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The Effect of Annealing Temperature on the Structural Properties and Color Properties of Tin Oxide Thin Films by the Sol-Gel Method

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Abstract*: *Tin oxide thin films were produced by the (sol-gel) method, coated on glass substrates using the spin coating process, and plasticized at (200°C, 300°C, 400 °C, 500 °C). The required analyses, including UV-visible spectroscopy, AFM, and XRD, were carried out. In order to research the produced films' optical, structural, and color characteristics. All of the produced films possessed a tetrahedral crystalline structure, according to X-ray diffraction data. Studies using AFM technology showed that when the annealing temperature rises, transmittance falls and the rate of surface roughness increases. In this study, the CIE 1931 method was used to examine the color coordinates of tin oxide films. Three parameters related to color were measured: brightness, dominating wavelength, and purity.

Keywords: Annealing Temperatures, Tin Oxide, CIE 1931, Dominating Wavelength.

1. INTRODUCTION

Novel materials with unique properties are produced by recent advances in science and technology, which are applied to the creation of gas sensors [1], optoelectronic devices [2], and other gadgets. Thus, several research initiatives have concentrated on creating novel materials in the form of thin films derived from oxides of semiconducting metals. The second half of the seventeenth century began the work in the field of preparing thin films, when many scientists prepared them. The method of thermal evaporation was used in 1857 to prepare thin films, and the scientist (Adams) prepared thin films of selenium deposited on platinum in 1876, and in 1887. The scientist (Narwold) discovered the possibility of evaporating metals using the vacuum evaporation technique by heating a platinum wire. The

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scientist (Kentt) used this method to prepare membranes in 1888 and studied their refractive indexes. Transparent conducting oxide thin films of superior quality are unique materials because of their unique thermal, optical, and electrical characteristics [3]. Thin films are characterized by their small mass, size, and thinness. These features have given thin films an important role for use in industrial fields. Thin film synthesis for most polycrystalline materials. There are several factors that affect the growth and structure of thin films when preparing them, which must be taken into account, including the surface temperature of the substrate, the concentration of the solution, and the evaporation rate of the solution. One of the most promising options among many metal oxide-based thin films is tin oxide thin film [4]. Transparent conducting oxide thin films are made using a variety of deposition processes, including spray pyrolysis, chemical vapors deposition, sol-gel [5], and others. Sol gel spine coating is one of these techniques that is easy to use and reasonably priced for producing good parity material. Tin oxide has a huge band gap(3.62ev) and is an (n-type) semiconductor[6] .

2. RELATED WORKS

The researcher [3], prepared (SnO_2) films using the (sol_gel) technique, and the XRD results showed that all the prepared films had a single phase with a tetrahedral crystalline structure, Thin films were characterized by a variety of techniques. The film surface is formed homogeneously of nano-sized particles withdense microstructure confirmed by TEM images. The X-ray diffraction pattern of the crystalline SnO_2, thin films reveals the existence of single-phase rutile type tetragonal crystal structure. The increase in crystallinity with thickness is attributed to the improvement of stoichiometry or reduction of impurities or both. The film properties are highly dependent on their structural characteristics. All the films exhibit transmission of 85% in the visible region. The electrical conductivity of the films strongly depends on crystalline structure quality. In conclusion, varying the thickness of the tin oxide films affects its optoelectronic properties, and it may he considered that the deposited SnO_2, thin film is suitable for many optical devices, such solar cells, gas sen- sors, surface acoustic devices, transparent electrodes. .[7] Tin Oxide thin films were deposited by sol gel dip coating method using the acrylamide route. The films were post heated at different temperature in the range of 350 - 525 ℃ . X-Ray diffraction (XRD) studies indicatyed the formation of tetragonal SnO_2. The Optimum temperature for the formation of the films was 450 ℃ .Microstructural parameters were estimated from the XRD data. XPS studies indicated the peaks corresponding to Sn 3d and 01s. Transmission spectra exhibited interference fringes. Refractive Index was in the range of 2.05-2.18. Optical band gap value was around 3.68 eV. Three fundamental Raman lines are observed which agree well with that of the bulk material. Using the CIE 1931 system, the color characteristics, dominant wavelength values, purity and luminance of thin films were studied by researchers [5] , The results showed that the purity increases with increasing annealing temperatures, The findings illustrated that the color purity and the dominant wavelength decrease with increasing annealing temp, and these values ranged between (0.7-0.51) and (563-556), respectively, when the temp increased from 300°C to 500°C, in contrast to the brightness values, which increased with increasing annealing temps. A comparative analysis was performed of

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fluorine-doped tin oxide (FTO) thin films deposited through two different systems: pneumatic spray pyrolysis and ultrasonic spray pyrolysis. The films were deposited on glass substrates at 460 °C with varying weight ratios of fluorine to tin (F /Sn = 0.35 ,F/ Sn = 0.5 and F /Sn = 0.65) The investigation focuses on the evolution of the film's crystallinity, structural, morphological, transmittance, optical, and electrical properties. Resonant nuclear reaction (RNR) and energy dispersive spectroscopy (EDS) techniques were used to confirm the presence of fluorine in the FTO samples. The results show that the sample with F / Sn = 0 deposited through pneumatic spray pyrolysis, with a figure of merit of 34.5 X 10^{-3} Ω^{-1} exhibits the best characteristics for use as electrodes in optoelectronic devices, particularly in the fabrication of solar cells [8].

3. METHODOLOGY

Materials Used in Preparing Sno_2 Films

- Aqueous tin chloride ($SnCl_2.2H_2O$): It is a solid substance in the form of a white powder, its molecular weight is (225.63g/mol), and it is produced by the Indian company (THOMAS BAKER), with a purity of (97 %).
- Diethanolamine as a stabilizer $[CH_2(OH)_2CH_2]_2NH$: It is a transparent, colorless, viscous liquid with a molecular weight of (105.14 g⁄mol), produced by the Indian company (THOMAS BAKER), with a purity of (98.0%).
- Absolute ethanol (C_2 H_5 OH) as a solvent: It is a transparent, colorless liquid, its molecular weight is (46.07g/mol), produced by a Spanish company, and its purity is (99%).

Preparing the Glass Floors

This research used glass floors produced by a Chinese company with a thickness of (1.1 mm) and dimensions (26 x 76 mm). The floors on which the material was deposited were started as follows:

- The floors were washed well with detergents and plain water to get rid of plankton caused by weather factors.
- The floors were washed with distilled water to get rid of traces of detergents and plain water.
- It was placed in ethanol alcohol for (20 minutes), then it was taken out, washed with distilled water, and left to dry in an electric oven at (150°C) for (20 minutes) in order to get rid of suspended materials and impurities that may prevent the adhesion of the membrane, leading to distortion. The prepared membrane or its composition has changed.

Preparation and Deposition of Sno_2 Thin Film Solution

To prepare a solution of tin oxide thin films using (aqueous tin chloride, diethanolamine, and absolute ethanol), at a concentration of (0.5M). (5.64g) of aqueous tin chloride was dissolved in (40ml) of absolute ethanol. The mixture was placed on a magnetic mixer for 15 minutes, with the temperature gradually raised to (60 °C), after which a mixture of (0.25g) diethanolamine was added as a stabilizer in 10ml of absolute ethanol, and it was mixed with a

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magnetic mixer for 10 minutes. The addition was made in drops with Burette on the solution. Mix for two hours until the solution is homogeneous and becomes a light yellow color. The solution is stored in a tightly closed glass bottle for 24 hours. The mixing ratio of materials in the solution was 2:1 for both $SnCl_2.2H_2O$ and $[CH_2(OH)_2CH_2]_2NH$. The solution is then filtered using filter paper to get rid of undissolved substances. The glass floors are placed in the middle of the rotating device, then the filtered solution is placed on the glass floors at a rotation speed of 3000 rpm. The solution is dried for 20 minutes at a temperature of (150 ℃), and the process is repeated for five times, after which the deposited membranes are annealed at temperatures of (200 ℃, 300 ℃, 400℃, and 500℃). Samples are then taken for the purpose of conducting the necessary tests.

4. RESULTS AND DISCUSSIONS

Structural Properties

Study of the structural properties of tin oxide films prepared and annealed at temperatures (200℃,300℃,400℃,500℃). Using X-Ray Diffractometer (Philips PW 1730/10), Netherlands. Wavelength device (λ=1.5406 °A) and a type objective (Cu Kα). Study of the structural properties of tin oxide films prepared and annealed at temperatures (200℃,300℃,400℃,500℃). The results were analyzed using the (x'pert highscore) program attached to the X-ray diffraction machine. The program analyzes the results automatically, taking into account when calculating the average grain size (Dav) of the prepared and annealed films at (200℃,300℃,400℃,500℃), adding a correction factor. The produced films' X-ray diffraction is displayed in Fig.1 . The results show that the spectrum reflected from the films is identical to pure tin oxide (SnO2). It was also shown that all the prepared films have a tetrahedral crystalline structure. These results match the international card (JCPDS.41-1445) [7,8]. The results showed the dominant crystalline levels (110), (101), (211), and (301) and the appearance of other levels with increasing annealing temperatures. The lattice constants (a=b≠c) were calculated through Equation (1) [3] and compared with the international card (JCPDS.41-1445) as shown in table 1.

$$\frac{1}{d^2} = \frac{h^2+k^2}{a^2} + \frac{l^2}{c^2} \quad \text{……. (1)}$$

Table 1 Lattice constants value for (SnO_2) films annealed at (200℃, 300℃, 400℃, 500℃).

A-T(℃)	***a*** (Å)	**c** (Å)
(JCPDS.41-1445)	4.738	3.187
200℃	4.952	3.198
300℃	4.737	3.224
400℃	4.748	3.181
500℃	4.748	3.184

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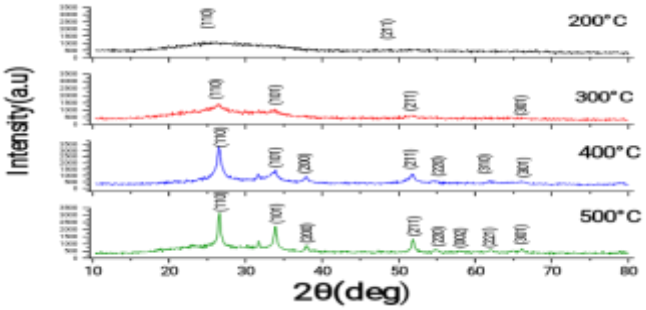

Fig.1.X-ray diffraction pattern of (SnO_2) thin films.

Through Equation (2) [3][9], the average grain size (D_{av}) was calculated, and it was found that the average grain size (D_{av}), increases with increasing annealing temperatures, as in Fig.2. These results match [9][10].

$$D_{av} = \frac{K\lambda}{B\cos\theta} \quad \ldots\ldots\ldots (2)$$

Where (B):is the full wide that half maximum(FWHM) of diffraction peaks,)λ):wavelength of x-rays($\lambda = 1.54056$Å),(K): Shape Factor, it depends on the shape of the granules and has a fixed value(K=0.9),(Θ):is the Bragg angle.

Table 2 X-ray diffraction results for (SnO2) films annealed at (200℃, 300℃, 400℃, 500℃).

(A-T)	**200($°C$)**	**300($°C$)**	**400($°C$)**	**500($°C$)**
2θ(deg)	25.4138	26.5884	26.5259	26.5257
(FWHM)(deg)	3.1488	0.4920	0.3936	0.2952
$D_{av}(nm)$	3.6	11.325	21.37778	29.24545
$\delta \times 10^3$	77.16049	7.796929	2.188139	1.169185
$N(nm)^{-2}$	51.05453	0.878488	0.182807	0.037973
ε	0.013403	0.002089	2.188139	1.169185
Where δ: dislocation density, ε: micro strain, N: number of crystals.				

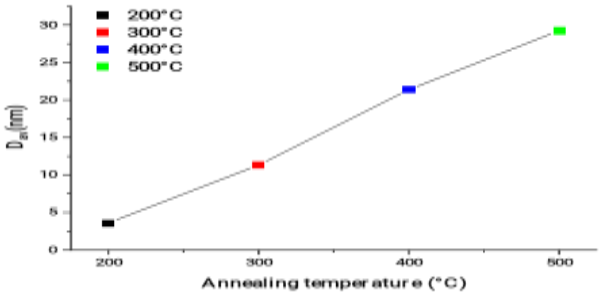

Fig.2.Variation of average grain size (D_{av}) with different annealing temperatures.

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Atomic Force Microscopy (AFM)

Atomic force microscopy (AFM) is used to study the surface morphology and surface crystal structure of deposited films, from which the average surface roughness (Sa), root mean square (RMS), and average grain size (D_{av}) can be calculated. Fig. 3 shows images Atomic force microscopy in two and three dimensions. Distribution of grains on the surface of films (SnO_2) deposited at different annealing temperatures. It was found that the average grain size (D_{av}), average surface roughness (Sa), and root mean square (RMS) values increase with increasing annealing temperature [13], as shown in the table 3 . Fig. 4.

Table 3 Atomic Force Microscopy (AFM) Results For (Sno_2) Films Annealed At (200℃, 300℃, 400℃, 500℃).

A-T (℃)	Root Mean Square (nm)	Surface roughness (nm)	Average Grain Size (nm)
200	9.288	7.264	127.6
300	20.342	22.7	165.5
400	52.13	31.43	304.2
500	29.86	22.70	200.8
500	52.13	31.43	226.3

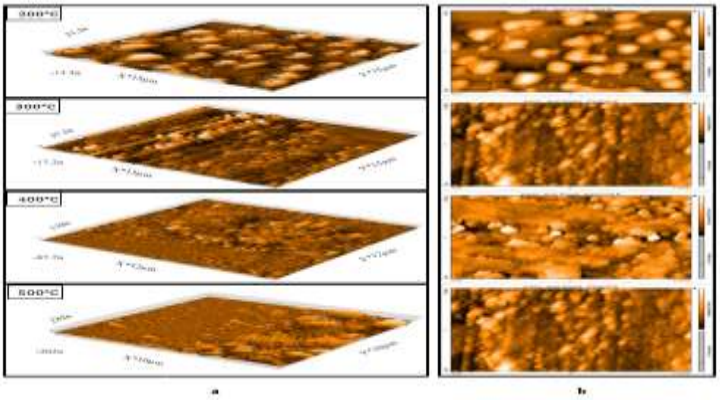

Fig.3. Atomic force microscope images: (a) in three dimensions, (b) in two dimensions, of (SnO_2) films annealed at (200℃, 300℃, 400℃, 500℃).

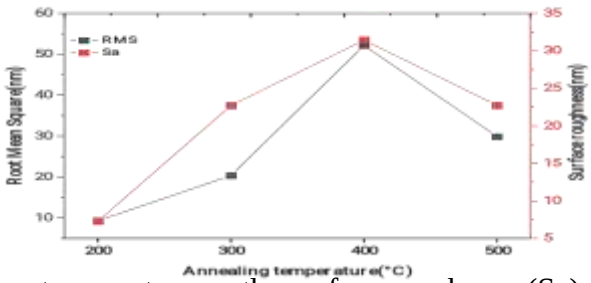

Fig.4. Effect of annealing temperature on the surface roughness (Sa) and root mean square (RMS) of the prepared (SnO_2) films.

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Optical Characterization

The transmittance (T) was calculated using an (UV-Visible Spector photometer), with a wavelength of (300nm-800nm), as shown in Fig. 5. The findings demonstrated that when the annealing temperature increased, the transmittance reduced [14], and the highest permeability was for membranes annealed at a temperature of (200℃).

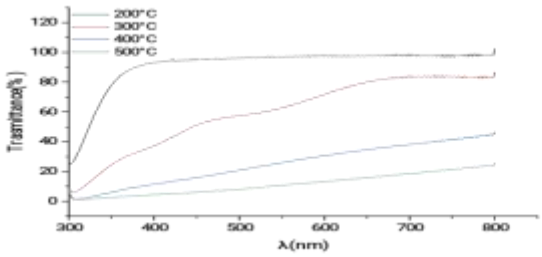

Fig.5. Transmission of (SnO_2) thin films annealed at different temperatures

Through equations (3) and (4) [14][15], the absorption coefficient (α) and extinction coefficient (K_0), were calculated, respectively. It turns out that both the absorption coefficient and the extinction coefficient increase with increasing annealing temperature, as shown in Fig. 6 and 7, respectively.

$\alpha = (2.303A)/t$ ……(3)

$K_0 = \alpha\lambda/4\pi$ ……..(4)

t: film thickness, A: absorptance.

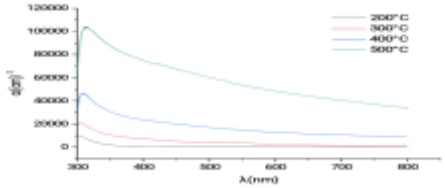

Fig.6. Absorption coefficient (α) of (SnO_2) thin films annealed at different temperatures.

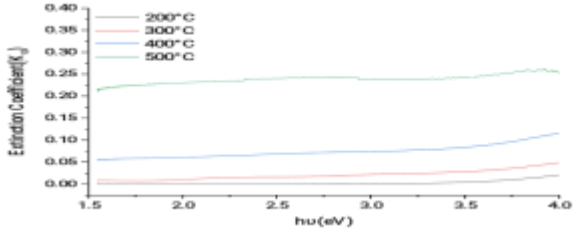

Fig.7. Extinction coefficient (K_0) of (SnO_2) thin films annealed at different temperatures.

Characteristics of Color Values

A table of T(λ) values for light with equal gradations of wavelengths for the range (380-770) nm can be produced by performing some mathematical conversions on the transmittance or

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absorbance values after obtaining the transmittance spectrum curve for tin oxide(SnO_2) using a UV visible spectrum device. Applying successive steps to the transmittance values T(λ) which were determined by CIE1931 [5][16], allows the computation of the transmitted light's tristimulus values (X, Y, Z) and color coordinates (x, y, z).

$$X = k\sum P(\lambda)\bar{x}(\lambda)T(\lambda) \text{ ..... (5)}$$
$$Y = k\sum P(\lambda)\bar{y}(\lambda)T(\lambda) \text{ .....(6)}$$
$$Z = k\sum P(\lambda)\bar{z}(\lambda)T(\lambda) \text{ .....(7)}$$
$$k = \frac{100}{\sum P(\lambda)\bar{y}(\lambda)} \text{ .....(8)}$$

The power distribution curve of the light source in use is denoted by P(λ), while the distribution coefficient values of the light source are represented by (X, Y, Z). The Tristimulus values of X, Y, and Z for the specimen are used to calculate the color coordinate magnitudes for the CIE system.

$$x = \frac{x}{x+y+z} \text{ ..... (9)}$$
$$y = \frac{y}{x+y+z} \text{ ..... (10)}$$
$$z = \frac{z}{x+y+z} \text{ ..... (11)}$$

The color coordinate values (x, y, z) of the CIE1931 color system are shown in table 4, and these values are used to determine three additional key color values: brightness, dominant wavelength, and color purity. Fig. 8 shows the color purity change at different annealing temperatures. A sample with a purity of (0%) signifies that all color has been eliminated, since a sample with a lower color purity number suggests that it contains less color. Fig.9 shows the brightness of (SnO_2) thin films. When a white diffuser reaches (100%) brightness, it is represented by a thin layer.

Table 4 The color values and color coordinate of (CIE1931) system of (SnO2) films annealed at (200℃, 300℃, 400℃, 500℃).

Purity	Brightness	Dominants Wave length	Color Coordinates (CIE)			T (°C)
			x	y	z	
0.259635	97.04353753	580	0.4088786	0.3127487	0.2783725	200
0.387184205	67.46196281	620	0.4633330	0.3236872	0.2129796	300
0.536718	28.17854994	617	0.4996118	0.3311421	0.1692459	400
0.56853	12.22346778	617	0.5276814	0.3257392	0.1465792	500

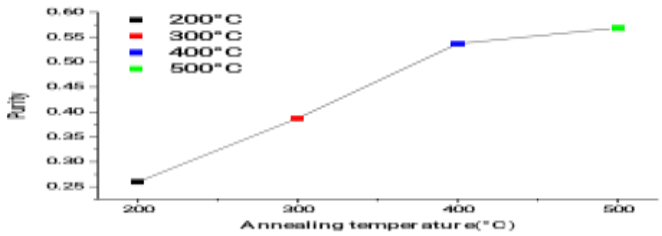

Fig.8 Color purity of (SnO_2) thin films annealed at different temperatures.

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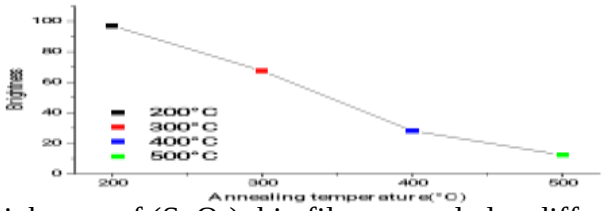

Fig.9 Color brightness of (SnO_2) thin films annealed at different temperatures.

5. CONCLUSIONS

Sol gel was used to create thin films of tin oxide, which were then spin-coated onto glass substrates. Tin oxide films made at various annealing temperatures were examined for their structural, optical, and color characteristics. The XRD results revealed that the films had a tetrahedral structure, with direction (110), (101), (211), and (301) being the dominating one. As the annealing temperature rises, the SnO2 films' surface roughness, grain size, and brightness increase while their transmittance, dominant wavelength, and purity drop. by raising the temperature during annealing. The temperature at which the maximum transmittance was achieved during annealing was (200°C).

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