Baghdad Science Journal **Vol.7(1)2010**

Structural and Optical Properties of Cobalt-Doped Zinc Oxide Thin Films Prepared By Spray Pyrolysis Technique

*M. K.Erhaima** *R. A.AL-ansari** *N. F.Habubi***

Date of acceptance 28 / 2 / 2010

Abstract:

Undoped and Co-doped zinc oxide (CZO) thin films have been prepared by spray pyrolysis technique using solution of zinc acetate and cobalt chloride. The effect of Co dopants on structural and optical properties has been investigated. The films were found to exhibit maximum transmittance (~90%) and low absorbance. The structural properties of the deposited films were examined by x-ray diffraction (XRD). These films, deposited on glass substrates at (400°C), have a polycrystalline texture with a wurtzite hexagonal structure, and the grain size was decreased with increasing Co concentration, and no change was observed in lattice constants while the optical band gap decreased from (3.18-3.02) eV for direct allowed transition. Other parameters such as Texture Coefficient (Tc), dislocation density (δ) and number of crystals (M) were also calculated .

Key words:Zno,Optical properties,spray pyrolysis

Introduction

Transparent conducting oxides (TCOs) thin films have been extensively studied because of their variety of applications. Keeping in view the need of low-cost TCOs that are required in various fields of science and technology [1]. Transparent conducting ZnO thin films are emerging as the most attractive alternative to ITO and various other TCOs [2]. ZnO is a very interesting material for many different applications in both microelectronic and optoelectronic devices [3]. It is a wide-band gap oxide semiconductor with a direct energy gap of about 3.37 eV [4], with high optical transparency in the visible and near-infrared region of electromagnetic spectrum, and has a high refractive index (1.9). Due to these properties, ZnO is a promising material for solar cell applications, such as antireflection coatings [5]. ZnO thin films can also be used for gas sensing because of high sensitivity to many gases [6]. Dilute magnetic semiconductors (DMS) produced by doping transition metal (TM) ions into non-magnetic semiconductors have attracted a great deal of interest [7]. Comparing with other TM (e.g., Fe, Ni, V, Cr, Mn) doped ZnO, the identical viewpoint is that the ZnCoO system is a promising material because of the highly solubility and the excellent ferromagnetic near room temperature [8]. ZnO thin films have been deposited by several techniques such as sputtering [9], pulsed laser [10], sole-gel [11], and spray pyrolysis [12]. In contrast, the spray pyrolysis technique has been only rarely used although this process presents many advantages: (i) it is a low-cost and simple technique, and (ii) it allows the possibility of obtaining films with a

*Physics Department, College of Science for Women, University of Baghdad.
**Physics Department, College of Edution, Al-Mustancrai University

large area [13]. Fitzgerald *et al.* [7] prepared single crystalline (CZO) films by pulsed laser with (110) preferred orientation and optical transmission of 70%.

In this work, we report the growth of $Zn_{1-x}Co_xO$ thin films (x=0, 2, 4, 6, 8) % on glass substrate by spray pyrolysis technique and the influence of cobalt doping on the structural and optical properties of ZnO thin films.

Experimental details

ZnO and CZO thin films were deposited using the spray pyrolysis technique. A homogeneous solution was prepared by dissolving zinc acetate ($Zn(CH_3COO)_2.2H_2O$) (0.1M) and cobalt chloride ($CoCl_2$) in (100 ml) distilled water. The solution was stirred for 15 min. The glass substrates were cleaned in acetone, rinsed in distilled water, and subsequently dried before deposition. The substrate is then placed on the hot plate which heated before progressively until the deposition temperature is reached. All films were deposited at 400 ˚C during 20 min with a flow rate fixed at 5 ml/min. The structures of ZnO and CZO samples were characterized by X-ray diffraction, Type Philips PW 1840, Target Cu. The optical measurements were performed using Shimadzu UV-VIS double beam spectrophotometer in the wavelength range (300-900) nm.

Results and discussion

In order to study the effect of the nominal Co concentration on the structural properties of $Zn_{1-x}Co_xO$ thin films, various dopants levels were used to obtain x values of (0, 2, 4, 6 and 8) %. The XRD patterns of the as deposited films with different doping concentrations are shown in Fig. 1. As can be seen from this data, all films are polycrystalline with hexagonal wurtzite structure and have preferred orientation along (002) direction. These results were in agreement with the results of (Bacaksiz *et al.*) [14]. No diffraction peaks of CoO or other impurity phases are found in these samples. It is to be noted that the intensities of the characteristic peaks increase with increasing Co concentration. The average grain size (G) decrease with increasing Co concentration while the lattice constants (a and c) and interplanner spacing (d) remain nearly constant. The values of the other structural parameters are shown in table (2.1)

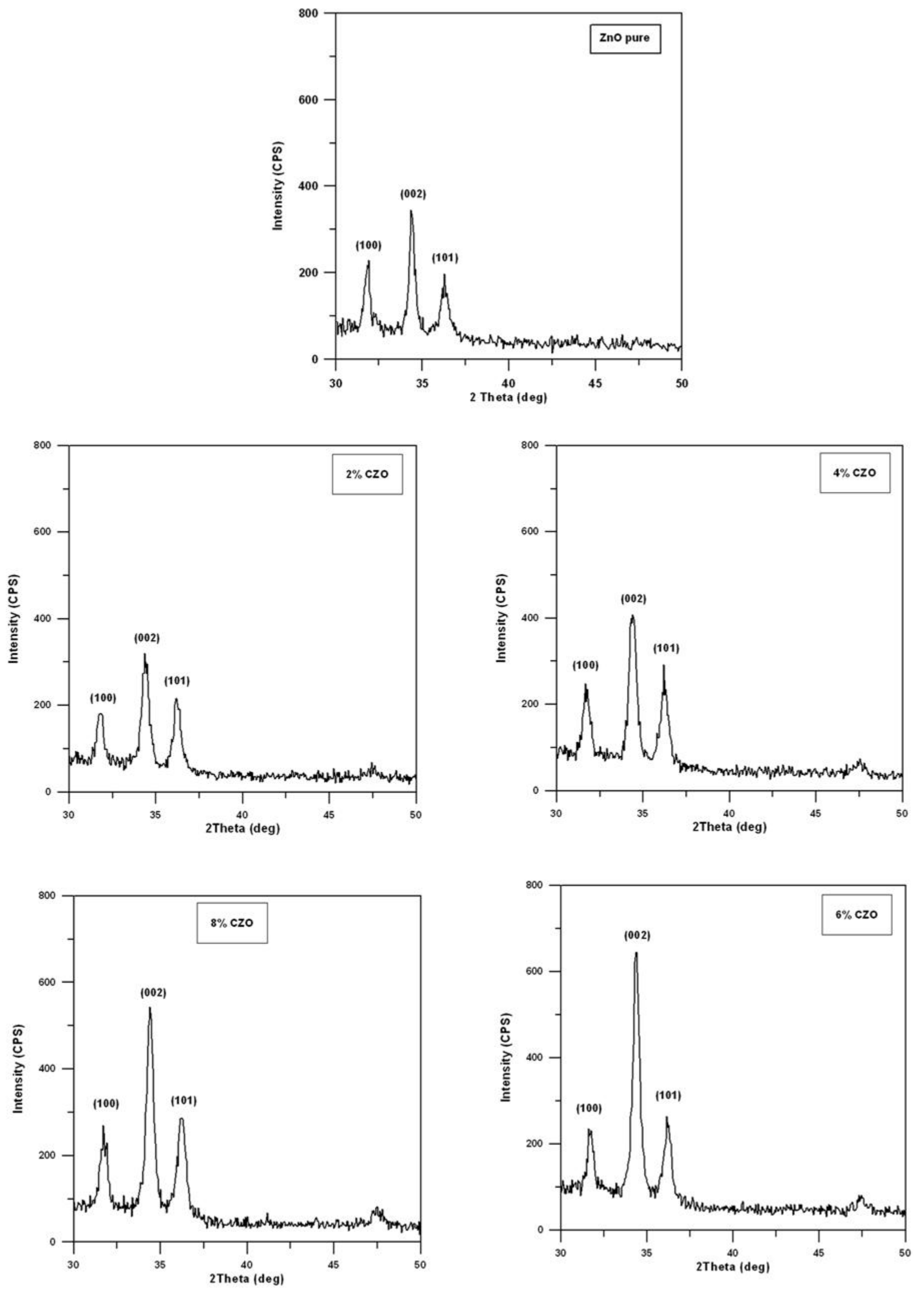

Fig.1. the XRD patterns of ZnO and CZO thin films deposited on glass substrate.

Table (2.1) the results obtained from XRD measurements

Sample	G nm	δ $m^{-2} *10^{15}$	M $m^{-2} *10^{15}$	Lattice Constants		d(002) (Å)	FWHM (002) (deg)	TC
				a(Å)	c(Å)			
Pure	24	1.8	43	3.244	5.210	2.605	0.355	1.9
2%Co	17	3.3	110	3.245	5.210	2.605	0.481	1.8
4%Co	17	3.6	122	3.251	5.210	2.605	0.504	1.9
6%Co	20	3.4	59	3.252	5.212	2.606	0.417	2.2
8%Co	18	3.1	82	3.251	5.208	2.604	0.475	2

Fig.2. shows the transmittance of all the as deposited films. It's clearly seen that the transmittance increase with increasing Co concentration. This interesting feature can be related to the solubility of Co-atoms in the ZnO structure [14]. There are three small Co^{2+} characteristic absorption bands at 560 nm, 610 nm, and 660 nm. These absorption bands are correlated with the d–d transitions of tetrahedrally coordinated Co^{2+} ions which are assigned as $^4A_2(F)$-$^2E(G)$, $^4A_2(F)$-$^4T_1(P)$, and $^4A_2(F)$-$^2A_1(G)$ transitions in a high spin state Co^{2+} (d^7), respectively. The observation of these characteristic absorption bands indicates that the Zn^{2+} ions are replaced by Co^{2+} ions. In other words, Co ions exist in a tetrahedral crystal field in the +2 state without destroying the wurzite crystal structure of ZnO [15].

Fig.3 shows the optical band gap of all the as deposited films. It can be seen that the optical band gap decrease with increasing Co concentration. The decrease in optical band gap is mainly due to the sp–d exchange interaction between the localized d-electrons of Co^{2+} ions and band electrons of ZnO [16]. This result was in good agreement with the result of (Fitzgerald *et al.)* [7] .

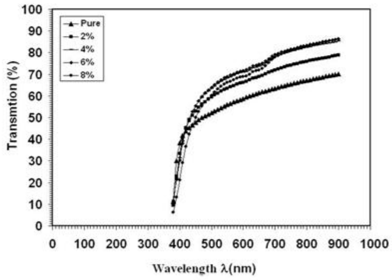

Fig.2. optical transmittance spectra of ZnO and CZO thin films deposited on glass substrate.

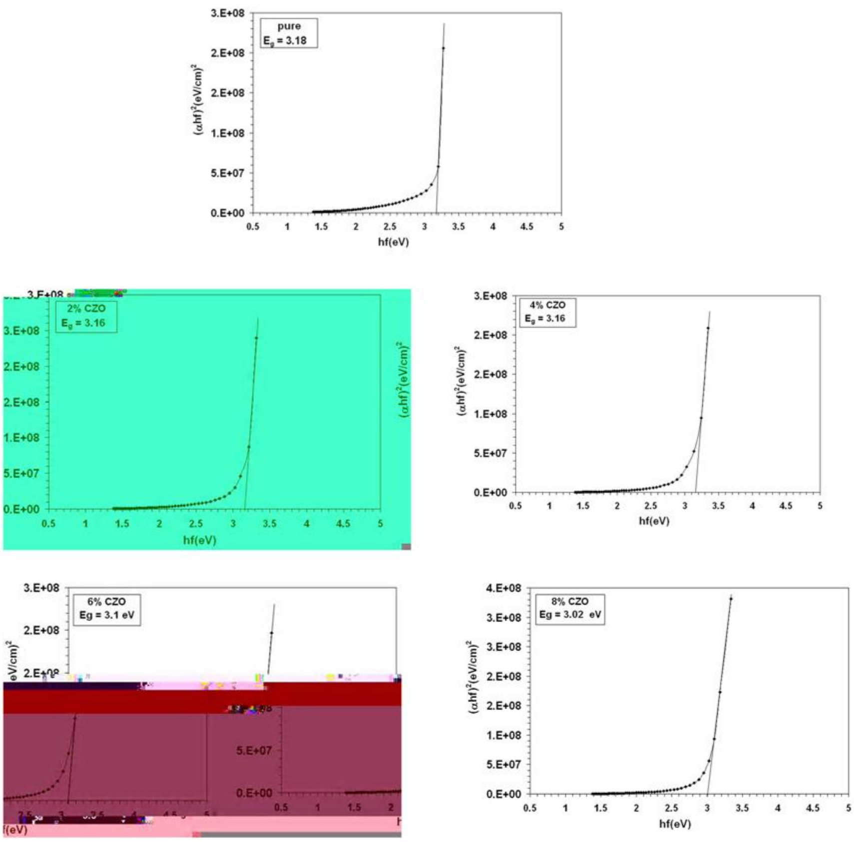

Fig.3. the optical band gap of ZnO and CZO thin films

Conclusion

ZnO and CZO films were deposited by spray pyrolysis technique on glass substrate at 400°C. XRD results showed that the structure of all films were hexagonal with a strong (002) preferred orientation. The adding of Co dopant led to a decrease in the average grain size and a stable maximum increase in the transmittance in (IR) region which can be useful in optoelectronic devises.

References

1. S.S. Shinde, P.S. Shinde, S.M. Pawar, A.V. Moholkar, C.H. Bhosale, and K.Y. Rajpure, ***"Physical properties of transparent and conducting sprayed fluorine doped zinc oxide thin films"***, Solid State Sciences 10, p. 1209-1214, 2008.
2. W.M. Tsang, F.L. Wong, M.K. Fung, J.C. Chang, C.S. Lee, and S.T. Lee, ***"Transparent conducting aluminum-doped zinc oxide thin film prepared by sol-gel process followed by laser irradiation treatment"***, Thin Solid Films 517, p. 891-895, 2008.
3. Ashour, M.A. Kaid, N.Z. El-Sayed, and A.A. Ibrahim, ***"Physical properties of ZnO thin films***

deposited by spray pyrolysis technique", Applied Surface Science 252, p.7844–7848, 2006.

4. Wei Lin, Ruixin Ma, Wei Shao, and Bin Liu, ***"Structural, electrical and optical properties of Gd doped and Undoped ZnO:Al (ZAO) thin films prepared by RF magnetron sputtering"***, Applied Surface Science 253, p. 5179–5183,2007.
5. M.C. López, J.P. Espinos, D. Leinen, F. Martín, S.P. Centeno, R. Romero, and J.R. Ramos-Barrado, ***"Growth and characterization of the ZnO/ZnS bilayer obtained by chemical spray pyrolysis"***, Appl. Surf. Sci., APSUSC-17511; No of Pages 7, 2008.
6. M.A. Kaid, and A. Ashour, ***"Preparation of ZnO-doped Al films by spray pyrolysis technique"***, Applied Surface Science 253, p.3029–3033, 2007.
7. C.B. Fitzgerald, M. Venkatesan, J.G. Lunney, L.S. Dorneles, and J.M.D. Coey, ***"Cobalt-doped ZnO – a room temperature dilute magnetic semiconductor"***, Applied Surface Science 247, p.493–496, 2005.
8. Ling Wei, Zonghui Li, and W.F. Zhang, ***"Influence of Co doping content on its valence state in $Zn_{1-x}Co_xO$ ($0 \leq x \leq 0.15$) thin films"***, Applied Surface Science 255, p. 4992–4995, 2009.
9. Jeng-Lin Chung, Jyh-Chen Chen, and Chung-Jen Tseng, ***"The influence of titanium on the properties of zinc oxide films deposited by radio frequency magnetron sputtering"***, Applied Surface Science 254, p. 2615–2620, 2008.
10. B.D. Ngoma, T. Mpahane, N. Manyala, O. Nemraoui, U. Buttner, J.B. Kana, A.Y. Fasasi, M. Maaza, and A.C. Beye, ***"Structural and optical properties of nano-structured tungsten-doped ZnO thin films grown by pulsed laser deposition"***, Applied Surface Science 255, p. 4153–4158, 2009.
11. Yaodong Liu, Lei Zhao, and Jianshe Lian, ***"Al-doped ZnO films by pulsed laser deposition at room temperature"***, Vacuum 81, p. 18-21, 2006.
12. Young-Sung Kim and Weon-Pil Tai, ***"Electrical and optical properties of Al-doped ZnO thin films by sol-gel process"***, Applied Surface Science 253, p. 4911-4916, 2007.
13. Y. Belghazi, M. Ait Aouaj, M. El Yadari, G. Schmerber, C. Ulhaq-Bouillet, C. Leuvrey, S. Colis, M. Abd-lefdil, A. Berrada, and A. Dinia, ***"Elaboration and characterization of Co-doped ZnO thin films deposited by spray pyrolysis technique"***, Microelectron. J., doi:10.1016/j. mejo. 2008.07.051,2008.
14. E. Bacaksiz, S. Aksu, B.M. Basol, M. Altunbaş, M. Parlak, and E. Yanmaz, ***"Structural, optical and magnetic properties of $Zn_{1-x}Co_xO$ thin films prepared by spray pyrolysis"***, Thin Solid Films 516, p.7899–7902,2008.
15. Xiao-Hong Xu, Xiu-Fang Qin, Feng-Xian Jiang, Xiao-Li Li, Ya Chen, G.A. Gehring, ***"The dopant concentration and annealing temperature dependence of ferromagnetism in Co-doped ZnO thin films"***, Applied Surface Science 254, p. 4956–4960,2008.
16. Sunil Kumar, R. Kumar, D.P. Singh, ***"Swift heavy ion induced modifications in cobalt doped ZnO thin films: Structural and optical studies"***, Applied Surface Science 255, p. 8014–8018, 2009.

الخواص التركيبية والبصرية لأغشية اوكسيد الخارصين المشوبة بالكوبلت (CZO) المحضرة بتقنية التحلل الكيميائي الحراري

مرفت كاظم ارحيمة*   رامز احمد الانصاري*   نادر فاضل حبوبي**

*قسم الفيزياء، كلية العلوم للبنات، جامعة بغداد
** قسم الفيزياء، كلية التربيه، الجامعة المستنصريه

الخلاصـــة:

تم ترسيب أغشية اوكسيد الخارصين النقية والمشوبة بالكوبلت(CZO) بتقنية التحلل الكيميائي الحراري، وباستخدام محلولي اسيتات الخارصين وكلوريد الكوبلت. وقد تمت دراسة تأثير التشويب بالكوبلت على الخواص التركيبية والبصرية للأغشية المحضرة. وكانت الأغشية المحضرة ذات نفاذية عالية (~90%) وامتصاصية واطئة. دُرست الخواص التركيبية باستخدام حيود الاشعة السينية، وكانت هذه الأغشية المرسبة على قواعد زجاجية عند درجة حرارة (400°C)، ذات تركيب متعدد التبلور ومن النوع السداسي المتراص، وقد وُجد أن الحجم الحبيبي يقل مع زيادة تركيز الكوبلت(Co) ، ولم يتم ملاحظة تغيير كبير في ثوابت الشبيكة، بينما قلت فجوة الطاقة البصرية ذات الانتقال المباشر المسموح من (3.18eV) الى (3.02eV). وقد تم حساب بقية المعلمات التركيبية مثل عامل التشكيل(Tc) وكثافة الانخلاعات (δ) وعدد البلورات(M).