted in red shifting of UV emission and the reduction in the UV and visible emissions intensity. Ours thin films shows the best photocurrent properties.

Keywords: Sol–gel technique; TM-doped Zinc Oxide thin film; Structural properties; Optical properties; Luminescence; Defects

INTRODUCTION

In recent years, Zinc oxide has attracted great interests because of their potential applications in optics and optoelectronic devices such as ultraviolet (UV) photodetectors, light-emitting diodes (LEDs), laser diodes (LDs), catalysts, gas sensors and transparent conducting electrodes (Hou *et al*., 2014; Mahroug *et al*., 2014; Abeda *et al*., 2015; Vijayalakshmi *et al*., 2014) due to its wide band-gap (3.37eV) and large exciton binding energy (60 meV) (Özgür *et al*., 2005). Additionally, the excellent optical properties of ZnO and the possibility of band gap engineering through transition metal ions (TM = Co; Mn; Ni …) doping strongly encourages the exploration of the magneto-optical properties of the TM-doped ZnO system. Various deposition techniques have been used to prepare ZnO thin films. Among these techniques, sol-gel method has a distinct advantage: simple, economic and easy to perform doping incorporation (Mahroug *et al*., 2014). In this study, ZnO and ZnCoO thin films have been deposited on glass substrates by sol– gel spin coating process and the effects of the Co doping on the structural morphological, and optical properties of the films have been investigated.

EXPERIMENTAL DETAILS

ZnO and ZnCoO (3%mol Co) thin films were prepared on glass substrates, using sol-gel spin coating technique, Zinc acetate dihydrate ($Zn(CH_3COO)_2.2H_2O$) with 0.6mol/L, cobalt acetate tetrahydrate [$Co(CH3COO)_2.4H_2O$] (3%mol) isopropanol and monoethanolamine (MEA) were used as a precursors, solvent and stabilizer, respectively. The solutions underwent a stirring at 55°C for 2 hours to be homogenous

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and clear, followed by aging at room temperature during 24h. The resulting solutions were deposited at 2500 rpm for 30 s. After each coating, the films were preheated at 250°C for 10 min. Finally, these films were annealed at 500°C for 1h.

Structural and morphological properties of the films were analysed using XRD with Cu Kα line (λ= 0.154 nm) and atomic force microscopy AFM with tapping mode. The optical properties were obtained by transmission spectra (UV-Vis in 300- 800 nm region), photoluminescence spectroscopy (using a 325 nm xenon lamp as excitation source). The photocurrent measurements were performed in an electrochemical cell using a UV light of 365nm.

RESULTS AND DISCUSSION

Structure and Surface Morphology of ZnO Thin Films

Figure 1a shows the XRD patterns of ZnO and ZnCoO thin films. The results indicate that both samples are polycrystalline hexagonal wurtzite structure and no other crystalline phase was found. The intensity of the diffraction peaks is decreased with Co content, indicating that the film crystallinity is deteriorated. The preferential orientation was determined using a texture coefficient TC(hkl) (Caglar, 2013). A sample with randomly oriented crystallite presents TC(hkl) = 1, while values higher than 1 indicate the abundance of crystallites in a given (hkl) direction. After the calculation of texture coefficients, It is seen that the highest TC values (TC = 1.5) are in (002) plane for both films. which indicates that the films grew preferential *c*-axis orientation. The crystallite size of the films was estimated by the Scherrer formula (Mahroug *et al.*, 2014): $D = K\lambda / \beta\cos\theta$, where D is crystallite size, K is constant of 0.9, λ is X-ray wavelength, β is full width at half maximum, θ is diffraction angle, respectively. The (002) peaks were used to estimate the crystallite size. The calculated average crystallite sizes of ZnO and ZnCoO thin films are 25, 24nm, respectively. Compared with undoped ZnO, cobalt doping in ZnO thin films resulted with a slightly decrease in crystallite size. The surface morphology of the films is studied by atomic force microscopy in tapping mode and it gives information about surface roughness and average grain size of the films. 2D and 3D surface images over a 1×1 μm^2 area and histogram of films are shown in Figure 1b. Good uniformity is observed for both films. The root-mean square (RMS) surface roughness strongly increased with Cobalt dopant. The roughness values of ZnO and ZnCoO thin films are 9 nm and 23 nm respectively. As remarked in the histograms, significant shift of the particle height distributions to high values with Co doping. Indeed a rough surface of the film shows an interest for certain applications such as solar cells.

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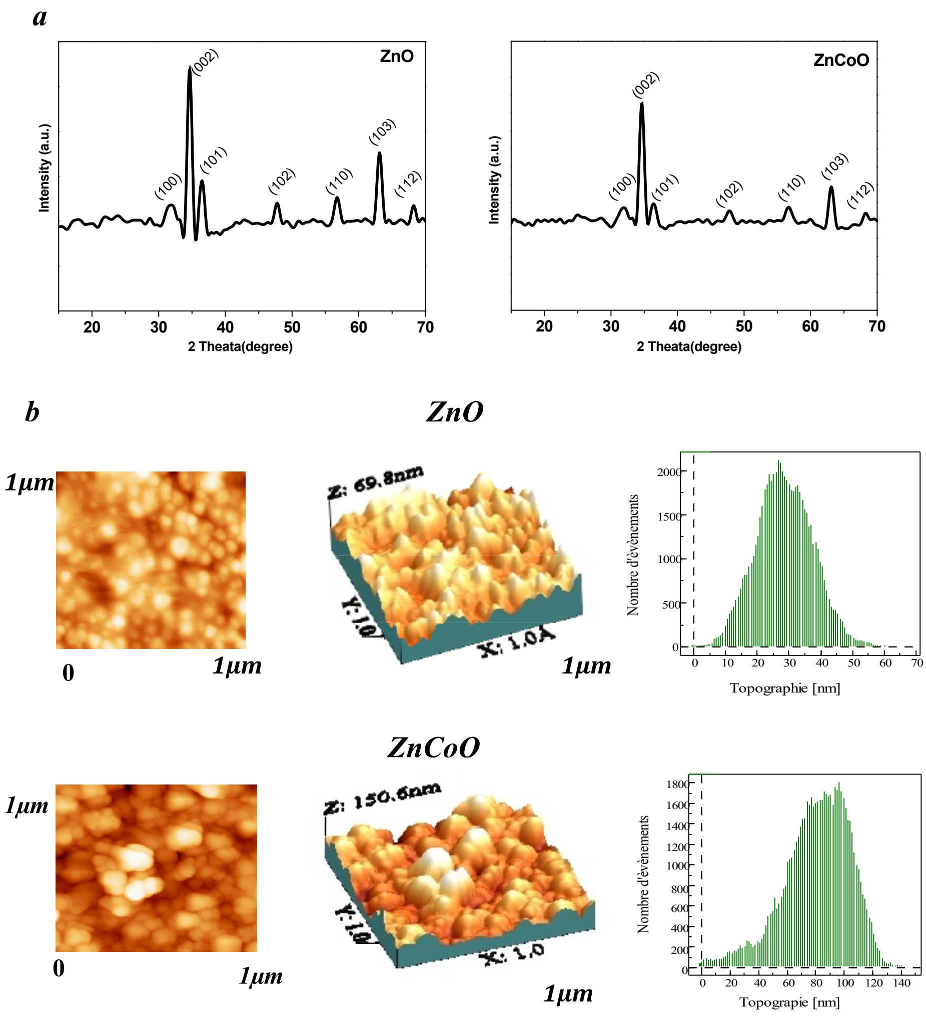

Figure 1. XRD patterns (a) and tapping mode AFM images (2D and 3D) of surface morphologies (b) of ZnO and ZnCoO thin films

Optical Properties

Transmittance

The optical transmittance spectra of thin films in the wavelength range 300- 800 nm at room temperature are shown in Figure 2a. The average transmittance in the visible region was higher than 85% for both films. Further, an red shift of the absorption edges can be observed in the doped thin film. Compared with pure ZnO film, three absorption

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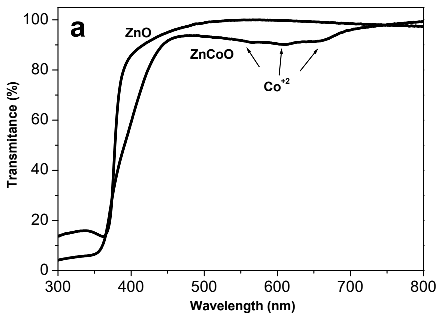
bands in visible region appear in the spectra of the ZnCoO thin films. These three absorption bands are attributed to the transitions of Co^{+2} ions substitute for Zn^{+2} ions in the hexagonal ZnO wurtzite structure (Weakliem, 1962). To evaluate the bandgap energy (E_g) from the optical absorption spectra, $(\alpha h\nu) = A(h\nu\text{-}E_g)^{1/2}$ (Mahroug *et al.*, 2014) relationship is employed, where α is the absorption coefficient ($\alpha = -1/D \ln T$, where T is the transmittance and D is the film thickness), A is a constant, hν is the photo energy, E_g is the optical bandgap. The bandgap is then evaluated by extrapolating the linear region of $(\alpha h\nu)^2$ vs. the photon energy. The optical band gap energy decreases from 3.28 to 3.25eV with Co dopant. This decrease can be attributed to the sp–d spin–exchange interaction between the band electrons and the localized d electrons of the Co^{2+} ions substituting Zn^{+2} ions (Belghazi *et al.*, 2009).

Luminescence Properties

Photoluminescence (PL) spectroscopy was used to study the luminescence properties of ZnO thin films. Figure 2b shows the room temperature photoluminescence emission spectra of ZnO and ZnCoO thin films. Both films exhibit an UV emission at 380nm, is originated from the exciton recombination corresponding to the near-band edge transition (NBE) of ZnO (Li *et al.*, 2012), and more visible emissions peaks are observed at 409nm, 442nm, 472 nm and 520 nm, which may be attributed to the energy of transition of electron from conduction band to the V_{Zn}, the energy of transition of electron from Zn_i to valence band, the electron transition from the level of the ionized oxygen vacancies to the valence band and the transition from Zn_i to O_i levels, respectively (Xu *et al.*, 2001; Elilarassi and Chandrasekaran, 2013; Sabri *et al.*, 2012). The UV emission is seen to display red shift and the emission peaks intensity decreased with Co dopant.



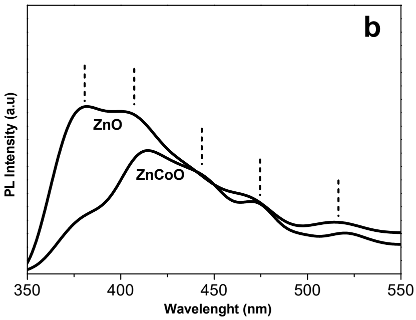


Figure 2. Transmittance spectra of ZnO and ZnCoO thin films (a), Photoluminescence (PL) spectra of ZnO and ZnCoO thin films (b)

UV Photodetection and Photocurrent Studies

Fig.3 shows the photo-response of the ZnCoO thin films obtained by a chronoamperometric method under intermittent illumination with a 365 nm wavelength light. The photocurrent curve has an almost rectangular response under light illumination with a significant increase of current. This is due to the increase of electrical conductivity of semiconductor material, by generating of electron-hole pair,

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when light with energy greater than the band gap energy is absorbed (Mahroug *et al.*, 2014).

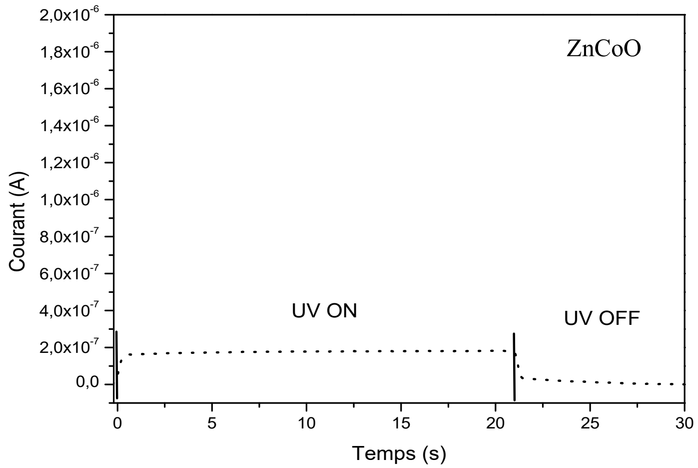

Figure 3. Photocurrent response of ZnCoO thin film

CONCLUSIONS

ZnO and ZnCoO thin films were prepared using a sol–gel spin coating method.

The X-ray diffraction spectra indicated that the films are polycrystalline with a hexagonal wurtzite structure, high *c*-axis orientation, along the (002) plane and the maximum crystallite size of about 25 nm. AFM studies revealed the good uniformity for both films, an increase of surface roughness is observed with Co. The average transmittance in the visible region was higher than 85% for both films and the optical band gap of Zinc oxide films decreased with Co doping. PL analysis of films shows an UV emission at 380nm, and violet, blue and green emission. Co doping causes a red shift of UV emission, a reduction in the intensity of UV and visible emissions. Our films presented photo-responses and a significant photocurrent was observed.

REFERENCES

Abeda, C. *et al.* (2015), "Mg doping induced high structural quality of sol–gel ZnO nanocrystals: Application in photocatalysis", *Appl. Surf. Sci.*, 349, 855, https://doi.org/10.1016/j.apsusc.2015.05.078.

Belghazi, Y. *et al.* (2009), "Elaboration and characterization of Co-doped ZnO thin films deposited by spray pyrolysis technique", *J. Microelectronics*, 40, 265, https://doi.org/10.1016/j.mejo.2008.07.051.

Caglar, Y. (2013), "Sol–gel derived nanostructure undoped and cobalt doped ZnO: Structural, optical and electrical studies", *J. Alloys Compd*, 560, 181, https://doi.org/10.1016/j.jallcom.2013.01.080.

Elilarassi, R. and Chandrasekaran, G. (2013), "Influence of Co-doping on the structural, optical and magnetic properties of ZnO nanoparticles synthesized using auto-combustion method", *Mater. Sci: Mater Electron*, 24(1), 96-105, https://doi.org/10.1007/s10854-012-0893-4.

Hou, Y., Mei, Z. and Du, X. (2014), "Semiconductor ultraviolet photodetectors based on ZnO and $Mg_xZn_{1-x}O$", *J. Phys. D: Appl. Phys.*, 47, 283001, https://doi.org/10.1088/0022-3727/47/28/283001.

Li, P. *et al.* (2012), "Structural and optical properties of Co-doped ZnO nanocrystallites prepared by a one-step solution route", *J. Luminescence*, 132, 220-225, https://doi.org/10.1016/j.jlumin.2011.08.019.

https://doi.org/10.24264/icams-2018.II.4

Mahroug, A. *et al*. (2014), "Structural, optical and photocurrent properties of undoped and Al-doped ZnO thin films deposited by sol–gel spin coating technique", *Mater. Lett.*, 134, 248, https://doi.org/10.1016/j.matlet.2014.07.099.

Özgür, Ü. *et al*. (2005), "A comprehensive review of ZnO materials and devices", *J. Appl. Phys.*, 98, 041301, https://doi.org/10.1063/1.1992666.

Sabri, N.S. *et al*. (2012), "Emission properties of Mn doped ZnO nanoparticles prepared by mechanochemical processing", *J. Lumin.*, 132, 1735, https://doi.org/10.1016/j.jlumin.2012.02.020.

Vijayalakshmi, K. *et al*. (2014), "Growth of high quality ZnO:Mg films on ITO coated glass substrates for enhanced H2 sensing", *Ceram. Int.*, 40, 6171, https://doi.org/10.1016/j.ceramint.2013.11.070.

Weakliem, H.A. (1962), "Optical Spectra of Ni2+, Co2+, and Cu2+ in Tetrahedral Sites in Crystals", *J. Chem. Phys.*, 36, 2117, https://doi.org/10.1063/1.1732840.

Xu, P.S. *et al*. (2001), "Electronic structure of ZnO and its defects", *Sci. China Ser.*, A44, 1174, https://doi.org/10.1007/BF02877436.

https://doi.org/10.24264/icams-2018.II.4