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Optical and Structural Properties of Vacuum Evaporated Tin Oxide (SnO_2) Thin Films

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Abstract - *Tin oxide (SnO_2) undoped and Cu, Al (each 5 %) doped SnO_2 thin films were synthesized by Thermal Evaporation Technique on a chemically and ultrasonically cleaned glass substrate at a pressure of high vacuum chamber $2x10^{-6}$ Torr and at a temperature of 350 ^{0}C. During evaporation the substrates were placed at 8 cm away from the source material. SnO_2 films with varying thicknesses (Sample-1, Sample-2, Sample-3) were prepared for a fixed substrate temperature, T_s= 350 ^{0}C. The films were annealed for 15 min at 350 ^{O}C. The optical properties of the films were investigated using a UV-3100 (dual beam) recording spectrophotometer. The wavelength range of the spectrophotometer is 300 nm to 2500 nm. All the films were characterized optically by UV-VIS-NIR spectrophotometer in photon wavelength ranging* from *300 nm to 2500 nm. The possible optical transition in these films was found to be direct and allowed. The optical transmittance and reflectance were utilized to compute the absorption coefficient, refractive index, extinction co-efficient and band gap energy of the films. The crystal structure, particle size and optical properties of the nanoparticles were investigated by X-ray diffraction (XRD), and UV absorption spectroscopy. X-ray diffraction study shows that the film was tetragonal rutile structure of SnO_2. The maximum transmittance was found to be 83.86% of the film for 1030nm wavelength. From XRD, the grain size in the range of 30-40nm was confirmed. The optical band gap was 3.4 eV for nearly 5% of Cu doping. The UV-VIS studies showed decrease in band gap with increasing doping concentration.*

Key Words*: *Optical Transmittance, Reflectance, SnO_2, Tetragonal, Thermal Evaporation

1. INTRODUCTION

Thin film solar cells is an active area of research at this time. Recently, much attention has been paid to the development of low cost, high efficiency thin film solar cells. Tin oxide, SnO_2 is one of the suitable candidates among the II–VI compounds for solar energy conversion due to its ideal band gap, high absorption coefficient, and ease of film fabrication.[1-5] Some beneficial properties such as, transparency for visible light, reflectivity for infrared light and a low electrical sheet resistance making them suitable for a wide variety of applications such as in transistors, photovoltaic cell, gas sensors, protective and wear-resistant coating on glass containers, Infrared reflectors for glass windows etc. Tin oxide is an inorganic compound of white, off-white or sometimes found grey. It is an amphoteric oxide, an n-type semiconductor having a wide band gap of about 3.6 eV, crystalline and diamagnetic in nature.

Various techniques such as screen printing [6], Sputtering [7], closed vapor deposition [8], chemical bath deposition [9], close-spaced sublimation [10-12], Metal organic chemical vapor deposition (MOCVD) [13], Spray pyrolysis, Sol-gel, electro deposition [14-16], and vacuum evaporation [17-19], have been investigated as suitable techniques for the fabrication of SnO_2 thin films. Enormous amount of work has been already reported on the study of structural, optical and electrical properties of SnO_2 thin films.[20-26]

The aim of this work is to prepare SnO_2 thin films on glass substrate by Vacuum Evaporation method and investigation of various properties such as electrical, optical and structural properties by varying film thickness and also varying substrate temperature. We investigate the effect of substrate temperature and thickness of vacuum evaporated SnO_2 films to optimize the growth condition for a good quality film which would be suitable for optoelectronic devices.

2. MATERIALS AND METHODS

SnO_2 thin film was deposited on glass substrate. The substrate was cleaned very carefully with detergent, acetone, de-ionized water and ultrasonic bath. The mask was placed in close proximity to the substrate for condensation of the evaporated vapor only in the exposed substrate areas.

The samples were prepared by vacuum evaporation method. The vacuum chamber was cleaned carefully with clothes soaked in acetone and then dried. The source material SnO_2 powder was inserted in a boat of turret source. The substrate with the mask was then mounted with a clamp above the boat. To vacuum the system, a rotary pump and a backing valve help to reach a pressure of 10^{-2} Torr as shown in Pirani guage. A roughing valve helps to reach a pressure of 10^{-3} Torr. Finally, high vacuum (10^{-6} Torr) was achieved with the help of a baffle valve as monitored in a Penning Gauge.

The substrate was heated with the help of radiant heater at a certain temperature called substrate temperature which was kept fixed at 350 ^{0}C. Then the low tension was switched on and current was controlled to become the boat red-hot

and the materials kept in the boat start to evaporate. The thickness monitor showed thickness of the film deposited. After getting the desired thickness the evaporation was stopped by placing a shutter above the evaporator source. The samples, prepared at a fixed substrate temperature 350 ^{0}C, were annealed at 350 ^{0}C for 15 minutes.

The transmittance (T) and reflectance (R) were calculated by using the following equations:

T% = {Transmitted intensity (I_t)/Incident intensity (I_0)}x100
R% = {Reflected intensity (I_R)/Incident intensity (I_0)}x100

Absorption coefficient and photon energy were calculated for the samples using the equations: $\alpha = (2.303xA)/t$, where α is absorption coefficient, A the absorbance, t the thickness of the films and $E = h\nu = hc/\lambda$, where h is Planck's constant, c the speed of light and λ is wavelength.

The extinction coefficient was calculated by using the values of $\boldsymbol{\alpha}$ and λ as: $K = \boldsymbol{\alpha}\lambda/(4\pi)$.

The band gap energy (E_g) for SnO_2 films was determined by plotting $(\alpha h\upsilon)^2$ versus photon energy ($h\upsilon$) for the graphs of corresponding wavelength λ. From the optical data, the absorption coefficient was calculated by using Lambert's law: $\boldsymbol{\alpha} = A(h\nu - E_g)^n / h\nu$, where n = 0.5 is used for SnO_2 as a direct band gap material. [34]

As there are diffraction peaks in XRD patterns, their grain size can be calculated by using the Debye-Scherrer formula: $D = k\lambda/(\beta\cos\theta)$, where Where D is the mean particle size, k is a constant whose value is 0.9, λ is the wavelength of X-ray used and β is the full-width at half-maxima (FWHM) of the peak of plane and is the diffraction angle.

3. RESULTS AND DISCUSSION

3.1 Optical Properties

We considered three samples of SnO_2 as: Pure tin oxide (SnO_2) (Sample-1), 5% Cu doped Tin Oxide (SnO_2) (Sample-2) and 5% Al doped Tin Oxide (SnO_2) (Sample-3) thin films. The thickness of the films was measured by using thin film measurement device. For all the samples, constant annealing temperature 350 ^{0}C and annealing time 15 min were maintained.

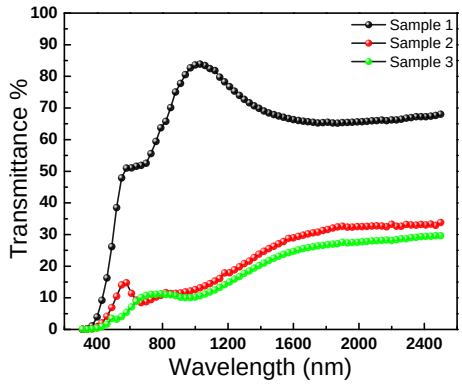

Fig-1: Variation of transmittance with wavelength of SnO_2 thin films of different samples

Fig-1 shows the variation of transmittance with photon wavelength varying from 310nm to 2500nm of SnO_2 thin films of different doping (Al, Cu) and thicknesses (50, 90, and 100 nm). The maximum transmittance (83.86%) is obtained for the wavelength 1030 nm. The films also show good interference pattern indicating better homogeneity and good quality. From 700-1030 nm for sample-1, transmittance increases sharply up to 80 - 84% whereas increases slowly upto 65-68% from 1030-2500 nm.

All the samples show optical transparency exhibiting interference pattern in the spectral region between 1000 nm to 1030 nm and display a clear explicit absorption edge interrelated to the optical band gap which agrees with Patil *et. al* [27]. Such behavior of the transmission spectra is an evidence of the increase in the thickness and uniformity of the films. The transmittance falls steeply with decreasing wavelength (310–580nm). This makes the materials useful in manufacturing optical components, windows, mirrors and lenses for high power IR laser.

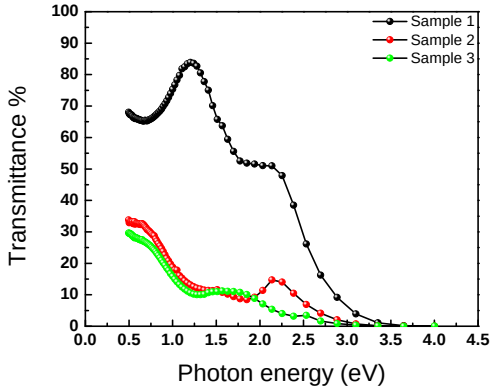

Fig-2: Variation of transmittance with photon energy of SnO_2 thin films of different samples

Fig-2 shows the variation of transmittance with photon energy 0.5-4eV of SnO_2 thin film of different doping by vacuum evaporation technique. The graph shows that the

films are highly transparent. The transmittance increases sharply up to 68% - 84% at photon energy 1.2 eV for sample-1. The interference pattern in the transmittance manifests a fairly smooth surface and relatively good homogeneity of the film.

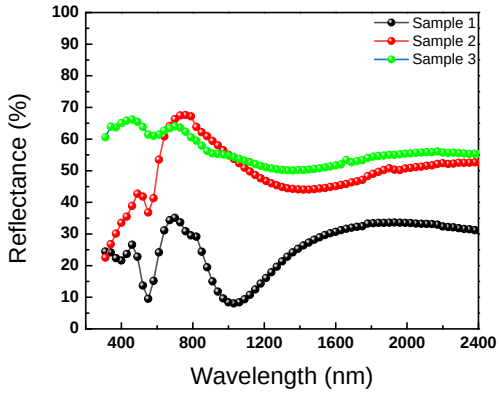

Fig-3: Variation of reflectance with wavelength of SnO_2 thin films of different samples

From Fig-3 we see that reflectance falls steeply with decreasing wavelength (460-610 nm). Sample shows consistent optical reflectance in the spectral region of 1200-2500 nm. The reflectance decreases in the NIR region. Maximum reflectance observed 67.55% at 760 nm is obtained for the Cu doped thin film (Sample-2). Reflectance spectra shows interference pattern in the range 580-2500 nm.

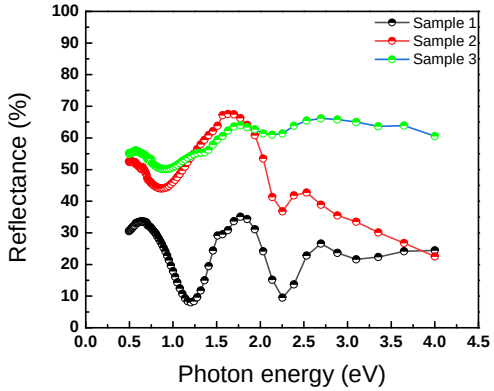

Fig-4: Variation of reflectance with photon energy of SnO_2 thin films of different samples

The reflectance spectra shown in Fig-4 indicates the interference pattern with distinct peaks and valleys. The reflectance decreases for all the films in the NIR-region. It is observed that maximum reflectance (67.55%) at 1.6323 eV is obtained for the film thickness 90 nm. Peak in the spectra indicates that photon energy in that region wasn't absorbed.

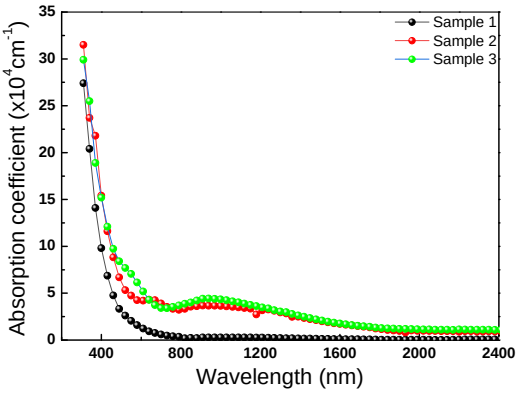

Fig-5: Variation of absorption coefficient with wavelength of SnO_2 thin films of different samples

Absorption coefficient as shown in Fig-5 decreases rapidly for shorter wavelength and slowly for longer wavelengths. The maximum values are obtained at 310 nm for three samples. The higher values of α (>10^4) at shorter λ means that, there is a larger probability of the allowed direct transition which agrees with M. Mott & E. Davis [28], then α decreases with increasing λ and remains consistent at higher wavelength. This will make the film a good window layer for Solar cell application. The low absorption co-efficient makes SnO_2 films useful for optical components in high laser window and multispectral applications, providing good imaging characteristics. [29]

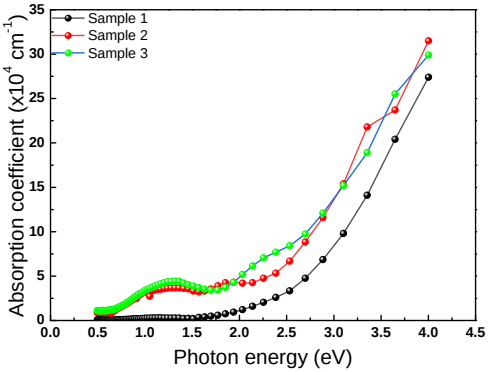

Fig-6: Variation of absorption coefficient with Photon Energy of SnO_2 thin films of different samples

As observed from Fig-6, the behavior of *α* versus *hν* can be attributed to free carrier absorption which increases with the increase of the photon energy due to inter band transition of electron from the valence to the conduction band as reported by E.L. Nahass *et al* [30]. All the films have high absorption coefficient (~3*10^5cm^{-1}) above the fundamental absorption edge. The high absorption coefficient and nearly optimum band gap energy of this material is favorable for solar photovoltaic application.

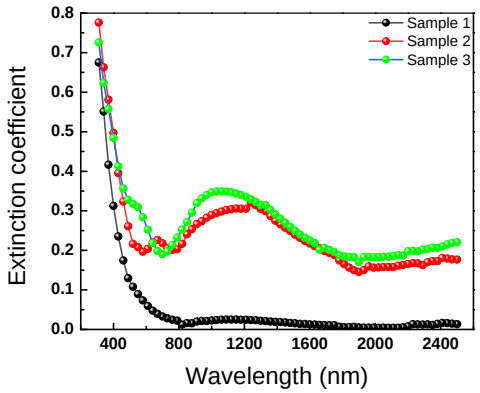

Fig-7: Variation of extinction coefficient with wavelength of SnO_2 thin films of different samples

The extinction coefficient is the imaginary part of the complex index of refraction related to the absorption of light. Fig-7 shows that extinction co-efficient falls sharply in the wavelength range 310-800 nm. The behavior of extinction co-efficient is nearly similar to the corresponding absorption co-efficient for SnO_2 thin films as reported [31]. The fall in extinction co-efficient may be due to the absorption of light at the grain boundaries. It is almost consistent in the higher wavelength region.

In Fig-8, extinction co-efficient increases rapidly with the increase of photon energy. Since the extinction co-efficient (K) describes the attenuation of light in a medium and increase of K with the increase of photon energy indicates the probability of raising the electron transfer across the mobility gap with photon energy. These optical properties makes SnO_2 thin films glazing material for maintaining cool interior in building in warm climate region while still keeping the room well illuminated. Extinction coefficient first increased slowly for shorter photon energy and rapidly for larger photon energy.

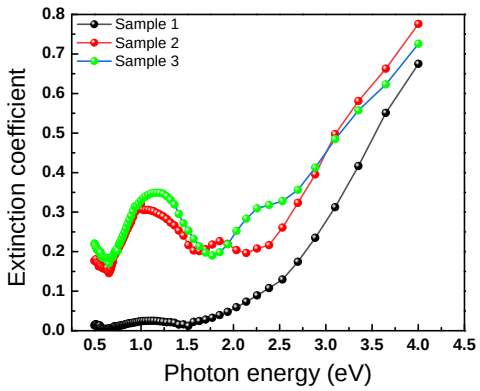

Fig-8: Variation of extinction coefficient with Photon Energy of SnO_2 thin films of different samples

Fig-9 shows the rapid fluctuations of the refractive indices in the visible range. The gradual decrease of refractive index with wavelength implies that the normal dispersion occurred before the absorption edge followed by anomalous dispersion. Low refractive index occurs due to successive internal reflections or due to the trapped photon energy within the grain boundary. [32]

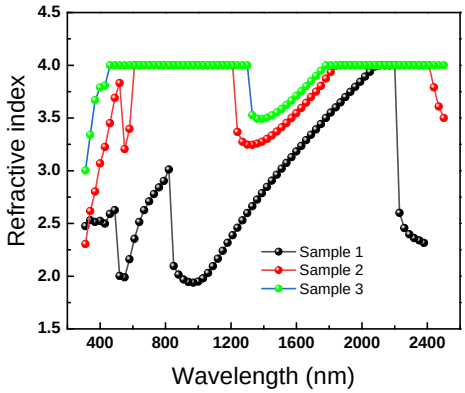

Fig-9: Variation of refractive index with wavelength of SnO_2 thin films of different samples

The variation of refractive indices with photon energy for SnO_2 thin films of different thicknesses is shown in Fig-10. The curves shift to shorter wavelength may be due to the increasing in the energy gap which causes the lattice reported by J. Bakar *et al* [33]. The initial sharp decrease of refractive index with wavelength indicates a rapid change in the absorption energy of the materials, which depends on the surface and volume imperfections.

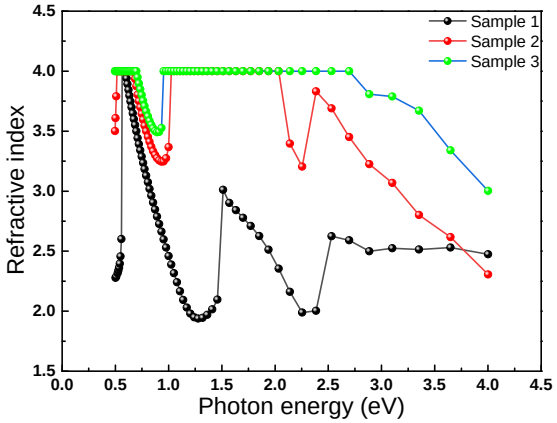

Fig-10: Variation of refractive index with photon energy of SnO_2 thin films of different samples

The band gaps (Eg) for SnO_2 films were determined by plotting $(\alpha h\nu)^2$ vs photon energy ($h\nu$) from the Lambert's law, where α is the absorption coefficient, A is a constant related to the effective masses associated with the bands. The value of n is 0.5 for direct band gap material and 2 for indirect band gap material [34]. Since SnO_2 is direct band gap material, we used n = 0.5. Extrapolating the straight line portion of the curve in energy axis gives the values of band

gap (E_g) as shown in Fig-11. This results are nearly similar to the reported band gap values 3.02 eV to 3.35 eV. [35]

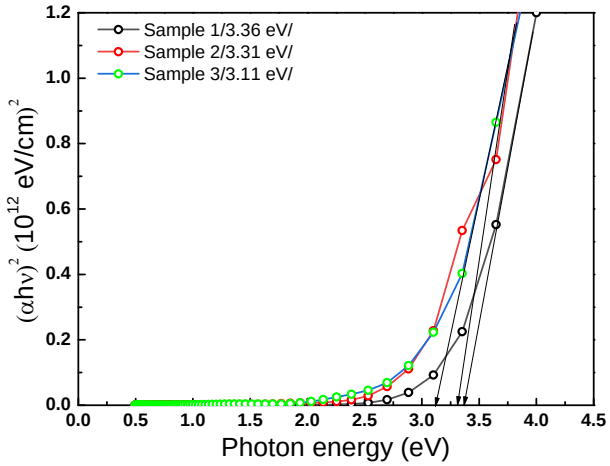

Fig-11: Variation of $(\alpha h\nu)^2$ with photon energy for SnO_2 thin films

Serial	Sample Name	Measured Band gap, E_g (eV)	Standard Band gap (eV)
Sample-1	Pure SnO_2	3.36	
Sample-2	5% Cu doped SnO_2	3.31	3.6
Sample-3	5% Al doped SnO_2	3.11	

Table-1: Band gap for the thin films

3.2 Structural Properties: X-Ray Diffraction Analysis

From the XRD patterns of prepared SnO_2 sample as shown in Fig-12, no diffraction peak is found. As the annealing temperature was limited to 350 °C, we may have only one peak of 2θ value at 43.33° corresponds to the [400] plane for 5% Cu doped SnO_2 sample. Moreover, the peak is not so sharp. The observed small, wide and low intensity peak indicates that the film structure has low degree of crystallinity. The [400] diffraction plane is localized approximately at 43.33° of cubic phase SnO_2 film which is in good agreement with the reported ones by several authors. [36] The number and sharpness of peaks could be increased by changing the annealing temperature and annealing time. From this result, it can be concluded that the elevated substrate temperature is the suitable optimum growth conditions to prepare good quality polycrystalline thin film.

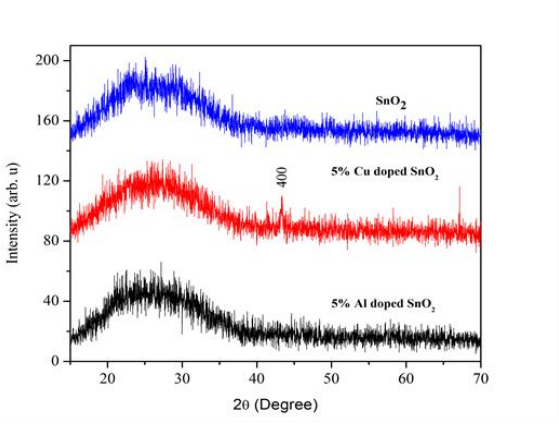

Fig-12: XRD spectra of (a) SnO2 , (b) 5% Cu doped SnO2 and (c) 5% Al doped SnO2 thin films (annealed), each of thickness 300nm deposited at 350 ºC

The wavelength of the target used in XRD instrument is 1.5406×10^{-10} m for Cu-K_α line. Using this value, the grain size for 5% Cu doped SnO_2 film is calculated as 34.7 nm.

4. CONCLUSIONS

Pure, Cu- and Al-doped Tin Oxide films were prepared by high vacuum thermal evaporation method. Optical characteristics of the thin films were determined from the transmittance spectra in the UV-VIS region. All the films show high absorption coefficient (~10^5 cm^{-1}) above the fundamental absorption edge. The high absorption coefficient and nearly optimum band gap energy of this material is favorable for solar photovoltaic applications.

The optical band gap of pure SiO_2 film is 3.36 eV, which indicates that the synthesized material of the film is a semiconducting oxide. The calculated band gap was found to decrease (3.36 to 3.11 eV) from pure and Cu/Al-doped samples. The range of band gap obtained from the studies is found to be suitable for optoelectronic devices. XRD study wraps up that the average grain size of the Cu-SnO_2 thin film was 35 nm. XRD study reveals one major peak in the film.

5. ACKNOWLEDGEMENT

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