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Preparation and Characterization of Spray-Coated Pure and Copper Doped Tin Oxide Thin Films

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Abstract

Pure and Copper (Cu) doped tin oxide thin films have been deposited from tin chloride ($SnCl_2$) as a precursor and Copper chloride ($CuCl_2$)for doping onto glass substrates by spray pyrolysis technique at the substrate temperature of 400°C. The doping concentration of Cu was varied from 2 to 5 wt.% while all other deposition parameters such as spray rate, carrier air gas pressure and distance between spray nozzle to substrate were kept constant. The structural properties and optical properties of the as-deposited thin films have been studied by X-ray diffraction (XRD) and UV visible spectroscopy. Also the chemical composition were analyzed by Fourier transform Infra-red Spectroscopy (FT-IR). The structural and optical studies were carried out on these films reveal their columnar and compact structure.

Keywords: Spray pyrolysis, Tin oxide, SEM, EDX, Optical band gap

1. Introduction

TCOs belong to a unique class of semiconducting materials that exhibit high optical transparency in the visible range and good electrical conductivity, simultaneously. These materials are widely used in several devices such as thin film solar cells, touch screens, flat panel displays, sensors, low emissive windows and flexible transparent electronic components. The most common TCOs include tin oxide, zinc oxide, indium oxide, cadmium oxide, titanium di-oxide and the like. TCOs find potential applications in electro chromic windows and oxide based thin film transistors (TFTs). To enhance the transparent conducting properties of TCOs, they are generally doped with suitable anionic or cationic impurities. The Cu doped SnO_2 thin films have been prepared by spray pyrolysis method and it was observed that the transmittance of the films was found to increase from 42% to 55 % on initial addition of Cu and then decreased for higher level of Cu doping [7]. To improve the quality of the films as well as the physical and chemical properties.

Various methods such as sol gel spin coating, spray pyrolysis, electron beam evaporation; vapour deposition, pulsed laser deposition, chemical vapour deposition, molecular beam epitaxy, magnetron sputtering, reactive evaporation and thermal evaporation etc. have been used for the preparation of pure or doped thin films. Among them spray pyrolysis deposition (SPD) technique provides a simple route of synthesizing thin films because of its simplicity, low cost experimental set up from an economical point of view. In addition, this technique could be used for the production of large-area thin film deposition without any high vacuum system. The main objective of this work is to prepare pure and Cu doped SnO_2 thin films from $SnCl_2.2H_2O$ precursor and to explore its structural and optical properties. In this paper we are reporting the effect of Cu doping on the structural

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and optical properties of SnO_2 films prepared by chemical spray pyrolysis technique (SPT).

2. Experimental details

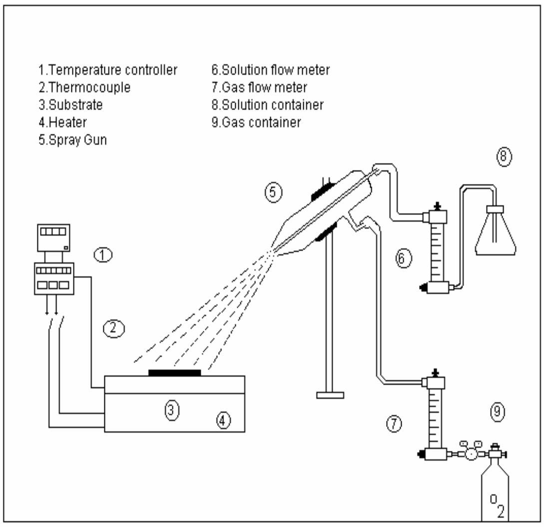
2.2.1. Sample preparation

By using absolute ethanol solvent, 0.1M tin chloride solution was prepared. And to dope copper chloride with prepared tin chloride solution, different atomic weight percentage was selected. The solution was stirred in magnetic stirrer for 20 minutes before deposition.

2.2.2 Spray pyrolysis technique

The precursor solution was deposited by simple and modified chemical spray pyrolysis technique. Before deposition, the hot plate and the spray gun were cleaned by hydrochloric acid (conc.HCL) and distilled water. The substrate was placed at the middle of the furnace and spray gun was focused to the substrate in order to get a uniform, coating. The distance between the nozzle and the substrate is 30 cm. The spray rate of 5ml/min was maintained constant by using compressed air as a carrier gas. The substrate temperature was kept constant at 400˚C and it was maintained by using temperature controller.

The substrate temperature was measured by using IR sensor. Now, the prepared precursor solution was deposited on the glass substrate for three minute continuously. Due to high temperature, the chloride and ethanol present in the precursor gets evaporated and oxidation takes place to gets a fine tin oxide thin film. The deposited tin oxide and copper doped tin oxide thin film where annealed at 400°c for one hour in open air atmosphere. Due to annealing, the atoms present in the molecule are properly arranged to get a fine and uniformed thin film.



2.2.3. Films deposition

Figure 1 shows the schematic diagram of the spray pyrolysis set up. Tin chloride ($SnCl_2.2H_2O$) and Copper chloride [$CuCl_2$] were used as source of Sn and Cu. In order to prepare precursor solution tin chloride ($SnCl_2.2H_2O$) was added with 50 ml of ethanol (CH_3CH_2OH). The amount of $CuCl_2$ was added from 2–5 wt%. The precursor solution was deposited by simple and modified chemical spray pyrolysis technique. Before deposition, the hot plate and the spray gun were cleaned by hydrochloric acid (conc.HCL) and distilled water. The substrate was placed at the middle of the furnace and spray gun was focused to the substrate in order to get a uniform coating. The distance between the nozzle and the substrate is 30-35 cm. The spray rate of 5ml/min was maintained constant by using compressed air as a carrier gas. The substrate temperature was kept constant at 400˚C and it was maintained by using temperature controller.

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3. Result and Discussion

3.1. Structural Analysis

3.1.1. X-Ray Diffraction

The XRD patterns of Pure and Cu doped SnO_2 films were shown in Figure 3.1. The films deposited showed five peak namely (110), (101), (200), (211) and (220). Since all the peaks are sharp it is evident that the films deposited are polycrystalline in nature and the positions of X-ray diffraction peaks fit well the tetragonal structure of SnO_2.**(JCPDS card:tin oxide, 41-1445)** [30]. As seen from Figure 3.1, the prepared orientations is (110) plane for Pure SnO_2 film. The addition of Cu atoms do not affect the prepared orientation along (110) plane and crystal structure. The dopant does not form extra peaks in the XRD pattern of doped SnO_2 films because dopant atoms incorporate homogeneously into the tin oxide matrix. In the present study, the most conspicuous feature observed in the XRD analysis of the films is orientation along the (110) plane. In literature published on SnO_2 films doped with different atoms such as Al, Zn and Co exhibited similar behaviors [28-30]. This result is consistent with the analysis of microstructure of Pure SnO_2 films prepared by spray pyrolysis from various solutions by Smith et al. [32].

From the diffraction pattern, the (h k l) values for each diffraction peak are indexed and the lattice parameters were calculated using 'check cell' software. Table 3.1 shows the calculated lattice constants of SnO_2 films. It was seen that they match well with the standard **JCPDS data card 41-1445**. It was also observed that the Cu doping atoms did not change the lattice parameters.

Table. 3.1. Lattice parameters and crystallite size values of SnO_2 films prepared for various dopant atoms

Doping Atoms	a (Å)	b (Å)	c (Å)
Pure	4.90	3.31	0.68
Cu	4.92	3.32	0.68

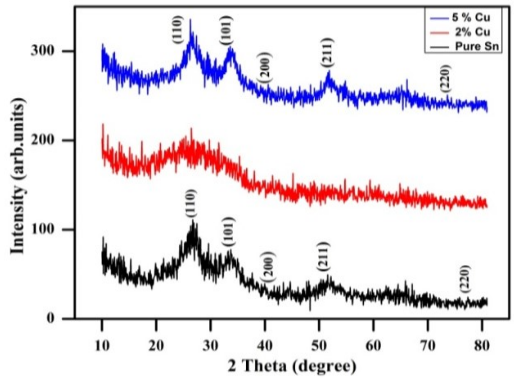

Figure 3.1. XRD spectrum of 0% (pure), 2% and 5% copper doped tin oxide thin films

3.2. Evaluation of Optical Constants

3.2.1. Fourier Transform Infrared Spectroscopy

Fourier Transform Infrared Spectroscopy has been used to analyze the functional groups present in the compound and to confirm the molecular structure of the compound. Functional groups with strong dipole interaction give rise to strong absorption in the IR region. In order to analyze qualitatively the presence of the functional in pure and copper doped SnO_2 was recorded using spectrum RXI FTIR spectrometer in the range 400-4000 cm^{-1}. The resultant spectra were shown in Figure 3.2.

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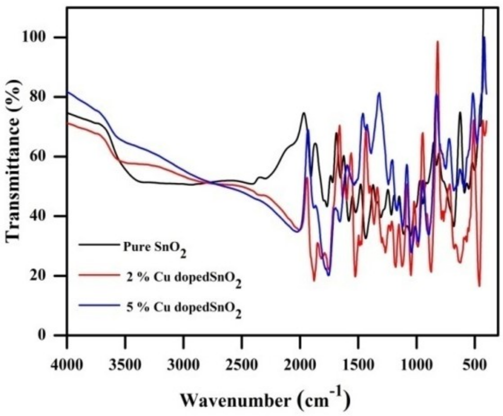

Figure 3.2. FTIR spectrum for pure and copper doped SnO_2 thin films

3.3. Optical Properties

The optical measurements of tin oxide thin films are studied using LAMBDA 35 UV-Visible Spectrophotometer wavelengths range from 300 nm to 1100 nm are shown Figure 3.3.

From this figure 3.3 the optical transmittance spectra of the SnO_2 films for pure and copper doped atoms. The transmittances of pure and copper doped films were increased in an apparent way with wavelength of entire visible and near the IR region. The absorption coefficients (a) were determined by means of the optical transmittance spectra using the relation. The transmittance threshold shift towards the higher wave length region indicates the reduction in optical band gap (E_g). From the transmission spectrum the absorption coefficient (α) is determined by the relation

$$\alpha = \frac{1}{t} \ln T$$

where t is the thickness and T is the transmittance of the film at a particular wavelength. The optical band gap E_g of the film was calculated using the Tauc relation, which is given as

$$\alpha h\upsilon = A(h\upsilon - E_g)^n$$

A is the energy dependent constant, E_g optical band gap energy of the material and n = 1/2, 2, 3/2, 3 corresponding to the allowed direct, allowed indirect and forbidden direct and forbidden indirect transitions respectively. The optical band gap depends upon the absorption coefficient (α). The plot of $(\alpha h\upsilon)^2$ versus $h\upsilon$ is shown in Figure 3.4. The optical band gap was obtained from extrapolating the linear portion of $(\alpha h\upsilon)^2$ versus $h\upsilon$ plot to $(\alpha h\upsilon)^2 = 0$ as 3.4 eV for Pure and 2.9 eV for Cu doped SnO_2 thin films.

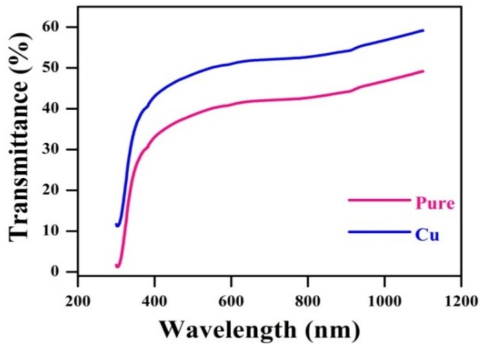

Figure 3.3. Transmittance spectra of SnO_2 films for pure and Cu doped thin films

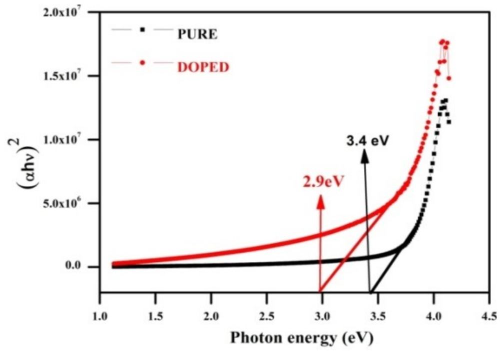

Figure 3.4 .The variation of $(\alpha h\nu)^2$ vs. $h\nu$ for SnO_2 films for pure and Cu doped thin films

4. Conclusion

In the present work, an attempt is made to prepare pure and copper doped tin oxide thin films by Spray pyrolysis techniques utilizing an ethonalic solution containing $SnCl_2.2H_2O$ and $CuCl_2$. The low cost spray pyrolysis deposition (SPD) technique has been used to obtain uniform conductive layers of pure and copper doped tin oxide thin films with good repeatability. The thickness of the synthesized films was found to be about 300 nm for 3 minutes deposition time. The average transmittance of copper doped tin oxide films in the visible region is higher than the tin oxide films and the higher transmittance is found at 2% copper doping and the lowest average transmittance at 5% of copper doping. The direct band gap of pure film is found to be 3.4eV and reduces to 2.9eV Cu doped SnO_2 films. In X-ray diffraction analysis, SnO_2:Cu films prepared at 400°c with various copper doped concentrations are polycrystalline in nature. Since the tin oxide thin films are highly transparent, it can be widely used to make optoelectronic displays and photocell devices.

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