Structural and electrical properties of cobalt doped SnO$_2$ thin films

Nadir Fadhil Habubi*, Ghuson H.Mohamed, Saad Farhan Oboudi

$^1$Al_Mustansiryah 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.

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**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.$^{11,21}$. Tin oxide SnO$_2$ films are technologically important materials.$^{3}$ It has been prepared using different preparation technique such as spraying pyrolysis, 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$_2$O$_3$ (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 ($E_g = 3.37$eV) at room
Structural and electrical properties of cobalt doped SnO₂ thin films

Full Paper

An Indian Journal

322

EXPERIMENTAL

Thin films of tin oxide SnO₂ 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 SnO₂ thin films.

Figure 1 : X-ray diffraction pattern of SnO₂ 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 Co$^{2+}$ or by Co$^{3+}$. It has to be noted that the probability for substituting Co$^{2+}$ is higher since the ion radius of Sn$^{4+}$ (0.83 Å) is similar to that of Co$^{2+}$ (0.79 Å for lower spin and 0.89 Å for the high spin state) rather than that of Co$^{3+}$ 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](image)

![Figure 3: Charge carrier compensation due to Co$^{3+}$ and Co$^{2+}$ doping (perfectly stoichiometric SnO$_2$ (a), oxygen vacancy with 2 donors (b), substituted Sn by Co$^{3+}$ (c) and Co$^{2+}$ (d) with two oxygen neighbors, substituted Sn by Co$^{3+}$ (e) and Co$^{2+}$ (f) with one adjacent oxygen vacancy$^{[14]}$](image)
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\(^1\). In order to study the mechanisms of conductivity, it is convenient to plot the logarithm of the conductivity (\(\ln \sigma\)) as a function of \(1000/T\). Figure 4 shows the relation between \(\ln \sigma\) versus \(1000/T\) for SnO\(_2\) thin films doped with different concentrations of Co in the range (393-473) K. It is clear from this figure that the values of conductivity increase 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-hole pairs resulting in 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 \(E_{a_1}\) and \(E_{a_2}\). The conduction mechanism of the activation energy \(E_{a_1}\) 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\(^1\).

In order to study the conductivity mechanisms, it is convenient to plot the logarithm of the conductivity (\(\ln \sigma\)) as a function of \(1000/T\) for all films. The activation energies 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\(^1\). The roughly constant intermediate \((E_{a_2})\) and increasing high values \((E_{a_1})\) can be assigned to oxygen donors\(^1\). 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\(^2\). Table 1 shows the effect of Co content on both activation energies \(E_{a_1}\) and \(E_{a_2}\) 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\(^2\).

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 \(\mu, n, \sigma, \rho\) 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: Ln σ versus 1000/T for Co doped SnO2 films](image-url)
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 ($v_d$), using equation ($σ = \frac{Nqv_d}{E}$) 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.

**TABLE 1 : The electrical properties of Co doped SnO$_2$ thin films**

<table>
<thead>
<tr>
<th>Sample</th>
<th>$σ×10^5$ (Ω.cm)$^{-1}$</th>
<th>$ρ×10^4$ (Ω.cm)</th>
<th>$R_0×10^7$ (cm$^2$/C)</th>
<th>$N×10^{11}$ (1/cm$^3$)</th>
<th>$μ_H×10^2$ (cm$^2$/V.s)</th>
<th>$v_d×10^3$ (cm/s)</th>
<th>$Ea1$(eV)</th>
<th>$Ea2$(eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>pure</td>
<td>4.82</td>
<td>2.07</td>
<td>1.4</td>
<td>4.46</td>
<td>6.76</td>
<td>1.5</td>
<td>0.103</td>
<td>0.34</td>
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<tr>
<td>3%</td>
<td>2.88</td>
<td>3.46</td>
<td>2.8</td>
<td>42.85</td>
<td>6.91</td>
<td>1.54</td>
<td>0.113</td>
<td>0.36</td>
</tr>
<tr>
<td>7%</td>
<td>1.92</td>
<td>5.21</td>
<td>4</td>
<td>1.56</td>
<td>7.68</td>
<td>1.71</td>
<td>0.115</td>
<td>0.39</td>
</tr>
</tbody>
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**REFERENCES**

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