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Physical properties of SnO_2: Co thin films prepared by chemical spray pyrolysis

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Abstract:

In this research, Co-doped SnO_2 thin films were prepared by chemical spray pyrolysis technique using $SnCl_4.5H_2O$ and $CoCl_2.6H_2O$, with impurity percentage are (0%-3%-6%-9%) on glass substrates preheated at (450°C) with spray rate 5sec./1min, and thickness (400nm). The investigation of (XRD) indicates that the (SnO_2) films are polycrystalline type of (tetragonal), the optical properties and band gap energy was observed and it`s found varied from (3.361-2.855 eV) when increasing in percentage impurity the energy band gap decreased. The Hall coefficient, concentration and mobility of charge carriers of SnO_2:Co films studied, and their results observed that the increase in impurity of cobalt caused increase in electrical properties generally.

Key words: thin films, SnO_2, chemical spray pyrolysis, cobalt.

Introduction:

Tin dioxide, SnO_2 , is an important n-type semiconductor SnO_2 is a wide-band gap semiconductor with band-gap of (E_g=3.6 ~ 4.2 eV) [1]. In addition to the excellent optical transparency, SnO_2 is very stable chemically. The applications of transparent conducting oxide (TCO) have been extensively studied, such as gas sensors [2], dye-sensitized solar cells, organic light emitting diodes, transparent electrodes for flat electrical resistance with high optical transparency in visible and near-IR region electromagnetic spectrum, transparent conducting electrodes, energy storage (e.g. lithium batteries) transistors and solar cells [3-8]. The purpose of the present work was to prepare Co-doped SnO_2 thin films by chemical spray pyrolysis technique and to investigate the effects of Co-doping levels on the structural, electrical and optical properties of the prepared samples have been studied.

Experimental

Material preparation and deposition of films:

Chemical techniques for the preparation of thin films have been studied extensively because such processes facilitate the designing of materials on a molecular level. Spray pyrolysis, one of the chemical techniques applied to form a variety of thin films, results in good productivity from a simple apparatus. In the current research, tin oxide thin films are deposited on glass substrates employing locally –made spray pyrolysis deposition chamber whose main components set up is illustrated in the schematic diagram of figure (1). It is essentially made up of a precursor solution, carrier gas assembly connected to a spray nozzle, and a temperature –controlled hot plate heater. The atomizer, illustrated in the photo plate 2-B, has an adjustable copper capillary tube nozzle of 0-0.3 mm inner diameter clamped to a holder and supported by a metal tripod. The nozzle is driven by a compressed atmospheric air. The prepared precursor solution is pumped through the metal nozzle with a solution flow rate ranging from 1 to 2 mL/min. Due to the air pressure of the carrier gas; a vacuum is created at the tip of the nozzle to suck the solution from the tube after which the spray starts [9]. To regulate spraying time, a 16 – Bar Tork solenoid valve controlled by an adjustable timer has been incorporated. The atomizer and the 1500 Watts hot plate heater are enclosed in a 1 ×1 ×1 m^3 ventilation hood, figure (1) (b). A 220 V a.c. power was applied to the heater and temperature was measured using a type K (nickel-chromium) thermocouple and precision digital temperature controller (GEMO DT109 figure (1) (c)).

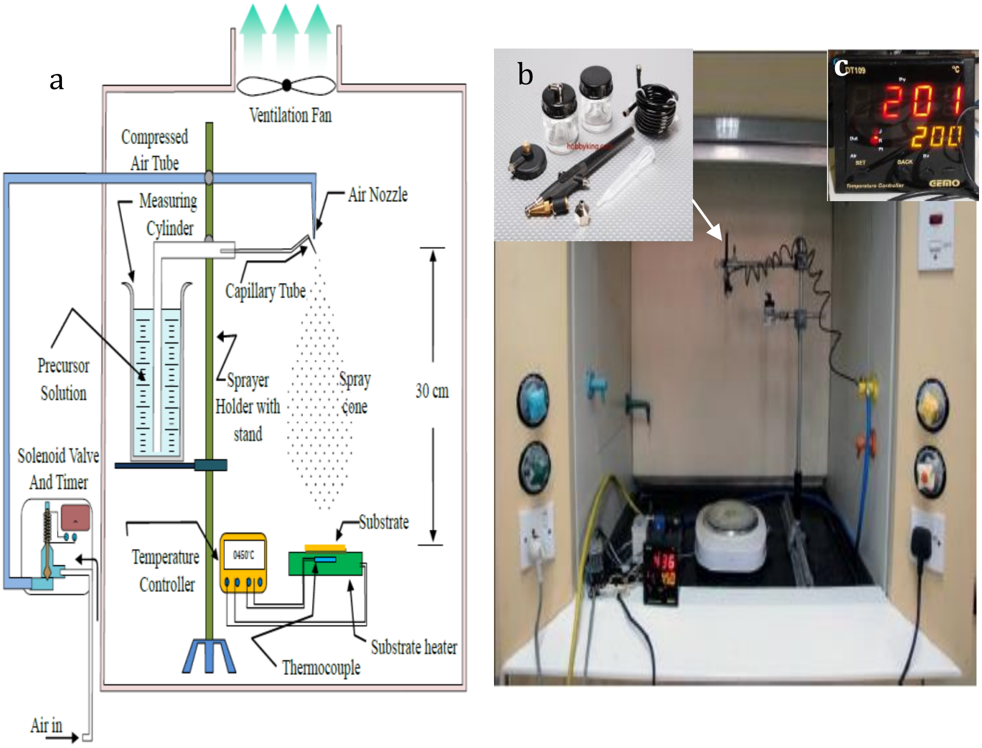

Fig. 1 Spray pyrolysis experimental set up.

A 0.1 M concentration precursor solution of Tin(IV) chloride pentahydrate ($SnCl_4.5H_2O$ (molecular weight 350.58 g/mol) has been prepared by dissolving a solute quantity of 3.5058 g of ($SnCl_4.5H_2O$ (as weighed by a 10^{-4} g -precision balance) in 100 mL dissolved in distilled water and ethanol alcohol C2H5OH have been employed in getting SnO_2 thin films. A magnetic stirrer is incorporated for this purpose for about 10 –15 minutes to facilitate the complete dissolution of the solute in the solvent. Organic solvents are preferable over distilled water because the former enables the attainment of homogeneous, highly – transparent, thin films of small grain size. Prior to depositing the films, the substrates, which are commercial glass slides of 76×25×1 mm^3 dimensions, are firstly cleaned by dipping in distilled water to remove the dust and then are ultrasonically cleaned in methanol for about 10 min. Finally they are soaked in distilled water, dried, and polished with lens paper. The pretreatment of the substrates is carried out to facilitate nucleation on the substrate surface. Presence of contamination on the substrate surface is one of the reasons of the appearance of pinholes and film inhomogeneity [10].The spray rate is usually in the range 10 cm^3. min^{-1}. The optimum carrier gas pressure for this rate of solution flow is around 10^5 N/m^2. At lower pressures, the size of the solution droplets becomes large, which results in the presence of recognized spots on the films and then reduction of transparency. This situation increases the scattering of light from the surface and then reduces the transmittance of the films. The spray pyrolytic substrate temperature is maintained within 450 ± 5 °C during the deposition. Film thickness is controlled by both the precursor concentration and the number of sprays, or alternatively, spraying time. Thus, a 5 – second spray time is maintained during the experiment. The normalized distance between the spray nozzle and substrate was fixed at 30 cm.Table (1) summarizes the optimized thermal pyrolysis deposition conditions for the preparation of SnO_2 thin films that were employed in the current research.

Table 1: Optimum thermal spray pyrolysis deposition conditions for the preparation of SnO_2 thin films.

Spray parameter	Value
Molecular weight $SnCl_4.5H_2O$	w_t=350.58 g/mol
Molecular weight $CoCl_2.6H_2O$	w_t= 237.93 g/mol
Molarity of SnO_2	0.1 M
Nozzle–substrate distance	30 cm
Solution flow rate	10 cm^3/min
Gas pressure	10^5 N/m^2
Substrate temperature	450 °C

Many methods have already been tested for this purpose, for example bulk doping during calcinations, sol-gel technology, spray pyrolysis deposition, thermal evaporation, CVD, laser ablation, magnetron sputtering, impregnation by salt solution, with the help of these methods, it was possible to form on a surface of metal oxides surface clusters of various components with sizes from 0.1 to 8 nm [11-13]. cobalt chloride was used as the source of dopant. The different dopant concentration of cobalt (Co) (3%, 6%, 9%) was prepared, then the prepared solution was sprayed on preheated glass substrate.

Structural Properties:

The crystalline structure of the thin films, obtained at different doping concentrations were examined by Philips instrument system at room temperature, X-ray diffractometer using CuK_α radiation with wavelength, λ=1·54056A°. The average grain size of tin oxide thin film samples were calculated by using the Scherrer's equation [14], and there values as table (2).

$$D = \frac{0.9\,\lambda}{\beta \cos\,\theta_B} \quad (1)$$

where **D** is the average grain size.

λ =1.54056 A° (X-ray wavelength).

β: the peak FWHM.

θ_B: the diffraction peak position, it means Bragg`s angle.

Co-doped SnO2 thin films in various Co from 0% to 9% are investigated; no peaks corresponding to the pure cobalt oxide film were observed, indicating that cobalt gets incorporated into the tin oxide lattice. There is no shift in the peak positions and all the diffraction peaks can be similarly assigned to the tetragonal cassiterite phase and preferred orientation (110) that may be followed by (101) plane as in figure (2) . Comparing the intensity of the series of XRD patterns, we noted that the intensities of diffraction peaks became weaker with increasing doping concentration but no impurity peak was observed. No diffraction peak related to other secondary phases was observed, indicating good purity of the final product.

Table 2: Effect of increasing in cobalt concentration on grain size($D_{ave.}$) and some of structural parameters.

SnO_2:Co	d_{110} A°	d_{101} A°	d_{200} A°	d_{211} A°	FWHM for d_{110} (degree)	$D_{ave.}$ A°
Pure SnO_2	3.34378	2.65403	2.33804	1.75680	1.8786	0.540713
3%Co	3.33633	2.65062	2.36091	1.77539	2.3000	0.427442
6%Co	3.30429	2.64873	2.36915	1.79205	2.0211	0.532095
9%Co	3.34571	2.72369	2.39063	1.80501	1.2000	0.858883

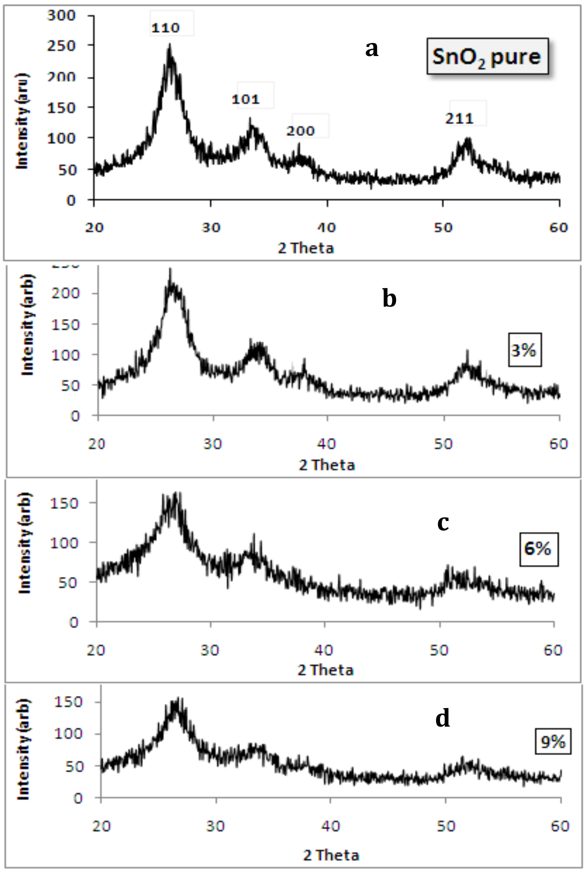

Fig. 3 XRD patterns of SnO_2:Co transparent for prepared films with various cobalt concentration as following (a) SnO_2:pure (b) SnO_2:3%Co (c) SnO_2:6%Co (d) SnO_2:9%Co.

Optical Properties:

The optical transmission spectra for undoped and SnO_2 doped Co thin films were obtained in the ultraviolet, visible region, using*(UV-1650PC Shimadzu software 1700 1650, UV-Visible recording Spectrophotometer), (Phillips), Japanese company in the wavelength range (300-850 nm)* as shown in figure (4) . The energy gap Eg values depend in general on the films crystal structure, the arrangement and distribution of atoms in the crystal lattice, also affected by crystal regularity. It was found in literature that SnO_2 film has a direct band gap and the values changes according to preparation parameters and conditions. The graphs of $(\alpha h\nu)^2$ vs. hν for direct band gap for pure and doped SnO_2 thin films are shown in figure (5). The values of E_g was obtained by extrapolation the curve to $(\alpha h\nu)^2=0$, the optical band gap of (3.361 eV) was estimated for pure SnO_2 film while the optical band gap decreases with increasing the doping concentration. This may be to increase the density of localized states near the conduction band in the energy band gap and consequently decrease the energy gap [15, 16]. From figure (6) the band gap energy of the films decreased significantly from (3.361 eV) for pure SnO_2 to (2.855 eV) for SnO_2:Co of 9% doped concentration.For estimating band gap, the optical absorption coefficient (□) was calculated from the absorption spectra (A) using the following equation [17]:

$$\alpha = 2.303\frac{A}{t} \qquad (2)$$

In which, t is thickness of the deposited film. Then, a self consistence rote based on the following relation was used for deducing optical band gap energy was calculated from relation [18]:

$$\alpha h\nu = B\left(h\nu - E_g\right)^r \qquad (3)$$

Where hυ : photon energy.

Eg : direct allowed photon energy.
B: is independent constant.
r:exponential constant, its value depended on type of transition,
r =1/2 for the allowed direct transition.
r =3/2 for the forbidden direct transition

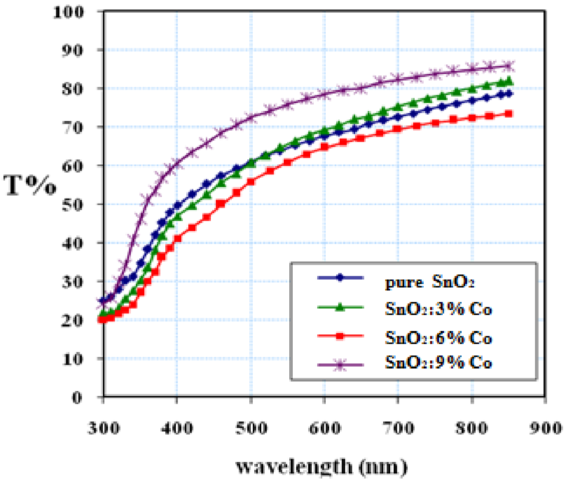

Fig. 4 Optical transmittance of pure and doped SnO2 films deposited on glass substrate

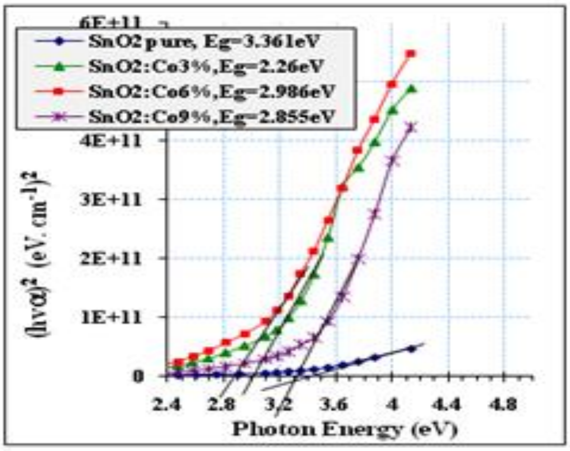

Figure 5 allowed direct electronic transitions of SnO2 films with Co various.

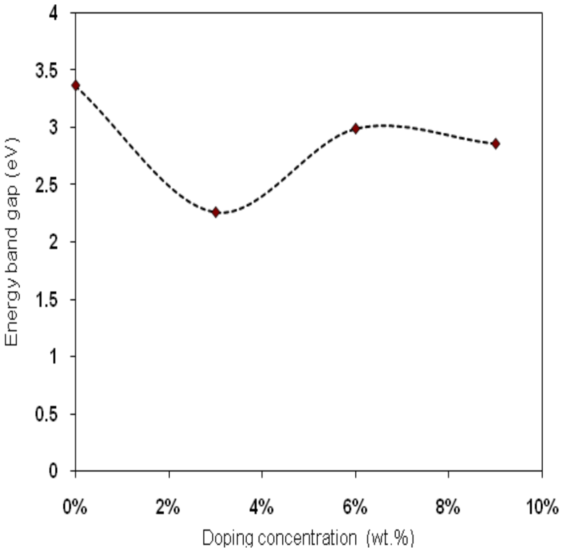

Fig. 6 Optical band gap as function with doping concentration

Electrical Properties

Electrical measurements consist of the resistivity; carrier concentration and mobility determination have been done from Hall's effect measurements were performed for distinction of the carrier type

Table 3. Hall coefficient, concentration and mobility of charge carriers of SnO_2:Co films:

SnO_2:Co	***Conductivity σ (1/ Ω.cm)***	***R_H (cm^3/C)***	***N_D (1/cm^3)***	***μ_H(cm^2/V.sec.)***	***Type***
pure SnO_2	*6.022×10^{-6}*	*7.529×10^{7}*	*8.291×10^{10}*	*4.534×10^{2}*	*n-type*
3%Co	*4.265×10^{-6}*	*1.908×10^{7}*	*3.271×10^{11}*	*1.192×10^{3}*	*n-type*
6%Co	*1.693×10^{-5}*	*1.722×10^{7}*	*3.181×10^{11}*	*3.932×10^{2}*	*n-type*
9%Co	*2.004×10^{-5}*	*1.692×10^{7}*	*3.690×10^{11}*	*2.262×10^{2}*	*n-type*

The conductivity and Hall mobility as a function of cobalt concentration is demonstrated in figure (7). It is clear that the values of conductivity increases with doping concentration, such as the general characteristics of the semiconductor with increasing doping concentration lead to an increase in the number of electron-holes pairs resulting on increased conductivity . The carrier concentration increases up to doping of 9wt %. The variation of carrier concentrations can ascribe to the substitution of Co for Sn, resulting in generation of conduction electrons and thus increasing the carrier concentration. It is that doping levels, the substitution of cobalt for_oxygen is the main defect in SnO$_2$:Co films. In the substituent, each Co- substitutes an O$_2$- in the lattice and the substituted O$_2$- provides more free electrons, which has an active effect on the free carrier initially.

The mobility of SnO$_2$:Co films shows a continuous decrease as the increasing of cobalt concentration. The actual value of mobility is determined by the interaction between the various scattering centers and free carriers. *This result in a good agreement with that obtained by .B.Zhang et al.* [19, 20].

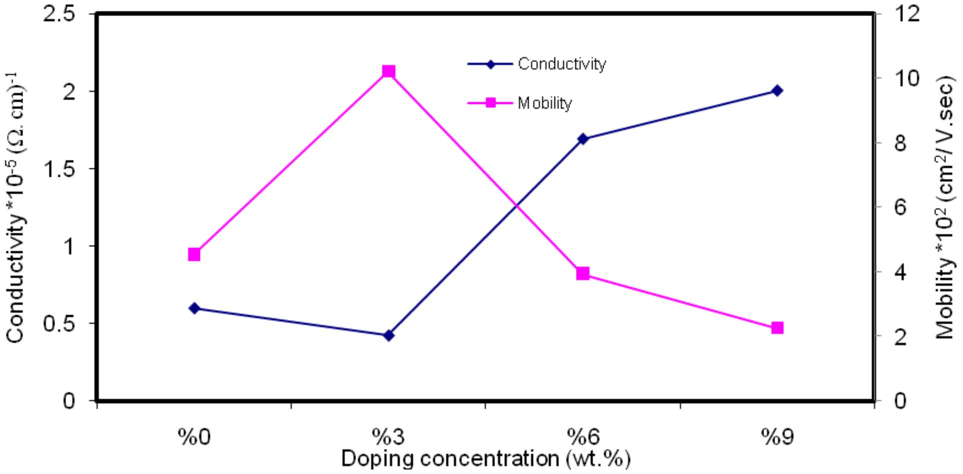

Fig. 7 The variation of conductivity and Hall mobility with doping concentration of SnO$_2$:Co films.

Conclusions:

SnO$_2$ thin films prepared by chemical spray pyrolysis technique, and they were doped with cobalt concentrations varied from (0% to 3%-6%- 9%), effect of varied cobalt concentration on structural, optical and electrical properties of SnO$_2$ were studied. Conclusions is including the following points:

1) The XRD results showed no peaks corresponding to the pure cobalt oxide film were observed, indicating that cobalt gets incorporated into the tin oxide lattice and there is no shift in the peak positions.

2) Electrical properties Hall coefficients, mobility and charge carriers concentration of SnO$_2$ were studied and show increasing in cobalt ratio improved all coefficients. And the high quality conductivity film is 2.004×10^{-5} Ω.cm for cobalt concentration is 9%.

3) Optical properties of prepared films show allowed indirect transitions were the most probable transition, and were found to vary from (3.361 to 2.855eV) for (0%-9%) respectively, that mean improvement in absorptance with increasing of cobalt concentration, although this behavior reversed in transmittance.

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