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# Synthesis and optical characterization of pure and Cu doped $SnO_2$ thin films deposited by spray pyrolysis

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Pure tin oxide ($SnO_2$) and copper (Cu) doped $SnO_2$ thin films have been deposited from tin chloride ($SnCl_2$) and cupric nitrate $Cu(NO_3)_2$ precursors onto glass substrates by spray pyrolysis technique at the substrate temperature of 350 C. The doping concentration of Cu was varied from 1 to 8 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 surface morphology and optical properties of the as-deposited thin films have been studied by Scanning Electron Microscopy (SEM) attached with an EDX and UV visible spectroscopy. The transmittance for the as-deposited films was recorded in the wavelength range of 290 to 1100 nm. The optical transmission of the films was found to increase from 71 % to 80 % for initial doping of Cu up to 4% for 200 nm thickness and then decreased for higher level of copper doping. The optical band gap of undoped film was found to be 3.75 eV and it was shifted to 3.50 eV for 4 wt. % of Cu doping and then increased on further increasing the concentration of the dopants. This paper discusses the optical properties of the as-deposited $SnO_2$ films with Cu doping.

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

## 1. Introduction

The study of $SnO_2$ transparent conducting oxide thin films are of great interest due to its unique attractive properties like high optical transmittance, uniformity, non-toxicity, good electrical, low resistivity, chemical inertness, stability to heat treatment, mechanical hardness, piezoelectric behavior and its low cost [1-3]. $SnO_2$ thin films have vast applications as window layers, heat reflectors in solar cells, flat panel display, electro-chromic devices, LEDS, liquid crystal displays, invisible security circuits, various gas sensors etc. [4–5]. Undoped and Cu, Fe and Mn doped $SnO_2$ thin films have been prepared by vapor deposition technique and reported that $SnO_2$ belongs to n-type semiconductor with a direct optical band gap of about 4.08 eV [6]. The Sb 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 Sb and then decreased for higher level of Sb doping [7]. To improve the quality of the films as well as the physical and chemical properties, the addition of some metal ions as impurities is expected to play an important role in changing the charge carriers concentration of the metal oxide matrix, catalytic activity, the surface potential, the phase composition, the size of crystallites, and so on [8-10].

Various methods such as sol gel 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 [11-20]. 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. Generally, $SnCl_4$ is used as precursor for Sn, and very few reports had been reported on the preparation of this material using $SnCl_2$ instead of $SnCl_4$ [15-16]. $SnCl_2$ is being cheaper than $SnCl_4$ and to be a cost effective precursor for preparing low-cost $SnO_2$ thin films. It is expected that various concentration of Cu in $SnO_2$ may affect the structural, optical and electrical properties of the films. From bang gap engineering point of view, suitable band gap is essential for the fabrication of optical devices. So far our knowledge is concerned there are very few reports available on the deposition of Cu doped $SnO_2$ thin films by spray pyrolysis method. In considering the importance of these materials in the field of optoelectronic devices, particularly for solar cells, we have synthesized both undoped and Cu doped $SnO_2$ films using a simple and locally fabricated spray pyrolysis system relatively at low temperature of 350°C and to see the change of optical band gap of as-deposited films for the doping of Cu.

## 2. Experimental details

**Films deposition:** Fig. 1 shows the schematic diagram of the spray pyrolysis set up. Tin chloride ($SnCl_2.2H_2O$) and Cupric nitrate [$Cu(NO_3)_2.3H_2O$] were used as source of Sn and Cu. Spray solution was prepared by mixing 0.2M of $SnCl_2.2H_2O$ in 50 ml $CH_3CH_2OH$ and 50 ml $H_2O$ for pure tin oxide films. In addition few drops of HCl were added to enhance the solubility of tin chloride salt. The pH of the solution was measured to be 6.5. Cupric nitrate [Cu $(NO_3)_2.3H_2O$] was dissolved in isopropyl alcohol and added to the precursor solution. The amount of Cu $(NO_3)_2.3H_2O$ was added from 1–8 wt. %. The deposition set up includes the precursor solution, carrier air gas assembly connected to a spray nozzle, reaction chamber in which substrate was heated and controlled by a variac. Precursor spray solution was first inserted in a syringe with a metallic needle and then transferred to the hot substrate kept at the deposition temperature of 350±5°C using a chromel-alumel thermocouple based digital temperature controller. Pressure of the carrier air gas was kept at 1 bar. The normalized distance between the spray nozzle and substrate was fixed at 30 cm. The spray rate of solution to the hot substrate was maintained at 5 ml/min throughout the experiment and the spray time was kept constant by 5 minutes. After deposition, films were allowed to cool at an ambient temperature slowly. The deposited films were found well adhered to the substrate and stable at room temperature. The as-deposited pure $SnO_2$ films were observed light grayish-white in color and dark grayish and blackening for Cu doped films. The possible chemical reaction that takes place on the heated surface to produce $SnO_2$ and $SnO_2$: Cu thin film may be as follows: when the droplets of the aqueous solution reached the heated substrate, chemical reaction of tin chloride with water vapor of solutions, stimulated by the temperature, takes place providing the formation of $SnO_2$ films and also $SnO_2$: Cu with the formation of oxides of nitrogen through some intermediate products [21].

$$SnCl_2.2H_2O \rightarrow SnO_2 \downarrow + H_2O \text{ (steam)} + 2HCl$$

$$SnCl_2.2H_2O + Cu\,(NO_3)_2.3H_2O \rightarrow SnO_2{:}\ Cu \downarrow + xN_yO_z + wO_2 + HCl + H_2O \text{ (steam)}$$

**Characterizations:** The thickness of the pure and Cu doped $SnO_2$ films were measured by Fizeau fringes method (Interferometer arrangement for producing reflection). The surface properties of the films were examined by using HITACHI S-3400N model Scanning Electron Microscope (SEM) attached with an EDX to measure quantitatively the sample stoichiometry. The optical spectra of transmittance, T (%) and absorbance, A (%) have been measured with respect to plain glass substrate (as a reference) for as-deposited and annealed thin films using UV-1631 Spectrophotometer (SHIMADZU) at wavelength ranges $290 \leq \lambda \leq 1100$ nm.

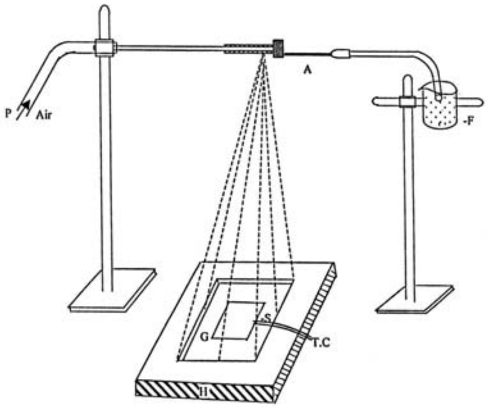
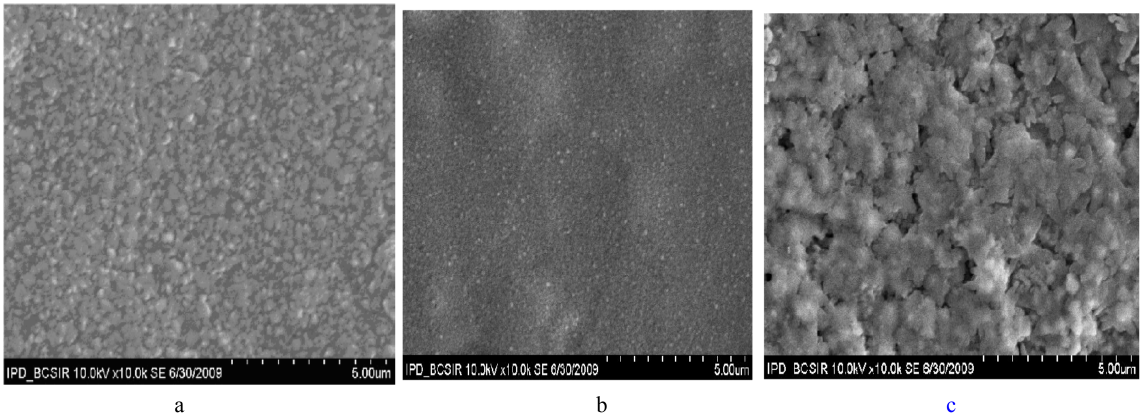


*Fig.1. Schematic diagram of thin film deposition by spray pyrolysis technique F (aqueous solution), A (nozzle), P (air pressure), G. S (glass substrate), T. C (thermo couple), H (heater).*

## 3. Results and discussion

**Surface Morphology:** Fig. 2 (a, b and c) shows the surface morphology of as-deposited pure and Cu doped $SnO_2$ thin film of thickness around 200 nm under 10 K magnifications. The SEM micrograph shows small crystallites and agglomeration of the grain particles for pure tin oxide samples but Cu doped $SnO_2$ (4 % Cu) films exhibit dense packed and homogeneous growth in the entire surface. When Cu doping is increased more than 4% then surface roughness increases and morphology is strongly affected.



a b c

*Fig.2. SEM images of (a) pure $SnO_2$, (b) 4 wt. % Cu doped $SnO_2$ and (c) 5 wt. % Cu doped $SnO_2$.*

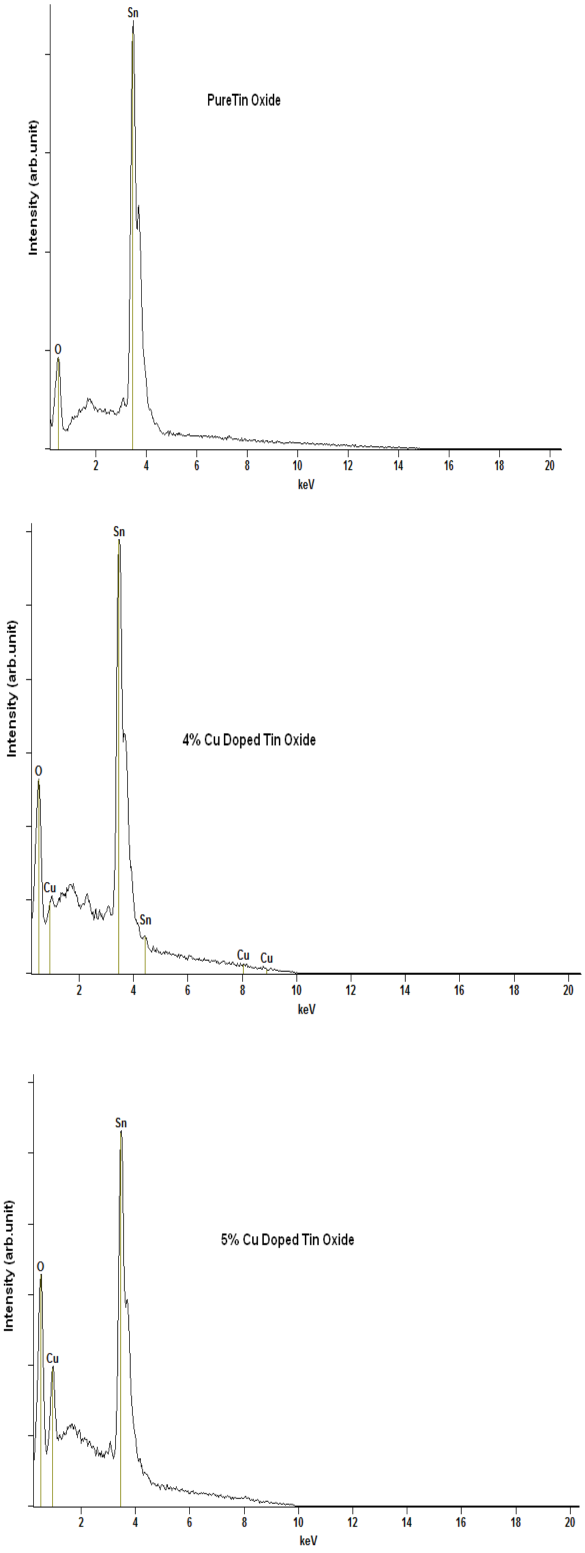


*Fig.3. EDX results of (a) pure $SnO_2$, (b) 4 wt. % Cu doped $SnO_2$ and (c) 5 wt. % Cu doped $SnO_2$.*

The quantitative analyses of the deposited films are carried out by EDX and images are shown in Fig. 3. In the spectrum, there are two strong peaks corresponding to Sn and O which confirms the purity of the $SnO_2$ thin films. An average atomic percentage of Sn and O were found to be 56.37 and 43.63 respectively. The percent of Sn, O, and Cu in the films for different concentrations of Cu are shown in Table 1. From EDX images it is observed that the height of the peak for Sn decreases while for Cu increases with increase of the Cu doping. From the result it is evident that the amount of Sn and O for pure and Sn, O and Cu for doped films are in good stoichimetric.

*Table 1. Quantitative results of pure and Cu doped $SnO_2$ thin films from EDX analysis.*

| Sample | Element | Weight % | Atom % |
|---|---|---|---|
| Pure $SnO_2$ film | O | 9.45 | 43.63 |
| | Sn | 90.55 | 56.37 |
| 4 wt. % Cu doped $SnO_2$ | O | 17.30 | 60.42 |
| | Sn | 81.12 | 38.19 |
| | Cu | 1.58 | 1.39 |
| 5 wt. % Cu doped $SnO_2$ | O | 20.50 | 63.30 |
| | Sn | 69.52 | 28.94 |
| | Cu | 9.98 | 7.76 |

**Optical properties:** The transmittance and absorbance spectra of $SnO_2$ films were recorded in the UV-visible near infrared regions (290 nm to 1100 nm.). Optical properties of pure and Cu doped $SnO_2$ thin films such as transmittance, absorbance, direct band gap, refractive index, etc. were calculated on as-deposited films. Fig.4 (a, b) shows the variation of transmittance with wavelength for as-deposited pure and Cu doped $SnO_2$ thin films as well as for annealed samples. It is seen that the values of transmittance is high in the visible and IR region and minimum at wavelength ~ 300 nm. The transmittance increases gradually, after the initial increase, till 4 wt. % Cu doping and shows the highest transmittance about 80 %. The transmittance values are decreased for the next higher levels of doping. This suggests that the decrease in the transmittance of $SnO_2$:Cu films with increasing in doping concentration may lead to increase in the degenerate (metallic) nature of the films, which results in light absorption. For higher doping levels, the samples were found light to deep blackish gray in colour and less transparent to naked eye. The transmission spectra were also taken on the samples annealed at 450º C for 1 hr. as shown in Fig. 4 (b). The transmittance of the films increases as 5-10% after annealing and it may be due to the transition of the $SnO_2$: Cu films from amorphous to polycrystalline structure.

The absorption coefficient (α) was calculated from the transmission spectra using the relation,

$$\alpha = \frac{1}{t}\ln\left[\frac{1}{T}\right]$$

Where T is the optical transmission and t is the film thickness. The absorption coefficient was found in the order of $10^6$ $m^{-1}$ which may be suitable for a transparent conducting film. The value of the absorption coefficient decreases as the concentration of Cu increases gradually up to 4 % but it starts to increase with further increasing of Cu doping. This reduction of absorption coefficient in Cu doped samples may be due to the removal of defects and disorderness in the as-deposited film by Cu doping. The direct optical band gap *Eg* was determined by fitting the transmittance data to the equation, $\alpha h\nu = B(h\nu - Eg)^{1/2}$ shown in Fig. 5. The lowest optical band gap was found to be 3.5 eV for 4 wt. % Cu doping whereas optical band gap is 3.75 eV for pure tin oxide films. Again the band gap increases with the increase of Cu concentration. The variations of band gap for as-deposited and annealed $SnO_2$ thin films with Cu doping are shown in Fig. 6.

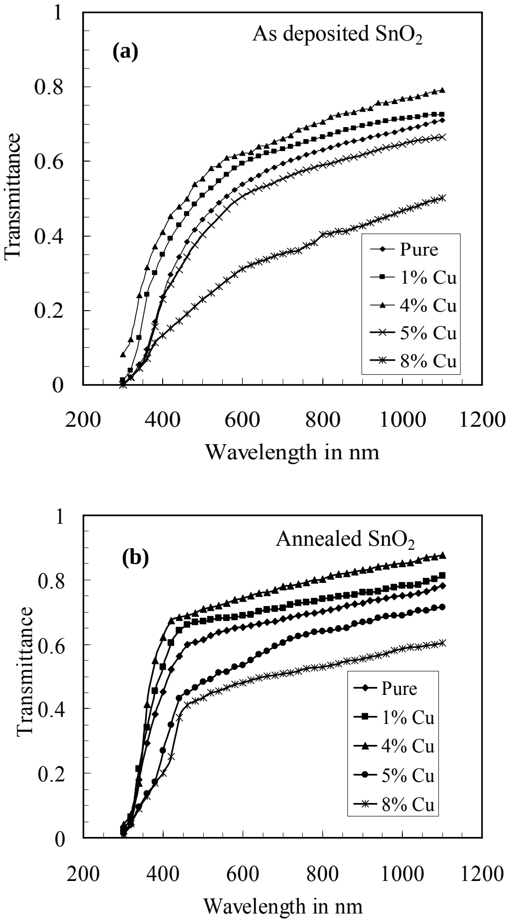


*Fig. 4 (a) as-deposited pure and Cu-doped tin oxide films, (b) annealed pure and Cu-doped tin oxide films.*

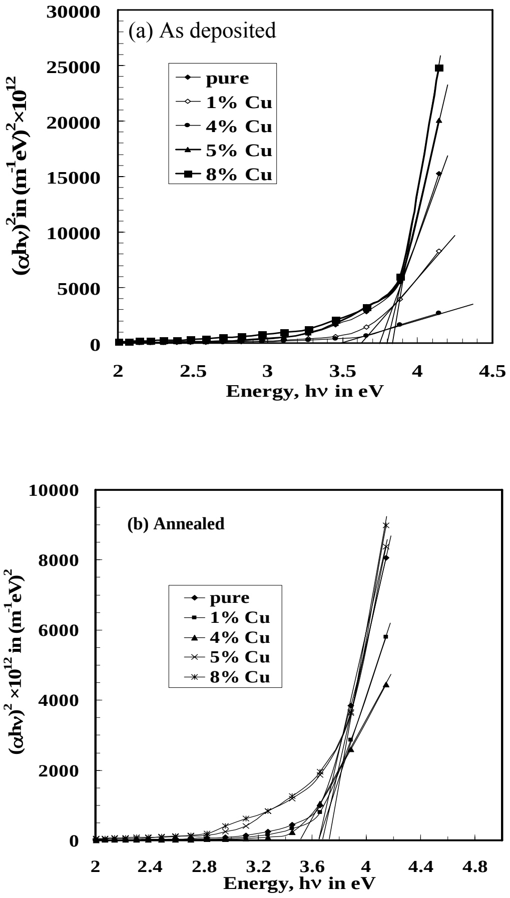


*Fig. 5 (a) Optical band gap for as deposited films and (b) for annealed samples*

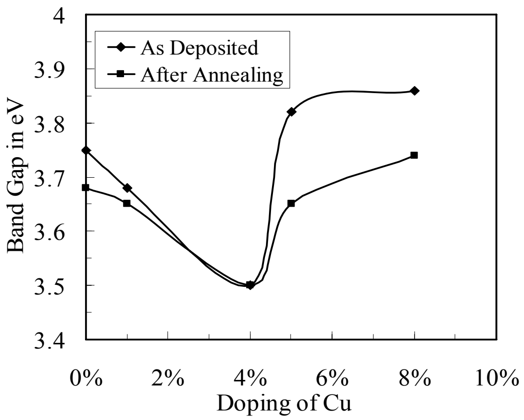


*Fig. 6 Variation of band gap for as-deposited and annealed $SnO_2$ thin films with Cu doping.*

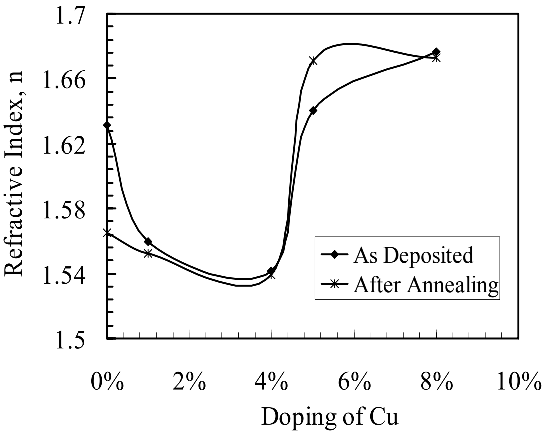


*Fig. 7 Variation of refractive index for as-deposited and annealed $SnO_2$ thin films with Cu doping.*

The refractive index of the films was calculated from the transmission spectra using the relation [22].

$$n^2=\left(\frac{n_a^2+n_g^2}{2}+2n_a n_g T_o\right)+\left\{\left(\frac{n_a^2+n_g^2}{2}+2n_a n_g T_o\right)^2-n_a^2 n_g^2\right\}^{1/2}$$

where, $T_o=\left(\frac{T_{\max}-T_{\min}}{T_{\max}\times T_{\min}}\right)$, $n_a$ = Refractive index of air, and $n_g$ = Refractive index of glass

The refractive index of the pure $SnO_2$ films was found to be 1.63 and 1.54 for 4 wt. % Cu doped film, shown in Fig. 7. This low value of refractive index may probably due to the increase of packed density and homogeneity of the film surface. It was also observed that refractive index increases for higher Cu concentrations which may be due to the increase of inhomogenity and surface roughness of the films. The refractive index is found low for annealed samples and it may be due to transition of polycrystalline nature from amorphous during annealing.

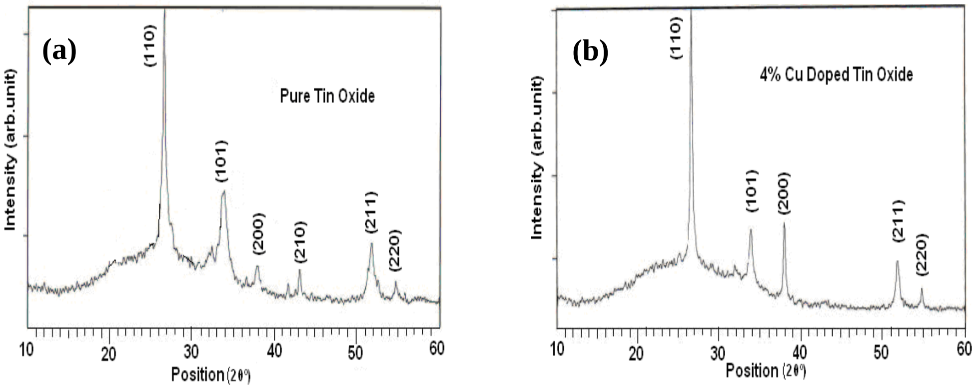


*Fig. 8 XRD spectra for pure and Cu doped $SnO_2$ thin film.*

The X-ray diffractogram of pure $SnO_2$ and Cu doped $SnO_2$ samples are shown in Fig. 8 (a & b). Using the $d_{hkl}$ (interplanar distance) values, their corresponding <hkl> values have been identified as (110), (101), (200), (210), (211), and (220) for pure $SnO_2$ films which indicate the tetragonal structure of $SnO_2$. The lattice parameters are a = b = 4.7522 Å, c = 3.1804 Å respectively. From X-ray diffraction patterns, it is clear that the $Cu^{2+}$ ions are acting as dopants in the $SnO_2$ structure. The preferred crystal face orientation of the undoped $SnO_2$ thin film is (110). Hence Sn forms an interstitial bond with oxygen and exists either as SnO or $SnO_2$; accordingly it has a valency of +2 or +4, respectively. During the initial addition of Cu into the film, the Cu substituted on $Sn^{4+}$ sites act as donors and releasing excess electrons into the conduction band. Thus the carrier concentration (n) increases and the band gap decreases with the addition of Cu up to a certain level (i.e 4 wt %). Above 4 wt %, the largest carrier concentration causes more carrier collision probability during charge transport which, in turn reduces photoconduction mechanism. At 4 wt % the charge concentration seems to be optimal for photoconduction.

## 4. Conclusions

The low-cost spray pyrolysis deposition (SPD) technique has been used to obtain uniform conductive layers of pure and Cu doped $SnO_2$ thin films with good repeatability. The thickness of the synthesized films was found to be about 200 nm for 5 minutes deposition time. SEM surface studies exhibit a smooth and homogeneous growth in the entire surface for Cu doped $SnO_2$ (4 wt. % Cu) films. The change of surface and adaptation of films clearly observed for higher level of Cu concentrations. EDX result reveals that the deposited films have the periodicity of the Sn, O and Cu matrix and stoichiometric. The average transmittance of Cu doped $SnO_2$ films in the visible region is higher than the undoped $SnO_2$ films and the highest transmittance is found at 4 wt. % Cu doping and the lowest average transmittance at 8 wt. % Cu doping. The direct band gap of pure film is found to be 3.75 eV and reduces to 3.50 eV for 4 % Cu doped $SnO_2$ films. It increases with further increasing of Cu concentrations. The refractive index of the pure films is being into 1.63 and for 4 % Cu doped film is 1.54. The best transparent and conducting $SnO_2$ film is possible to deposit by doping with 4 wt. % of Cu. In conclusion, we can state that the SPD could be employed for large-scale synthesis of $SnO_2$ films because of its high yield and purity, simple reaction mechanism, simple apparatus and relatively low deposition temperature. The obtained experimental results also discuses the suitability of $SnO_2$: Cu thin films as transparent and conducting window materials in solar cells applications.

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