

Structural and Optical Properties of Copper-Doped Tin Oxide Films through Spray Techniques

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Abstract

Spray pyrolysis was used to create copper-doped tin oxide (Cu-SnO_2) thin films, which were then analysed for their morphological, structural, optical, and electrical characteristics. With crystallite diameters ranging from 8 to 31 nm, X-ray diffraction revealed lattice strain and verified a tetragonal rutile phase devoid of secondary phases. The substitution of Cu into the SnO_2 lattice was confirmed by Fourier transform infra-red spectra. The optical studies revealed in the absorption edge with a bandgap 3.88 eV (1 at% Cu) and a high transmittance (85%). Due to the equilibrium between carrier production and scattering, electrical characterisation showed a minimum resistivity of approximately $6.34 \Omega \cdot \text{cm}$ at 1 at% Cu doping. At 1% doping, scanning electron microscope images showed homogeneous grains; at greater concentrations, agglomeration and surface roughness were observed. These results show that 1 at% Cu doping maximises conductivity and transparency, making Cu-SnO_2 thin films attractive options for solar cells, transparent electrodes, and optoelectronic devices.

1. Introduction

Thin films are now essential to modern technology, being used in everything from photovoltaic devices and display technologies to storage devices and communication systems [1, 2]. Their distinct characteristics, namely their enormous surface-to-volume ratios and nanoscale dimensions, allow for customised functionality for particular applications [3]. Tin oxide (SnO_2) is a transparent conducting oxide (TCO) that is extensively researched among many materials used for thin films because of its exceptional chemical stability, strong electrical conductivity, and outstanding optical transparency in the visible range [4, 5]. Because of these characteristics, SnO_2 is a material of choice for solar windows, gas sensors, and transparent electrodes in electrochemical systems, among other applications [6, 7].

Doping SnO_2 with transition metals, such as copper (Cu), has been demonstrated to increase its electrical and optical properties by introducing non-stoichiometry and electron degeneracy [8]. Doped SnO_2 films are appropriate for sophisticated applications where high transparency and conductivity are crucial because copper doping can regulate the bandgap, increase conductivity, and improve carrier mobility [9, 10]. Doped SnO_2 thin films' adaptability and smooth integration into current systems highlight their potential to propel technological advancements in the modern era [11, 12].

The current study utilises a low-cost spray pyrolysis approach to improve the structural, optical, and electrical properties of Cu-doped SnO_2 thin films. We specifically want to achieve high optical transmittance and low electrical resistivity, which are suitable properties for transparent electrodes in solar cell topologies. Various films serve as window layers in various applications, necessitating low resistivity for efficient charge transport and high transparency for optimal light harvesting.

This work uniquely determines the ideal Cu doping concentration that simultaneously improves optical and electrical performance without producing secondary phases, in contrast to previous publications that commonly suffered from phase separation, greater resistivity, or limited transparency [13, 14]. The films showed the best conductivity and transparency at 1 at% Cu doping, which made them viable

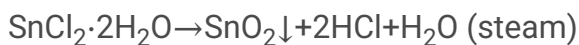
options for optoelectronic uses. We systematically examine how Cu doping affects the structural, optical, electrical, and morphological characteristics of SnO₂ thin films in order to illustrate this. We assess how Cu concentration affects electrical resistivity, bandgap variation, surface morphology, and crystal structure using spray pyrolysis, a scalable and repeatable technique. All of these results support the potential of Cu-doped SnO₂ films for use in energy devices including solar cells and sensors as well as transparent electronics.

2. Materials and Methods

2.1. Film Preparation

Cu-doped SnO₂ thin films were deposited on glass substrates using a chemical spray pyrolysis unit. The substrates were cleaned sequentially with HCl, deionized water, acetone, and ethanol to ensure a contaminant-free surface. A precursor solution was prepared by dissolving 1.13 g (0.1 M) of tin chloride (SnCl₂·2H₂O) in a mixture of 25 ml ethanol and 25 ml distilled water, with a few drops of HCl added to enhance solubility. For Cu-doped films, cupric chloride (CuCl₂·2H₂O) was added to the precursor solution at concentrations of 1–4 at%. A digital temperature controller was used to regulate the substrate temperature during the spray pyrolysis process, which was set at 320 ± 5°C. The nozzle was placed 30 cm from the heated substrate, and the precursor solution was sprayed over it at a rate of 5 ml/min for 5 minutes. The chemical reactions during the pyrolysis process can be summarized as follows:

1. Decomposition of SnCl₂·2H₂O:



2. Reaction of SnCl₂·2H₂O with CuCl₂·2H₂O:



After deposition, the films were allowed to cool slowly to room temperature. Every synthesis was carried out in triplicate under the same circumstances in order to evaluate repeatability. The films' uniform surface shape, thickness, and optical clarity across batches attested to the spray pyrolysis technique's dependability. The weight gain method was used to measure thickness at various spots on the substrate and visually assess film homogeneity. The results showed a difference of less than 5%. Achieving consistent film deposition required careful management of the spray parameters, such as substrate temperature, flow rate, and nozzle-substrate distance. High homogeneity and reproducibility were guaranteed by these procedures, which are crucial for scalable optoelectronic applications.

2.2. Characterization Techniques

The weight increase method was used to determine the thickness of the film. Using X-ray diffraction (XRD) with Cu-K α radiation ($\lambda = 1.5406 \text{ \AA}$), structural characteristics were examined. UV-Vis spectroscopy was used to investigate optical characteristics in the 300–800 nm wavelength range. Fourier-transform infrared (FTIR) spectroscopy was performed to detect functional groups and validate the inclusion of Cu into the SnO₂ lattice. Scanning electron microscopy was used to analyse the surface morphology (SEM). A four-probe technique was used to assess electrical characteristics, such as resistivity. The resistivity measurements were carried out on rectangular film samples of 10 mm $\times$ 10 mm area with an average thickness of 500 nm.

3. Results and Discussion

3.1. Structural Properties

The XRD patterns showed significant peaks corresponding to the (110), (101), (200), and (211) planes, confirming the tetragonal rutile structure of Cu-doped SnO₂ films (Fig. 1). It is evident from the XRD patterns that Cu²⁺ ions were successfully integrated into the SnO₂ lattice without generating distinct copper oxide phases since there were no secondary phases. At higher Cu doping concentrations, the crystallite size decreases compared to the lightly doped film. The dopants do not form extra peaks in the XRD pattern of doped SnO₂ films because dopant atoms incorporate homogeneously into the tin oxide matrix. Hence Sn forms an interstitial bond with oxygen and exists either as SnO or SnO²; accordingly it has a valence of + 2 or + 4, respectively. During the initial addition of Cu into the film, the Cu substituted on Sn⁴⁺ sites act as donors and release excess electrons into the conduction band. The lattice parameters are $a = b = 4.7269 \text{ \AA}$, $c = 3.9247 \text{ \AA}$ respectively. From x-ray diffraction pattern, it is clear that Cu²⁺ ions are acting as dopants in the SnO₂ structure. The lattice tetragonal phase structure is determined by the relation (1)

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

1
,

where, d and (hkl) are the interplaner distance and miller indices, respectively. It was also observed that the various doping atoms did not change the lattice parameters.

The Scherrer Eq. (2) was used to determine the crystallite size, which varied from 8 to 31 nm.

$$D = \frac{0.9\lambda}{\beta \cos\theta}$$

2
,

In this context, D represents grain size, while β denotes the full width at half maximum of the observed peak, λ means the wavelength of X-ray used for diffraction, and θ means the angle of diffraction. The smallest crystallites were found at greater doping concentrations. These results are in line with [8], which demonstrated that Cu doping in SnO_2 films reduced crystallite size. Lattice strain from replacing smaller Sn^{4+} ions with bigger Cu^{2+} ions, which prevents crystal development, is responsible for the decrease in crystallite size. The main development here is the use of spray pyrolysis to produce a phase of up to 4 at% Cu doping, which is a major improvement over sol-gel and other techniques where secondary phases frequently show up at lower concentrations. This offers a perfect solution for property research by demonstrating excellent dopant solubility and uniform inclusion into the SnO_2 matrix.

3.2. FTIR Studies

The presence of Cu and the SnO_2 lattice structure are both confirmed by the unique absorption peaks seen in the FTIR spectra (Fig. 2). The broad absorption peaks around $2000\text{--}3000\text{ cm}^{-1}$ are attributed to normal polymeric O-H stretching vibration of H_2O in Cu-Sn-O lattice which may be due to moisture in the solution and the atmosphere.

The Sn-O stretching vibration, a fundamental mode of the SnO_2 matrix, is shown by the peak at 537 cm^{-1} . The successful substitution of Cu^{2+} into the SnO_2 lattice is indicated by the extra peak at 640 cm^{-1} , which is ascribed to Cu-O vibrations and becomes more noticeable with doping. Weak C-O vibrations from leftover precursors or metal oxide bridging modes could be the cause of a notable absorption at 812 cm^{-1} . The C = C and C = O stretching modes are associated with the bands at 1466 cm^{-1} and 1752 cm^{-1} , indicating trace organic molecules from the synthesis environment. H-O-H bending from adsorbed water or hydroxyl groups is represented by a wide band around 1600 cm^{-1} . The structural integrity of SnO_2 and the successful incorporation of copper ions into the lattice without the formation of secondary phases are confirmed by the combination of these observed FTIR features, which include Sn-O stretching, Cu-O vibration, and other minor absorption bands [14]. Chemical evidence of successful substitutional doping is provided by the FTIR spectra. Together with the steady Sn-O peak, the expanding Cu-O peak at 640 cm^{-1} verifies that Cu is integrated into the lattice bonds rather than existing as distinct oxide phases. One significant benefit of our synthesis approach over those that produce composite films is highlighted by this clear spectroscopic signal of efficient doping.

3.3. Optical Properties

The absorption edge, and the band gap slightly increased to 3.88eV (1 at% Cu doping), according to UV-Vis spectroscopy. The inclusion of defect states, such as oxygen vacancies and Cu-induced impurity levels, which produce extra energy states for electron transitions, may account for the observed bandgap value 3.88eV (1 at% Cu-doped) [8, 9]. Sub-bandgap optical transitions can be facilitated by these impurity levels acting as intermediate energy states inside the SnO_2 bandgap [10, 11]. The density of localised states close to the conduction band edge may rise as a result of lattice distortions brought on by substituting Cu^{2+} for Sn^{4+} [12].

It is also plausible that the Burstein–Moss (B–M) effect could contribute if Cu doping raises the number of free carriers, which would move the Fermi level into the conduction band and thus reduce the apparent optical bandgap [15]. According to published Hall measurements for comparable Cu-doped SnO₂ systems [16], these band structure changes usually correlate to carrier concentrations between 10¹⁹ and 10²⁰ cm⁻³. The trend in optical transmittance and bandgap narrowing is consistent with these previously documented effects, despite the fact that direct Hall measurements were not conducted in this investigation [17]. As the Fermi level moves closer to the conduction band, the red shift also indicates a higher carrier concentration brought on by Cu doping [18, 19].

In the UV-visible-NIR range (300–800 nm), the transmittance and absorbance spectra of Cu-doped SnO₂ thin films were captured. The transmittance change with wavelength for as-deposited films is displayed in Fig. 3. The visible and infrared spectrums exhibit high transmittance, with a minimum at 300 nm. At greater doping levels, transmittance drops, indicating increasing metallic nature and light absorption, yet it increases up to 1 at% Cu doping. The concentration of Cu doping affects these variations in optical characteristics, such as transmittance and absorbance [10, 11]. The transmittance increases gradually up to 1 at% Cu doping, but decreases at higher doping concentrations. This suggests that the decrease in the transmittance of Cu–SnO₂ films with increasing doping concentration may lead to an increase in the degenerate (metallic) nature of the film, which results in light absorption.

The absorption coefficient (α) was calculated from the transmission spectra using the relation (3).

$$\alpha = \frac{1}{t} \ln \frac{1}{T}$$

3

where T is the optical transmittance and t is the film thickness. The absorption coefficient (α) was found in the order of 10⁶ m⁻¹, which is typical for transparent conducting films. The value of the absorption coefficient increases as the concentration of Cu increases gradually up to 1%, But it starts to decrease with further Cu doping. This reduction of absorption coefficient in Cu doped samples may be due to the removal of defects and disorders in the deposited film by Cu doping. The direct optical band gap E_{g1} was determined by the Eq. (4) given below.

$$(\alpha h\nu)^2 = A(h\nu - E_{g1})$$

4

where α is the absorption coefficient, $h\nu$ is the photon energy, A is a constant, and E_{g1} is the optical band gap.

UV-visible absorption spectroscopy was used to investigate the optical properties of Cu-doped SnO₂ thin films. Tauc plot analysis was used to calculate the associated band gap energies in Fig. 4. As is common for direct bandgap semiconductors, all films show a distinct and sharp absorption edge, signifying little sub-bandgap absorption and good crystallinity. [20, 21]

The Cu doped SnO₂films have an optical band gap of 3.88 eV with 1 and 2 at% Cu doping (Table 1). The band gap is slightly reduced (3.76 eV for 3 at% and 3.75 eV for 4 at%) when doping is increased beyond 2 at%. This shift in the absorption edge can be explained by the Burstein–Moss effect, which requires higher energy photons for electronic transitions because the substitution of Cu²⁺ for Sn⁴⁺ introduces more carriers that fill the lower conduction band states. This could be because of the creation of localised defect states or Cu-related impurity levels that produce band tailing and marginally reduce the effective optical gap.

The optical transmittance of all films remains high, with values above 80% in the visible region, confirming the excellent transparency of the deposited layers. A maximum transmittance of 85% is achieved at 1 at% Cu doping, suggesting that moderate Cu incorporation enhances the optical quality of the films by reducing light-scattering centers. At higher doping levels, a marginal decrease in transmittance is observed, which could arise from increased defect density or surface roughness introduced by excessive Cu incorporation [22]. The results demonstrate that low-level Cu doping effectively tunes the band gap while maintaining high optical transparency, making these films suitable for applications in optoelectronic devices such as transparent conducting oxides, solar cell window layers, and UV photodetectors.

Table 1
The electrical, and band gap analysis details of Cu doped SnO₂ Thin films.

Concentration	Resistivity	Band gap energy(Eg)	Optical transmittance
(at%)	Ω.cm	eV	(%)
1	6.3406	3.88eV	85
2	8.1522	3.88eV	82
3	9.5109	3.76eV	81
4	10.869	3.75eV	80

3.4. Electrical Properties

The conductivity improvement at this doping level is due to the optimal balance between defect states and carrier concentration. The resistivity rose to about 10.87 Ω·cm (Fig. 5) at higher doping levels (e.g., 4 at%) because of the formation of defect states that obstruct electron mobility and serve as scattering centres.

The observed trends in electrical resistivity suggest an increase in carrier concentration at low Cu doping levels (up to 1 at%) because substitution of Sn^{4+} with Cu^{2+} introduces additional free carriers (electrons) into the system, even though direct Hall measurements were not carried out. This increase in carrier density lowers the resistivity and enhances conductivity. However, beyond the optimum doping concentration, excess Cu likely forms interstitial states or defect clusters, which act as scattering centres and electron traps, reducing mobility and thereby increasing resistivity. For a more comprehensive understanding of these transport pathways, future work should quantitatively evaluate carrier mobility and carrier concentration through Hall effect measurements. These findings are consistent with previous reports [9, 14], which demonstrated that excessive doping deteriorates electrical properties due to increased carrier scattering and the formation of defect-related localized states.

At the 1 at% doping level, the ideal balance between low resistivity and good optical transparency both essential for solar cells and transparent conducting electrodes was reached. The transmittance dramatically dropped (as shown in Fig. 3) and the resistivity rose to about $8.15 \Omega \cdot \text{cm}$ at higher Cu concentrations (e.g., 2 at %), signifying the start of defect-induced absorption and greater carrier scattering. Consequently, 1 at% Cu doping is found to be the most efficient concentration within the range under study for maximising both optical and electrical performance.

The resistivity minimum observed at 1 at% is attributed to an optimal balance between carrier generations and scattering, which enhances electrical conductivity at this doping level. By encouraging the creation of charge-compensating oxygen vacancies, substitutional Cu^{2+} increases electron concentration. After this, too much dopant reduces mobility and raises resistivity by acting as electron traps and scattering centres. Our research shows that, at this particular optimum, spray pyrolysis can provide a very low, device-ready resistivity, in which a difficult outcome for solution-based techniques [23].

3.5. Morphological Properties

SEM micrographs of Cu-doped SnO_2 thin films at various doping concentrations are shown in Fig. 6. Images (a) to (d), on the other hand, represent films doped with 1%, 2%, 3%, and 4% Cu, respectively. Of these, the 1% Cu-doped sample (Fig. 6a) has a comparatively homogeneous grain structure with less agglomeration, indicating enhanced crystallinity and film quality at this doping concentration. Higher doping levels (2–4%), however, cause the surface to become more uneven with observable grain boundaries and clusters (Fig. 6b–d). This is probably because secondary phases and defects connected to Cu are forming. This non-systematic morphological evolution shows that too much Cu interferes with the film's ability to grow uniformly, leading to an increase in surface roughness and inhomogeneity. The degradation of electrical and optical properties at increasing doping levels is in line with the SEM data. Therefore, although the trend is not strictly linear, 1% Cu doping appears to promote more favourable surface morphology for device applications [15]. By lowering scattering at grain boundaries, the smooth, uniform morphology at 1 at% Cu suggests effective charge transport and shows no lattice distortion. Increased strain from higher doping levels causes agglomeration and surface roughness, which in turn

produce electrical traps. The immediate microstructural explanation for the macro-scale property increases we observed is provided by this obvious visual link between the peak optoelectronic performance and the optimum shape at 1 at% [24].

4. Conclusion

Cu–SnO₂ thin films were successfully fabricated by spray pyrolysis, and the effects of Cu doping on their properties were systematically studied. The tetragonal rutile structure and effective Cu inclusion without secondary phases were verified by X-ray diffraction and Fourier transform infra-red spectroscopy. At 1 at% Cu doping, optical investigation showed bandgap decreasing to 3.88eV and high transmittance (85%). Scanning electron microscope images revealed homogeneous grains and better shape, while electrical investigations found a minimum resistivity of 6.34Ω·cm at the same concentration. Higher doping levels, however, introduced defects, agglomeration, and increased resistivity. Overall, the ideal condition was determined to be 1 at% Cu doping, which provided the best balance between conductivity and transparency. These findings validate Cu–SnO₂ thin films as promising and reasonably priced materials for solar cells, transparent electrodes, and other optoelectronic applications.

Declarations

Funding Declaration

No funding was received for this research work.

Credit Authorship Contribution Statement

S. Rosepriya conducted all experiments and analyzed the data. C. Vignesh wrote the manuscript. K. Vinoth performed the data analysis and interpretation. G. Anburaj and A. Premkumar supervised the experiments and provided technical guidance, R. Sugumar and L. Guganathan revised the manuscript.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have influenced the work reported in this paper.

Data Availability

Data will be made available upon request.

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Figures

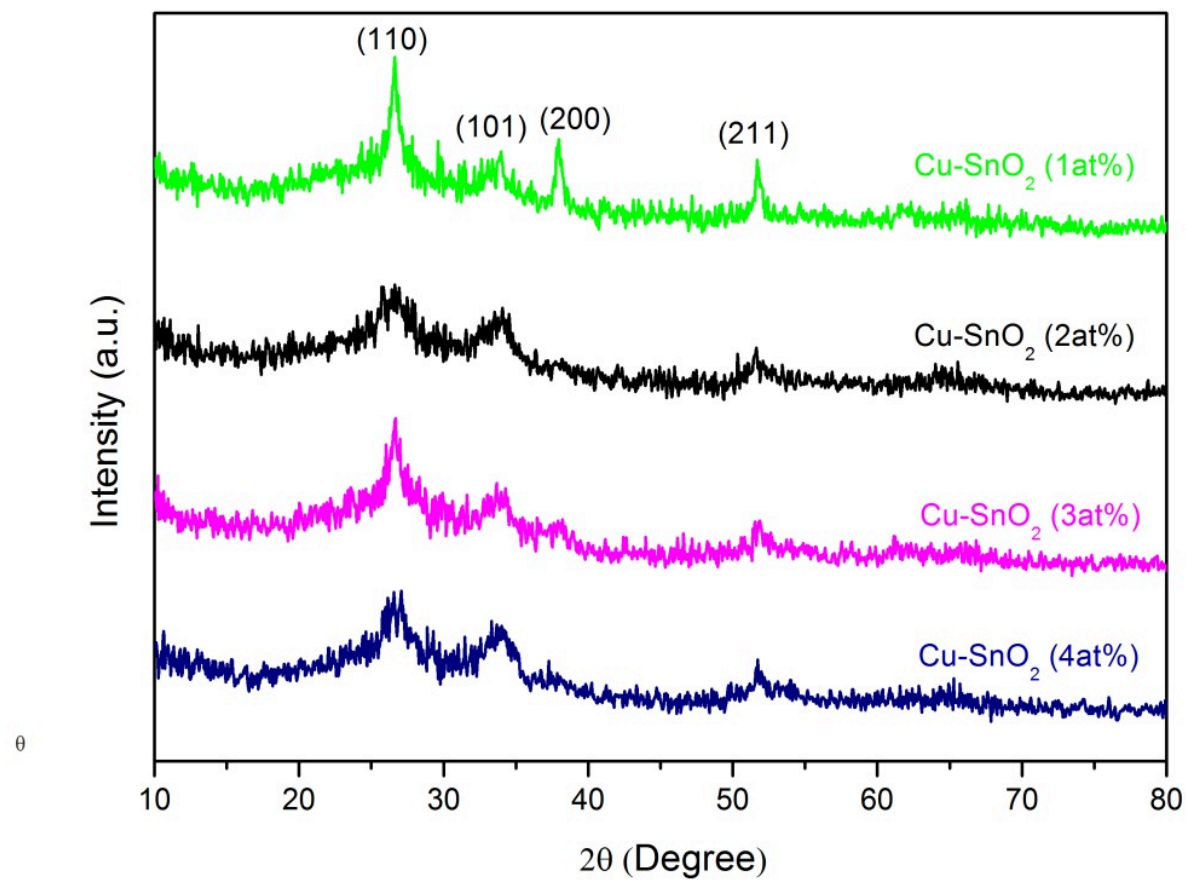


Figure 1

XRD Spectra of Cu doped SnO₂ Thin films

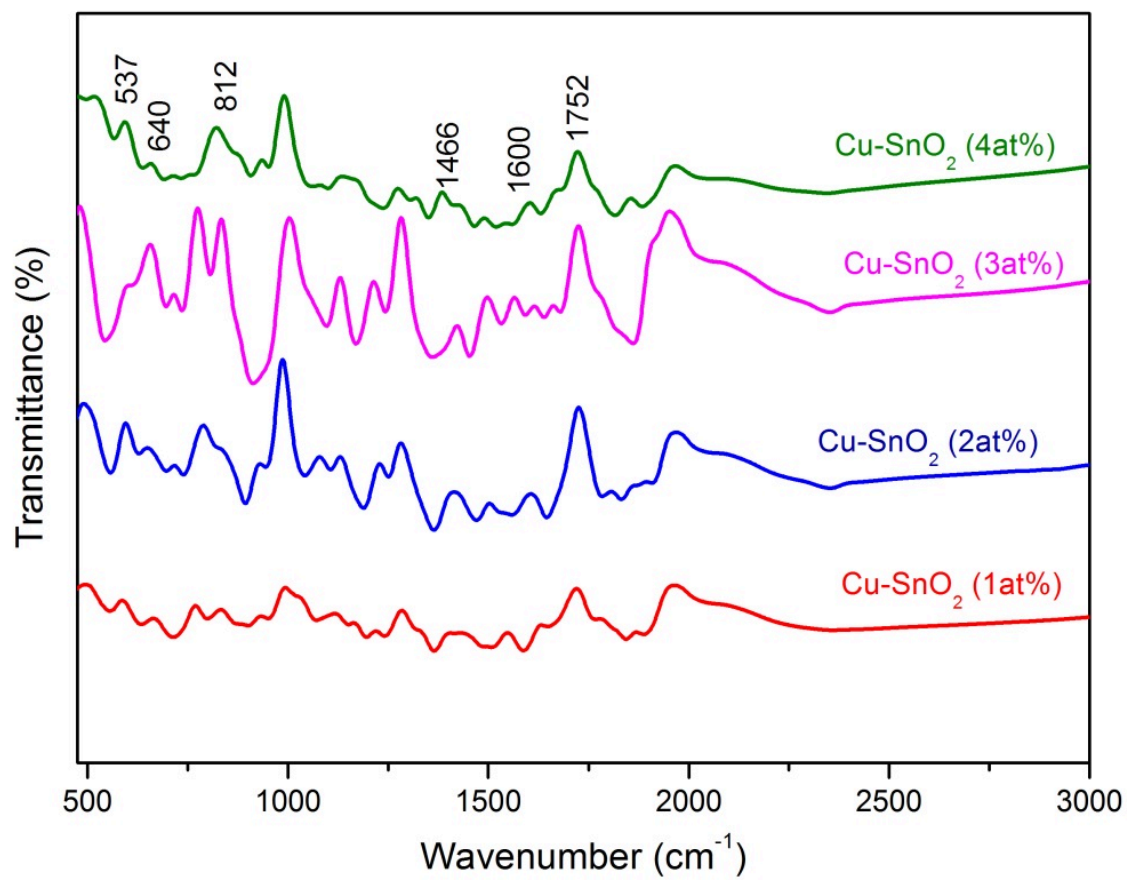


Figure 2

FTIR- Spectra of Cu doped SnO₂ Thin films

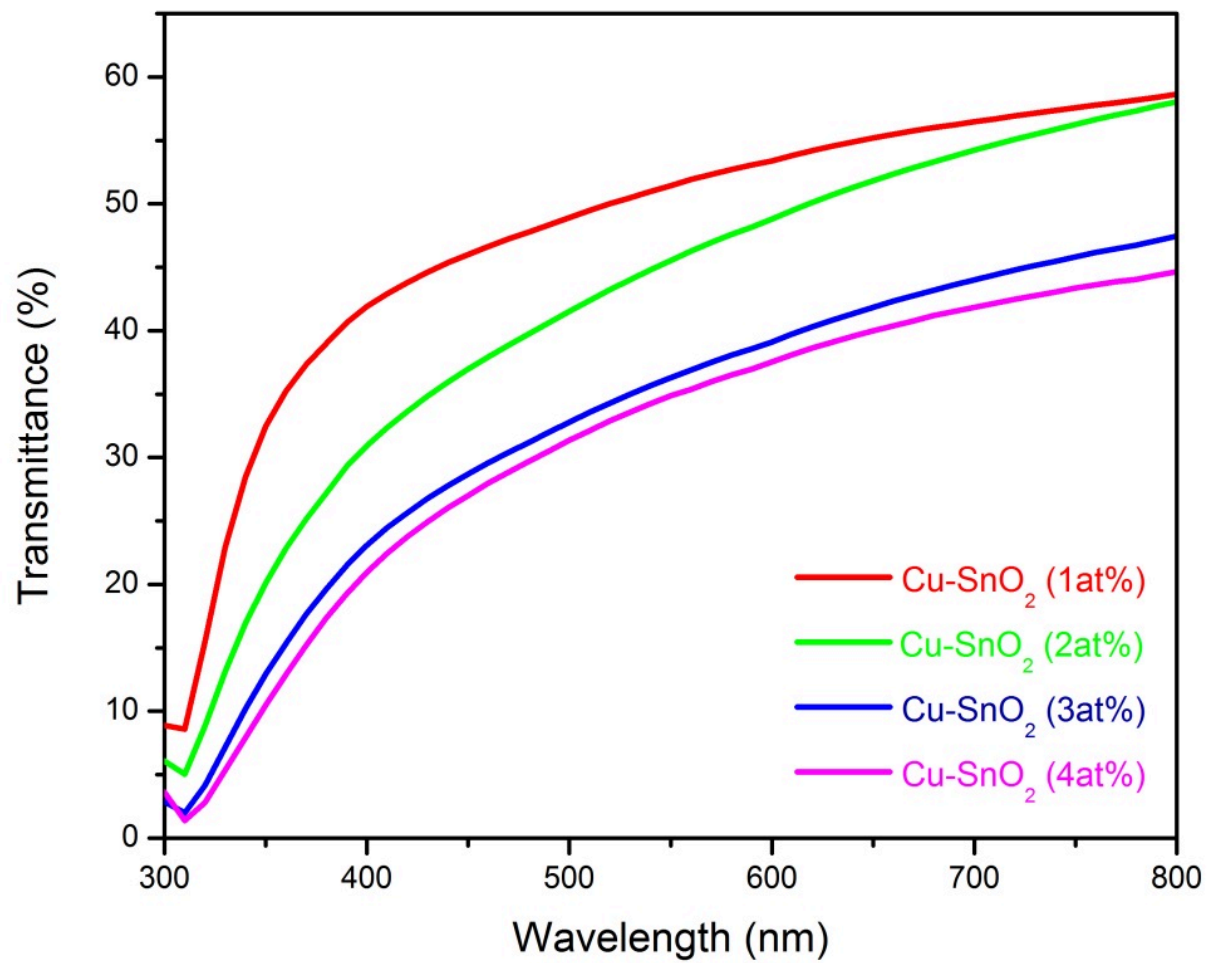


Figure 3

UV-Transmittance Spectra of Cu doped SnO₂ Thin films

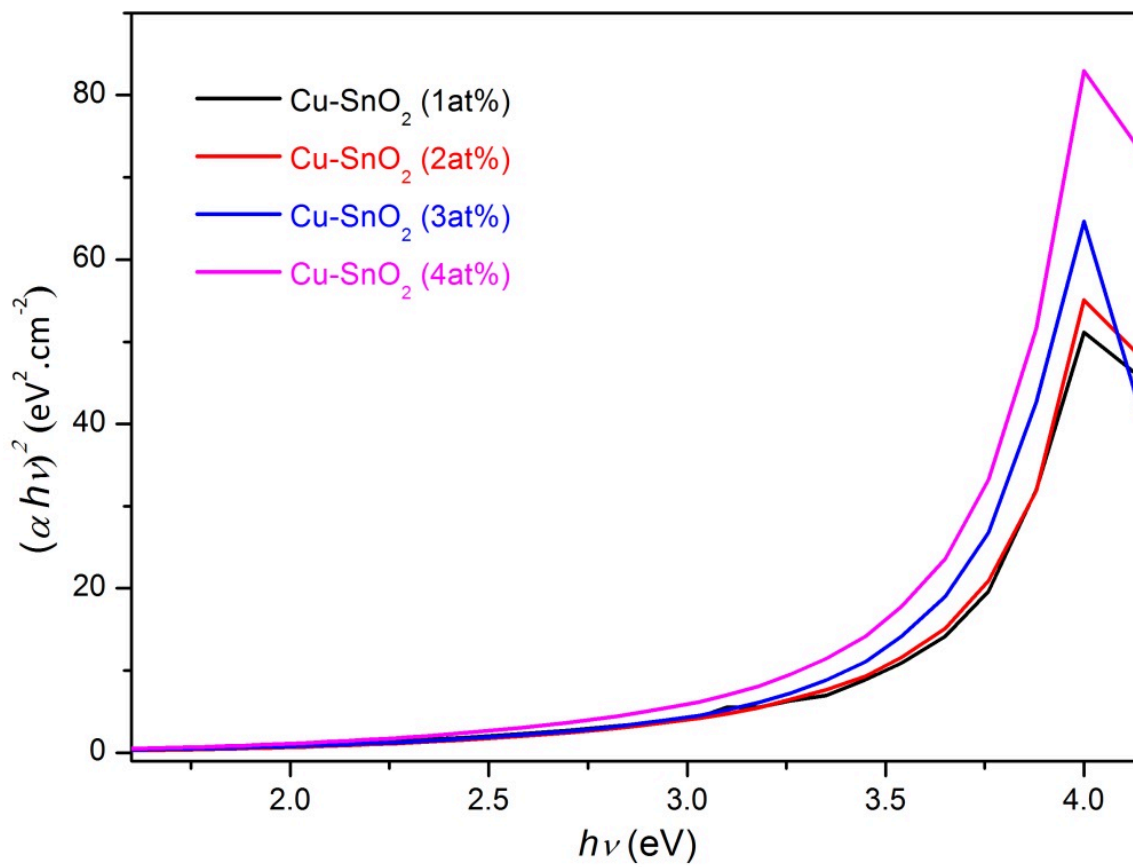


Figure 4

UV-Band Gap - 2 Spectra of Cu doped SnO₂ Thin films.

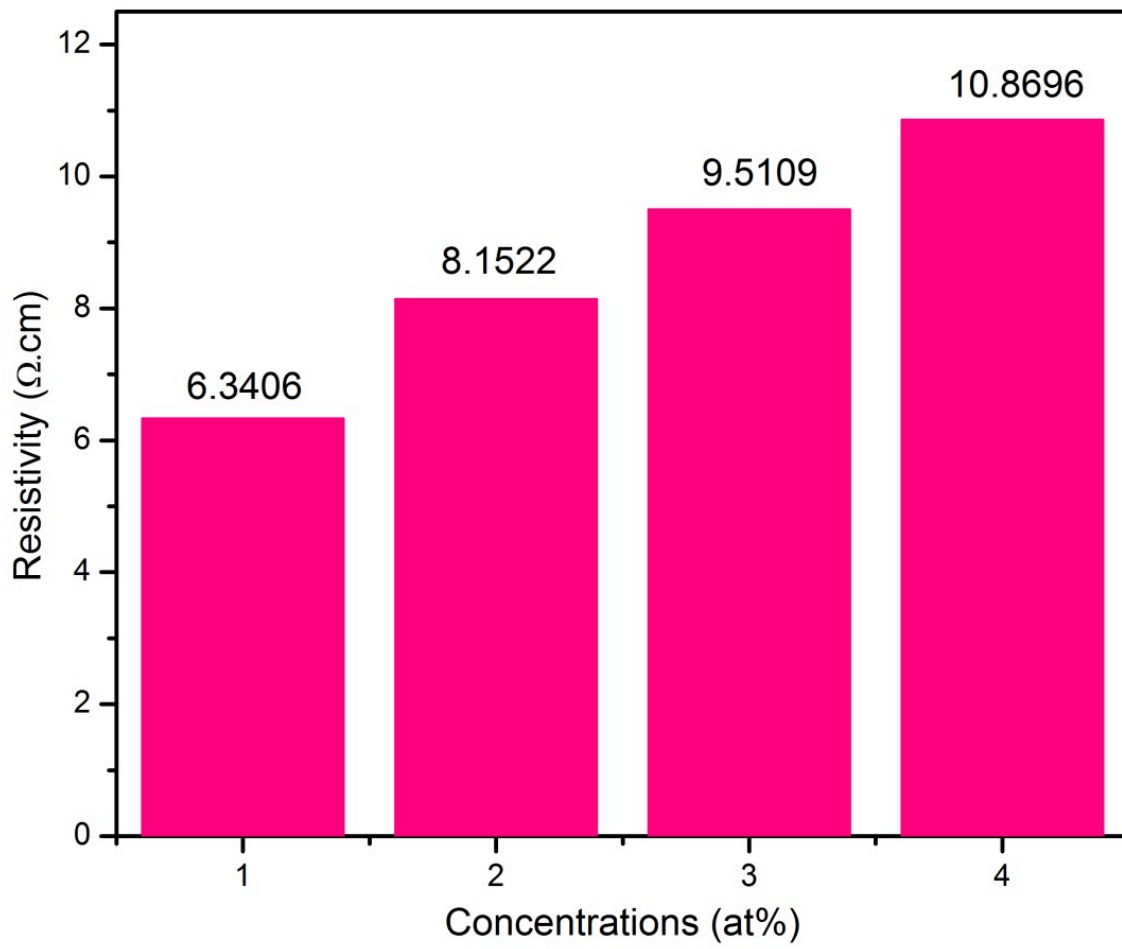


Figure 5

Electrical Spectra of Cu doped SnO₂ Thin films

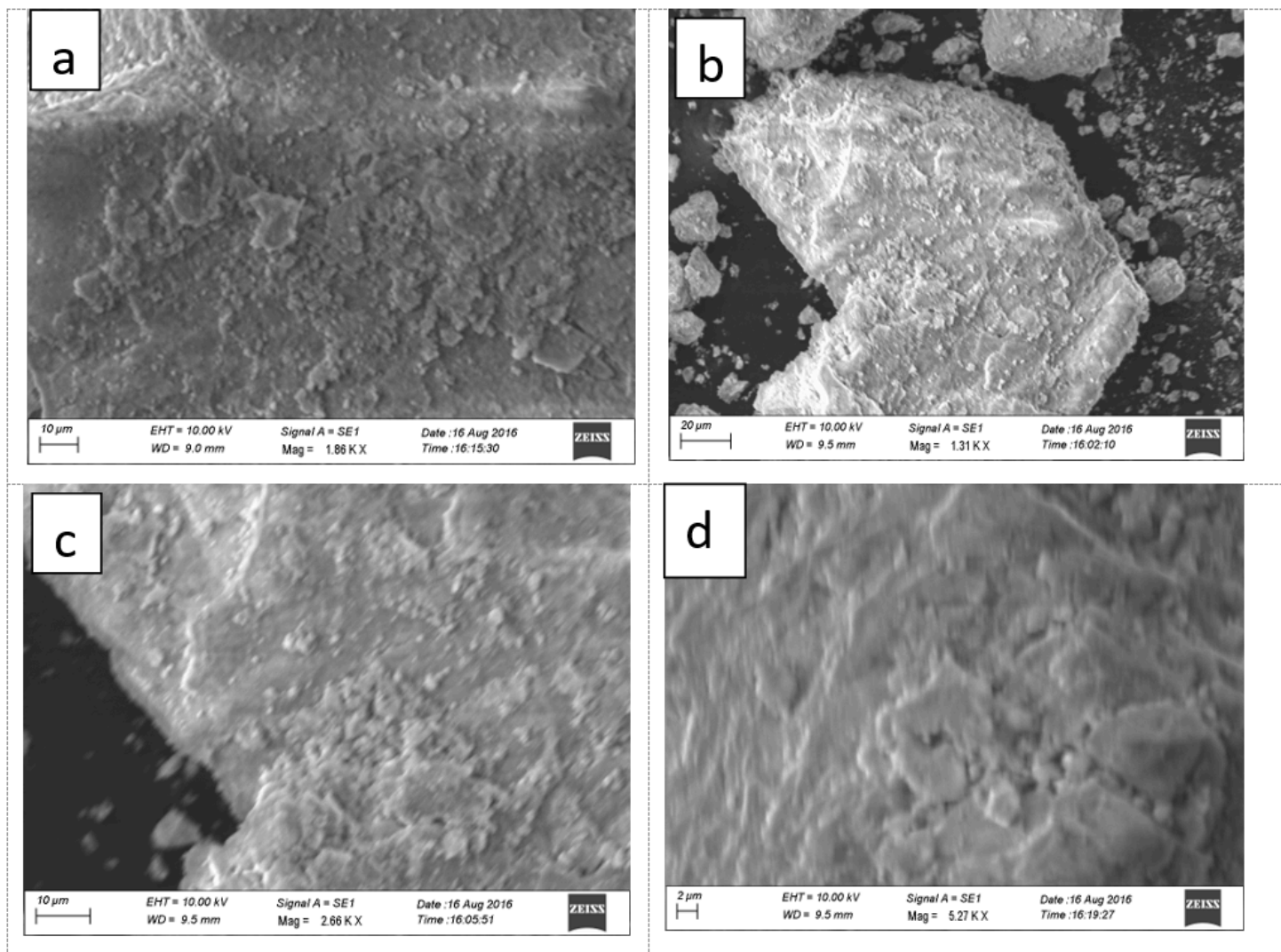


Figure 6

SEM images of Cu doped SnO_2 Thin films observed at different magnifications. 6(a, b,c, d) 1,2,3,4 at% Cu doped SnO_2 Thin films