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STUDIES ON TIN OXIDE (SnO_2) AND CU DOPED SnO_2 THIN TILMS DEPOSITED BY SPRAY PYROLYSIS TECHNIQUE FOR WINDOW MATERIALS IN SOLAR CELLS

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ABSTRACT

SnO_2 thin films have been deposited onto glass substrates by spray pyrolysis technique. Tin chloride and copper nitrate were used as source of Sn and Cu respectively. The structural, optical and electrical properties of SnO_2 films have been investigated as a function of Cu-doping (1~8 wt. %). The SEM micrographs of film show uniform deposition and EDX results show the stoichiometry and elemental composition of the films (viz. Cu, Sn and O, etc.). The optical transmission was found to increase from 71 % to 79 % for 200 nm thickness with the addition of Cu up to 4 % and then decreased for higher concentration of copper doping. The optical band gap for pure SnO_2 film was found 3.75 eV. Due to Cu doping, the band gap was shifted to lower energies and then increased with further increasing of doping concentrations. X-ray diffraction studies show the polycrystalline nature of the films with preferential orientation along the (101) planes and an average grain size of 7.244 Å. The resistivity of SnO_2 films was found to decrease initially from 4.5095×10^{-4} Ωm to 1.1395×10^{-4} Ωm. The experimental results discussed the suitability of this material for using as transparent and conducting window materials in solar cells.

Keywords: Spray Pyrolysis, Sno_2 Thin Film, Optical Band Gap

1. INTRODUCTION

Transparent and conducting oxides (semiconductors) have been extensively studied because of their novel properties and wide range of applications including architectural windows, polymer-based electronics, etc. [1]. SnO_2 semi-conducting transparent thin films have various appealing features for technical applications in solar energy conversion, flat panel displays, electro-chromic devices, invisible security circuits, LEDs, etc. Hence large area SnO_2 films on cheap and easily available substrates are of considerable interest for the formation of most of the photonic structures.

There are various methods such as chemical vapour deposition, sol gel, spray pyrolysis, electron beam evaporation, vepour deposition, pulsed laser .deposition, molecular beam epitaxy, thermal evaporation, reactive evaporation and magnetron sputtering, etc. for the preparation of pure or doped thin films [2-6]. The structure of SnO_2 in its bulk form is tetragonal rutile with lattice parameters of a = b = 4.737 Å and c = 3.816 Å [7]. However, in thin film form, depending on the deposition technique, its structure can be polycrystalline or amorphous. Generally, $SnCl_4$ is used as a precursor for Sn, and limited work had been reported using $SnCl_2$ instead of $SnCl_4$. The SnO_2 films close to stoichiometric conditions have low free carrier concentration and high resistivity, but non-stoichiometric SnO_2 films have high carrier concentration, high conductivity, and high transparency. Usually there is an oxygen vacancy in the structure, so that the formula for the thin film of the material is SnO_{2-x}, where x is the deviation from stoichiometry. Conventional n-type transparent conducting oxide (TCO) thin films are In_2O_3: Sn (ITO), SnO_2: F (FTO), and ZnO:Al (AZO) [8]. SnO_2 thin films with electrical resistivity of 2.7×10^{-4} Ω-m at a deposition temperature of 500ºC and the minimum resistivity for the doped SnO_2 films was found to be 0.381× 10−4 m deposited

at 575° C with 3 wt. % of Fe doping [9]. The transmittance value for the pure tin oxide films is found to increase from 42.24 % to 54. 48 % (at 800 nm) on the addition of 0.5 wt. % of antimony. But the transmittance is found to decrease gradually if the antimony concentration is increased above 0.5 wt. % [10]. The highest transmission observed in the films was 75% and the band gap varied between 2·7 and 3·4 eV for Mn doped tin oxide [11]. The main objective of this work is to prepare high conducting Cu doped SnO_2 thin films from $SnCl_2$ precursor and to explore its optical and electrical properties. In this paper we are reporting the effect of Cu doping on the structural, optical, and
electrical properties of SnO_2 films prepared by a simple spray pyrolysis technique (SPT).

2. EXPERIMENTAL DETAILS

Pure SnO_2 and SnO_2: Cu films were deposited using a locally fabricated spray pyrolysis system. 0.2M $SnCl_2.2H_2O$ was added with 50 ml water and 50 ml ethanol for precursor solution of pure SnO_2 thin film. 1~8 wt % of Cu $(NO_3)_2.3H_2O$ was dissolved in $SnCl_2.2H_2O$ solution for Cu doped thin film. To enhance the solubility of prepared solution, a few drops of HCl were added [12]. The distance between substrate to nozzle was 30 cm. Air pressure was 1 bar, spayed time was 5 min. and spray rate was kept constant at 5 ml/min. For each concentration the reproducibility of the films were verified by repeating the experiments several times. Microscope glass slides were used as substrates. The substrate temperature was fixed at 350 °C. Scanning Electron Microscope (SEM) model HITACHI, S-3400N JAPAN, was used to see the surface morphology. The transmission and absorption spectra for the as-deposited films were recorded using a UV-1631 spectrophotometer (SHIMADZU) as a function of wavelength ranging from 290 to 1100 nm. The electrical resistivity was measured using Van der Pauw method in the range of 300~475K.

F (aqueous solution)
A (nozzle)

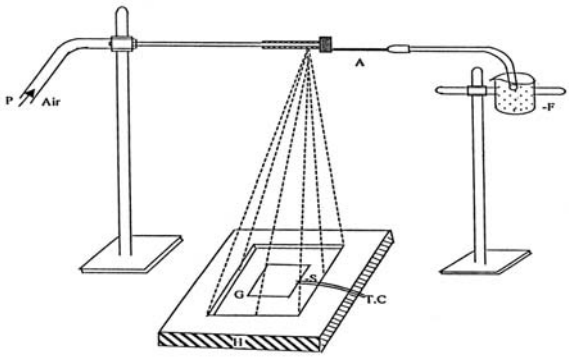


Fig 1. Experimental setup of spray pyrolysis technique.

3. RESULTS AND DISCUSSION

The thickness of the as de-posited film was estimated to be about 200 mm by Fizeau fringes method weight % of Sn, O and Cu are found as 69.52, 20.50 and
dopant concentration was increased, the films became denser and closely packed. This clearly indicates that the metal dopant inhibits grain growth. The micro structural 9.98 respectively. The morphology of the films was found that for lower dopant concentration, films were non-uniform. As the images are shown in Figure 3. In pure SnO_2 films, weight % of Sn and O are found to be 90.55 and 9.45 respectively. On the other hand for 4% Cu doping,

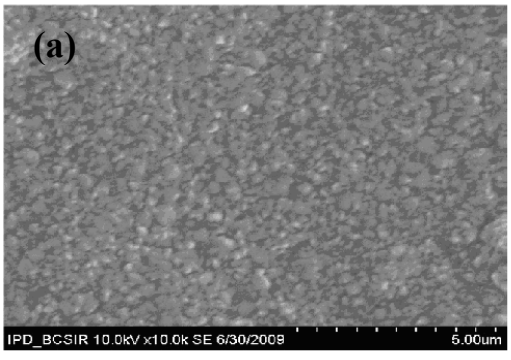


Fig 2. SEM images for 4 wt. % Cu doped SnO_2 thin film

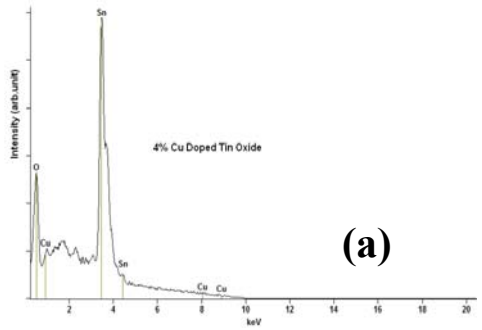
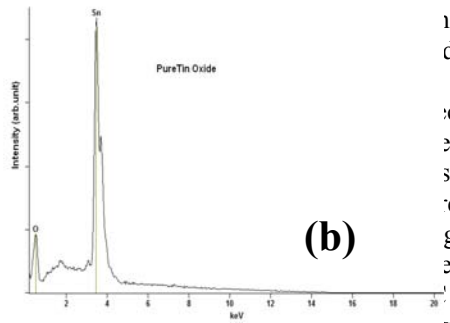


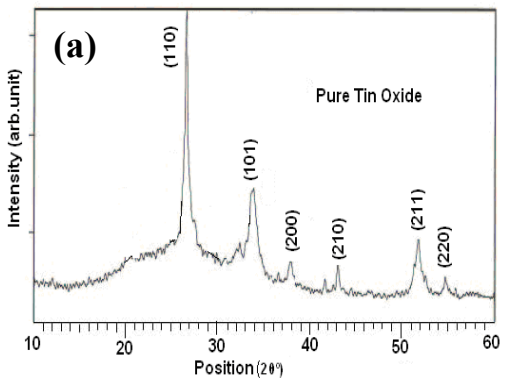
Fig 3. EDX images for 4 wt. % Cu doped SnO_2 thin film.

Further evidence is found in the X-ray diffraction patterns shown in Figure 4. From this figure it is observed that the reflection peaks in the doped films shifted from their standard positions in the presence of the dopant. The deviation in the lattice parameters is mainly due to occupying of doping atoms into the interstitial positions of the lattice. Hence from the EDX, optical absorption spectra and X-ray diffraction patterns, it is clearly



obser Cu^{2+} ions are acting as dopants in the SnO_2 ...e range of 7.24... diffraction patte...

O ...ectra were taker... 5. From figur... sent in the abso... ...e is a shift in th... ...gnifying a cryst... ...decreased after ... exhibit a transmission of > 60% in the visible and IR region, again it is found > 70% in the visible and IR region for Cu doped film, which is found to be greater than that of undoped film. The refractive index of pure SnO_2 thin film has been obtained 1.6316 and refractive index became 1.5417 for 4% Cu doping (Figure 6.). This low value of refractive index may probably due to the smaller density of the films. It is observed that refractive index increases further for higher doping of Cu. Among these transmittance plots it is seen that films deposited at 4% Cu doped have the highest transmittance value.



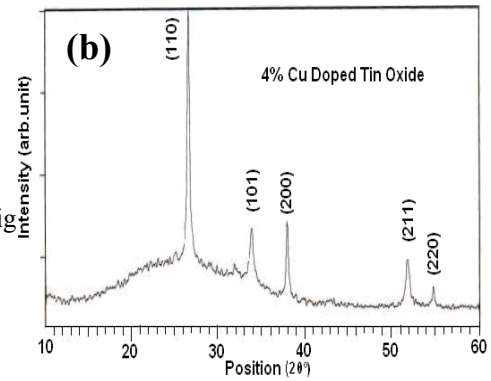


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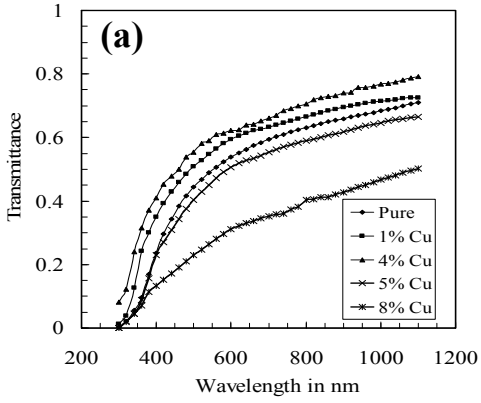
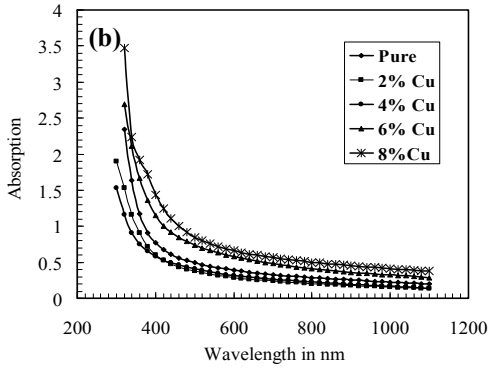
Fig 4. XRD images (a) for pure and (b) for 4% Cu doped SnO_2 thin film





The lowest direct optical transition corresponds to energy about 3·75–3.50 eV. The indirect transitions dominate as Sn^{2+} increases in the system and occurs within the conduction band at 1·75–1·25 eV causing transparency in the visible range (Figure 6). The resistivity of the as-deposited SnO_2 thin films is decreased (close to linear) with increasing temperature. This behavior indicates the semiconducting nature of the films. All the films exhibited resistivity in the range of 10^{-4} ohm-cm. The resistivity was dependent on dopant concentration and similar oscillatory behaviour in resistivity has been observed in the case of Sb doped SnO_2 thin films. In this work the variation has been related to the increase in mobility at a particular concentration. Other work on Nb and Al doped SnO_2 thin films also report similar resistivity behavior. It is clear that the doped SnO_2 films in the current study exhibit the properties of transparency and semiconductivity.

At room temperature, the electrical resistivity and sheet resistance of pure SnO_2 films is found to be $5.1065 \times 10^{-4}\Omega$-m, and 2.5532×10^{3} Ω/□ respectively. Conductivity of pure films is varied in the range of 1.9582×10^{3} $(ohm\text{-}m)^{-1}$ to $2.4065 \times 10^{3}(ohm\text{-}m)^{-1}$ in the temperature range 305-475K. For Cu doping the resistivity is reduced and then its range becomes 1.1395×10^{-4} Ω-m to 0.5080×10^{-4} Ω-m (Figure 7). On Cu doping, carrier concentration increases and conductivity enhances remarkably. The conductivity behaviour is, however, an oscillatory nature depending on the level of dopant concentrations. It was proposed that Sn interstitials produce a donor level inside the conduction band due to their loosely bound outer electrons which gives rise to donor ionization and conductivity. Oxygen vacancies on the other hand would tend to produce deep levels inside the band gap. Sn interstitials have very low formation energy, therefore, they can exist in significant quantities and they are stable due to the intrinsic multivalency of Sn.

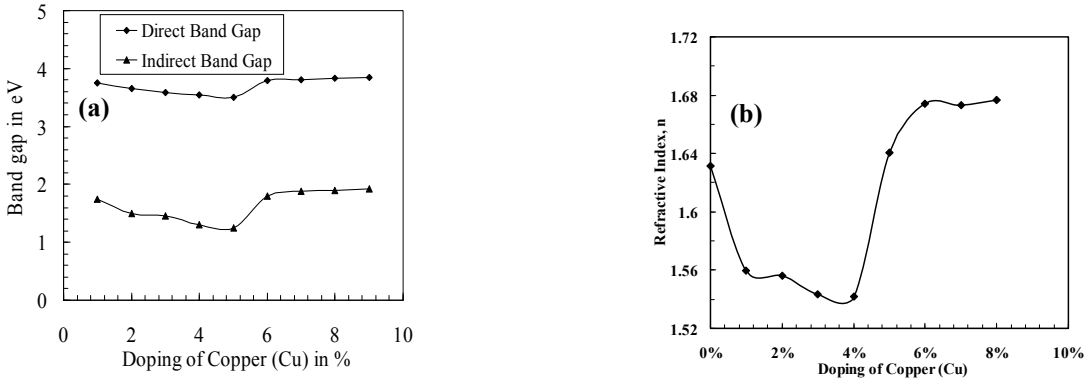


Fig 6. Variation of (a) band gap (b) refractive index of pure and Cu doped SnO_2 thin films

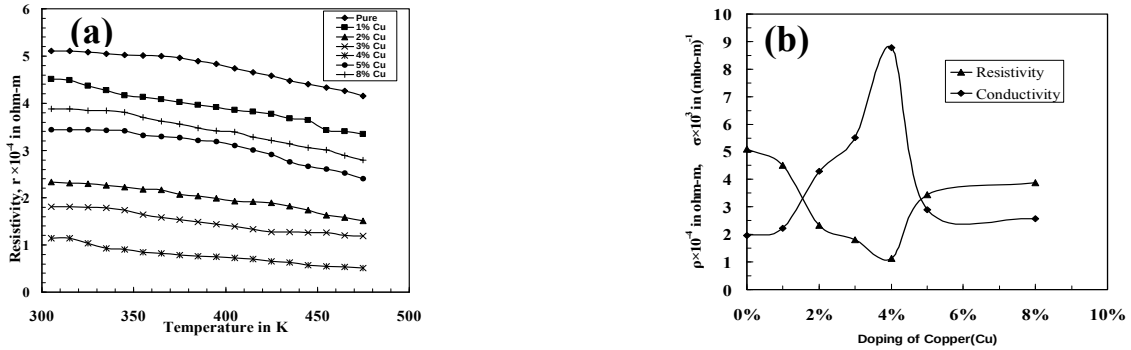


Fig 7. Variation of resistivity with (a) temperature and (b) Cu doping.

4. CONCLUSION

The pure and Cu doped tin oxide thin films are prepared by spray pyrolysis technique from $SnCl_2$ precursor. XRD patterns of SnO_2 films is pound to have a better polycrystalline nature oriented along the (110), (101), and (200), (211) planes at $2\theta = 26.591^{o}$, 33.888^{o}, 37.959 and

51.787º respectively with single phase of SnO_2. Average grain size of the film is found to be 7.244579 Å, which is agreed well with previous reported value. The transparency is ~ 80% for the best films with resistivity of the order of 10^{-4} ohm-m. The transmittance increases initially with increase in doping concentration and then decreases for higher doping levels which is attributed to light absorption. The behaviour of the films has been explained within the frame work of current model for the coexistence of transparency and conductivity in SnO_2 based systems. The sheet resistance of the undoped films is decreased with 4% doping of copper to attain a minimum value and increased for higher level of 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. The refractive index of the pure films is being into 1.63 and for 4% Cu doped film is 1.54. The obtained experimental results infer the suitability of this material as transparent and conducting window materials in thin film solar cells and optoelectronic devices.

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