ISSN : 0974 - 7486 Volume 11 Issue 10

Materials Science

An Indian Journal

Full Paper

MSAIJ, 11(10), 2014 [321-326]

Structural and electrical properties of cobalt doped SnO_2 thin films

Nadir Fadhil Habubi*[1], Ghuson H.Mohamed[2], Saad Farhan Oboudi[2]

[1]Al_Mustansiriyah University, College of Education, Physics Department, Baghdad, (IRAQ)

[2]Baghdad University, College of Science, Physics Department, Baghdad, (IRAQ)

E-mail : nadirf61@gmail.com

ABSTRACT

During this work, pure and doped SnO_2 thin films with different concentration of Co (3 and 7)% wt. have been prepared by chemical spray pyrolysis method on glass substrates preheated to 500°C. The structure of these films has been examined using X-Ray diffraction analysis and the results show that the pure films were amorphous and converted to polycrystalline after doping with Co with strong crystalline orientation (110) and it is affected slightly with increasing of Co content. The electrical properties of these films were studied with different concentration of Co. The d.c. conductivity for all deposited films was decreased with increasing Co contents while the resistivity increased. Also, it was found that there is tow region of activation energy and the electrical activation energies increase with increasing the concentration of Co. Hall measurements showed that all the films are n-type and carrier concentration decreases with the increasing of Co concentration. Furthermore, we observe that the mobility increases with increasing of Co content while drift velocity is increased.

KEYWORDS

SnO_2 thin films;
Electrical properties;
Spray pyrolysis technique.

INTRODUCTION

Tin oxide is one of the semiconductors that have been widely investigated over the past three decades. It is employed in a wide range of applications, including solid state gas sensors, liquid crystal displays, photovoltaic cells, transparent conducting electrodes, infrared reflectors, plasma display panels (PDPs) etc.[1,2]. Tin oxide SnO_2 films are technologically important materials[3]. It has been prepared using different preparation technique such as spraying pyrolsis, CVD technique and vacuum deposition. In addition, SnO_2 is useful as a hard film material for applications requiring high refractive and reflective properties. SnO_2 films are low cost, chemically and environmentally more stable than other TCOs such as ZnO, and Sn-doped In_2O_3 (ITO)[4]. SnO_2 is a material of wide ranging application It is used in UV light emitting diodes (LEDs), transparent conducting electrodes of laser diodes (LDs), photovoltaic devices, optical wave guides, gas sensors, etc[5-8]. Also, It is interested as transparent conductor, because the n-type SnO_2 thin films which does not result in corrosion when it is brought into contact with the electrolyte (SnO_2) a tetragonal rutile structure with lattice parameters a = b = 4.737 Å and c = 3.826 Å[9]. SnO_2 has a direct band gap semiconductor (E_g=3.37eV) at room

temperature with high exaction binding energy (60 meV). It has transmission in the visible range, and SnO_2 thin films can take place of ITO and ZnO because of their electrical and optical properties and its excellent stability which has been mentioned widely[10,11]. SnO_2 layers also can be used as the top layer of a solar cell with multilayers, since the top layer of a multilayer usually absorbs photons with high energies in the solar spectrum SnO_2 films are highly conductive material with negative charged conductivity. It resistivity found to decrease rapidly through annealing in vacuum or air also by suitable doping with different opant. Also this dopant material could be used to convert the conductivity to positive type[12].

EXPERIMENTAL

Thin films of tin oxide SnO_2 have been prepared by chemical pyrolysis method. The spray pyrolysis was done by using a laboratory designed glass atomizer, which has an output nozzle about 1 mm. The films were deposited on preheated glass substrates at a temperature of 500°C, the starting solution was achieved by an aqueous solutions of 0.1M tin(IV) Chloride Pentahydrate provided from BDH chemicals England and 0.1M of Cobalt Chloride Hexahydrate from Sigma-Aldrich USA used as a doping agent with a concentration of 3% and 7%, these materials were dissolved in demonized water and ethanol, few drops of HCl were added to speed up the dissolving, formed the final spray solution and a total volume of 50 ml was used in each deposition. With the optimized conditions that concern the following parameters, spray time was 8 sec lasted by two minutes to avoid excessive cooling and the spray interval (3min) was kept constant. The carrier gas (filtered compressed air) was maintained at a pressure of 105 Nm^{-2}, distance between nozzle and substrate was about 30 cm ±1 cm, solution flow rate 5 ml/min. Thickness of the sample was measured using the weighting method and was found to be around 500nm.

RESULTS AND DISCUSSION

The XRD spectra of pure of SnO2 thin films and doped with different Co concentrations (3% and 7%) recorded in 2θ angle in the range of 20-60 are shown in Figure 1. It can be seen that the pure film obtained has amorphous structure. With increasing of Co content one may observe a weak diffraction peak for [110] direction, which is characteristic of the tetragonal structure of the SnO_2 thin films.

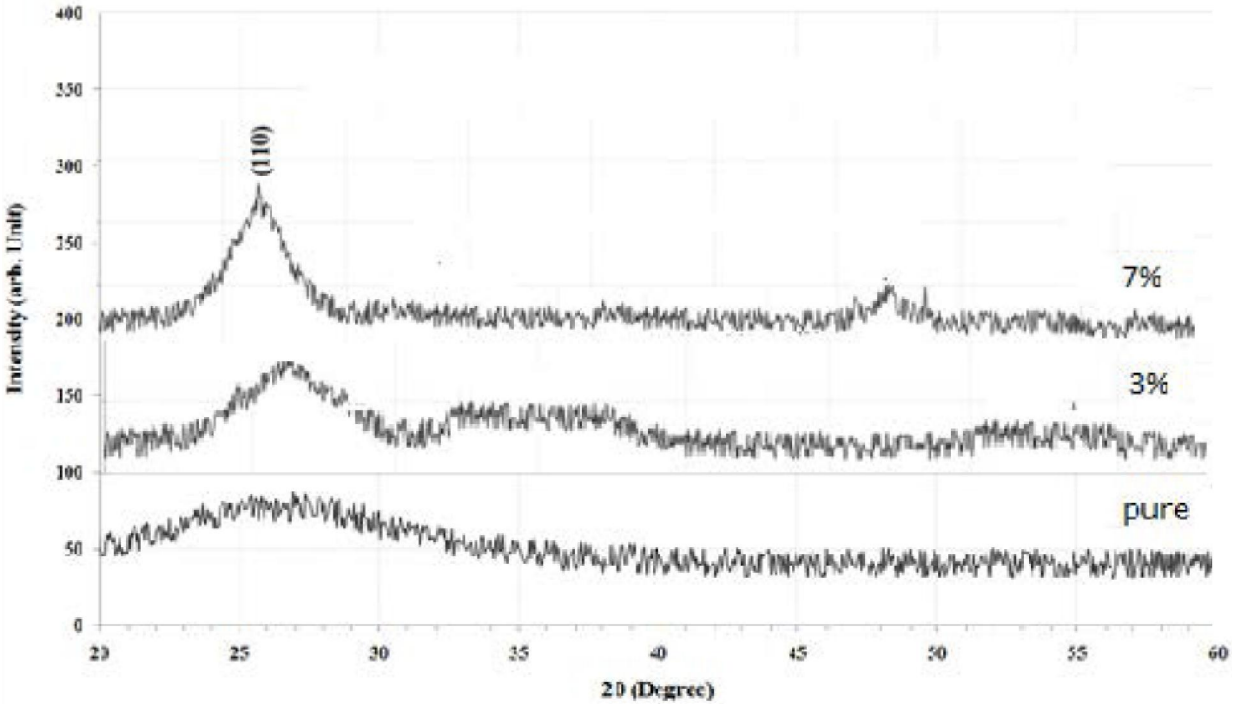

Figure 1 : X-ray diffraction pattern of SnO_2 films with different Co content

The variation of resistivity of Co doped SnO_2 thin films as a function of temperature in the range of (298-400) K at different doping of Co is shown in Figure 2. It is clear from this figure that the resistivity shows the negative temperature coefficient of resistance for all deposited films. Also, the resistivity decreases markedly as the concentration of Co increases. The increase of the resistivity with the Co concentration indicates a decrease of the number of free charge carriers.

When Co atoms are implanted into the host SnO_2 lattice, they either occupy interstitial sites or they substitute Sn atoms. In the latter case the Sn atoms can easily move to interstitial sites since the formation energy for Sn interstitial is small[13,14]. The Sn is substituted either by Co2+ or by Co3+. Is has to be noted that the probability for substituting Co2+ is higher since the ion radius of Sn4+ (0.83 Å) is similar to that of Co2+ (0.79) Å for lower spin and 0.89 Å for the high spin state) rather than that of Co3+ which is considerably smaller[15]. Perfectly stoichiometric SnO_2 is an insulator [16] in which four Sn valence electrons are transferred to the oxygen Figure 3(a). In real SnO_2 a slight oxygen deficiency provides free charge carriers originating from two shallow donor levels due to the oxygen vacancies Figure 3(b). Doping with Co inserts ions into the host lattice with a lower valence compared to Sn. This reduces the number of potential binding electrons to neighboring oxygen atoms Figure 3(c,d). The high electronegativity of the oxygen causes a free-electron capture into the localized acceptor states. Therefore, the conductivity decreases as a function of the Co concentration which is observed in the experiment.

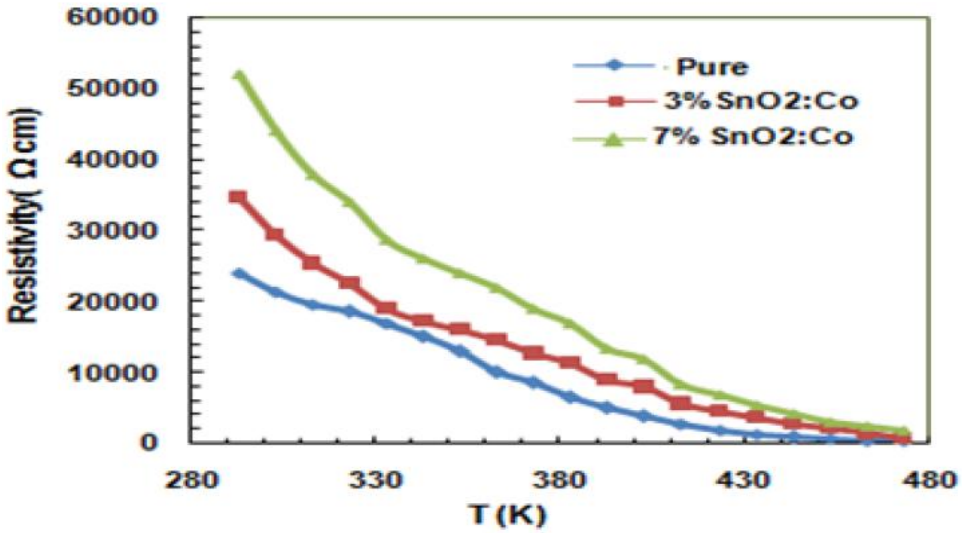

Figure 2 : Variation of resistivity versus temperatures for Co doped SnO_2 films

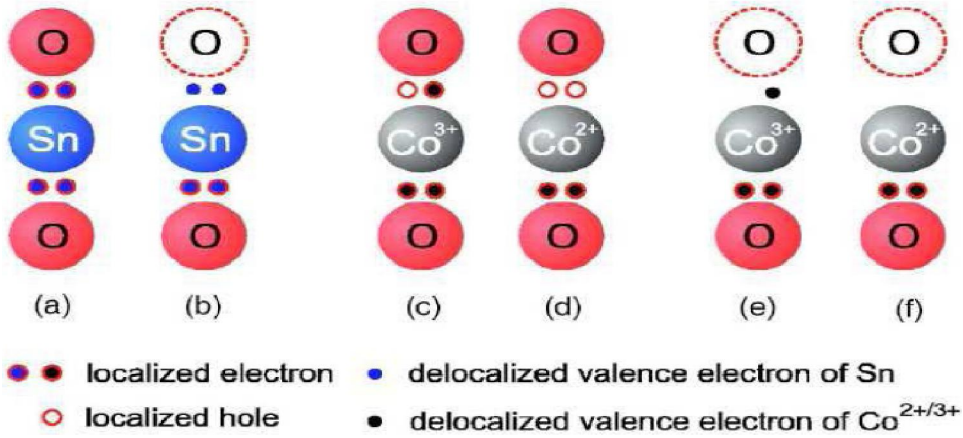

Figure 3 : Charge carrier compensation due to Co3+ and Co2+ doping (perfectly stoichiometric SnO_2 (a), oxygen vacancy with 2 donors (b), substituted Sn by Co3+ (c) and Co2+ (d) with two oxygen neighbors, substituted Sn by Co3+ (e) and Co2+ (f) with one adjacent oxygen vacancy[14]

Full Paper

This decrease in conductivity can be understood on the basis of the fact that the conductivity generally decreases when the carrier concentration of the heavily doped semiconductor increases[17]. In order to study the mechanisms of conductivity, it is convenient to plot logarithm of the conductivity (lnσ) as a function of 1000/T. Figure 4 shows the relation between of lnσ versus 1000/T for SnO_2 thin films doped with different concentration of Co in the range (393-473) K. It is clear from this figure that the values of conductivity increases with the increasing of temperature, such as the general characteristics of the semiconductor with increasing temperature lead to an increase in the number of electron-holes pairs resulting on increased conductivity. The linear proportionality in the curve is related to the increase in the number of ionized carriers from the valence band to the conduction band as the substrate is heated. Also, it is seen that the conductivity decreases with increasing of Co concentration. Furthermore, it is clear from this figure that there are two transport mechanisms, giving rise to two activation energies Ea_1 and Ea_2. The conduction mechanism of the activation energy (Ea_2) at the higher temperatures range (403-503)K is due to carrier excitation into the extended states beyond the mobility edge and at the lower range of temperatures (293-393)K, the conduction mechanism is due to carrier excitation into localized state at the edge of the band[16].

In order to study the conductivity mechanisms, it is convenient to plot logarithm of the conductivity (lnσ) as a function of 1000/T for all films. The activation energy of the samples can be determined from the slopes as shown in Figure 4. The evaluation of the conductivity data yields the activation energies of the donor levels, which are given by an Arrhenius plot. For all doping concentrations two activation energies can be derived as listed in TABLE 1. In all samples a very low donor level may be attributed to interstitial Sn[13]. The roughly constant intermediate (Ea_2) and increasing high values (Ea_1) can be assigned to oxygen donors[19]. The increase of the high energies with the Co doping concentration results from a considerable coulomb attraction between the electron and the ionized impurities which increase with the donor concentration[20]. TABLE 1 shows the effect of Co content on both activation energies Ea_1 and Ea_2 for SnO_2 thin films. It is clear that the activation energies increase with the increasing of the Co concentration. This may be due to changes in the localized states, structure, and composition of films as well as to the re-arrangement of atoms which yields fewer defects. The value of the activation energy has been estimated in our work is agreed with the result[21].

In this measurement, the Hall Effect will be used to study some of the physics of charge transport in thin film samples. Hall mobility, carrier type and concentration were measured from Hall coefficient (R_H) data and d.c conductivity. The complete data of μ_H n σ, ρ for the undoped and doped films with doping concentration of Co (3 and 7) % wt are tabulated in TABLE 1. The results indicate that the materials under study are n-type

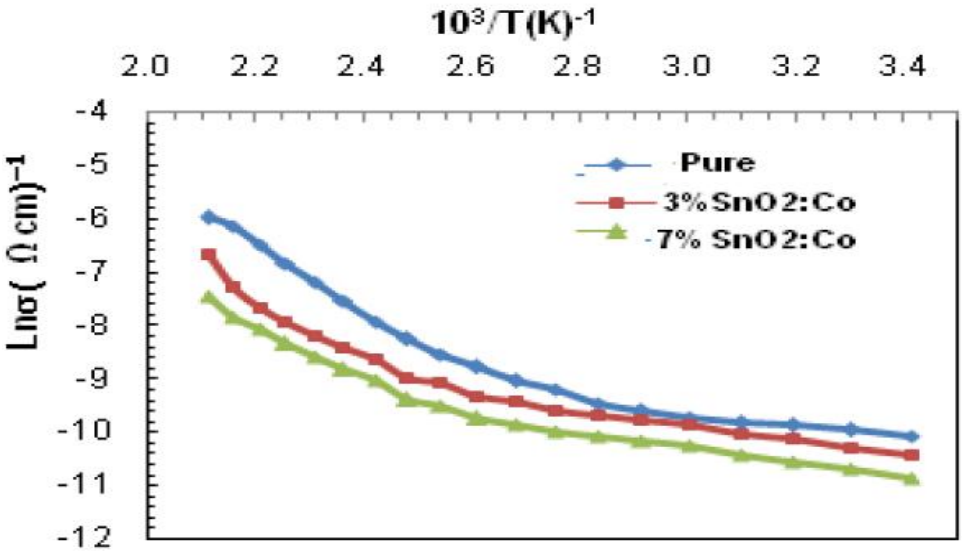

Figure 4 : Lnσ versus 1000/T for Co doped SnO2 films

TABLE 1 : The electrical properties of Co doped SnO_2 thin films

Sample	$\sigma\times10^{-5}$ $(\Omega.cm)^{-1}$	$\rho\times10^{4}$ $(\Omega.cm)$	$R_H\times10^{7}$ (cm^2/C)	$N\times10^{11}$ $(1/cm^3)$	$\mu_H\times10^{2}$ $(cm^2/V.s)$	$v_d\times10^{3}$ (cm/s)	Ea1(eV)	Ea2(eV)
pure	4.82	2.07	1.4	4.46	6.76	1.5	0.103	0.34
3%	2.88	3.46	2.8	42.85	6.91	1.54	0.113	0.36
7%	1.92	5.21	4	1.56	7.68	1.71	0.115	0.39

semiconductor possibly due to the donor formation by O_2 vacancies, these results correspond to the published literatures[22]. From the table, it can be seen that the carrier mobility increases with decreasing the carrier concentration which is due to increase in the (Co) content. The interpretation of this increase is attributed to the decrease in the localized state near band edge, and also decrease in carrier concentration, then leads to increase in $\mu_{H,}$ From the Hall mobility measurements, we can calculate the drift velocity (υ_d), using equation ($\sigma = \frac{Nqv_d}{E}$) where N is the carrier concentration,q is the electron charge, E is the electric field. It is found that drift velocity is increased with the increasing of Co concentration and the result is due to increase in the value of mobility and decreases in the carrier concentration. In summary, Co implantation leads to a homogeneous dopant distribution without formation of clusters. The Co doping causes a compensation of charge carriers by localized holes. The resulting decrease of the conductivity is reflected in the decrease of the ordered moment, which supports the model in which the magnetic exchange is mediated by delocalized charge carriers. The results in this report have been agreed with the result obtained by Awada et al[14].

CONCLUSION

In this report, the influence of doping with cobalt was studied for tin oxide thin films grown by chemical spray pyrolysis technique with different doping concentrations of Co (3 and 7) % wt on glass substrate. The electrical properties which include conductivity and Hall measurements were investigated for these films. The films have high resistivity, high resistance and high mobility with increasing of Co content. We demonstrated experimentally that the selectivity of the resistance response is improved for the tin oxide properties by high amounts of the Co.

REFERENCES

[1] W.Gopel, K.D.Schierbaum; SnO_2 sensors: Current status and future prospects, Sensors and Actuators B: Chemical, **26(1-3)**, 1-12 **(1995)**.

[2] K.L.Chopra, S.Major, D.K.Pandya; Transparent conductors-A status review, Thin Solid Films, **102(1)**, 1-46 **(1983)**.

[3] P.M.Gorley, V.V.Khomyak, S.V.Bilichuk, I.G.Orletsky, P.P.Horley, V.O.Grechko; SnO2 films: Formation, electrical and optical properties, Materials Science and Engineering: B, **118(25)**, 160-163 **(2005)**.

[4] Mounir Gaidi, Anouar Hajjaji, My Ali El Khakani, Brenard Chenevier, Michel Labeau, Brahim Bessaïs; Optical properties tuning of SnO_2 films by metal incorporation (Pt,Pd): Correlation with microstructure change, Jpn.J.Appl.Phys., **48**, 072501 **(2009)**.

[5] C.R.Gorla, N.W.Emanetoglu, S.Liang, W.E.Mayo, Y.Lu; Structural, optical, and surface acoustic wave properties of epitaxial ZnO films grown on (01[REMOVED EQ FIELD]2) sapphire by metalorganic chemical vapor deposition, J.Appl.Phys., **85**, 2595-2602 **(1999)**.

[6] T.Minami, T.Yamamoto, T.Miyata; Highly transparent and conductive rare earth-doped ZnO thin films prepared by magnetron sputtering, Thin Solid Films, **366(1-2)**, 63-68 **(2000)**.

[7] Q.Chen, J.W.Yang, A.Osinsky, S.Gangopadhyay, B.Lim, M.Z.Answer, M.Asif Khan; Schottky barrier detectors on GaN for visible-blind ultraviolet detection, Appl.Phys.Lett., http://dx.doi.org/10.1063/1.118837, **70**, 2277 **(1997)**.

[8] S.C.Lee, J.H.Lee, T.S.Oh, Y.H.Kim; Fabrication of tin oxide film by sol-gel method for photovoltaic solar cell system, Sol.Energy Mater.Sol.Cells, **75**, 481-487 **(2003)**.

[9] S.Majumder; Synthesis and characterization of SnO_2 films by wet chemical process, Materials Science-Poland, **27(1)**, 123-129 **(2009)**.

Full Paper

[10] F.K.Shan, Y.S.Yu; Band gap energy of pure and AL-doped SnO_2 thin films, Journal of the European Ceramic Society, **24**, 1869-1872 **(2004)**.

[11] P.Samarasekaral, A.G.K.Nisanthal, A.S.Disanayake; (High photo-voltage Zinc Oxide thin films Deposited by DC Sputtering), Chinese Journal of Physics, **40(2)**, 196-199 **(2002)**.

[12] E.Elangovan, K.Ramesh, K.Ramamurthi; Studies on the structural and electrical properties of spray deposited SnO_2:Sb thin films as a function of substrate temperature, Solid State Commun., **130**, 523-527 **(2004)**.

[13] C.Kilic, A.Zunger; Origins of coexistence of conductivity and transparency in SnO_2, Phys.Rev.Lett., **88**, 95501-1 - 095501-4 **(2002)**.

[14] A.Awada, D.Menzel, H.Dierke, J.Schoenes, F.Ludwig, M.Schilling; Free-carrier compensation in ferromagnetic ion-implanted SnO_2:Co, J. of Appl.Phys., **103**, 07D106 **(2008)**.

[15] R.D.Shannon; Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides, Acta Cryst.A32, **751**, 751-767 **(1976)**.

[16] C.Terrier, J.P.Chatelon, R.Berjoan, J.A.Roger; Sb-doped SnO_2 transparent conducting oxide from the sol-gel dip-coating technique, Thin Solid Films, **263**, 37-41 **(1995)**.

[17] S.Y.Lee, B.O.Park; Structural, electrical and optical characteristics of SnO_2:Sb thin films by ultrasonic spray pyrolysis, Thin Solid Films, **510**, 154-158 **(2006)**.

[18] J.I.Langford, A.J.C.Wilson; Scherrer after sixty years: A survey and some new results in the determination of crystallite size, J.Appl.Cryst., **11**, 102-113 **(1978)**.

[19] S.Samson, C.G.Fonstad; Defect structure and electronic donor levels in stannic oxide crystals, J.Appl. Phys., http://dx.doi.org/10.1063/1.1662011, **44**, 4618 **(1973)**.

[20] G.L.Pearson, J.Bardeen; Electrical properties of pure silicon and silicon alloys containing boron and phosphorus, Phys.Rev., **75**, 865-883 **(1949)**.

[21] Marwa A.Hassan; Construction, characterization of MIS Heterojunction devices, MSC Thesis, Department of Physics, College of Science, **(2009)**.

[22] H.He Jr., Te.H.Wu, Cheng L.Hsin, Kun M.Li, Lih J.Chen, Yu L.Chueh; Beaklike SnO_2 nanorods with strong photoluminescent and field-emission properties, Small, **2(1)**, 116-120 **(2006)**.