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Structural and Morphological Characterization of Cu-Doped SnO_2Thin Films

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Abstract

This study investigated the structural and morphological properties of Cu-doped SnO_2 films grown on glass and FTO (fluorine tin oxide) substrates by RF magnetron sputtering and annealed at a temperature of 600 ºC. The techniques of X-ray diffraction (XRD), atomic force microscopy (AFM), field emission scanning electron microscopy (FESEM), and energy dispersive X-ray spectroscopy (EDX) were employed to characterize the structural and morphological properties of the films. The XRD results verified the formation of a polycrystalline SnO_2 in a tetragonal structure for all samples. The sample deposited on the FTO exhibited a larger crystallite size compared to the sample deposited on a glass substrate. AFM and FESEM images exhibit that the type of the substrates influences the morphology, roughness, and grain sizes of the films. The EDX analysis confirmed the presence of Sn, O, and Cu elements in the films. The results show that the choice of substrate can significantly impact the structural and morphological characteristics of deposited films, influencing their potential applications in various fields such as solar cells and gas sensors.

Keywords: Cu-Doped SnO_2, Glass, FTO, Thin Film, RF Sputtering, Nanocrystalline.

1. Introduction

These days, the study of materials based on metal oxides [1-3] has received attention due to their characteristics, including being low cost, simple preparation and environmental friendliness [4-6]Among the transition metal oxides, tin oxides (IV) (SnO_2) is an n-type semiconductor with a rutile tetragonal crystal structure that has received a great deal of attention owing to its wide band gap (3.6 eV), highly transparent (in the visible range), high excitation energy, stable structure, low cost, fast kinetics, chemical stability and, reproducibility [7-9]. SnO_2 thin films have found various applications such as gas sensors and optoelectronic devices [10,11]. Researchers incorporated various transition metals such as Cu, Ni, Co, and F, to explore the structural, optical, and electrical properties of SnO_2 [12]. The incorporation of Cu into SnO_2 thin films has shown significant enhancements in properties such as conductivity and energy-level alignment, leading to improved performance in perovskite solar cell devices. Various methods have been employed to synthesize SnO_2 thin filmsincluding chemical and physical methods [2, 13, 14]. The advantages of each of these techniques vary depending on the specific application of interest. Chemical methods are predominantly employed to fabricate pure and doped SnO_2 thin films. However, these methods often involve the use of substances or solvents that introduce impurities and are not environmentally friendly.

In contrast, physical methods offer contamination-free alternatives. We used a physical method to produce layers with high purity and save time. Among physical methods, RF sputtering is a straightforward and efficient technique that enables the creation of nanostructures in thin films. It offers precise control, high yield, low pollution, and uniform particle size [2,15,16]. In this investigation, we employed the RF sputtering technique to fabricate thin films of Cu-doped SnO_2 on glass and FTO substrates. Furthermore, the study explores the impact of substrate type (glass or FTO) on the characteristics of prepared Cu-doped SnO_2 thin films.

2. Materials and Methods

In this study using the RF magnetron sputtering technique and a SnO_2/Cu target, we deposited Cu-doped SnO_2 thin films on glass and FTO substrates. Then the samples were annealed at 600 ºC for 1 h in the electric furnace. FTO serves as a transparent substrate for transferring electric charge to crystals.This type of substrate exhibits characteristics such as low surface resistance, high conductivity, thermal stability, and chemical stability. It finds widespread use in various application areas, including energy materials and solar cells [17,18].The Cu/SnO_2 target was composed of a SnO_2 target with a diameter of 76.2 mm and a thickness of 1.5 mm and also contained four bonded Cu square chips with dimensions of 8.24 mm, the purity of the Cu chips was 99.99%. Before being introduced substrates into the deposition chamber, the substrates underwent

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ultrasonic cleaning in ethanol for 10 minutes. Base pressure and deposition pressure were 2×10^{-4} and 2.7×10^{-3} mbar respectively, the target to substrate distance was 6 cm and deposition time was 86 min. The plasma power was kept at 70 w. Atomic force microscopy (AFM, Park Scientific Instruments Auto Prob CP USA) and field emission scanning electron microscopy (FESEM; Hitachi S-4160) were employed to investigate the surface topography and microstructure of the films. The elemental composition of the films was analyzed using energy-dispersive X-ray spectroscopy (EDAX) attached to the field emission scanning electron microscopy (FESEM). X-ray diffraction analysis (XRD) using CoKα radiation (λ Co kα = 0.1789 nm) was used to determine the crystallographic structure of the samples.

3. Results and Discussion

3.1. Structural Characterization

Fig. 1.a and Fig. 1.b display the XRD patterns of the Cu-doped SnO_2 films on glass and FTO substrates respectively. We can observe that all the films are polycrystalline with tetragonal structures.

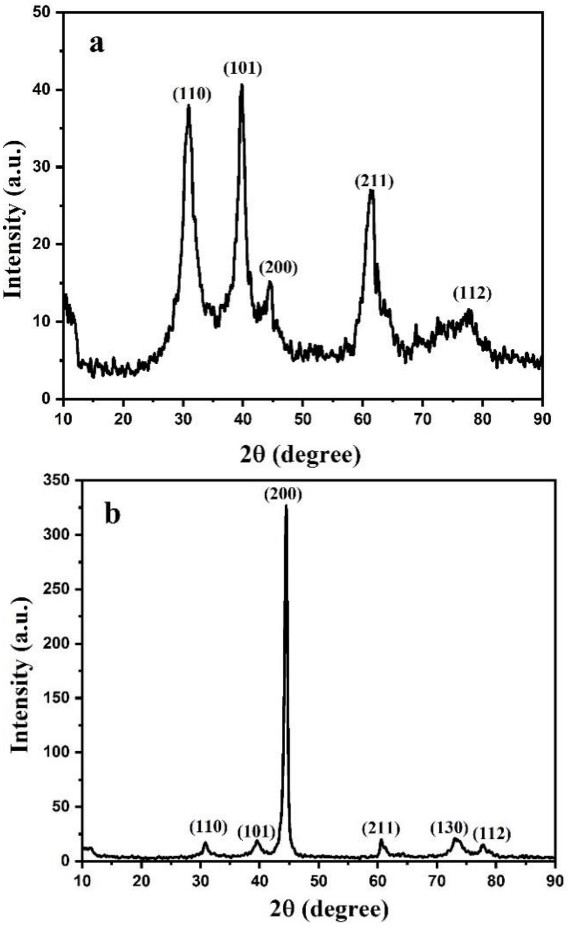


Fig. 1. X-ray diffraction results of Cu-doped SnO_2 on glass (a) and on FTO (b) substrates.

According to the XRD spectra in Fig. 1.a there are peaks of (110), (101), (200), (211), and (112) related to the tetragonal lattice construction of SnO_2 (with the reference pattern JCPDS 00-001-0625). In Fig. 1.b in addition to the mentioned peaks in Fig. 1.a there is a (130) peak of the tetragonal structure of SnO_2. The average crystallite size (D) was calculated using the Scherrer equation formula in Eq. 1. [2] and the micro-strain (ε) was calculated according to the relation Eq. 2. [2].

$$D = \frac{0.9\lambda}{\beta \cos\theta} \text{Eq. (1).}$$

$$\varepsilon = \frac{\beta}{4\tan\theta} \text{Eq. (2).}$$

Where λ is the X-ray wavelength of Co-Kα (0.1789 nm), θ is the Bragg diffraction angle and β is the full width at half maximum (FWHM). The calculated data are provided in Table. 1.

Table. 1. The structural parameters of Cu-doped SnO_2 films.

Samples	Substrate	Peak	2θ (deg)	Peak Intensity	FWHM	D (nm)	ε $\times10^{-2}$
Cu-doped SnO_2	glass	(101)	30.77	40.69	0.62	16.73	2.02
Cu-doped SnO_2	FTO	(200)	44.49	325.93	0.33	30.98	0.74

The obtained results showed that the use of FTO as a substrate gives a big crystallite size compared to glass as a substrate. When FTO is used as a substrate, the resulting thin film tends to have a more homogeneous surface.

The uniform surface promotes the growth of larger crystallites during deposition compared to the glass substrate. On the other hand, the sample deposited on glass substrates exhibits greater microstrain compared to that on FTO substrate, indicating a superior alignment of growth films on FTO due to its lower mismatch with the deposited lattice structure, as opposed to the randomly oriented atoms on the glass substrate [13].

3.2. Morphological Characterization

The atomic force microscopy (AFM) technique was employed to conduct an in-depth investigation of the cu-doped SnO_2 surface morphology. Fig. 2. shows the 2D and 3D AFM images of Cu-doped SnO_2 thin films on glass (a) and FTO (b) substrates. It is evident that the layers deposited on glass and FTO substrates display well-advanced and regularly distributed surface grains with more uniform surface morphology. The root mean square roughness (RMS) and average roughness (Ave) values were determined from AFM observations and tabulated in Table. 2.

Table. 2. The result of roughness values from AFM analysis and grain size calculated from FESEM analysis.

Samples	Substrate	RMS Roughness (nm)	Average Roughness (nm)	grain size from FESEM (nm)
Cu-doped SnO_2	glass	10.31	7.31	6
Cu-doped SnO_2	FTO	9.26	6.11	11

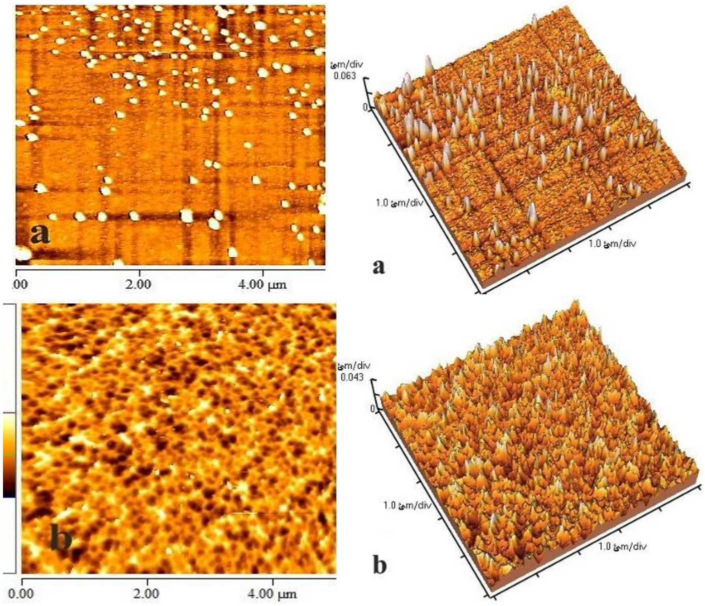


Fig. 2. 2D and 3D AFM images of Cu-doped SnO_2 on glass (a) and on FTO (b) substrates.

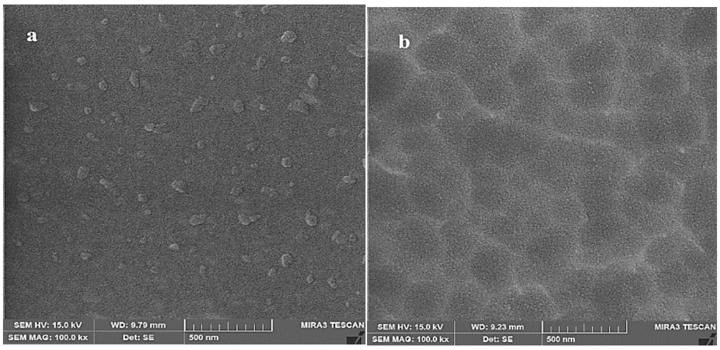
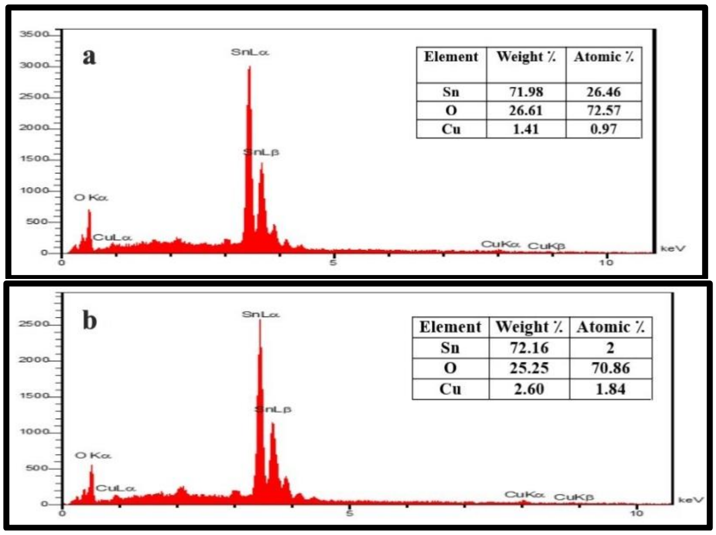


Fig. 3. FESEM images of Cu-doped SnO_2 films on (a) glass and (b) FTO substrates.



Element	Weight %	Atomic %
Sn	71.98	26.46
O	26.61	72.57
Cu	1.41	0.97

Element	Weight %	Atomic %
Sn	72.16	2
O	25.25	70.86
Cu	2.60	1.84

Fig. 4. The EDX spectra of the Cu-doped SnO2 films on glass (a) and on FTO (b) substrates.

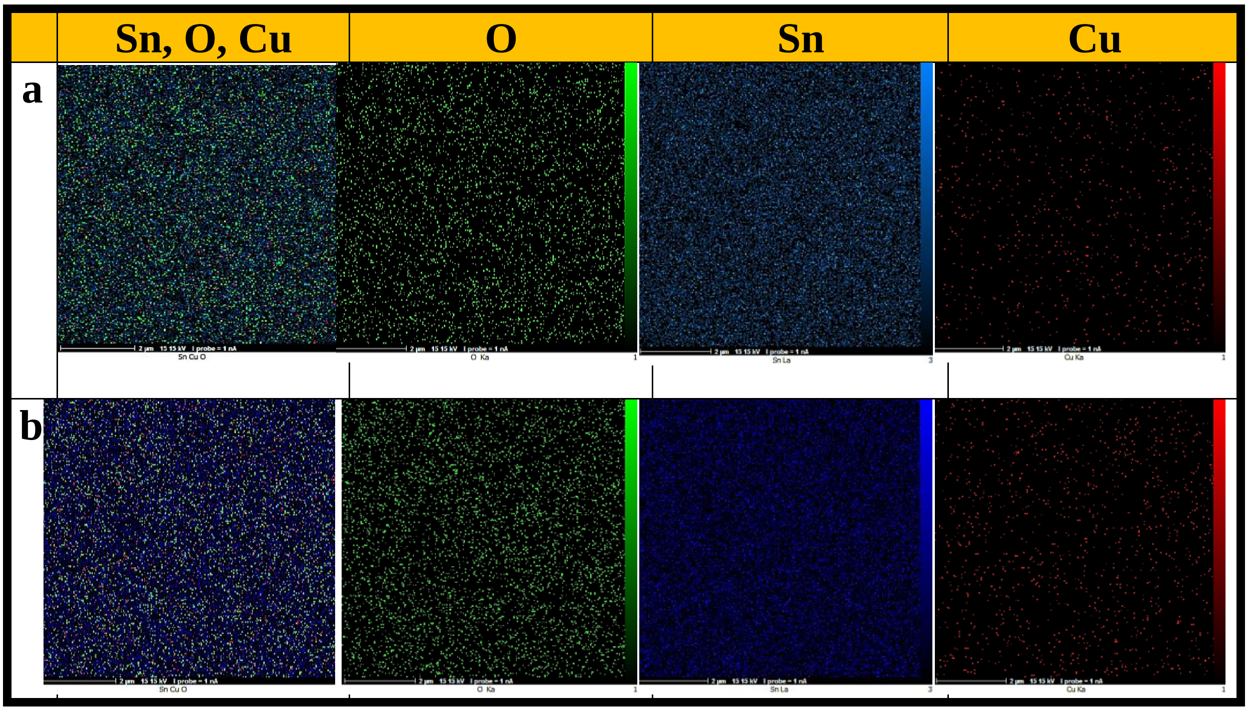


Fig. 5. EDX elemental mapping images of Cu-doped SnO_2 films on glass (a) and on FTO (b) substrates.

The roughness of the films deposited on a glass substrate is more than the roughness of films on the FTO substrate. Generally, larger crystal sizes lead to less grain boundaries and, consequently, reduced surface roughness, which is in agreement with XRD analysis [13, 17]. FESEM analysis is employed to determine the grain size of the prepared samples. The FESEM images are presented in Fig. 3. and the grain sizes of the Cu-doped SnO_2 films deposited on glass and FTO substrates are collected in Table. 2. These results were obtained by calculating the average size of 20 grains for each sample. In the case of Cu-doped SnO_2 films deposited on glass and FTO substrates, the FESEM images show uniform and granular surfaces with tightly packed grains, indicating good crystallinity.

The grain sizes obtained for these films are different, with a particle size distribution of 6 nm for the glass substrate and 11 nm for the FTO substrate which approves the construction of nanograins in the films. On Fig. 4. shows EDX spectra of the prepared Cu-doped SnO_2 films. These figures exhibit the presence of Sn, O and Cu elements in the films deposited on glass and FTO substrates. The composition of elements in the samples is listed and shown in the energy-dispersive X-ray (EDX) spectra in Fig. 4. The EDX spectra show no additional impurity peaks or extra elements, confirming the purity of the samples and confirmed the XRD results. The EDX elemental mapping images of Cu-doped SnO_2 thin films deposited on both glass and FTO substrates were shown in Fig. 5. These images clearly depict the presence and distribution of Sn, O, and Cu in all samples. The absence of any additional elements confirms the purity of the prepared film and is in agreement with the XRD results [2].

4. Conclusion

In this study, Cu-doped SnO_2 films were deposited on glass and FTO substrates by using the RF magnetron sputtering method. The XRD results exhibited that the type of substrate influenced the average crystallite size. AFM analysis also revealed that the type of the substrate influenced by the surface roughness, Utilizing FTO as a substrate yields a more uniform surface, facilitating larger crystallite growth in Cu-doped SnO_2 thin films. The grain size distribution analysis of Cu-doped SnO_2 thin films on different substrates showed that films deposited on FTO exhibited larger grain sizes compared to those on glass substrates. The FTO substrate's lattice mismatch contributed to higher grain sizes and increased surface roughness which is in good agreement with XRD and AFM results. Our findings highlight the choice of substrate plays a crucial role in determining the grain sizes, surface roughness, and structural properties of Cu-doped SnO_2 thin films deposited on glass, FTO substrates. In addition, the prepared nanocrystalline Cu-doped SnO_2 films can be useful for solar cells and gas sensors.

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