Copper Doping Effect on Nanocrystalline Tin Oxide (SnO_2) Thin Films for Gas Sensing Applications

Arshad Ahmed Mahmoud[1], J.F. Mohammad[2]*

Abstract

In this work, Nanocrystalline SnO_2 and copper doped SnO_2 with (SnO_2: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.

DOI Number: 10.14704/nq.2022.20.5.NQ22228 **NeuroQuantology 2022; 20(5):723-728**

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_2, In_2O_3, 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_2) 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_2, among these chemical pyrolysis echnique, 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_2 and doped SnO_2 with Cu and the study the structural and, optical properties for gas sensor applications.

Experimental Part

To synthesize the films of pure SnO_2 and SnO_2:Cu, tin chlorides ($SnCl_2.2H_2O$) with a molar concentration (0.02 M) and copper chloride ($CuCl_2$:$2H_2O$) 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 ºC and Nozzle height is 30 cm. The dimensions of clean substrates are (2.5 cm×2.5 cm). After the depostion process is completed, the substrate is left for an hour to cool and then kept in a special container.

Corresponding author: J.F. Mohammad
Address: [1,2*]University of Anbar, College of Education for Pure Sciences, Physics Department, Iraq.
[2*]E-mail: esp.jamalf.mohamad@uoanbar.edu.iq
Relevant conflicts of interest/financial disclosures: The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.
Received: 26 March 2022 **Accepted:** 30 April 2022

Results and Discussion

1. XRD Analysis

Figure 1 shows XRD pattern of pure SnO_2 and SnO_2: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 (26.42º), (33.89º), (38.06º) and (54.01º) respectively. The crystal size (G.S.) calculated from the preferred (dominant) direction (110) using the Debye-Sparks equation [17].

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

β- (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.

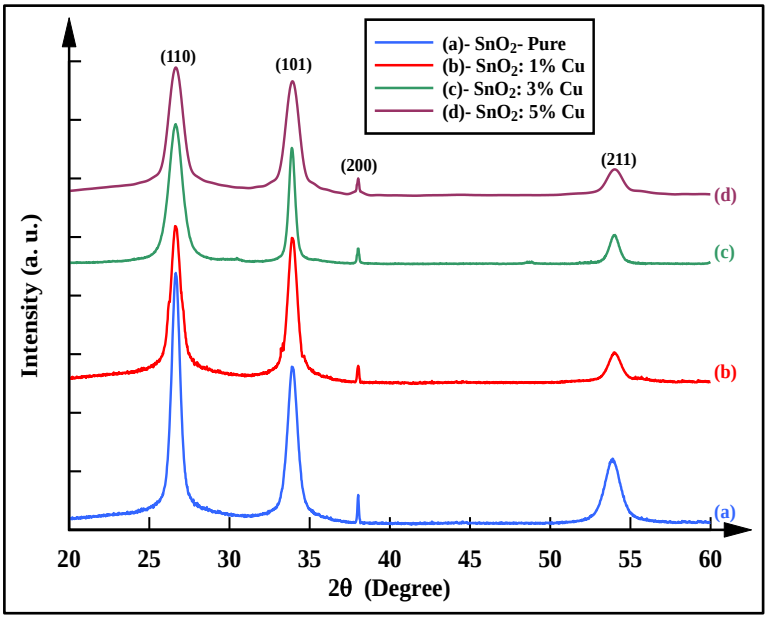

Figure 1. XRD pattern of pure SnO_2 and SnO_2:Cu (1, 3, 5%).

Table 1. XRD results of nanocrystalline SnO_2 and SnO_2:Cu thin films

Samples	Crystalline size(D)nm	2θ (Degree)	Hkl (Tetragonal)	$d_{(hkl)}$ (Å)
SnO_2 Pure	44.6	26.42	110	3.36
SnO_2: Cu 1%	16.9	26.60	110	3.34
SnO_2: Cu 3%	8.3	26.58	110	3.41
SnO2: 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_2 and SnO_2: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_2 and SnO_2: Cu thin films

Type of films	Root Mean Sq. (nm)	Roughness Ave. (nm)	Averge G. S. (nm)
SnO_2	6.56	4.3	38.25
SnO_2: 1% Cu	4.37	2.62	32.2
SnO_2: 3% Cu	2.61	1.81	21.03
SnO_2: 5% Cu	1.96	1.42	12.99

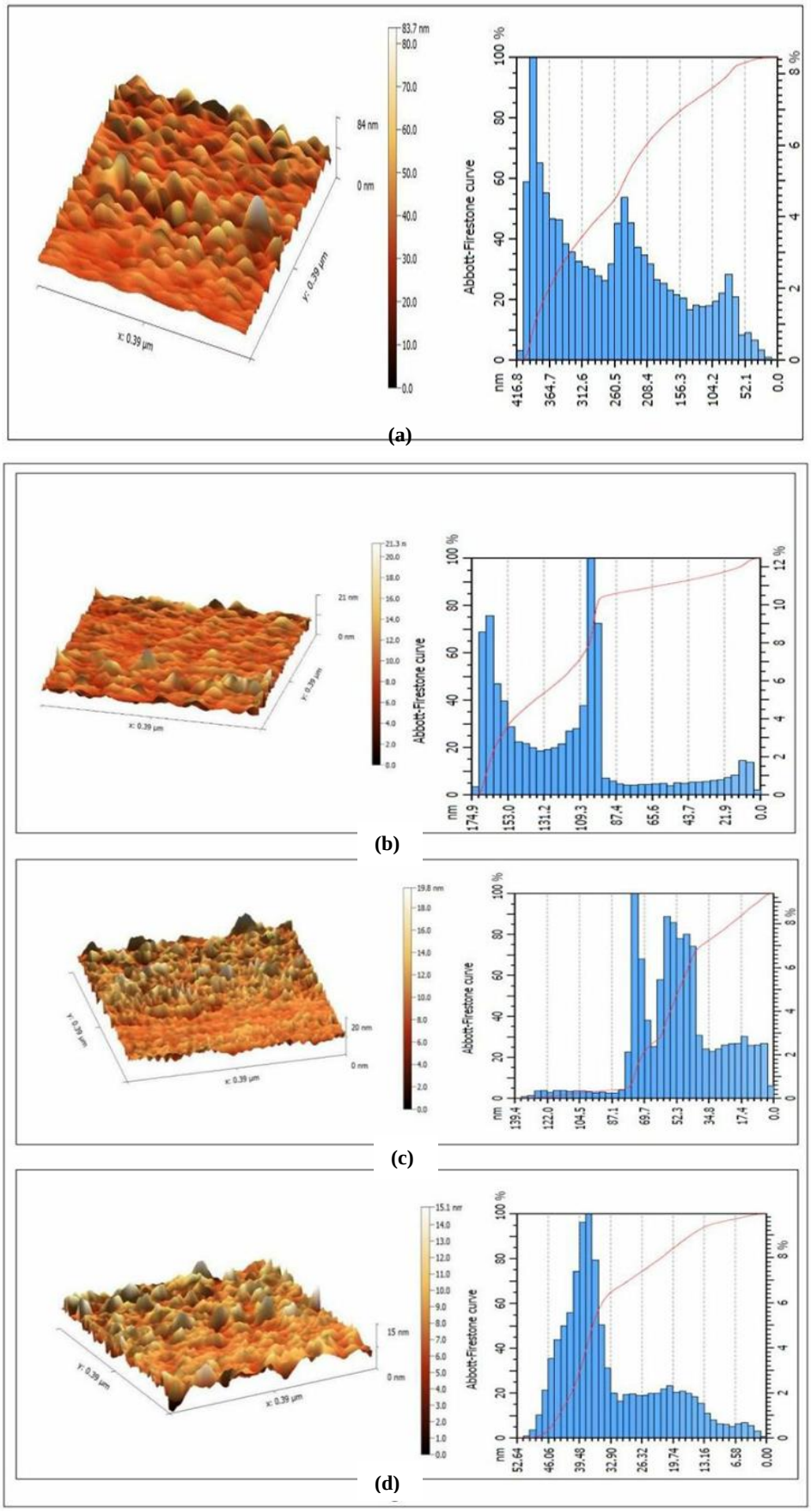

Figure 2. AFM images of SnO_2 and SnO_2: Cu (1, 3, 5%)

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_2 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_2 film thickness, which causes an increase in the film absorbance.

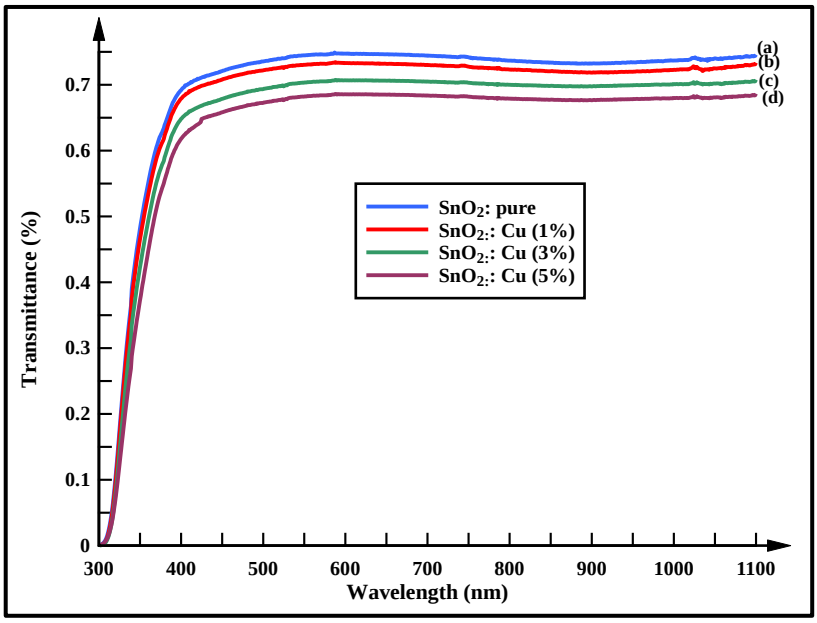

Figure 3. Transmittance of SnO_2 and SnO_2: Cu (1, 3, 5%)

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.

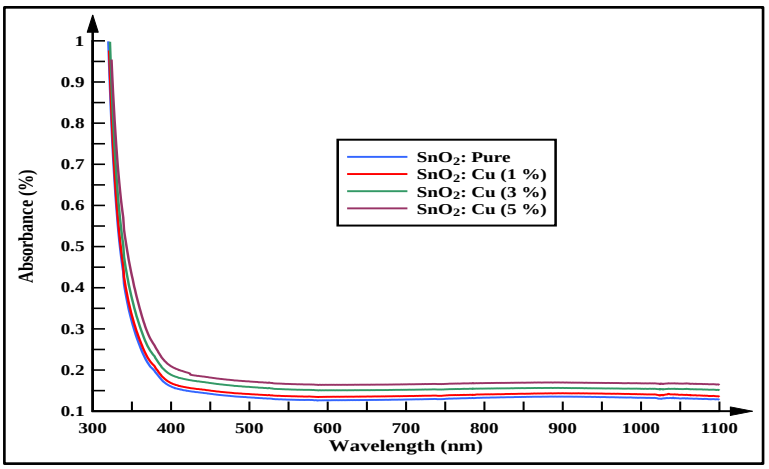

Figure 4. Absorbance of SnO_2 and SnO_2:Cu (1, 3, 5%)

Fig. (5) shows the calculated energy gap (E_g) of SnO_2 and (SnO2: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_2 was (3.86 eV), this value is large as compared with that of the corresponding bulk SnO_2 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 Eg are 3.84, 3.81 and 3.78 eV for the nanocrystalline SnO_2:Cu (1, 3 and 5 %) respectively. A decrease in the energy gap leads to an increase in the activation energy.

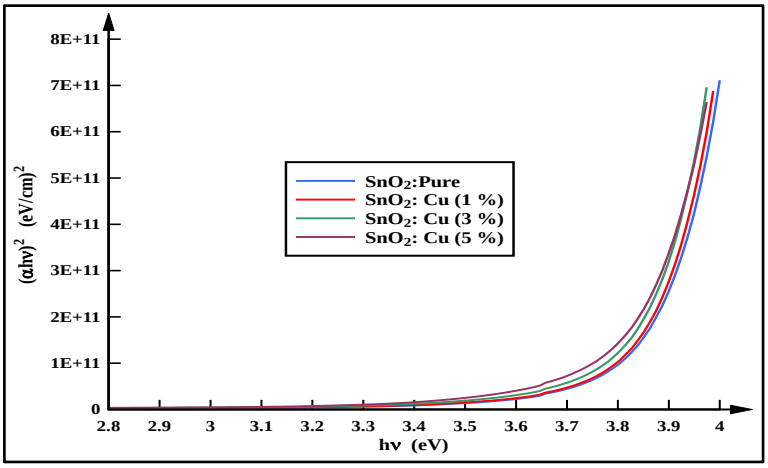

Figure 4. Optical band gap of SnO_2 and SnO_2: Cu (1, 3, 5%)

Conclusions

Nanocrystalline Tin oxide and Cu doped Tin Oxide films are synthesized successfully by CSPD method. XRD results shows that, the preparation of SnO_2 and SnO_2: 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_2 and SnO_2: 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.

References

J.R. Sheeba, S. Radhika, and C.M.Padma, Structure and Optical Properties of Quantum Confined Pureand Cu Doped SnO_2, *Advanced Materials Research,* Vol. 1159, pp 60-66, 2020.

Rakesh K. Joshi, F. Einar Kruis and Olga Dmitrieva, Gas sensing behavior of $SnO_{1.8}$:Ag films composed of size-selected nanoparticles, *Journal of Nanoparticle Research,* (2006) 8: 797–808.

Pankaj S. Kolhe, Pankaj M. Koinkar, Namita Maiti, Kishor M. Sonawane, Synthesis of Ag doped SnO_2 thin films for the evaluation of H_2S gas sensing properties, *Physica B,* 524 (2017) 90–96.

Sabah Ibrahim Abbas, Saba Farhan Hathot, Awatif Sami Abbas, A.A. Salim, Influence of Cu doping on structure, morphology and optical characteristics of SnO_2 thin films prepared by chemical bath deposition technique, *Optical Materials,* 117 (2021) 111212.

G.E. Patil et al., Preparation and characterization of SnO_2 nanoparticles by hydrothermal route, *Int. Nano Lett.,* 1(2) (2012) 46-51.

M.R. Vaezi and M. Zameni, The fabrication of a dip- coated tin oxide thin film via sol- gel processing and a study of its gas sensing properties, *Journal of Ceramic Processing Research,* Vol. 13, No. 6, pp. 778~782 (2012).

J.F. Mohammad, M.A.A. Sooud, S.M. Abed, Characteristics of pH Variation on the structural and optical properties of Nanocrystalline SnO_2 Thin films by CBD Technique, *Digest Journal of Nanomaterials and Biostructures,* Vol. 16, 2021, p. 311- 316.

Suresh Sagadevan, Zaira Zaman Chowdhury, Mohd. Rafie Bin Johan, Fauziah Abdul Aziz, L. Selva Roselin, Jiban Podder, J. Anita Lett, and Rosilda Selvin, Cu-Doped SnO_2 Nanoparticles: Synthesis and Properties, *Journal of Nanoscience and Nanotechnology,* Vol. 19, 7139–7148, 2019.

J. Divya, A. Pramothkumar, S. Joshua Gnanamuthu, D.C. Bernice Victoria, P.C. Jobe prabakar, Structural, optical, electrical and magnetic properties of Cu and Ni doped SnO_2 nanoparticles prepared via Co-precipitation approach, *Physica B: Physics of Condensed Matter,* 588(2020) 412169.

Kiran Jain, R.P. Pant, S.T. Lakshmikumar, Effect of Ni doping on thick film SnO_2 gas sensor, *Sensors and Actuators B,* 113 (2006) 823–829.

A. Tombak, Y.S. Ocak, F. Bayansal, Cu/SnO_2 gas sensor fabricated by ultrasonic spray pyrolysis for effective detection of carbon monoxide, *Applied Surface Science,* 493 (2019) 1075–1082.

J.E. Dominguez, L. Fu, X.Q. Pan, Effect of crystal defects on the electrical properties in epitaxial tin dioxide thin films, *Appl. Phys. Lett.,* 81 (2002) 5168–5170.

N. Bhardwaj, A. Pandey, B. Satpati, M. Tomar, V. Gupta, S. Mohapatra, Enhanced CO gas sensing properties of Cu doped SnO2 nanostructures prepared by a facile wet chemical method, *Phys. Chem. Chem. Phys.,* 18 (2016) 18846–18854.

C.M. Ghimbeu, R.C. van Landschoot, J. Schoonman, M. Lumbreras, Preparation and of SnO_2 thin films prepared by spray pyrolysis, *Bull. Mater. Sci.,* 34 (2011) 1–9.

G.E. Patil, D.D. Kajale, S.D. Shinde, V.G. Wagh, V.B. Gaikwad, G.H. Jain, Synthesis of Cu-doped SnO_2 thin films by spray pyrolysis for gas sensor application, *Advancement in Sensing Technology,* (2013) 299 – 311.

C. Thanachayanont, V. Yordsri, Chris Boothroyd, "Microstructural investigation and SnO nanodefects in spray pyrolyzed SnO_2 thin films" Mater. Lett. 65, 2610-2613, 2011.

G.W. Scherer, "Recent Progress in Drying of Gels", *Journal of Non- Crystalline Solids,* 147-148, 363-374, (1992).

C. Zapata, M. Khalid, G. Simonelli, M. Villafuerte, S.P. Heluani, P. Esquinazi, Magnetic field influence on the transient photo resistivity of defect-induced magnetic ZnO films, *Appl. Phys. Lett.,* 99 (2011) 112503.