



# Copper Doping Effect on Nanocrystalline Tin Oxide (SnO<sub>2</sub>) Thin Films for Gas Sensing Applications

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## Abstract

In this work, Nanocrystalline SnO<sub>2</sub> and copper doped SnO<sub>2</sub> with (SnO<sub>2</sub>:Cu, Cu: 1%, 3%, 5%) was grown on glass substrates at (350 °C) via chemical pyrolysis method. The results of the structural properties using XRD analysis showed that The films have diffraction angles of different intensities and have a tetragonal crystal structure. The intensity decreases with an increased doping ratio. Atomic force microscopy showed that with increasing copper doping, the average grain size decreased. Transmittance of the prepared films is greater than 70% at 550 nm. The energy gap of the calculated tin oxide is 3.9 eV and decreases with increasing copper doping, while the absorption coefficient increases with increasing Cu ratio.

**Key Words:** Tin Oxide, Nano-thin Film, Doping, Optical Properties, Spray Pyrolysis.

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## Introduction

Nanocrystalline Semiconductors have received great interest from many researchers due to their variety usage in optical devices such as sensors, biomedicine and nanoelectronics.. etc. [1-3]. Transparent conductive oxides (TCOs) such as (SnO<sub>2</sub>, In<sub>2</sub>O<sub>3</sub>, ZnO,...) are well-known and well researched due to their high conductivity and high optical transparent [4]. Therefore, it has been used in many electro-optical applications [5]. Tin dioxide (SnO<sub>2</sub>) has an unique properties with direct optical bandgap ( 3.6 to 4.1 eV), n-type semi-conducting layer, chemical stability and sensitive substance to various gases [6-9]. These good properties of tin dioxide enable it to be used in many applications, especially in gas sensors [10-13]. Many different techniques were used to synthesize pure and doped SnO<sub>2</sub>, among these chemical pyrolysis technique, due to cost-effective, low cost and large areas of thin

films can be produced [14-16]. This paper includes the preparation of pure SnO<sub>2</sub> and doped SnO<sub>2</sub> with Cu and the study the structural and, optical properties for gas sensor applications.

## Experimental Part

To synthesize the films of pure SnO<sub>2</sub> and SnO<sub>2</sub>:Cu, tin chlorides (SnCl<sub>2</sub>.2H<sub>2</sub>O) with a molar concentration (0.02 M) and copper chloride (CuCl<sub>2</sub>:2H<sub>2</sub>O) as an impurity substance were used. The solution is mixed for 30 minutes. The parameters of chemical spray were fixed as follows; The temperature of the heater is approximately 350 °C and Nozzle height is 30 cm. The dimensions of clean substrates are (2.5 cm×2.5 cm). After the deposition process is completed, the substrate is left for an hour to cool and then kept in a special container.

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## Results and Discussion

### 1. XRD Analysis

Figure 1 shows XRD pattern of pure SnO<sub>2</sub> and SnO<sub>2</sub>:Cu films with three different doping ratios (1%, 3%, 5%) synthesis using CSPT. The prepared films have several peaks with different intensities as a result of the polycrystalline structure. Diffraction peaks of samples are (110), (101), (200) and (211) which correspond to the diffraction angles (26.42°), (33.89°), (38.06°) and (54.01°) respectively. The crystal size (G.S.) calculated from the preferred

(dominant) direction (110) using the Debye-Sparks equation [17].

$$G.S. = (K\lambda)/\beta \times \cos(\theta) \quad (1)$$

$\beta$ - (FWHM): represents the measurement of the bandwidth at 50% of the maximum intensity of prominent peak. As evident, the (G. S.) is directly related to the width of the peak. As the dopant ratio increase from (1% to 5%), the crystalline size decreases due to the increase in the FWHM, and the intensity decreases. Table (1) summarizes the results of X-ray diffraction.

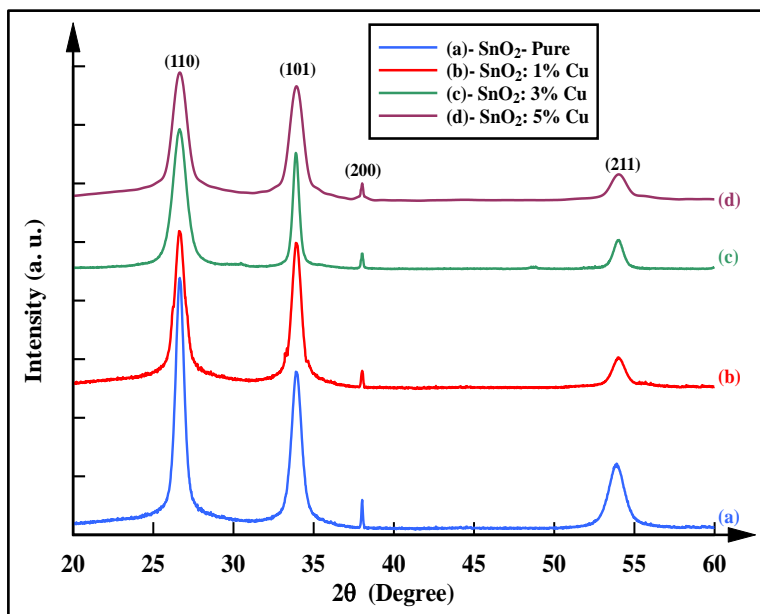


Figure 1. XRD pattern of pure SnO<sub>2</sub> and SnO<sub>2</sub>:Cu (1, 3, 5%).

Table 1. XRD results of nanocrystalline SnO<sub>2</sub> and SnO<sub>2</sub>:Cu thin films

Samples	Crystalline size(D)nm	2θ (Degree)	Hkl (Tetragonal)	d <sub>(hkl)</sub> (Å)
SnO <sub>2</sub> Pure	44.6	26.42	110	3.36
SnO <sub>2</sub> : Cu 1%	16.9	26.60	110	3.34
SnO <sub>2</sub> : Cu 3%	8.3	26.58	110	3.41
SnO <sub>2</sub> : Cu 5%	8	26.39	110	3.37

### 2. Atomic Force Microscopy (AFM) Analysis

AFM is a helpful tool that enables us to study the topography of surfaces with nano and micro dimensions. Fig. (3) shows 3- dimensional images of SnO<sub>2</sub> and SnO<sub>2</sub>:Cu (1%, 3%, 5%) films deposited at (350 °C) with a molar concentration (0.02 M). Obviously, the grains cover the all surface and it has a homogeneous distribution without cracks. With increasing doping ratio with copper, the surface roughness decreases. Table 2 shows the most important parameters of AFM analysis such as grain size and root mean square.

Table 2. AFM results of the nanocrystalline SnO<sub>2</sub> and SnO<sub>2</sub>: Cu thin films

Type of films	Root Mean Sq. (nm)	Roughness Ave. (nm)	Average G. S. (nm)
SnO <sub>2</sub>	6.56	4.3	38.25
SnO <sub>2</sub> : 1% Cu	4.37	2.62	32.2
SnO <sub>2</sub> : 3% Cu	2.61	1.81	21.03
SnO <sub>2</sub> : 5% Cu	1.96	1.42	12.99



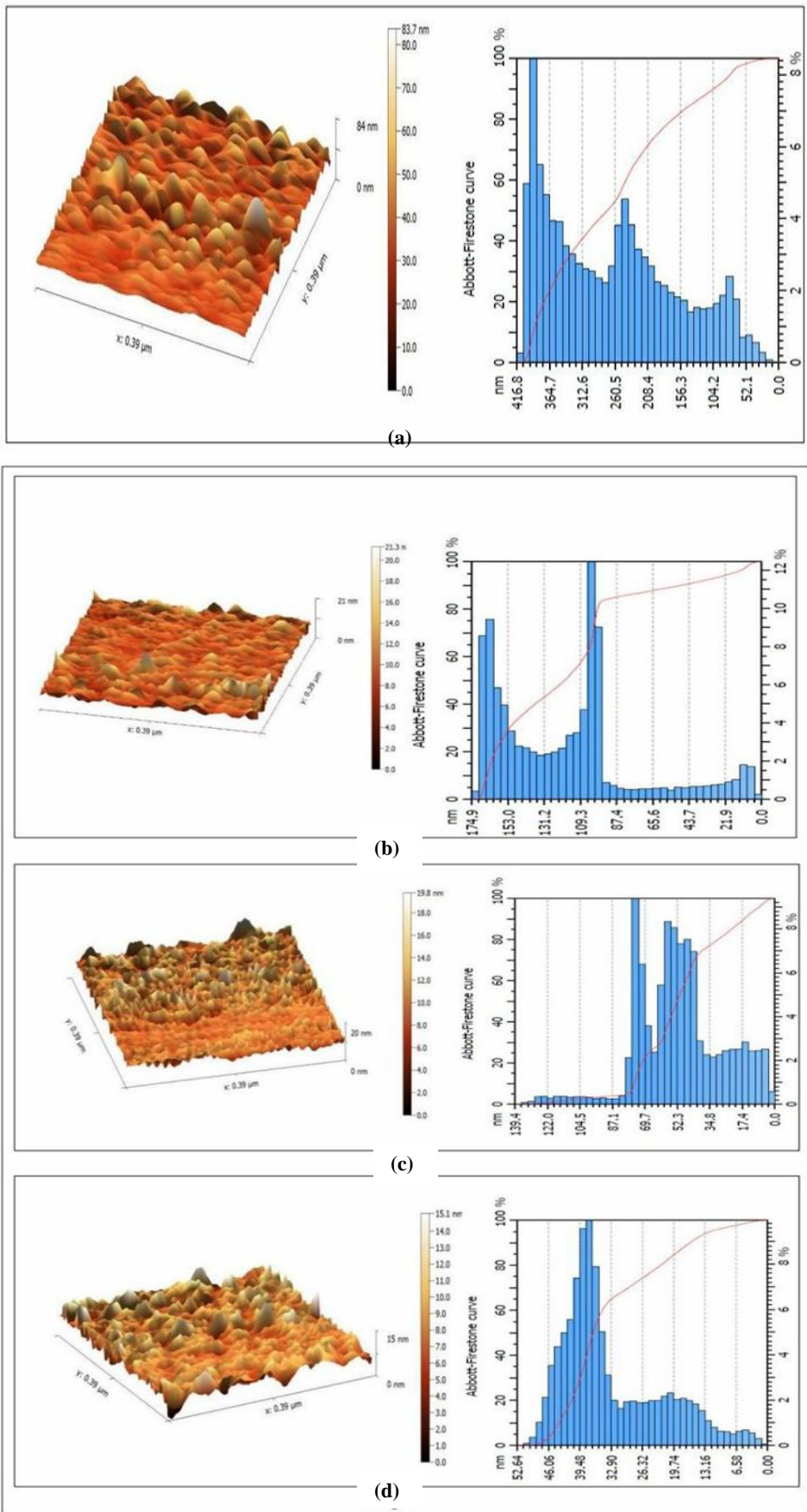


Figure 2. AFM images of SnO<sub>2</sub> and SnO<sub>2</sub>: Cu (1, 3, 5%)

### 3. Optical Properties

Fig. (4) shows the transmittance versus wavelength (300-1100 nm) of tin dioxide and copper- tin dioxide with three different dopant ratio of copper (1%, 3%, 5%). The pure SnO<sub>2</sub> film has high

transmittance (74 %) at 550 nm. As the Cu doping ratio increases the transmittance decreases and this may be due to as a result of the increase in the crystalline levels of the film resulting from the increase in SnO<sub>2</sub> film thickness, which causes an increase in the film absorbance.

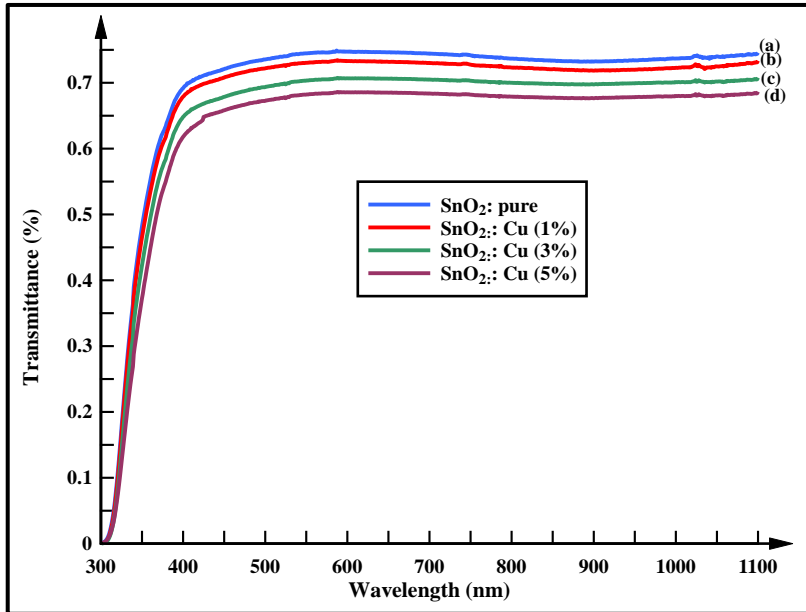


Figure 3. Transmittance of SnO<sub>2</sub> and SnO<sub>2</sub>: Cu (1, 3, 5%)

Absorbance versus wavelengths of nanocrystalline tin oxide and Cu (1%, 3%, 5%) doped tin oxide n films is shown in figure (4). It clear that the absorbance increases with the increasing the doping ratio of Cu from (1% to 5%). This increase in absorbance is perhaps attributed to Increasing the thickness of the film due to increasing the percentage of copper doping, which leads to an increase in the optical path length inside the film.

The absorption edge shifts towards lower energies (Red shift) with increasing doping of tin oxide with copper. The absorption edge happens almost at 340 nm wavelength region (UV-region) is related to transfer of charge from the lower band (valence band) to the upper band (conduction band) of nanoparticles tin oxide. In the visible region, very low absorbance was observed.

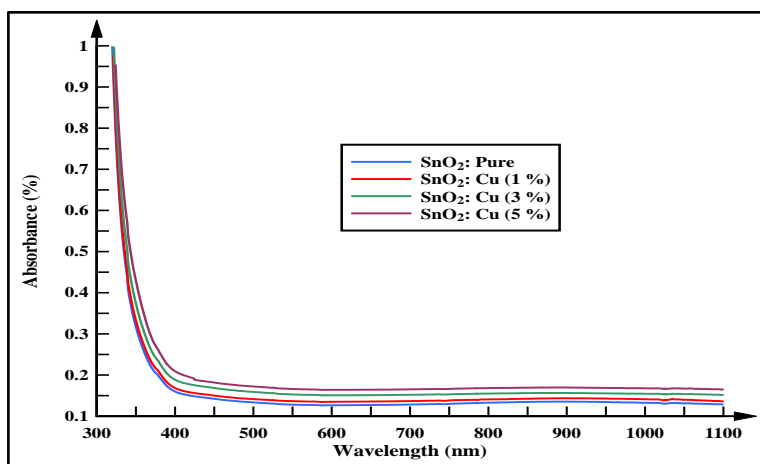


Figure 4. Absorbance of SnO<sub>2</sub> and SnO<sub>2</sub>:Cu (1, 3, 5%)



Fig. (5) shows the calculated energy gap ( $E_g$ ) of SnO<sub>2</sub> and (SnO<sub>2</sub>:Cu) films by using Tauc plot relation (equation 2) [18]. The energy gap decreases with the increase of copper doping.

$$\alpha h\nu = K(h\nu - E_g)^{\frac{1}{2}} \quad (2)$$

The value of band gap for pure SnO<sub>2</sub> was (3.86 eV), this value is large as compared with that of the

corresponding bulk SnO<sub>2</sub> value, This result may be due to the quantum restriction phenomenon of particles. As the copper dopant ratio increase, the band gap decreases. Values of  $E_g$  are 3.84, 3.81 and 3.78 eV for the nanocrystalline SnO<sub>2</sub>:Cu (1, 3 and 5 %) respectively. A decrease in the energy gap leads to an increase in the activation energy.

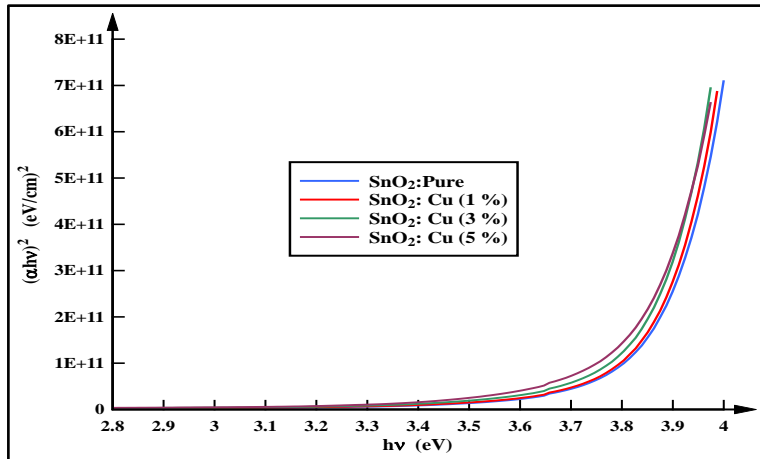


Figure 4. Optical band gap of SnO<sub>2</sub> and SnO<sub>2</sub>: Cu (1, 3, 5%)

## Conclusions

Nanocrystalline Tin oxide and Cu doped Tin Oxide films are synthesized successfully by CSPD method. XRD results shows that, the preparation of SnO<sub>2</sub> and SnO<sub>2</sub>: Cu films have nanostructure and Tetragonal Phases with favorite orientation in (110) direction. Atomic force microscopy analyzes showed that the surface roughness changes with the increase of copper doping. The prepared nanocrystalline SnO<sub>2</sub> and SnO<sub>2</sub>: Cu films have good optical properties. The transmittance is greater than 70 % with low absorbance in the visible (VIS) and infrared (IR) regions. These results promote the synthesized films promising candidates for sensor applications.

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