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Optical and Structural Characteristics of Copper Doped Tin Oxide Thin Film Prepared by Thermal Evaporation Method

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***Abstract*— The present paper discusses the optical and structural properties of copper doped tin oxide thin film prepared on a glass substrate by thermal evaporation technique at a pressure of Vacuum chamber 2x10^{-5} torr and at a temperature 32^{0}C to 38^{0}C. The film was annealed at 300^{0}C for two hours. Optical characteristics were studied by UV/VIS Spectrophotometer and observed that the transmission value was more than 80% at a wavelength greater than 450nm. X-ray diffraction study shows that the film was tetragonal rutile structure of SnO_2. From XRD and SEM micrograph it was confirmed, the grain size in the range of 35-40nm. The study reveals polycrystalline structure with prominent peaks. The optical band gap was 3.55eV for nearly 5wt % of Cu doping.**

***Index Terms*— Band gap, SEM, Spectrophotometer, Tin Oxide, XRD.**

I. INTRODUCTION

The study and application of thin film technology is entirely entered in to almost all the branches of science and technology. Present study which describes the synthesis and study of optical and structural characteristics of copper doped Tin Oxide (SnO2) is really more interesting for researchers due to its vast applications. Due to the properties like reflectivity, transparency, low electrical sheet resistance etc., tin oxide thin films has immense applications such as gas sensing material for photovoltaic cell [1] gas sensors devices [2-4], in transistors [5], transparent conductive electrode for solar cells[6-7], photochemical and photoconductive devices in liquid crystal display[8] etc. Till today so many methods were adopted to synthesize doped or un-doped tin oxide films such as R.F. Magnetron Co- sputtering [9] Thermal Evaporation [10 -11], Chemical Vapor Deposition [12-13], Laser Pulse Evaporation [14-15], Sol-Gel [16-18], Spray Pyrolysis [19-21] and ultrasonic spray pyrolysis [22]. Undoped tin oxide and Fe and Mn doped SnO_2 thin films have been prepared by vapor deposition technique[23] and reported that SnO_2 is an n-type semiconductor with a band gap of about 4.08 eV. The Sb doped SnO_2 thin films have been prepared by spray pyrolysis method and it is reported that the transmittance of the films was found to increase on initial addition of Sb and then decreased for higher level of Sb doping [24]. The addition of some metal ions as impurities play a vital role in changing the phase composition, the charge carriers concentration of the metal oxide matrix, catalytic activity, the size of crystallites, and the surface potential[24-26] Therefore to improve the quality, physical and chemical properties of thin film doping is highly essential . It is expected that the doping of copper with tin oxide increases gas sensing property as well as changes structural and optical properties and since there are rare evidences of synthesis of copper doped tin oxide by thermal evaporation method, we made an effort to fabricate copper doped tin oxide films by thermal deposition method.

II. EXPERIMENTAL DETAILS

Copper doped tin oxide film with doping level about 5 wt% was fabricated on corn glass substrate by thermal evaporation unit model 12A4D **(**Fig.1) at a pressure of vacuum chamber 2x10^{-5} torr and at a temperature of 32^{0}C to 38^{0}C. Tin oxide powder 99% and copper powder 99% pure from Aldrich are considered as source materials and were taken separately on two tungsten boats which are connected to the respective electrodes. The pressure of the vacuum chamber was maintained at 2 x 10^{-5} torr, rate of deposition 4-6 A°/sec and target- substrate separation of 8cm was maintained during the entire deposition process. Before the deposition, the glass substrate was thoroughly cleaned with cleaning liquid soap and then with acetone to remove organic particles on the surface and then washed with distilled water. To prevent local hydrolysis the substrates were then soaked with TEA diluted isopropyl alcohol for 10 minutes and then dried. After fabrication the film was annealed at 300^{0}C for two hours.

Optical characterization was studied from transmission% Vs. wavelength curve which was plotted from the data obtained from transmission spectrum analysis of the film by ELICO UV/VIS spectrophotometer Model- SL 159 in the wavelength range 300nm to 1100nm. The refractive index and the thickness of the film were calculated using the formula [27]

$$n = \left\{ N + \left(N^2 - \mu^2 \right)^{1/2} \right\}^{1/2} \quad \text{----------------------------(1)}$$

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Where, $N = 2\mu \frac{T_u - T_l}{T_u T_l} + \frac{\mu^2 + 1}{2}$

and $d = \left| \frac{\lambda_1 \lambda_2}{4(n_1 \lambda_2 - n_2 \lambda_1)} \right|$ ----------------------(2)

Where 'n' and 'd' are the refractive index and thickness of the thin film 'μ' refractive index of the substrate, T_u and T_l be the transmission maximum at upper envelop and transmission minimum at lower envelop for a particular wavelength λ, n_1 and n_2 be the refractive index of the thin film at maxima(for wave length λ_1) and corresponding minima (for wave length λ_2) where phase difference is π. The optical band gap was obtained from the plot of $(\alpha h\nu)^{1/2}$ Vs. hν in thin film deposited on glass substrate. It has been observed the band gap was 3.55eV . XRD measurement was carried out by using SIEMENS Diffract meter and study of morphology was done by Scanning Electron microscope.

Fig.1. Thermal Evaporation Unit

III. RESULT AND ANALYSIS

A. OPTICAL ANALYSIS

Optical analysis of copper doped SnO_2 thin film on glass substrate was studied from transmission% Vs. wavelength curve in the wavelength range 300nm to 1100nm which is shown in the fig.2.

From fig.2 it was clear that the surface quality and homogeneity of the thin film were excellent and this confirms that copper doped tin oxide thin film exhibits semi conducting properties also as it was established by Nowak that the pure semi conducting compounds have a sharp absorption edge [28]. In the visible region of the spectra, the transmission of film was very high, due to the fact that the reflectivity is low and there is less absorption due to excitation of electrons from the valence band to conduction band [29].

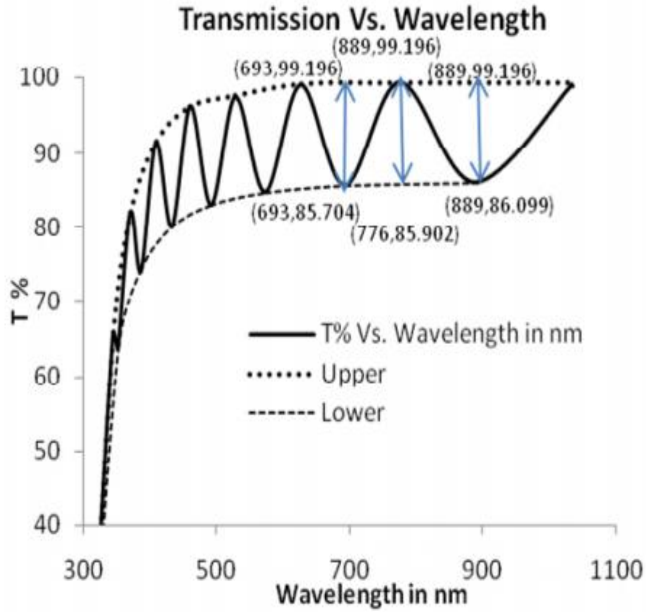

Fig.2. T%Vs. λ in nm in the wavelength range 300nm-1100nm.

From fig.2 it may be concluded that the transmittance was more which may be due to high porosity and larger grain size and less absorption in the film. The lower and upper envelop were used to find out refractive index of the film material and thickness of the film. From the Transmission Vs. wavelength data average refractive index and thickness were measured by the above mentioned formula (1) and (2). The calculated refractive index and thickness of the film were 1.754 and 937.69nm respectively. The higher value of refractive index may probably due to high porosity and surface roughness of the films which is mainly attributed to larger grain size. Sensitivity of thin semi conducting film is highly dependent on film porosity, film thickness, operating temperature, presence of additives and crystallite size. But porosity is expected to have a large impact on sensor sensitivity. The absorption coefficient (α) was calculated from the expression [30].

$$\alpha = \frac{1}{d} \ln\left(\frac{1}{T}\right)$$

Where'd' thickness of the film and 'T' optical transmission. The calculated absorption co-efficient was about 10^4 cm^{-1}. Which may be suitable for a transparent conducting film. Fig.3. shows the plot of $(\alpha h\nu)^{1/2}$ Vs. hν in Cu- doped SnO_2 thin film. It has been observed that the graph was linear over a wide range of photon energies which was due to direct type of transition. When the linear portion was extrapolated to the hν axis the intercept gives the band gap which was 3.55eV. The reported band gap values for SnO_2 thin film for single crystal 3.6eV [31]. The less value may be due to the addition of Cu- dopant and also may be due to growth of grain and improvement of the degree of crystallization.

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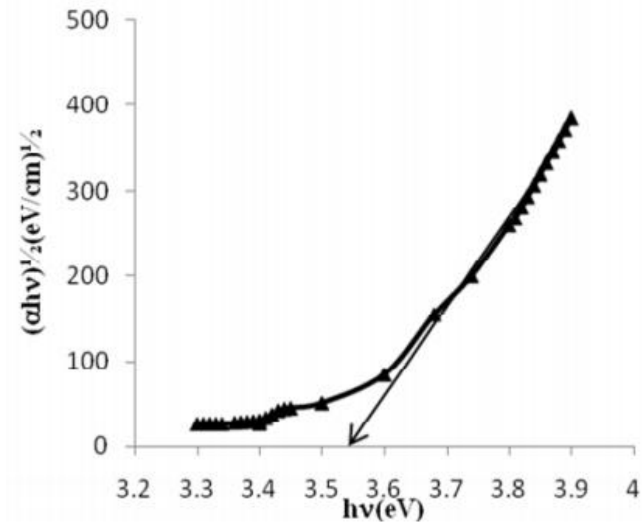

Fig.3. (αhν)½ Vs. hν for SnO2 films

B. STRUCTURAL ANALYSIS

The XRD spectra of the sample was recorded by Siemens Diffractometer Model- D 5000 using CuKα radiation of wavelength λ= 0.1540nm. With a diffraction angle 10^0 to 70^0 and is shown in the Fig.4.

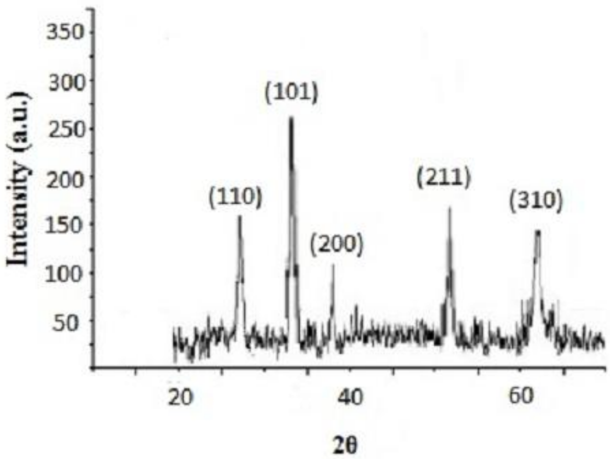

Fig.4. XRD Pattern of Cu-doped SnO_2 thin film

From fig.4. it was observed that well defined sharp diffraction peaks are obtained which indicates that the film is polycrystalline in nature. The peaks are observed nearly at same angle of 2θ which may be considered to be the tetragonal rutile structure of SnO_2 (JCPDS Card No. 88-0287). No characteristics peaks of Cu- dopant was observed which may be due to less dopant percentage. The main aspect of the spectra is the sharpness of the XRD peaks. This variation is related to grain size raise and higher crystalline quality due to annealing condition The peaks which match the standard interplanar spacing JCPDS card no. 88-0287 is given as 26.6^0 for (110) plane, 33.9^0 for (101) plane, 38^0 for (200) plane, 51.8^0 for (211) plane, and 61.9^0 for (310) plane. The (101) peak has the largest intensity, but others like (110), (200), (211) and (310) are clearly identified. Since the intensity of (101) plane is more it may be believed the preferential growth along direction (101). Using the back ground noise level as a reference the (hkl) orientation parameters γ was calculated from the relative heights of the peaks using the expression [32]

$$\gamma = \frac{I_{(hkl)}}{I_{(110)} + I_{(101)} + I_{(200)} + I_{(211)} + I_{(310)}}$$

and observed that orientation parameter is more for (101) plane. XRD spectra were analyzed with Gaussian function where FWHM was determined. By using Debye-Scherrer formula [33] $D = \frac{0.9\lambda}{\beta\cos\theta}$, Where D= Mean grain size, β = FWHM(Full width and half maxima) of the observed peak, λ = wavelength of X-Ray used for diffraction, θ = angle of diffraction. Using the above formula the average grain size of the deposited film was calculated as 36nm. Strain of Cu-SnO_2 thin films was calculated by using the formula[34], $\beta\cos\theta = \frac{C\lambda}{D} + 2\varepsilon\sin\theta$, where C correction factor which is taken as 1, D is the particle size, ε is the strain. From calculation it was found that the value of strain of Cu-SnO_2 film deposited on glass substrate is 0.0095. The amounts of defects in the film known as dislocation density (δ) was calculated using the relation[35] $\delta = \frac{1}{D^2}$ where D is the particle size. The calculated value shows that dislocation density is randomly varied and is less along (101) plane.

C. MORPHOLOGICAL ANALYSIS

The study of surface morphology of Cu- SnO_2 thin film has been carried out using Scanning Electron Microscope Model- Philips XL 30. Fig.5. shows SEM micrographs of Cu-SnO_2 films. SEM micrograph shows agglomeration of the grain particles and domes like structure. This dome like structures may be believed as the top surfaces of the grains of the film. It also shows canal like structure with islands which may be due to contact angle, thickness and drying stresses. This is not only due to annealing process but also may be expected depends on other factors like large thickness of the deposited film.

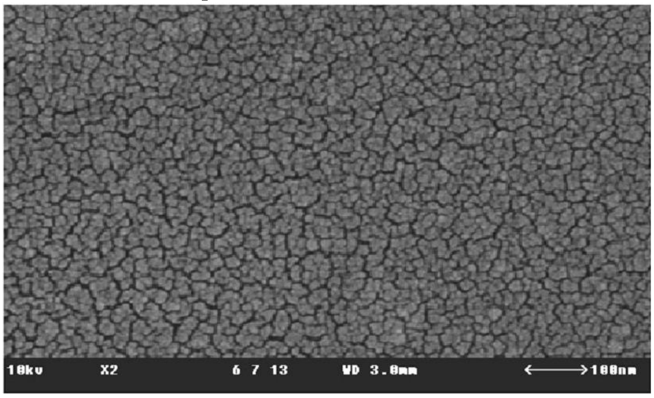

Fig.5. SEM image of Cu-SnO_2 film

D. EDS ANALYSIS

The quantitative analysis of the film was carried out by Energy Dispersive Spectroscopy and the spectrum obtained shown in the figure.6. From the spectrum it is clear that only Sn and O are present along with small quantity of copper.

We observed percentage of Sn, O and Cu in the film as 75.71% and 19.28% and 5.01% respectively.

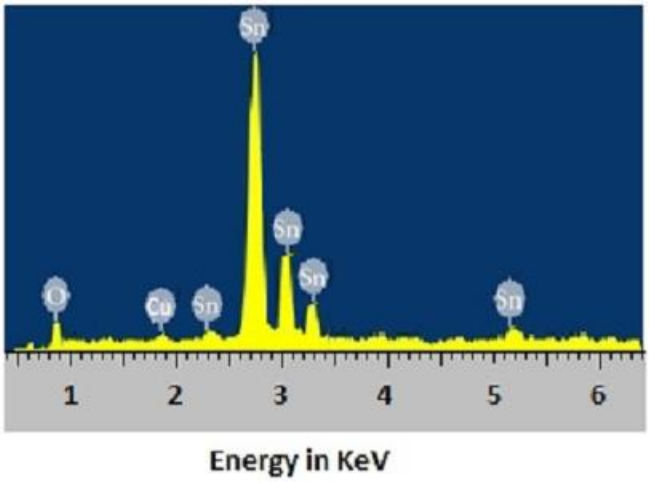

Fig.6. EDS spectrum of Cu- SnO_2 thin film

IV. CONCLUSION

Summarizing briefly, Copper doped Tin Oxide film was prepared by thermal evaporation method. Optical characteristics of the thin film were determined from the transmittance spectra in the UV-VIS region. Film thickness and the refractive index of the film was determined by using the envelop method. It is calculated that thickness of the film was 937.69 nm and average refractive index 1.754. It was also observed that transmission values were more than 0.80 at wave length greater than 450nm. The optical band gap value of the film is 3.55eV which indicates that the synthesized material of the film is semiconducting oxide material. XRD study wraps up that grain size of the Cu-SnO_2 thin film varies from 35 to 40nm however the average grain size was calculated as 36nm. XRD study reveals polycrystalline nature with canals in the film. Five major peaks were clearly observed. XRD result also confirms that the product was tetragonal rutile structure. EDS analysis conforms the presence of Copper. No other impurities were found.

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