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Optical Characterization of $SnO_2$and SnO_2:CoDeposited by Spray Pyrolysis Technique

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Abstract : The optical properties of the pure SnO_2 and SnO_2:Cothin films deposited on a glass substrate by spray pyrolysis technique at a substrate temperature (673±10) K have been investigated by the transmittance spectra at room temperature at wavelength range from (320 to 1100) nm.The optical parameters of the prepared films astransmittance, absorbance, absorption coefficient, optical energy gap, refractive index and extinction coefficient were found.
Keywords: Spray pyrolysis, Tin dioxide, Cobalt ,optical properties , Thin film.

Introduction

Tin dioxide has the unique properties of being transparent and at the same time conducting. The conductivity arises from the oxygen deficient sites and the conductivity could be modulated from normal semiconducting to degenerate one by suitably doping the material and maneuvering the oxygen deficient sites[1]. There are many techniques that have been used to prepare the tin oxide films. Spray pyrolysis is a reliable and cheap method. It is a known technique that is closely related to chemical vapor deposition (CVD).SnO_2 is a remarkable n-type semiconductor material having wide band gap (3.6 eV) with electrical resistivity varying from 10 to 10^6 (Ω. cm) , depending on the temperature and the stoichiometry of the oxide and is sought for a wide variety of applications[2].Tin oxide (SnO_2) a tetragonal rutile structure with lattice parameters a=b = 4.737 Å and c = 3.826 Å.A substance with white color has a molecular weight of (150. 69 g/mole). Its density (6.95 g/cm^3), its melting point (1903 K) and its boilingpoint (2173 K) .A chemical spray deposition process can be described with six parameters[3]. Temperature of the gaseous environment, flow of carrier gas, distance between nozzle-substrate, droplet radius.solution concentration and solution flow. Direct deposition of thin films of SnO_2 at a temperature of 673K by simple and inexpensive chemical spray pyrolysis technique [4].Cobalt is a transition metal with a hexagonal close-packed (HCP) crystal structure at room temperature. The lattice parameters of the unit cell are a = 2.50 Å and c =4.06 Å. However,Co will undergopolymorphic transformation above 450°C into a FCC crystal structure of lattice parameter a= 3.54 Å[5].In this study, spray pyrolysis technique was adopted to deposit Cobalt doped SnO2 coatings onto glass substrates. Films thus produced were characterized by measuring optical properties.

2- Experimental Details

To prepared pure tin oxide (SnO_2) and doped Cobalt (Co) thin films. Which used procures material ($CoCl_2.6H_2O$) is a solid material which has a green color and its molecular weight (257.15 gm/mole). Cobalt was added with different doping concentrations (2,4,6and 8 Vol.%) to different concentrations of tin chloride and also dissolved in 50 ml of distilled water. The mixture was stirred by (Magnetic stirrer) at 40 ^oC for 30 min and then it was allowed to cool to the room temperature with continuous stirring. The deposition parameters such as spray nozzle-substrate distance (30 cm), spray time (4 s) and the spray interval (1 min) were kept constant.Optical transmittance spectra in the wavelength ranging 300–1100 nm were recorded using UV Visible spectrometer (UV-IR 1800 Spectrophotometer).

3- Results and Discussion

A. Transmittance

Figure (1) show the optical transmittance as a function of wavelength in the range (320 – 1100 nm) for pure and doped thin films.The maximum transmittance observed for undoped SnO_2 was almost (95%) at wavelength (1100), while for the doped films was maximum transmittance equal (94 ± 3%) for SnO_2:2%Co at the same wavelength. The optical transmission values are decrease with the increase cobalt concentration this behavior is may be due to the increase in free electrons with the increase in cobalt concentration,this result is in agree with X.Liu[6].

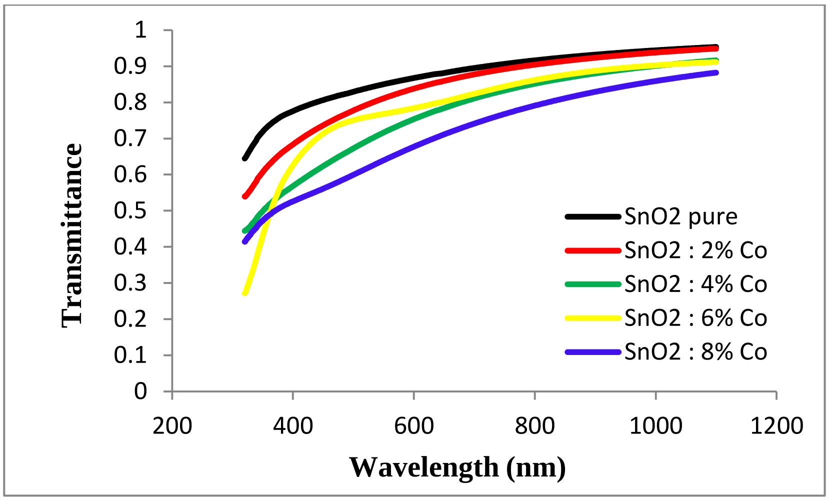

Figure (1):Transmittance as a function of wavelength for pure and doped SnO_2thin films.

B. Absorbance

Absorbance materials are affected by several factors such as the type of material , thickness, and the wavelength of the incident beam.

Figure (2) show the variation of absorbance as a function of wavelength, with in the range (320 – 1100nm) for all samples under investigation. It is observed that the absorbance increases as doping percentage increases. In general, It was found that the absorbance decreases with increasing wavelength for all the prepared thin films. This physically means that an incident photon was not able to excite the electron and transfer it from valence band to the conduction band because the energy of incident photon less than the value of the energy gap value of the semiconductorthis lead to the absorbance decrease with increasing of wavelength. In general the absorbance of all undoped and doped films has low values in the visible and near infrared region. When the wavelength decreases, the interaction between incident photon and material will occur, and then the absorbance will increase.Also we can observed that the absorbance increases as doping percentage increases because the energy gap will decrease as doping increase,this result is in agree with X.Liu[6].

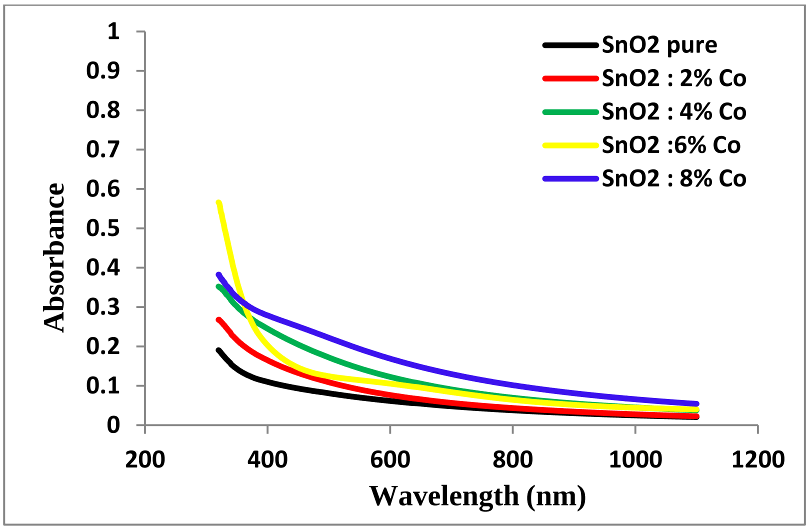

Figure (2):Absorbance as a function of wavelength for pure and doped SnO_2 thin films.

C. Absorption Coefficients

The absorption coefficient (α) for the prepared thin films wascalculated from equation [7] :

$$\alpha = \frac{2.303 \times A}{t} \text{..................} (1)$$

where:

t: is the thickness of thin film in (cm), A: absorption.

Figure (3) shows the absorption coefficient verses wavelength for different Co doping concentrations . In general the absorption coefficient

decrease with the wavelength increase while it will be increased especially for doping concentrations greater than (4Vol.%) and for the direct transfer this confirms that the large values of the coefficient of absorption that are ($\alpha > 10^4$ cm^{-1}).This behavior is typical for many semiconductors and can occur for a variety of reasons, such as internal electric fields within the crystal, deformation of lattice due to strain caused by imperfection and inelastic scattering of charge carriers by phonons, this result is in agree with Ali[8,9].

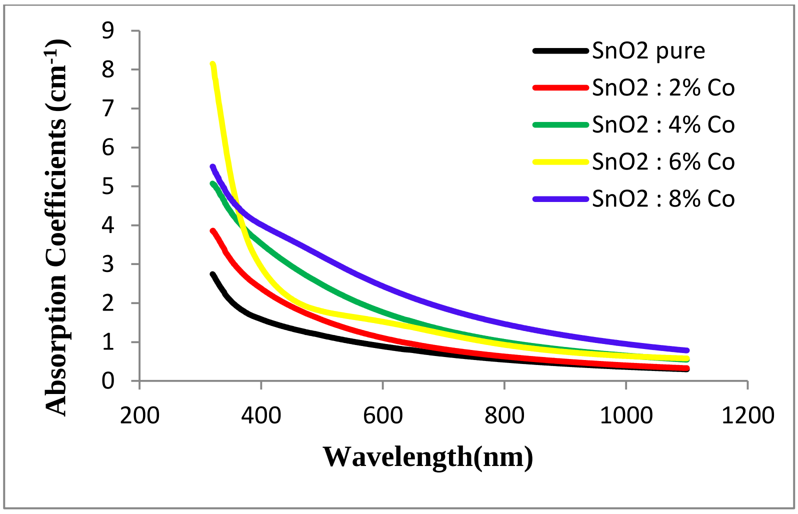

Figure (3):Absorption coefficients as a function of wavelength for pure and doped SnO_2thin films.

D. Optical Energy Gap

The band gap energy *(E_g)* of materials is always one of two types, either direct band gap or indirect bandgap. The energy gap values and its type values depend in general on the films crystal structure, deposition temperature, the arrangement and distribution of atoms in the crystal lattice. The energy gap is calculated for all prepared thin films by draw between $(\alpha h\nu)^2$ as a function of (hν) as shown in figure (4), by extended straight line of the curve and intersection with x-axis gives the value of the energy gap for prepared thin films. From figure (4) shows by extrapolatingthe linear part of the plot to α = 0.The optical band gap was found to decrease with increasing cobalt concentrations, as shown in Table (1), this mean shift absorption edge red shift (toward energies photonic low), which are attributed to the exchange interactions (sp-d), this means interaction of electrons Level (d positional ions cobalt (Co^{2+}) and electrons package of tin dioxide, and this shows the compensation ions cobalt (Co^{2+}) for tin ions (Sn^{4+}) in the lattice quartet of tin oxide, this result is in agree with X.Liu[6].

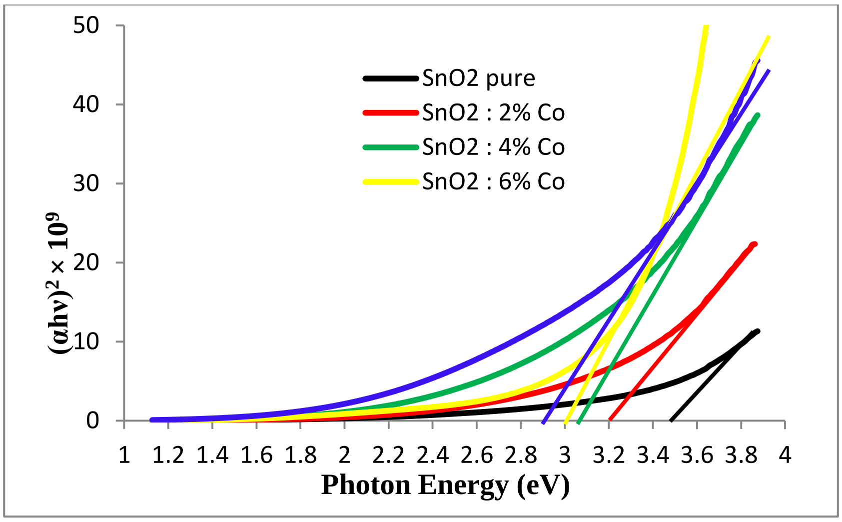

Figure (4): $(\alpha h\nu)^2$ as a function of photon energy for pure and doped SnO_2 thin films.

Table (1): The values ofoptical energy gap for pure and doped SnO_2 thin films.

Sample	E_g (eV)
SnO_2 pure	3.5
SnO_2 : 2% Co	3.2
SnO_2 : 4% Co	3.18
SnO_2 : 6% Co	3
SnO_2 : 8% Co	2.9

E. Refractive Index (*n*)

The refractive index is the ratio between the speed of light in vacuum to its speed in material which doesn't absorb this light. The refractive index (n) was calculated from the following relation[7].

$$n = \left[\left(\frac{1+R}{1-R}\right)^2 - (k_o^2+1)\right]^{\frac{1}{2}} + \frac{1+R}{1-R} \quad \cdots\cdots\cdots\cdots (2)$$

where :

R: is reflectance.

It has been shown in figures (5) as a function of wavelength of pure and doped SnO_2 thin films. We can notice that the behavior of refractive index with wavelength is the same behavior reflection, which means that the reflective index increase with increase photon energy. Also we can notice in general from the figures that the refractive index increases with the increasing of doping with cobalt,the behavior of refractive index with wavelength is the same behavior reflection, which means that the reflective index increase with increase photon energy[10].

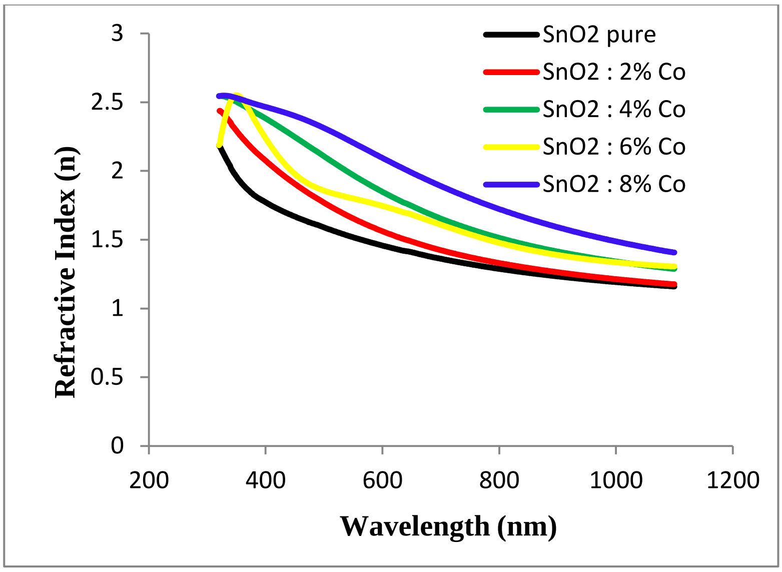

Figure (5): Refractive indexcoefficients as a function of wavelength of pure and doped SnO_2 thin films.

F. Extinction Coefficient

The extinction coefficient could be calculated by using followingequation :

$$k_o = \frac{\alpha \lambda}{4 \pi} \quad \text{.......................} \quad (3)$$

Where:

λ : is the wavelength of incident photon rays.

α : absorption coefficient .

Figure (6) shows the variation of (k) as a function of wavelength for all the pure and doped tin dioxide samples prepared thin films,in general, it is clear that the extinction coefficient (k) decreases with the increasing of wavelength (λ) for all prepared samples.As well as the figure show that the extinction coefficient increases with increasing doping concentration . This behavior can be attributed to the increasing of carrier density which confirms the increasing in the absorption coefficient with doping concentration and that leads to increase the extinction coefficient with doping with cobalt[11].

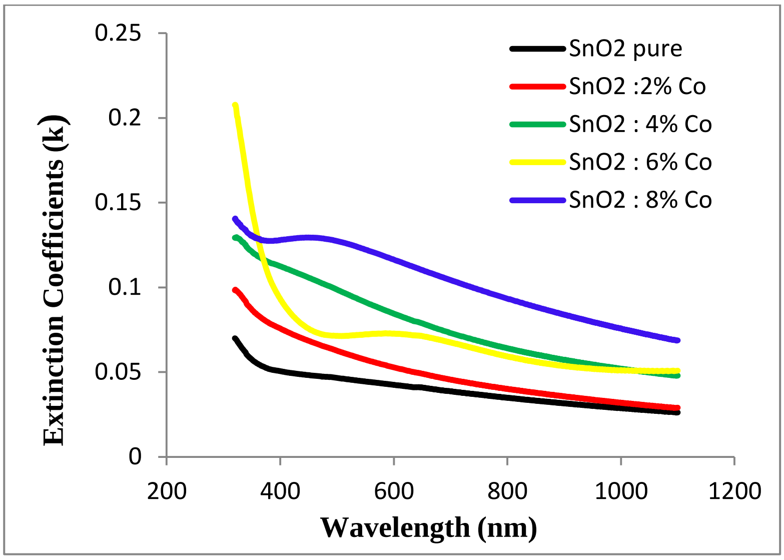

Figure (6): Extinction coefficients as a function of wavelength for pure and doped SnO_2 thin films.

4- Conclusion

Pure and doped SnO_2thin films have been successfully deposited using spray pyrolysis technique . The optical properties show that the optical transmittance and optical energy gapdecrease with the increasing of cobalt concentration and absorption coefficient increased with increasing Co doping concentration. The films have optical transmittance (up to 80% at 800 nm)

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