Synthesis of Tin Oxide Thin Films by Sol-gel Spin Coating Method and Study of Their Color Properties Using CIE 1931 and CIE LAB systems

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The primary objective of the project was to study the color characteristics of tin oxide thin films produced with varying concentrations (0.25M, 0.5M, and 0.75M) by the sol-gel (spin coating) method and 400°C annealing. Using the CIE 1931 system, the color coordinates of the tin oxide (SnO_2) thin films were determined, and three key color attributes (purity, dominant wavelength, and brightness) were measured. The results indicated that the dominant wavelength and brightness values decreased with increasing film concentration, whereas the purity values increased as the film concentration rose. To further differentiate between the colors, the color angle and chrominance were calculated using the CIE LAB system. Additionally, XRD and UV-visible spectrophotometry were employed to analyze the structural and optical characteristics. XRD data revealed that all annealed films exhibited a tetragonal structure. The UV-visible spectrophotometry results showed that transmittance values decreased with increasing film concentration, with the highest transmittance observed at a concentration of 0.25M, reaching approximately 89.9%.

***Keywords*:** CIE LAB; Tin oxide; Color coordinates; Spin coating
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1. Introduction

In recent years, thin film technology has been widely researched and applied across various branches of science and technology due to the rapid advancements in nanotechnology. Tin oxide (SnO_2) thin films, which are the focus of this study, offer numerous benefits for researchers due to their wide range of applications. SnO_2 thin films are particularly useful in applications such as transistors because of their infrared reflectivity, visible light transparency, and low electrical sheet resistance. Semiconductors are often used as transparent films in electronic devices, including gas sensors, thin film (solar cells), electrochromic displays, display devices, and defogging windows for cars and airplanes.

Recent studies have explored the synthesis and properties of thin films using various techniques such as spray pyrolysis [1], sol-gel [2,3], and chemical precipitation [4]. In this work, the sol-gel method was chosen for film preparation due to its low cost and ability to produce large, homogeneous films with controlled properties, depending on the material type, concentration, and annealing temperature. The sol-gel process is ideal for creating thin films on solid, flat substrates. It is based on chemical colloids, where solid raw materials are dissolved in specific solvents to form homogeneous materials.

The primary objective of this study is to examine the color characteristics of tin oxide films using the CIE 1931 [5,6] and CIE LAB [7] systems to control color values and intensity. This is crucial, as many thin film applications rely on optical coatings, which often require precise control over the amount of color or its removal. It was determined that the optimal color removal occurred at a concentration of 0.25M for tin oxide films. Additionally, characterization tests such as UV-visible spectroscopy, x-ray diffraction (XRD), atomic force microscopy (AFM), and energy-dispersive x-ray spectroscopy (EDX), were performed to analyze the optical and structural properties of SnO_2 films.

2. Experimental Part

In this investigation, the materials used were absolute ethanol (Scharlab S. L, Spain), $SnCl_2.2H_2O$ (THOMAS BAKER, India), and $[CH_2(OH)CH_2]_2NH$ (THOMAS BAKER, India).

The first step involves dissolving 0.25M, 0.5M, and 0.75M of tin chloride in 50 ml of absolute ethanol keeping the temperature at 50°C for 20 minutes while using a magnetic stirring tool. Then, ethanolamine is added in a 2:1 mass ratio, and the solution is stirred continuously for 2 hours using the magnetic stirrer until a homogeneous light yellow solution is obtained. The weight of each component is calculated using the following equation:

$$M=W/M_{wt}\times1000/V \quad (1)$$

In this equation, M represents the molarity of the substance, M_{wt} denotes the molecular weight, and V refers to the volume of the prepared solution. The solution is then left in a sealed container at room temperature for 24 hours, after which it is filtered using filter paper to remove any sediment.

The glass substrates are first cleaned before depositing the solution. The cleaning process involves washing the substrates with a solution of soap, absolute ethanol, and distilled water, Afterward, it was dried for 20 minutes at 150 °C in the oven. After that, the substrates are positioned in the middle of the spin coating apparatus and rotated for 30 s at a speed of 500 rpm, and the solution is gradually dropped onto the glass substrates to form uniformly coated thin films of tin oxide (SnO_2). The deposited films are dried at 150°C for 20 minutes to remove volatile solvents. This process is repeated five times.

Finally, the deposited tin oxide films are annealed at 400 °C for 60 minutes to enhance the crystallization process.

3. Results and Discussion

The x-ray diffraction (XRD) analysis was performed on all samples of tin oxide films prepared using the sol-gel method at different concentrations. This was done to determine the crystal structure and estimate the average grain size. Figure (1) shows the XRD patterns of SnO_2 films prepared at concentrations of 0.25M, 0.5M, and 0.75M. All prepared films display tetragonal structure and it is clear that at concentrations of 0.5 and 0.75M, the dominant and preferred crystal plane was (110), which means that growth occurred faster at this crystal plain and thus gave a greater intensity of x-ray reflection according to the JCPDS card no. 00-041-1445, a=b=4.7382Å, and c=3.1871Å (table 1). With a decrease in the concentration of the precipitating solution to 0.25 M, the dominant crystal plane became (020), which means that the growth occurred faster at this level according to the JCPDS card no. 00-029-1484. Other common crystal planes observed for all three concentrations (0.25M, 0.5M, 0.75M) were (110), (101) and (211), in line with findings of previous studies [8,9].

Table (1) Lattice constants of SnO_2 thin films annealed at 400°C

Concentrations	a (Å)	c (Å)
JCDPS SnO_2	4.7382	3.1871
0.25M	4.7471	3.1854
0.5M	4.7483	3.1819
0.75M	4.7328	3.1984

As seen in Fig. (1), the intensity of the peaks increases, the film thickness increases, leading to improve crystallization. The lattice constants of the SnO_2 films, determined by applying Eq. (2) [10,11], are consistent with the JCPDS card no. 00-041-1445, a=b=4.7382Å, and c=3.1871Å, confirming the high structural quality of the prepared films.

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

where d is the inter-planer distance and (hkl) are Miller indices. The average grain size was calculated using the Scherrer's formula as [10,12]:

$$D_{av} = \frac{k\lambda}{\beta cos\theta} \quad (3)$$

where D_{av} is the average grain size in nm, k is the shape factor, which depends on the shape of the granules and has a fixed value of 0.9, λ represents the wavelength of x-rays (1.5406Å), β is the full-width at half maximum (FWHM) in radians, and θ is Bragg's angle of diffraction at the peak position in degrees

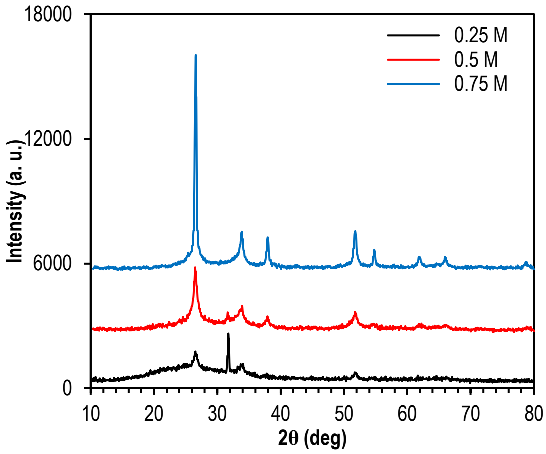


Fig. (1) XRD patterns of SnO_2 thin films prepared using different concentrations

It was found that the particle size increases with increasing concentration, as shown in Fig. (2). These results are consistent with those of previous researchers [2,13].

The number of dislocation lines that intersect a unit area in a crystal is called the dislocation density. It represents the ratio between the total length of all dislocation lines and the volume of the crystal. The dislocation density, denoted by δ, is calculated using Williamson and Smallman's relationship as [14]

$$\delta = \frac{1}{D_{av}^2} \quad (4)$$

The results of from Eq. (3) showed that the dislocation density values decrease with increasing film concentration as shown in Fig. (3). These results are consistent with those of other researchers [15].

Figure (4) shows 3D images and the distribution of grains on the surface of SnO_2 films prepared at concentrations of 0.25 M, 0.5 M, and 0.75 M with an annealing temperature of 400 °C. The surfaces of the films were found to be homogeneously distributed, featuring a porous structure with no voids. Table (2) and figure (5) present the average diameter, roughness average, and root mean square, their values increasing as the concentration increases. These results are consistent with the results of researchers [16,17].

Through EDX examination of the prepared SnO_2 thin films, it was observed that the films are composed solely of tin (Sn) and oxygen (O_2), with no trace of other elements. This confirms the purity of the prepared films, consistent with previous researcher [18]. As shown in Fig. (6), table (3) presents the atomic and weight ratios of SnO_2 films prepared at concentrations of 0.75M, 0.5M, and 0.25M, respectively.

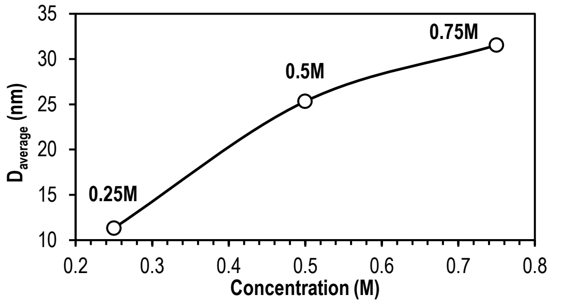


Fig. (2) Variation of average grain size (D_{av}) with concentration for SnO_2 thin films annealed at 400°C

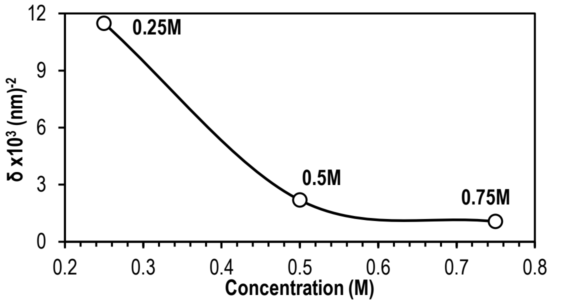


Fig. (3) Variation of dislocation density (δ) with concentration for SnO_2 thin films annealed at 400 °C

Table (2) Morphological characteristics from AFM images for SnO_2 thin films

Concentration	Average Roughness (nm)	Root mean square Roughness (nm)	Average Diameter (nm)
0.25M	0.301	0.348	74.74
0.5M	0.912	1.03	81.41
0.75M	1.42	1.68	88.32

Figure (7) shows the transmittance of SnO_2 thin films prepared at different concentrations and annealed at a temperature of 400°C. The transmittance was measured using UV-visible spectroscopy in the range of 300-800 nm, with a maximum transmittance value of 89.8%, this is a prerequisite for materials made of transparent conduction oxide (TCO). These films are therefore excellent candidates for application in optical applications. From Fig. (7), it was observed that transmittance increases with wavelength and decreases with increasing concentration, according to Lambert's law. In Fig. (7), we notice that there is a sudden increase in transmittance for the wavelength range 430-550 nm, especially at a concentration of 0.25 M. The reason for this is due to the increase in the particle size and the diameter of the particles. We know that the condition for occurring the scatter to light is $D_{av} \leq \lambda$. Therefore, the intensity of the scattered light depends on the diameter of the particles, as the particle diameter becomes greater than the wave length, which means the particle size and diameter of the particles become incompatible with the occurrence of the scattering phenomenon, which will help to increase the intensity of the transmitted light for this range. Also, the same thing happens with Fig. (8), where the absorption coefficient is inversely proportional to the transmittance, and for this reason we notice a sudden decrease in the value of the absorption coefficient (α) for the wavelength range of 430-550 nm. The absorption coefficient (α) was calculated using Eq. (5):

$$\alpha = \frac{2.303A}{t} \quad (5)$$

where t is the thickness, A is the absorbance

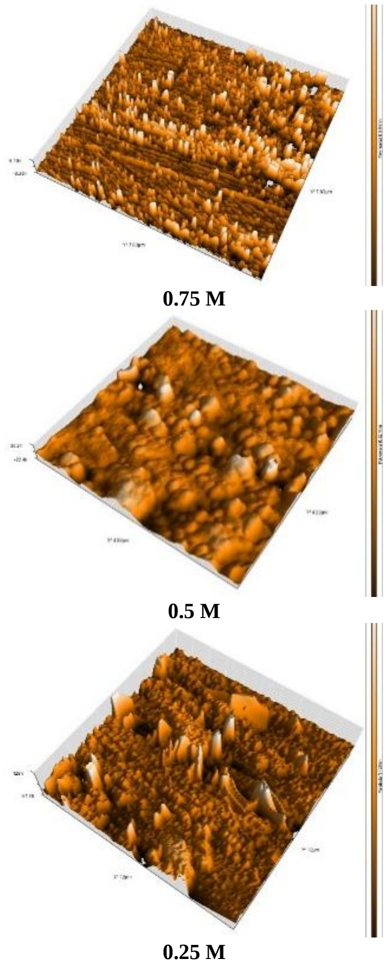


Fig. (4) 3D AFM images for SnO_2 thin films prepared using different concentrations and annealed at 400°C

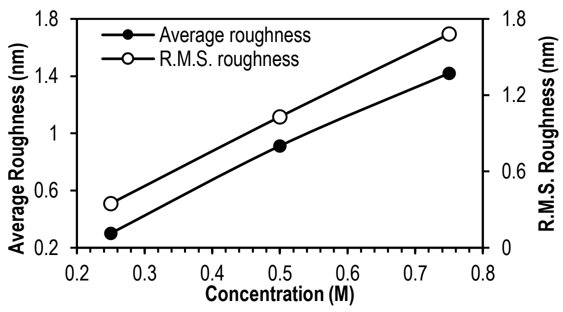
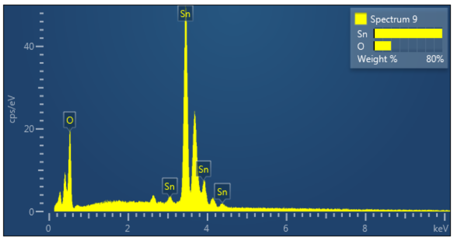


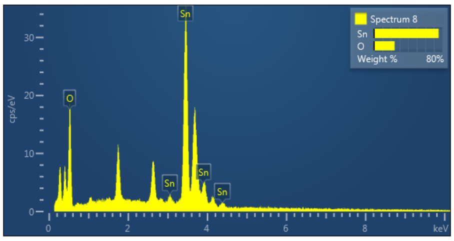
Fig. (5) Variation of average roughness and root-mean-square roughness with concentration of SnO_2 used to prepare thin films annealed at 400°C

Table (3) Values of the atomic and weight ratios of the prepared SnO_2 thin films

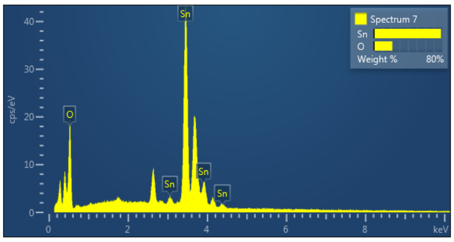
Concentrations(M)	Element	Weight %	Atomic %
0.25M	O	67.19	21.63
	Sn	32.81	78.37
0.5M	O	70.42	24.29
	Sn	29.58	75.71
0.75M	O	65.17	20.14
	Sn	34.83	79.86



0.75 M



0.5 M



0.25 M

Fig. (6) EDX spectra of SnO_2 thin films prepared at different concentrations (0.25M, 0.5M, and 0.75M)

Figure (8) shows the increase in absorption coefficient values with increasing concentration.

With a wavelength range of 380-780 nm, the tristimulus values are computed using the following equations:

$$X = k\sum P(\lambda)\bar{x}(\lambda)T(\lambda) \quad (6)$$

$$Y = k\sum P(\lambda)\bar{y}(\lambda)T(\lambda) \quad (7)$$

$$Z = k\sum P(\lambda)\bar{z}(\lambda)T(\lambda) \quad (8)$$

$$k = \frac{100}{\sum P(\lambda)\bar{y}(\lambda)} \quad (9)$$

where $\bar{x}(\lambda)$, $\bar{y}(\lambda)$ and $\bar{z}(\lambda)$ of the CIE color system are the values of the (CIE) color matching functions for the standard observer at wavelength λ, and T(λ) is the sample's transmittance factor at wavelength λ, and P(λ) is the illuminant's spectral power distribution value at wavelength λ

The trisitimulus value is normalized by factor (K), resulting in a value of 100 for the ideal light in y. The specimen's trisitimulus value of x, y and z is used to calculate the color coordinate values (x, y and z) for the (CIE) system. Utilizing the color coordinate values (x, y, z) of the CIE color system [19-21]:

$$x = \frac{x}{x+y+z} \quad (10)$$

$$y = \frac{y}{x+y+z} \quad (11)$$

$$z = \frac{z}{x+y+z} \quad (12)$$

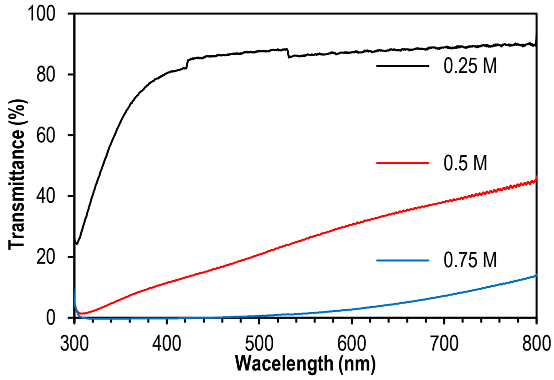


Fig. (7) Transmission spectra of SnO_2 thin films prepared using different concentrations and annealed at 400°C

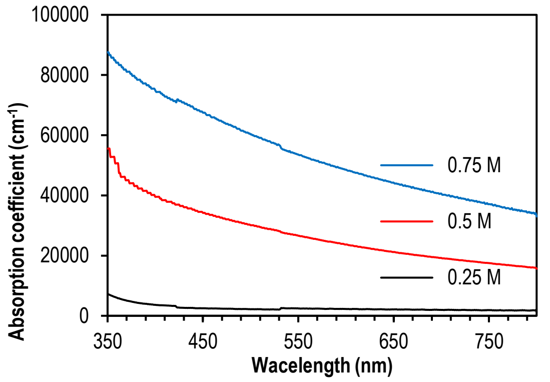


Fig. (8) Variation of absorption coefficient of SnO_2 thin films prepared using different concentrations and annealed at 400°C

The CIE system of color coordinate values (x, y, z) is used to determine three important color values: brightness, dominant wavelength, and color purity and table (4) displays these values. The results presented in figures (9-11) showed that as concentration increased, the dominant wavelength and brightness values decreased, while the purity values increased.

Three color values (a^*, b^* and L^*) are obtained from the CIE LAB system, which provides a uniform color space. From these three values, two significant color metrics are derived: the metric Chroma (C_{ab}) and the metric hue angle (h_{ab}), as shown in table (5).

Trial and error methods were used to construct the mathematical conversions from tristimulus values to CIELAB coordinates. The tristimulus values for a sample that fully reflects light at all wavelengths, under a specific standard illuminant and observer, are provided.

$$a^* = 500[(\frac{X}{X_n})^{\frac{1}{3}} - (\frac{Y}{Y_n})^{\frac{1}{3}}] \quad (13)$$

$$b^* = 200\left[\left(\frac{Y}{Y_n}\right)^{\frac{1}{3}} - \left(\frac{Z}{Z_n}\right)^{\frac{1}{3}}\right] \quad (14)$$

$$L^* = 116\left(\frac{Y}{Y_n}\right)^{\frac{1}{3}} - 16 \quad (15)$$

$$h_{ab} = tan^{-1}\left(\frac{b^*}{a^*}\right) \quad (16)$$

$$C_{ab} = \left({a^*}^2 + {b^*}^2\right)^{\frac{1}{2}} \quad (17)$$

where X_n, Y_n, and Z_n, are the tristimulus values for a perfect reflecting diffuser under a specific standard illuminant and observer. These values are well-documented in standard literature and are integrated into the software of modern color-measuring reflectance spectrophotometers.

Other transformations of tristimulus values are available to account for the departures of CIELAB space from perceptual uniformity, although this compromises the conceptual simplicity of the CIELAB space. Using the CIE LAB system [22], the metric hue angle and Chroma values were found to be in the ranges of 67.62–61.92 and 23.78–32.15, respectively. The data in Fig. (12) showed that the best decolorization occurred at a concentration of 0.25 M.

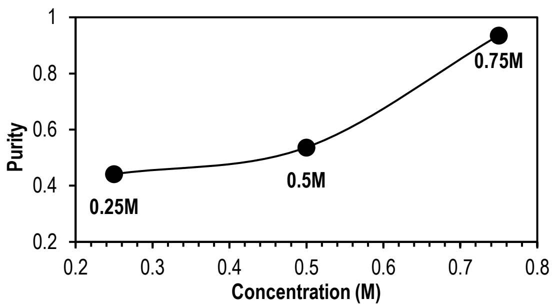


Fig. (9) Purity of SnO_2 thin films prepared using different concentrations

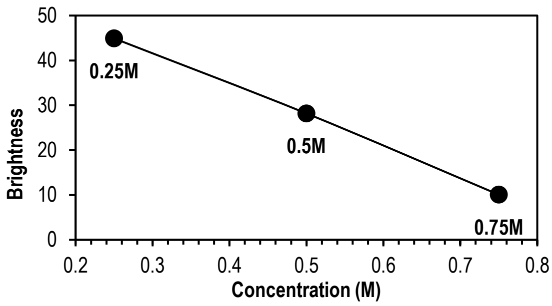
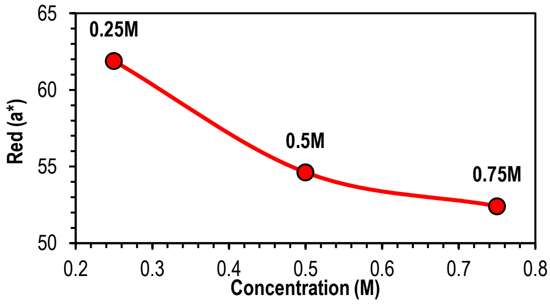
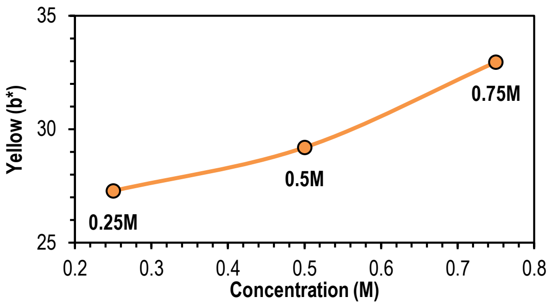


Fig. (10) Brightness of SnO_2 thin films prepared using different concentrations



(a)



(b)

Fig. (11) (a), (b) Effect of concentration on the color values of the CIE LAB system for SnO_2 thin films annealed at 400°C

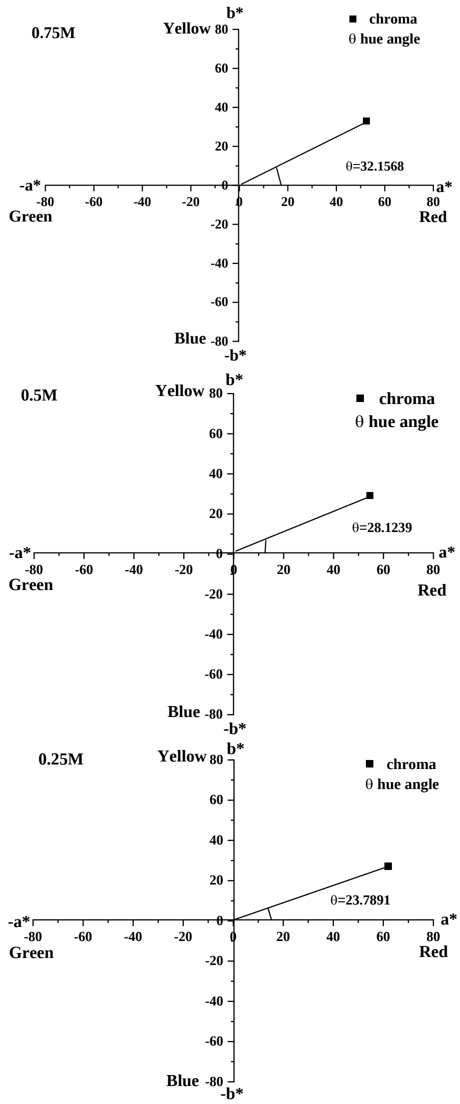


Fig. (12) Metric Chroma and metric hue angle of the CIE LAB system for SnO_2 thin films annealed at 400°C

4. Conclusions

Using the sol-gel technique, tin oxide thin films were prepared on glass substrates at various concentrations (0.25 M, 0.5 M, and 0.75 M) and annealed at 400 °C. All prepared films exhibited a tetragonal structure, with dominant crystal planes in the

(110) and (101) directions. The results confirmed that the grain size and surface roughness increase with increasing concentration. At a concentration of 0.25 M, the highest transmittance of 89.9% was obtained. It was observed that the dominant wavelength and brightness values decreased with increasing film concentration, while the purity values increased. The metric Chroma and hue angle values were found within the ranges of 67.62–61.92 and 23.78–32.15, respectively. The results confirmed that the best decolorization was achieved at a concentration of 0.25 M.

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Table (4) The CIE color system and color coordinate of SnO_2 thin films at various concentrations

Purity	Brightness	Dominant Wavelength (nm)	Color coordinates (CIE)			Concentrations (M)
			x	y	z	
0.4414	44.9073	620	0.48146	0.32325	0.19527	0.25
0.5367	28.1785	617	0.49961	0.33114	0.16924	0.5
0.9355	10.0537	580	0.57495	0.32877	0.09627	0.75

Table (5) The CIE LAB color system of SnO_2 thin films at various concentrations

Hue angle (h_{ab})	Chroma (C_{ab})	Color values of (CIE LAB) system			Concentrations (M)
		a^*	b^*	L^*	
23.7891	67.6323	61.8860	27.2809	72.8308	0.25
28.1239	61.9352	54.6225	29.1950	60.0497	0.5
32.1568	61.9212	52.4221	32.9569	37.9387	0.75