

The effect of thickness on the structural and optical properties of SnO₂ thin films Prepared by chemical spray pyrolysis method

Nadia Jasim Ghdeeb

College of science for Women, University of Baghdad, Jadriya, Baghdad, Iraq

Abstract: SnO₂ thin films with different thickness have been deposited on glass substrate by chemical spray pyrolysis technique at RT. X-ray diffraction studies reveal that the films are polycrystalline in nature with tetragonal structure and preferential orientation along (110). The grain size of the films is found to increase from (56.1056 to 93.9) nm with increasing thickness while the strain and the dislocation density of the films are found to decrease from

(61.78 to 36.9025) 10^{-4} rad and from (3.1847 to 1.1312)

lines.m⁻² respectively. The transmittance spectrums of SnO₂ thin films reveal very pronounced interference effects for photon energies below the fundamental absorption edge by exhibiting interference pattern. The optical energy gap for SnO₂ thin films decreases as the thickness in the films increased.

Key word: SnO₂ films, structure properties, optical properties

I. Introduction

Semiconductor oxide thin films are materials with numerous applications in electronic and optoelectronic devices as well as some other applications such as protective coatings, heat mirrors, and catalysis [1,2]. SnO₂ is widely used as transparent electrodes in solar cells, flat panel displays, and chemical sensors. Recently, SnO₂ has been integrated into micromachined silicon devices as a sensing element of microsensors [3]. As is known, tin dioxide (SnO₂) is a crystal of white color, the density is 7.0096 g/cm³, melting point is about 2000°C [Kunians, 1964]. The SnO₂ films have

(predominantly amorphous or polycrystalline structure with a tetragonal lattice of rutile with parameters $a = b = 0.4737$ nm, $c = 0.3185$ nm, with two tin atoms and four oxygen atoms in the unit cell. Depending on the method of film synthesis, the band gap varies in the range (3.35–4.3) eV and the refractive index in the range (1.8–2) [1]. Since the last decade there has been a great deal of interest in the preparation of inexpensive thin films of SnO₂. This is because tin dioxide based thin films with SnO₂ large band gap ($E_g > 3$ eV) n-type semiconductors are attractive from the scientific and technological point of view [4]. A variety of techniques has been used to deposit tin oxide (SnO₂) thin films. These include spray pyrolysis [5], chemical vapor deposition [6], ion-beam assisted deposition, sputtering [7], and sol-gel methods [8, 9]. Among these techniques, spray Pyrolysis has proved to be simple, reproducible and inexpensive, As well as suitable for large area applications. Besides the simple experimental arrangement, high growth rate and mass production capability for large area coatings make them useful for industrial as well as solar cell application. In addition, spray pyrolysis opens up the possibility to control the film morphology and

particle size in the nm range [10]. Tin dioxide (SnO₂) with the rutile structure is an n-type semiconductor with a wide band gap ~ 3.6 eV. Due to its electrical, optical, and electrochemical properties, SnO₂ is widely used as transparent electrodes in solar cells, flat panel displays, and chemical sensors. Recently, SnO₂ has been integrated into micromachined silicon devices as a sensing element of microsensors. SnO₂ thin films have been fabricated using different techniques including electron beam evaporation, rf sputtering, and chemical vapor deposition. One of the major challenges in synthesizing SnO₂ thin films is the control over stoichiometry. Since most depositions are carried out in high vacuum condition at high temperatures, the SnO₂ films obtained are nonstoichiometric and frequently consist of metastable phases such as SnO and Sn₃O_{4.3}. The existence of these metastable phases and crystal defects will strongly affect the properties of the films. Therefore, a postdeposition annealing in air is necessary to obtain the stoichiometric SnO₂ phase with the rutile structure.[11]

II. Experimental

Tin dioxide (SnO₂) were prepared by spray pyrolysis glass substrates at temperatures (Ts) of 400°C. The effective area of the substrates was approximately 2.5 cm². The deposition parameters such as solution flow rate; carrier gas flow rate and nozzle to substrate distance were kept constant at 5 ml/min, 8 l/min and 30 ± 1 cm, respectively. The starting solution was prepared using SnCl₂.5H₂O. Firstly Tin Chloride (SnCl₂.5H₂O) was dissolved in a Water. Secondly, solutions were mixed and diluted with deionized water, so that the final concentration was 0.1 M.

Which were then sprayed onto the heated substrates. . The substrates were ultrasonically cleaned, first

with trichloroethylene and then with acetone and methyl alcohol followed by rinsing in distilled water. The solution was stored in a volumetric reservoir at room temperature and connected to one side of the spray nozzle. The carrier gas, air was allowed to flow (8 l/min.) through the pressure-monitoring gauge, connected to the other side of the spray nozzle. The spray nozzle was moved in the (x–y) plane using the microprocessor controlled stepper motor system in order to achieve uniform film coating. Moving the spray nozzle is just an option so, it is possible to work in a stationary position too with the same setup. The structural characterization of tin oxide (SnO₂) thin films were investigated using X-ray.

III. Result and discussion

The X-ray diffraction patterns of SnO₂ thin film deposited by chemical spray pyrolysis method on glass substrate at R.T with thickness (500 , 700 & 900) nm are shown in Fig. (1 a , b & c) respectively . All XRD patterns reveal polycrystalline nature of prepared materials . Our results agree with [12],[4], [13]. Table (1) illustrates bragg's angles , inter planers spacing , relative intensity and miller indices of SnO₂ thin film From Fig. (1 a) where (x=500) corresponding to SnO₂ thin film , it can be observed that the dominant phase was tetragonal with preferential orientation along (110) at 26.346 °, from Fig.(1b) where (x=700) . All these crystals exhibit tetragonal structure with preferential orientation along (110) at 26.6007 ° for SnO₂ and the dominant orientation for SnO₂ crystals was along (101) at 33.807 °. From Fig. (1c) where (x=900) , it can be also observed a crystals with tetragonal structure and the dominant orientation for SnO₂ crystals was along (110) , (101) at 26.683 ° and 33.657 ° respectively. it is clear that the SnO₂ tetragonal structure was dominated for all peaks as matched with the ASTM card of SnO₂ with preferential orientation along (110) at 26 °. From Fig. (1a-b-c) it can be observed a crystals with tetragonal structure and the dominant orientation for SnO₂ crystals was along (110) , (101) at 26 ° and 33 ° respectively. it is clear that the SnO₂ tetragonal structure was dominated for all peaks as matched with the ASTM card of SnO₂ ,but the Intensity increasing with increase the thickness.

Table(1)
The Structural Parameters Of SnO₂ Thin Film

| X | 2θ Exp (deg) | 2θ Stan (deg) | d Exp.(Å) | d Stan.(Å) | I/I _o Exp. | I/I _o Stan. | (hkl) |
|-----|-----------------|------------------|--------------|---------------|--------------------------|---------------------------|-------|
| 500 | 26.346 | 26.578 | 3.380 | 3.5808 | 100 | 100 | 110 |
| | 33.0844 | 33.772 | 2.7054 | 3.1609 | 88 | 50 | 101 |
| 700 | 26.6006 | 26.611 | 3.347 | 3.6200 | 100 | 100 | 110 |
| | 33.807 | 33.893 | 2.648 | 3.5100 | 32 | 75 | 101 |
| 900 | 26.683 | 26.611 | 3.3381 | 3.6200 | 100 | 100 | 110 |
| | 33.657 | 33.893 | 2.6606 | 3.2000 | 51 | 75 | 101 |

The lattice constants calculated from the following equation [14] :

$$+ \frac{l^2}{c^2} \quad (1) \quad \left[\frac{h^2 + k^2}{a^2} \right]$$

Where , *hkl* : miller indices , *a , c* : lattice constants .

The calculated values of lattice constants for SnO₂ thin films are in good agreement with ASTM data . Similar results have been reported by [1],[15].

It is clear from XRD patterns of SnO₂ thin films, that the full width at half maximum (FWHM) decreases with the increasing of thickness in these films. This decreasing in (FWHM) indicates an increasing in the grain size of SnO₂ thin films as given in table (2) according to Scherrer's formula where the relation between the grain size (D) and (FWHM) is reversal as follows [16]:

$$D = \frac{0.9 \lambda}{\beta \cos \theta} \dots \dots \dots (2)$$

Where, β is the full width at half maximum (FWHM) in radian and λ is the X-ray wavelength (1.5406 Å).

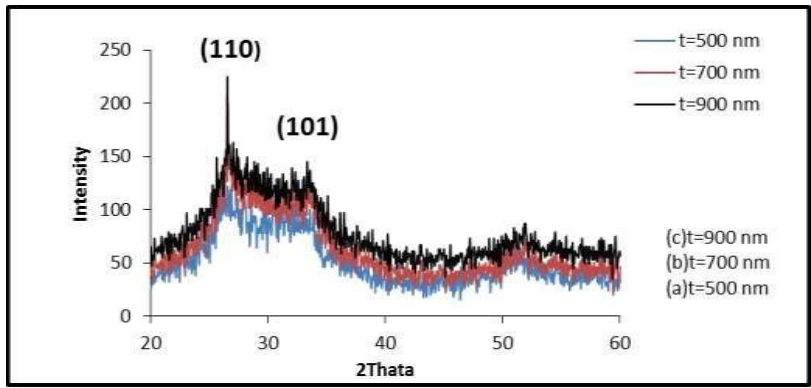


Fig.(1) The XRD patterns of SnO₂ thin films

(a) t=500, (b) t=700, (c) t=900

The dislocation density (δ) of SnO₂ thin films which defined as the length of dislocation lines per unit volume of the crystal was calculated from this equation [17]:

$$(3) \delta = \frac{1}{D^2} \dots \dots \dots$$

The values of the dislocation density of SnO₂ thin films are given in table (2). It is evident from this table that the dislocation density of SnO₂ thin films decreases with increasing in thickness which can be also deduced from the increasing in the grain size where the dislocation density is proportion reversely with the square of the grain size according to eq.(3). This decreasing in the dislocation density indicates an improvement in the crystallinity of SnO₂ thin films and their homogeneity as increasing in thickness. The strain (ξ) developed in SnO₂ thin films can calculated from the relation [18]:

$$\xi = \frac{\beta \cos \theta}{4} \dots \dots \dots (4)$$

The origin of strain is related to lattice misfit which in turn depends upon the growing condition of the films. The values of the strain of SnO₂ thin films are given in table

(2). It is clear from this table that the strain in SnO₂ thin films decreases with increasing in thickness which can be also deduced from the increasing in the grain size, where the decreasing in the strain and the dislocation density with the increasing in the grain size is a well-known phenomenon. In addition the films with lower strain and dislocation density improves the stoichiometry of the films which inturn causes the volumetric expansion of the films. In polycrystalline films, the dislocated atoms occupy the regions near the grain boundary. Due to large number of grain boundaries and short distance between them, the intrinsic strains are always associated with such interface. The increasing in the grain size causing reduction in the number of grain boundaries and that leads a reduction in the intrinsic strains associated with the grain boundaries interface.

Table (2)
Variation Of The Full Width At Half Maximum , Grain Size , Lattice Constants, Dislocation Density And Strain Of SnO₂ thin Films With Thickness

| thickness | (FWHM) rad | Grain size (nm) | Lattice Constants | | Dislocation density (lines.m ⁻²) x 10 ¹⁶ | Strain (rad) x 10 |
|-----------|------------|-----------------|-------------------|-------|--|-------------------|
| | | | a(Å) | c(Å) | | |
| 500 | 0.025382 | 56.1056 | 4.781 | 3.141 | 3.1847 | 61.78 |
| 700 | 0.020951 | 58.04 | 4.733 | 3.093 | 2.9726 | 50.9726 |
| 900 | 0.015176 | 93.9 | 4.720 | 3.080 | 1.1312 | 36.9025 |

Optical properties

The transmittance spectrum of SnO₂ thin films where thickness equal (500 , 700 & 900)nm are shown in Fig.(2). All spectrums reveal very pronounced interference effects for photon energies below the fundamental absorption edge by exhibiting interference pattern . Such behavior of the spectrum is evidence of the thickness uniformity of the films. It is clear from the same figure that the transmittance decreases with increasing in thickness. In addition the variation of the transmittance of SnO₂ thin films with the wavelength is very important because this variation will limit the transmitted wavelengths which play an important role in determination the category/type of the optical filters . The absorbance spectrums of SnO₂ thin films where x equal (500 , 700 & 900)nm are shown in Fig. (3). It is clear that as the thickness increases the absorbance of SnO₂ thin films is increased . which results in an increase of the depth of donor levels associated with these vacancies and these levels will be available for the photons to be absorbed therefore the absorbance of SnO₂ thin films will increase with increasing in thickness . As well as from the same figure , it can be seen that the absorption edge shifts to the higher wavelengths corresponding to the red region as the Se concentration increased .

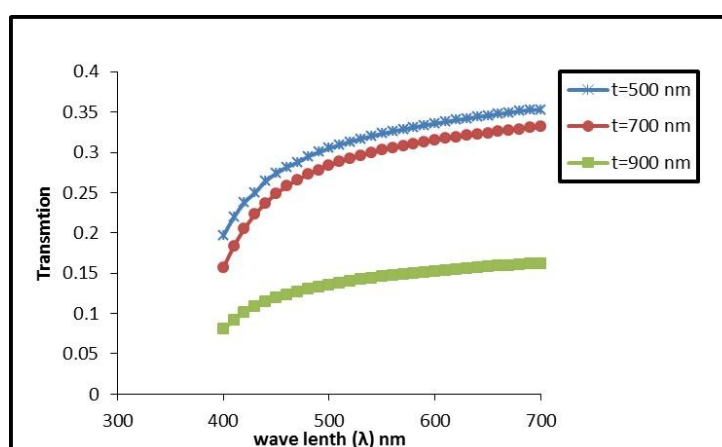


Fig.(2) Transmittance spectrums of SnO₂ thin films

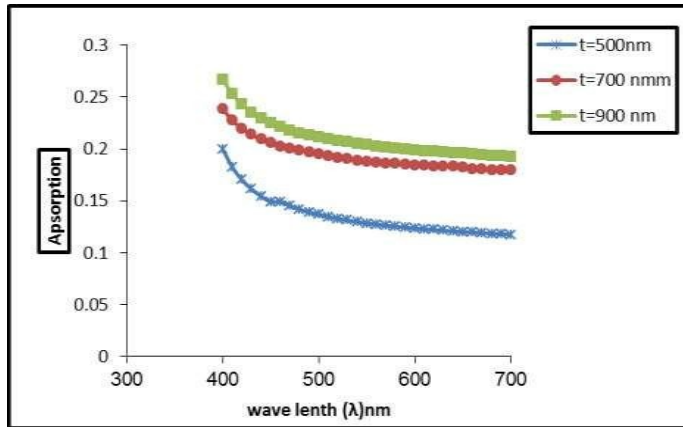


Fig.(3) Absorbance spectrums of SnO₂ thin films

The optical energy gap values (E_g) for SnO₂ thin films prepared by chemical spray pyrolysis method have been determined from the region of the high absorption at the fundamental absorption edge of these films by using Tauc equation [19]:

$$\alpha h\nu = B_o (h\nu - E_g)^r$$

Where, α is the absorption coefficient, $h\nu$ is the incident photon energy in eV, B_o is a constant depends on the nature of the material (properties of its valence and conduction band) [19] and r is a constant depends on the nature of the transition between the top of the valence band and bottom of the conduction band.

This equation is used to find the type of the optical transition by plotting the relations $(\alpha h\nu)^2$, $(\alpha h\nu)^{2/3}$, $(\alpha h\nu)^{1/2}$ and $(\alpha h\nu)^{1/3}$ versus photon energy ($h\nu$) and select the optimum linear part. It is found that the first relation yields linear dependence, which describes the allowed direct transition, then E_g was determined by the extrapolation of the portion at ($\alpha=0$) as shown in Fig.(7). It is clear that the optical energy gap for SnO₂ thin films decreases as the thickness of the films increased. This decreasing in the optical energy gap have been also reported for brush plated [3], pulse plated films [20] and chemical bathed films. The optical energy gap values

for SnO₂ thin films were 2.5 eV, 2.45 eV, 2.35 eV respectively.

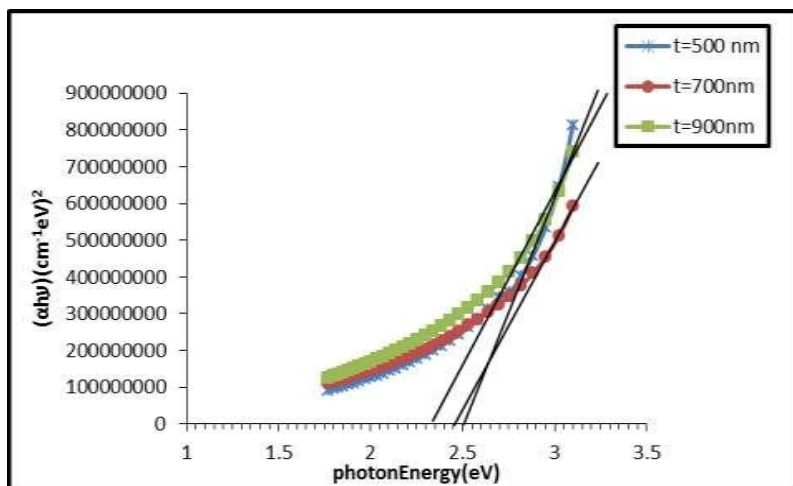


Fig.(4) $(\alpha h\nu)^2$ as a function of $h\nu$ for SnO₂ thin films

(a) $t=500$, (b) $t=700$, (c) $t=900$

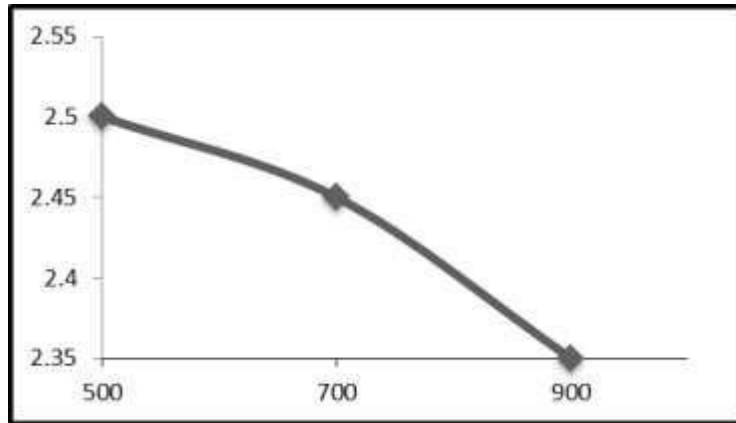


Fig.(5) Variation of the optical energy gap for SnO₂ thin films

with thickness

The refractive index (n_s) of SnO₂ thin films have been determined by using the following equation [19]:

$$(6) \quad n_s = \sqrt{\frac{4R}{(R-1)^2} - k_s^2} - \left(\frac{R+1}{R-1}\right)$$

Where, R : is the reflectance of the films and k_o : is the extinction coefficient.

The variation of the refractive index as a function of the photon energy for SnO₂ thin films is illustrated in Fig. (6). It is clear from this figure that the refractive index increasing with the decreases in the photon energy. Also it can be observed, that the refractive index of SnO₂ thin films decreases with the increasing in the thickness. This increasing is attributed to the increasing in the grain size of the films with the increasing in the thickness which interns causing an increment in the compactness of the films which in turns reduces the speed of light in the material of the thin film and then leads to an increasing in the refractive index. Where (n_s) varies according to the grain size even if the crystalline structure is itself of the material.

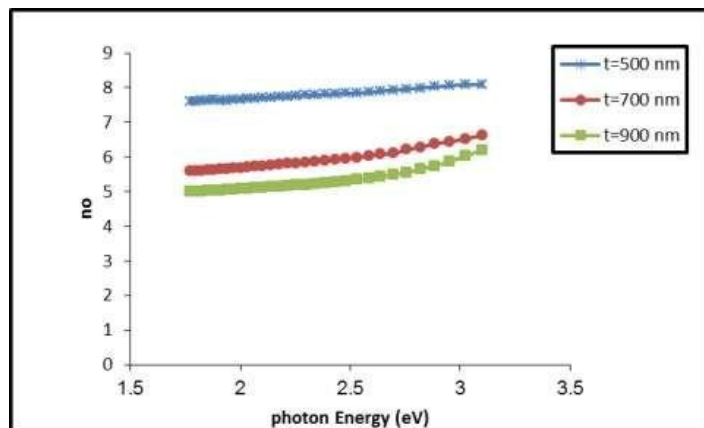


Fig.(6) The variation of the refractive index as a function of the photon energy for SnO₂ thin films

The extinction coefficient (k_s) have been determined by using the following equation [19]:

$$k_s = \frac{\alpha \lambda}{4\pi} \quad (7)$$

Where, α : is the absorption coefficient and λ : is the wavelength of the incident photon .

It is clear from this equation that k_s depends on α and has a similar behavior to α .

Fig. (7) illustrates the variation of the extinction coefficient of SnO₂ thin films with photon energy for thickness (500 , 700 & 900) nm . From this figure , it can be noted that k_s varies slightly with the increasing in the photon energy corresponding to the decreasing in the absorption coefficient. Then k_s increases highly at the absorption edge region and this increasing is attributed to the increasing of the absorption coefficient due to the direct electronic transitions thereafter k_s reaches to its maximum value at the high absorption region corresponding to the increment in the photons' energy and the increasing in the absorption coefficient with the decreasing in the wavelength . In addition , it is clear from this figure that with the increasing in the thickness the extinction coefficient k_s increases . This is attributed to the increasing in the absorption coefficient due to the increasing of the depth of donor

levels associated with tin vacancies and these levels will be available for the photons to be absorbed causing an increment in the absorbance and leads to increase in the absorption coefficient. Therefore k_s will increase with the increasing in the

thickness since it has a similar behavior to α and depends on it .

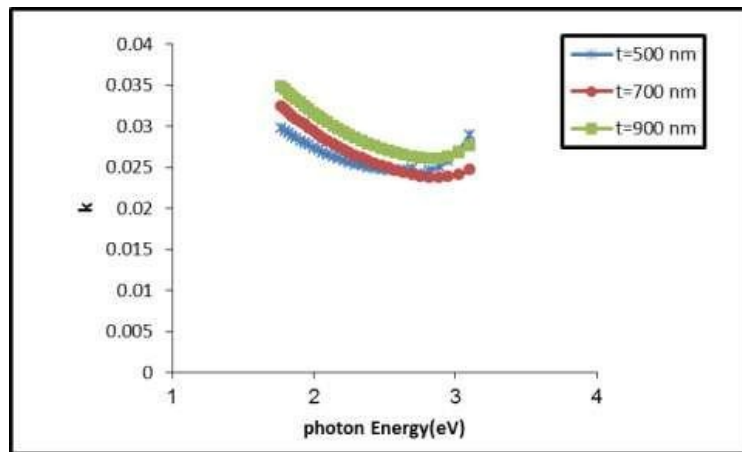


Fig.(7) Extinction coefficient as a function of photon energy

for SnO₂ thin films

figure(7)It is clear that the real part of the dielectric constant of SnO₂

thin films decrease with the thickness increases due to the dependence of the real part of the dielectric constant on the refractive index values , where the refractive index decrease with the thickness increases.

figure (8) . It is clear that the increase in the thickness leads to an increase in the imaginary part of the dielectric constant of SnO₂ thin films . This is attributed to the dependence of the imaginary part of the dielectric constant on the extinction coefficient values , where the extinction coefficient increases with the increase in the thickness.

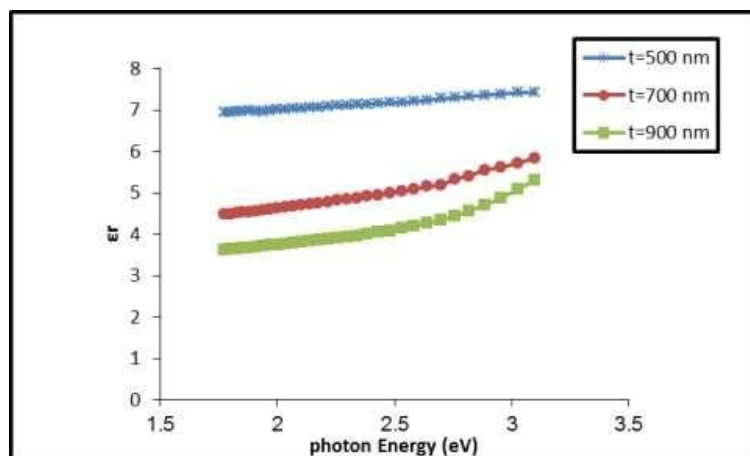


Fig.(8):The real part of the dielectric constant of SnO₂ thin films

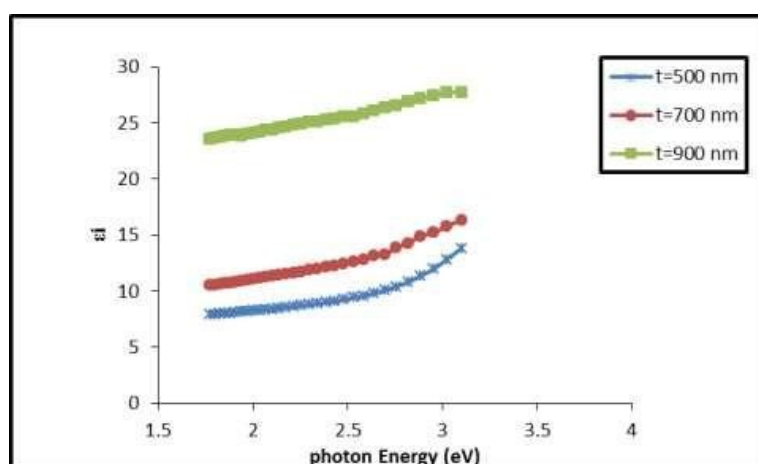


Fig.(9) Fig.(8):The imaginary part of the dielectric constant of SnO₂ thin film m

IV. Conclusion

chemical spray method technique can be successfully employed for the deposition of uniform polycrystalline SnO₂ thin films with tetragonal phase at R.T . The increasing of thickness in these films has improved the crystallinity of the films and their homogeneity because the decreasing in the strain and the dislocation density with the increasing in the grain size according to the increasing of thickness . Optical studied indicates that SnO₂thin films exhibit direct band gap which is strongly depends on the thickness almost cover the entire visible spectral that makes these films are suitable for optoelectronic devices especially for solar cell and optical filters .

References

- [1]. Daniya M. Mukhamedshina and Nurzhan B. Beisenkhanov, "Influence of Crystallization on the Properties of SnO₂ Thin Films", "Institute of Physics and Technology ", Kazakhsta (2012) ISBN: 978.
- [2]. Brito G.E.S., Ribeiro S.J.L., Briois V., Dexpert-Ghys J., Santilli C.V., Pulcinelli S.H, " Short range order evolution in the preparation of SnO₂ based materials", " Journal of Sol-Gel Science and Technology" , (1997),Vol.8, pp. 261–268.
- [3]. J. E. Dominguez, X. Q. Pan,a) and L. Fu, "Epitaxial SnO₂ thin films grown on .1⁻ 012. sapphire by femtosecond pulsed laser deposition", , VOL. 91, N. 3 1 , 2002.
- [4]. Manal Madhat Abdullah*, Mahdi Hassan Suhail* and Sabah Ibrahim Abbas **, "Fabrication and Testing of SnO₂ Thin Films as a Gas Sensor, Scholars Research Library", " Archives of Applied Science Research", 2012, 4 (3):1279-1288.
- [5]. J. P. Chatelon, C. Tenier, E. Bemstein, R. Berjoan , J. A. Roger, "Thin Solid Films",1994, 247, 162.
- [6]. B. Oreal, U. Lavrencic-Stangar, O. Cmjak, P. Bukovec, M. Kosec J. Non-Cryst. Solids ,1994,167, 272. P. S. Patil, Mater. Chem. Phys.,1999, 59, 185.
- [7]. G. Korotcenkov, A. Cornet, E. Rossinyol, J. Arbiol, V. Brinzar , V. Blinov, "Thin Solid Films ",2005,471,310.
- [8]. J. E. Dominguez, X. Q. Pan,a) and L. Fu, " FuEpitaxial SnO₂ thin films grown on .1⁻ 012. sapphire by femtosecond pulsed laser deposition", " JOURNAL OF APPLIED PHYSICS", VOLUME 91, NUMBER 3 1 FEBRUARY (2002)
- [9]. Jochan JOSEPH1, VargheseMATHEW1, Jacob MATHEW2, K. E. ABRAHAM2, " Studies on Physical Properties and Carrier Conversion of SnO₂:Nd Thin Films", 33 (2009) , 37 – 47.
- [10]. E. Horváth,*, J. Kristófb, N. Heiderb, R.L. Frostc, Á. Rédeya, A. De
- [11]. Battistid, " Investigation of SnO₂ thin film evolution by thermoanalytical and spectroscopic methods",
- [12]. Mario Alberto Sánchez-García1, Arturo Maldonado2, Luis Castañeda3, Rutilo Silva-González3, María de la Luz Olvera2*,

- Characteristics of
- [13]. SnO₂:F Thin Films Deposited by Ultrasonic Spray Pyrolysis: Effect of Water Content in Solution and Substrate Temperature ",
Materials Sciences and Applications", 2012, 3, 690-696.
- [14]. S. S. Roy¹ and J. Podder², STUDIES ON TIN OXIDE (SnO₂) AND CU DOPED SnO₂ THIN FILMS DEPOSITED BY SPRAY
PYROLYSIS TECHNIQUE FOR WINDOW MATERIALS IN SOLAR CELLS," International Conference on Mechanical
Engineering", 2009.
- [15]. E.N. Al-Jamal , "Solid State Physics" ,(1990).
- [16]. C. B. Fitzgerald, M. Venkatesan, L. S. Dorneles, R. Gunning, P. Stamenov, and J. M. D. Coey, Magnetism in dilute magnetic oxide
thin films based on SnO₂," PHYSICAL REVIEW ",B 74, 115307 ,2006.
- [17]. Y. Sitroin and M. Shaskolskaya, "Fundamental of crystal physics", (Mir publishers, Moscow, 1982).
- [18]. M.M.EL Nahass and A.M.A. EL Barry , "Effect of substrate temperature , deposition rate and heat treatment on structural and
carrier transport mechanisms of thermal evaporated p-Cu₂S/n-CdS heterojunction ", "Indian Journal of Pure & Applied Physics
",Vol. 45, May (2007) , p. 465-475 .
- [19]. Z.R. Khan , M. Zulféqar and M.S. Khan ," Effect of thickness on structural and optical properties of thermally evaporated
cadmium sulfide polycrystalline thin films" , Chalcogenide Letters Vol. 7, No. 6, June (2010) , p. 431-438 .
- [20]. N. F. Mott and E. A. Davis "Electronic Processes in Non-Crystalline Materials", (2nd, Clarendon Press, oxford, 1979).
- [21]. S. O. Kasap , "Principle of electronic materials and devices " , (2nd ed , McGraw-Hill , New York , 2002) .