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INFLUENCE OF COPPER DOPING ON THE STRUCTURAL AND OPTICAL PROPERTIES OF SPRAYED SnO_2 THIN FILM

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ABSTRACT

The influence of copper contents on the structural and optical properties of sprayed SnO_2 thin films has been investigated. The surface topography and structural properties of these films were studied by using atomic force microscopy (AFM) and X-ray diffraction techniques. According to the X-ray diffraction spectra, SnO_2 and copper doped SnO_2 thin films were formed with a rutile type phase and tetragonal unit cell with a preferred orientation along (110) plane. The optical dispersion parameters have been evaluated and analyzed by using Wemple-Didomenico equation. The average values of the oscillator energy, E_o, and the dispersion energy, E_d, were found to be in the range of (6.75-7.53) eV and (22.14-25.98) eV respectively. Also, the average values of the oscillator strength S_o, and average oscillator wavelength λ_o were estimated to be in the range of (4.16-5.48).10^{13} m^{-2} and (255-266) nm respectively.

Keywords: dispersion parameters, Urbach tails, SnO_2 thin films, chemical spray pyrolysis Technique

I. INTRODUCTION

Tin oxide has become a promising material due to its unique properties such as high electrical conductivity,high optical transparency in the visible part of the electromagnetic spectrum [1,2]. The IR reflectivity of stoichiometric SnO_2 thin films is low because of its low intrinsic free carrier concentration and mobility,which are thought to be due to doubly ionized vacancies serving as donors [3], which are stable at high temperatures. Tin oxide is also known to have high resistance to acids and bases,and have a very good adhesion to many substrates [4,5]. SnO_2 has a tetragonal structure, with a wide energy gap of E_g=3.7eV,and behaves as an n- type semiconductor [6]. This metal oxide has wide range of applications in low emission glass, electrodes, organic light emitting diodes optoelectronic devices, lithium batteries, gas sensors, heat reflectors and polymer based electronics [7-14], pure and doped SnO_2 thin films have been prepared by various techniques such as sol-gel method, chemical vapor deposition, pulsed laser deposition, plasma based evaporation and spray pyrolysis[15-20]. In the present work, we have investigated the optical and structural properties of SnO_2:Cu, thin films, grown by spray pyrolysis technique. The result of the present work will have an important application in the field of industry.

II. EXPERIMENTAL

SnO_2:Cu thin films were obtained by the spray pyrolysis in air atmosphere. A homogeneous solution was prepared by dissolving ($SnCl_4.5H_2O$)and ($CuCl_2$) in distilled water at room temperature in which the volumetric ratios of Cu were (0,3,7)% The glass substrate were cleaned with ethanol and acetone in ultrasonic cleaner. The optimized deposition parameters such as spray nozzle-substrate distance (30 cm), spray time (5 s) and the spray interval (90 s) were kept constant during deposition process. The resultant solution was sprayed onto the preheated substrate at 500 ^oC. The total duration of film coating was adjusted to get film thickness of a bout 400 nm.
The X-ray diffraction (XRD) data of the prepared films were taken using (Philips pw 1840 diffractometer) with Cuk$_\alpha$ radiation, λ = 1.5418 Å over the diffraction angle range 2θ=20-60 at room temperature. Surface morphology of the films was examined by atomic force microscopy (AFM) . The absorption and transmittance spectra were measured at room temperature using double beam spectrophotometer (Shimadzu UV- probe Japan) in the wavelength range (350-900) nm.

III. RESULTS AND DISCUSSION

The X-ray diffraction pattern for the pure SnO_2 and Cu doped SnO_2 deposited at 500^{o}C are shown in Fig. (1). The diffraction peaks in Fig. (1) ((110), (101), (200), (211)) planes are indexed to the rutile type phase of SnO_2 (JCPDS card No. 77.0450) with a tetragonal unit cell showing a preferred orientation along (110), which was in good agreement with Moudes and Radriguez [21], the preferred orientation of the films which depends on the substrate temperature, dopant concentration and other deposition parameters.
No traces of copper metal or oxides could be detected within the detection limit of XRD.
In order to determine the variation of the crystallites size with increasing copper contents, three methods were used, the first method is using Scherrer formula neglecting peak broadening due to residual stresses in the films is givens by [22]:

$$D = \frac{0.9\ \lambda}{\beta \cos\theta} \qquad \text{..........} \qquad (1)$$

where D is the size of crystallite, (β) is the broadening of the diffraction line measured at half its maximum intensity in radians.
The second and the third approaches were the use of the Lorentzian and Gaussian components of the integral breath which are given by:

$$\beta_{Lorentzian} = \beta - \beta_i \qquad (2)$$

$$\beta_{Gaussian} = \beta^2 - \beta_i^2 \qquad (3)$$

where β_i is the instrumental profile function.

The calculated values crystllite sizes by the three methods are given in table (1). From table (1) it can be noticed that the crystallite size decrease with the increasing of the copper contents. The lowest value of the crystallite size was obtained by Gaussian method.

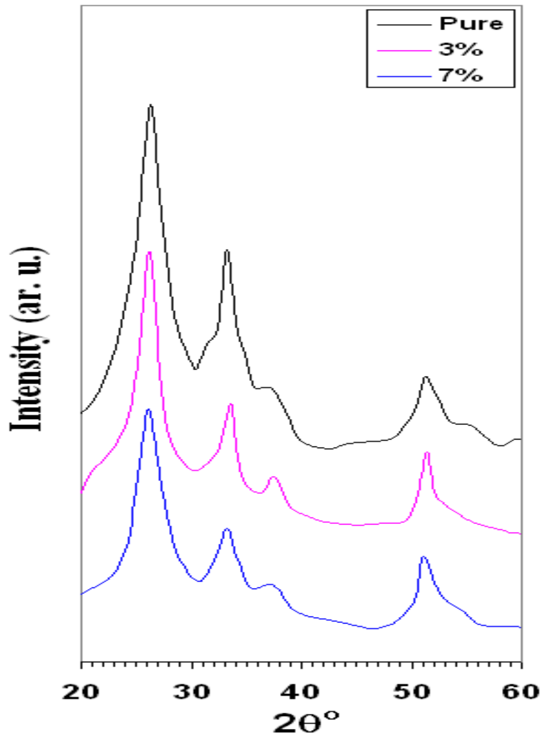


Fig. 1: XRD spectrum for the pure SnO_2 and (3%,(7%) copper doped SnO_2 thin films

Table 1: The average crystallite size of SnO_2 and (3%,7%) Cu doped SnO_2 thin films

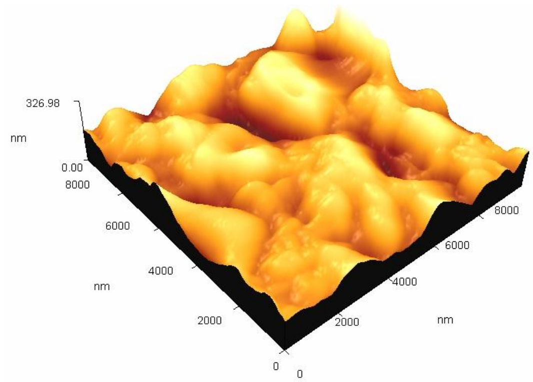
	Crystallite size method		
sample	Scherrer (nm)	Lorentzian (nm)	Gaussian (nm)
SnO_2	63.70	75.00	49.7
3 % Cu doped SnO_2	43.88	49.17	23.5
7 % Cu doped SnO_2	37.78	41.64	17.49

We have also measured the surface topography of the thin films as shown in Fig. (2), from which it can be noticed that the root mean square roughness of the thin films were decreased as the copper contents increased, the RMS value for SnO_2 thin film was 38.9 nm and for the 7% Cu doped SnO_2 was 18.8 nm which means that the crystallite size was also decreased, as the copper contents was increased. This results are in good agreement with XRD data.

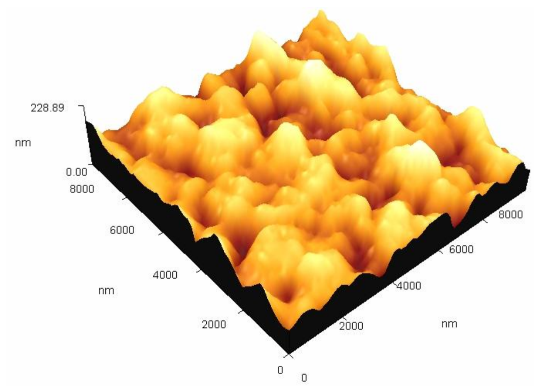
The dispersion of refractive index (n) with incident photon energy $(h\upsilon)$ can be explained mathematically via the single oscillator model proposed by Wemple–Didomenico [23], whom assumed that every particle in the medium is vibrating with the same natural frequency, (υ_o) and can be expressed by the relation:

$$n^2 - 1 = \frac{E_d E_o}{E_o^2 - (h\upsilon)^2} \qquad (4)$$

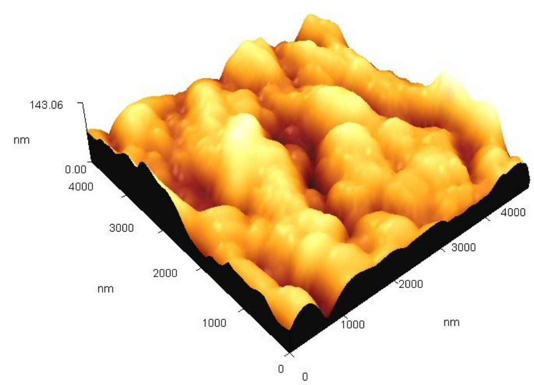
where $E_o = h\upsilon_o$ is the single effective oscillator energy, E_d is the dispersion energy which is a measure of the strength of the inter-band optical transitions, which simulates all the electronic excitations involved. By plotting $(n^2-1)^{-1}$ versus $(h\upsilon)^2$ and by fitting the result as straight lines, as shown in Fig. (3), then E_o and E_d can be determined directly from the gradient, $(E_o\, E_d)^{-1}$, and the y intercept, (E_o/E_d) .



Pure



3 %



7%

Fig. 2: The AFM micrographs for the pure SnO_2 and (3%,(7%) copper doped SnO_2 thin films

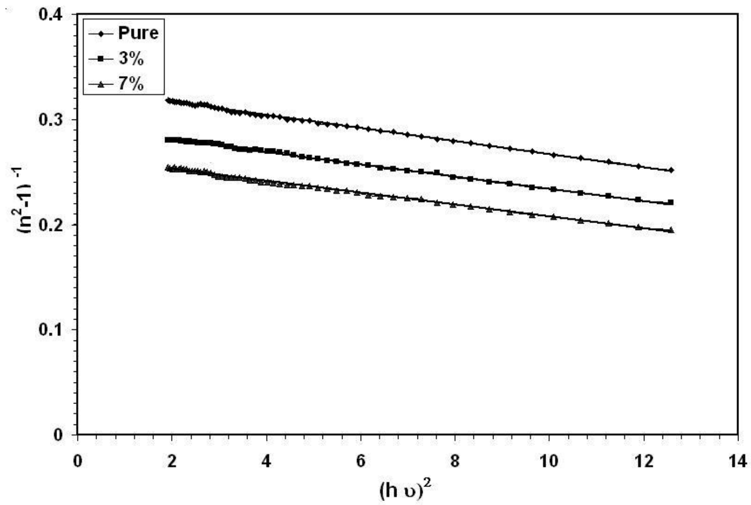


Fig. 3: $(n^2 -1)^{-1}$as a function of $(h\upsilon)^2$for the pure SnO_2 and (3% ,(7%) copper doped SnO_2 thin films

It can be observed from the results which are listed in table (2), the values of the static refractive index n_∞ and the static dielectric constant ε_∞ were found to be in the range of (1.99-2.2) and (3.94-4.85) respectively. The values of E_o were found to decrease with the increasing of Cu contents, while the values of E_d were found to increase from 22.14 eV to 25.98 eV. This might be attributed to the increase in the number of scattering centers due to the dissolving of copper atoms in the film matrix [24].
From the results listed in table (2), it can also noticed that the values of E_o and E_g are decreased with the increasing of the copper dopant, with the approximated empirical behavior, $E_g \approx 0.5\ E_o$.

Table 2: the dispersion parameters and Urbach tails for SnO_2 and Cu doped SnO_2

sample	**E_d eV**	**E_o eV**	**E_g eV**	E_U meV	n_∞	ε_∞	**$S_o x10^{13}$ m^{-2}**	λ_o nm	**M_{-1}**	**M_{-3} $x10^{-2}$ (eV^{-2})**
SnO_2	22.14	7.53	3.67	526	1.99	3.94	4.16	266	2.94	5.19
3 % Cu doped SnO_2	23.97	7.19	3.60	555	2.08	4.33	4.64	260	3.33	6.44
7 % Cu doped SnO_2	25.98	6.75	3.38	588	2.20	4.85	5.48	255	3.85	8.43

It is well known that The absorption coefficient near the band edge show an exponential dependence with the photon energy [25]:

$$\alpha = \alpha_o \exp\left(\frac{h\upsilon}{E_U}\right) \qquad (5)$$

where E_U is Urbach energy which corresponds to the width of band tail and can be evaluated as the width of localized states, (α_o) is a constant.
The E_U was calculated from the slope of Fig. (4) by using the relation:

$$E_u = \left(\frac{d(\ln\alpha)}{d(h\upsilon)}\right)^{-1} \quad \text{------------- (6)}$$

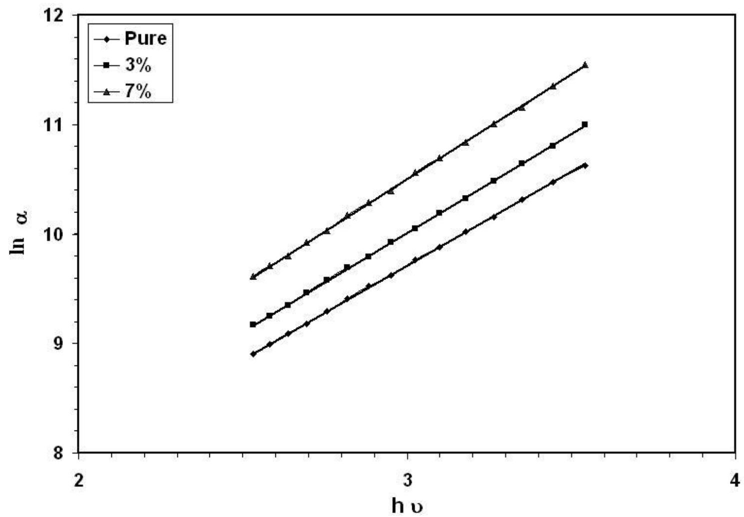


Fig. 4: ln α as a function of hυ for the pure SnO_2 and (3%,(7%) copper doped SnO_2 thin films

The obtained values are given in table (2). Urbach energy values of the films were observed to increase with increasing copper contents. The E_U values were change inversely with optical band gaps of the films. The decrease in E_g might be attributed to the increase in the disorder of the material occurred by the doping. This behavior is in good agreement with the XRD and AFM analysis.
The refractive index can be fitted to the well Known Sellmeier equation:

$$n^2 - 1 = \frac{S_o \lambda_o^2}{1-(\lambda_o/\lambda)^2} \quad (7)$$

Where S_o is the oscillator strength, λ_o is the average oscillator wavelength .

The plot of $(n^2-1)^{-1}$ against $(\frac{1}{\lambda^2})$ for the thin films, are shown in Fig. (5), where the values of S_o and λ_o are obtained from the slope, $(\frac{1}{S_o})$, and the y- intercept, $(So\lambda_o^2)^{-1}$, their values were listed in table (2).
A measure of interband transition can be provided from the M_{-1} and M_{-3} moments of the optical spectrum which are expressed as [26]:

$$E_o^2 = \frac{M_{-1}}{M_{-3}} \quad (8)$$

$$E_d^2 = \frac{M_{-1}^3}{M_{-3}} \quad (9)$$

The obtained values are given table (2), from which it can be noticed that the M_{-1} and M_{-3} moments have a tendency to increase with the increasing of the copper contents.

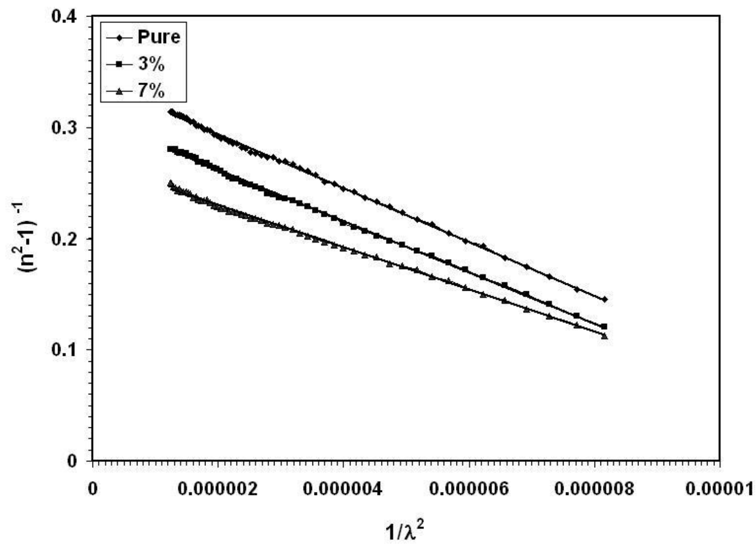


Fig. 5: $(n^2 -1)^{-1}$ as a function of $(1/\lambda^2)$ for the pure SnO_2 and (3% ,(7%) copper doped SnO_2 thin films

IV. CONCLUSIONS

In the present work pure and Cu-doped SnO_2 thin films were obtained using the spray pyrolysis technique. The XRD revealed that the preferred orientation was along (110) plane. The average crystallite size were estimated and found to decrease as the copper contents increased. The root mean squares of the surface roughness were also found to decrease with the increasing of copper contents. Values of the optical energy gap estimated from the oscillator energy, E_o were found to decrease while the values of Urbach tail were found to increase as the copper contents increased, which assures that the crystal disorder were increase.

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