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Research Article

Effect of annealing in nitrogen atmosphere on the topographic and structural properties of SnO_2 thin films produced by airbrush

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Abstract:

Tin oxide is a versatile material that is frequently used in temperature, gas, and photo-sensing applications. It is well-known for its beneficial physical and chemical properties. This work describes an economical fabrication technique that uses an airbrush to apply SnO_2 to a glass substrate in ambient circumstances. Important variables were carefully controlled, such as a constant 30 cm distance from the head of the airbrush to the preheated substrates, a 0.5 ml/minute deposition rate, and a 300 °C deposition temperature. Following that, annealing procedures were conducted at 350, 450, and 550 °C for 30 minutes in a nitrogen atmosphere to investigate the effects on optical, morphological, and structural characteristics. X-ray diffraction (XRD) structural investigation revealed a significant increase in crystallinity at higher annealing temperatures, with each thin film consistently displaying cassiterite phase matching with PDF number (PDF 00-041-1445). The produced tin dioxide thin films appear homogeneous in the images taken by the scanning electron microscope (SEM). However, there were visible structural defects. Additionally, an increase in surface roughness with higher annealing temperatures was found by atomic force microscopy (AFM) examinations. Such result holds significant value in fields like gas-sensing and photon absorption, which the surface properties are critical to overall sensor performance. Finally, extensive investigations combined with the economical fabrication approach present a potential path toward customizing tin oxide thin films for a range of applications. The material's advantage for practical applications is improved by the capacity to modify structural and morphological properties through annealing conditions (in a nitrogen gas ambience etc.), demonstrating its potential in emerging fields of technology.

1.Introduction

The exceptional physical and chemical characteristics of metal oxide semiconductors make them broadly applicable in a variety of applications [1]. The selection of material is determined by physical, chemical, technical, and economic factors, such as the need for a clean room and whether a vacuum is necessary [2]. Physical vapor deposition (PVD), atomic layer deposition (ALD), chemical vapor deposition (CVD), Sol-Gel, spin coating, and airbrush spray methods are a few instances of thin film growth procedures [3].

One of the simply used techniques for producing metal oxide semiconductors is the airbrush spray method [4], which only needs a sprayer (Airbrush) and substrate temperature tools. It is an inexpensive and straightforward production method that doesn't need a vacuum environment [5].

Tin oxide is a semi-conductive oxide material that is white, transparent, and highly resistant to both chemical and mechanical forces [6]. Fluorine and indium-doped materials are frequently utilized, particularly in commercial applications [7]. In addition to photovoltaic applications [8], it is used in gas sensors [9]. Thanks to its relatively high energy band gap (E_g = 3.6 eV), elevated mobility, and high donor concentration [10].

2. Experimental

This study employed a simple airbrush as a spray technology to fabricate tin oxide thin films. At 350, 450, and 550 °C, the thin films that developed were annealed in a nitrogen atmosphere. To examine the structural, morphological, and optical characteristics of tin oxide thin films as grown and annealed at various temperatures, XRD, SEM, AFM, and UV-Vis analyses were performed.

2.1 Solution Preparation

To achieve 0.1 M molarity, 1.753 g of high purity (~98%) tin (IV) chloride pentahydrate (Sigma) was dissolved in 50 ml of distilled water. The solution was stirred with a magnetic stirrer for 60 minutes at 300 rpm in ambient conditions. After only 15 to 20 minutes of mixing the solution, it began to be transparent. To improve the homogeneity of the precursor solution, it was mixed for 60 minutes.

2.2 Fabrication Method

A simple airbrush that is shown in Figure 1 was used to spray the prepared solution. The substrate was heated to 300 °C. The distance from the substrate to the head of the airbrush was 30 cm and at an approximate angle of 45 degrees.

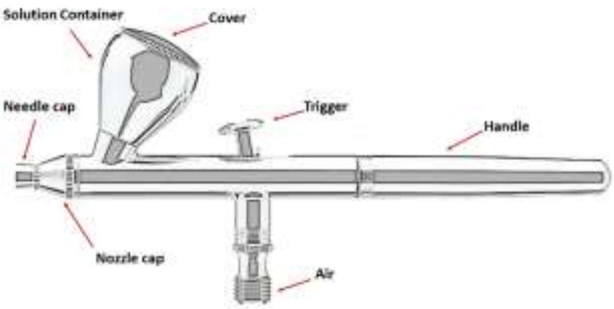

Figure 1. *Airbrush main components*

Measurements using experiments were performed to determine the rate of solution; on average, 0.5 ml of solution takes 60 seconds to spray. A thermocouple sensor was placed close to the substrate to monitor and record the substrate's temperature before, during, and after the deposition procedure. Finally, 50 psi of air pressure was set to ensure a smooth, uniform spray.

2.3 Deposition and Annealing of The Films

After setting the distance and preparing the solution, 5 ml of solution was sprayed to cover the preheated glass substrates. The spraying process continued for 10 minutes at the spray rate and conditions mentioned previously. After completing the spraying process, the substrates were left to cool gradually to room temperature to prevent cracks in the films due to sudden thermal contraction. Next, three out of four samples were chosen for annealing, which is a half-hour process carried out in a nitrogen atmosphere.

3. Results and Discussions

The produced thin films were examined using SEM, XRD, UV-Vis, and AFM. A FEI QUANTA FEG 250 scanning electron microscope was utilized to capture SEM images of SnO_2 thin films as they were grown and after they were annealed at 350, 450, and 550 °C, respectively. Figure 2, 3, 4, and 5 show the SEM images at ×5000 magnification of each sample. Examining each film's SEM images indicates that the tin dioxide film grows uniformly on the glass substrates. Yet again, the images show that the annealing effect leads to the circular structures becoming clear and cracks appearing in the structures which might be valuable for gas sensing applications [11]. The result of the EDS analysis showed the existence of oxygen (O) and tin (Sn) elements. There is no extra element that comes from impurities. The silicon (Si) element EDS signal comes from the glass substrate, see Figure 6.

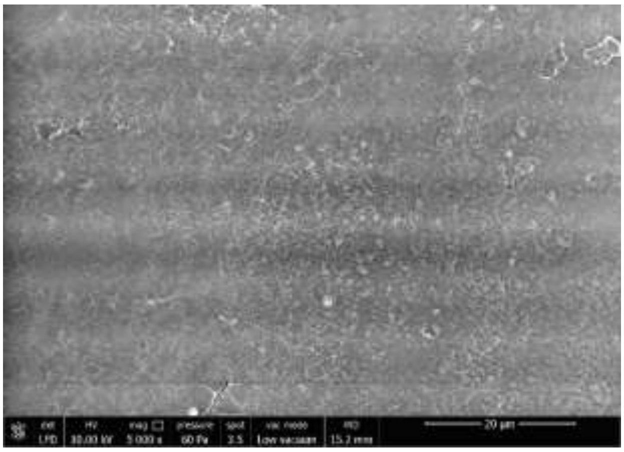

Figure 2. *SEM images of as-grown SnO_2*

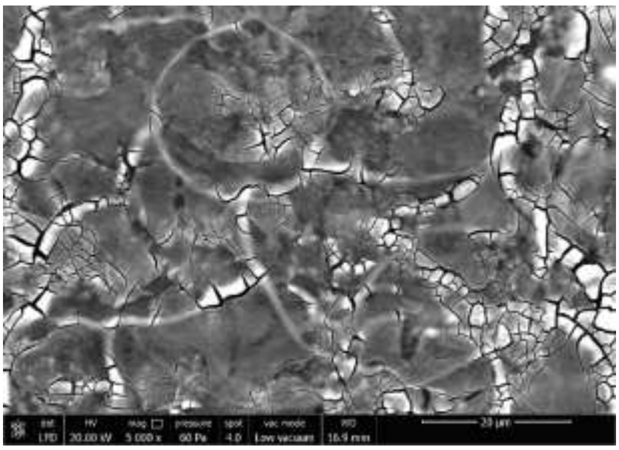

Figure 3. *SEM images of SnO_2 annealed at 350 °C*

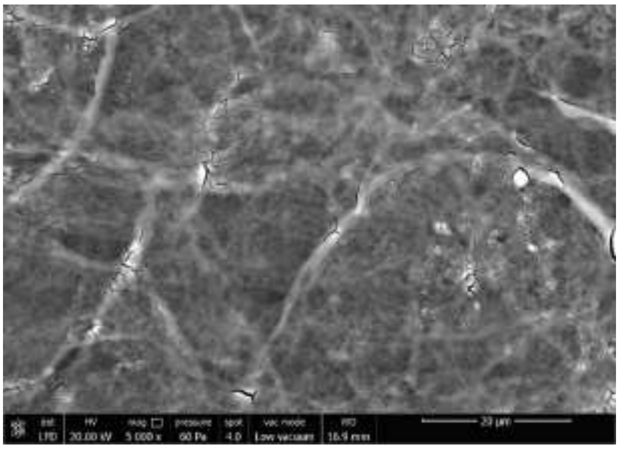

Figure 4. *SEM images of SnO_2 annealed at 450 °C*

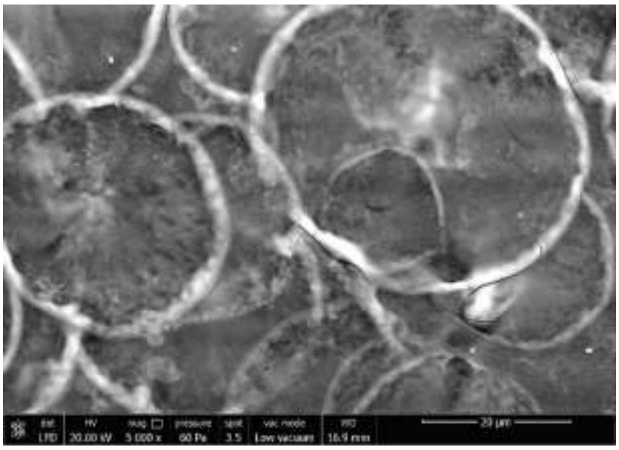

Figure 5. *SEM images of SnO_2 annealed at 550 °C*

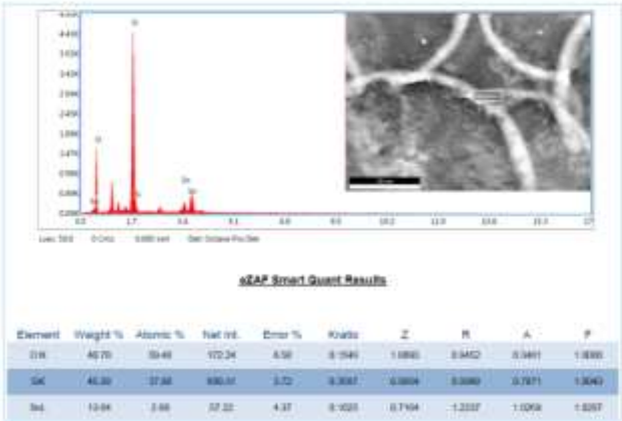

Figure 6. *EDS result of the SnO_2 thin films surface*

The related peaks of the crystallographic phases are displayed in Figures 7 and 8 which are the spectrum of XRD (Bruker D8 Advanced) analysis utilized to determine the crystallographic properties of the produced SnO_2 thin films. With an increase in annealing temperature in a nitrogen, it was found that more peaks started to appear, and the crystal structure became more obvious. This is a scenario that is anticipated. Upon reviewing the literature, it was found that as the annealing temperature increased, the structure went through a change from amorphous to crystalline [12]. It was also found that, for the tetragonal structure, the peak positions agreed well with the standard data with code number of (PDF 00-041-1445).

The crystallite sizes of the as grown and annealed thin films were found to be 25.6, 29.8, 33.6, and 49.9 Å, respectively, using the Scherrer formula. These findings showed that, as anticipated, annealing procedure increased the crystallinity.

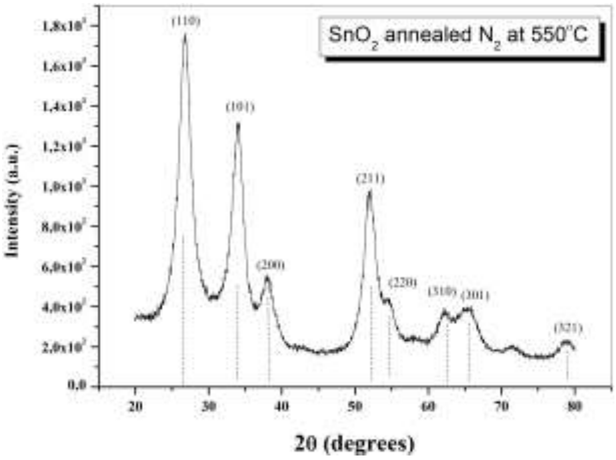

Figure 7. *XRD patterns of SnO_2 thin films annealed at 550 °C*

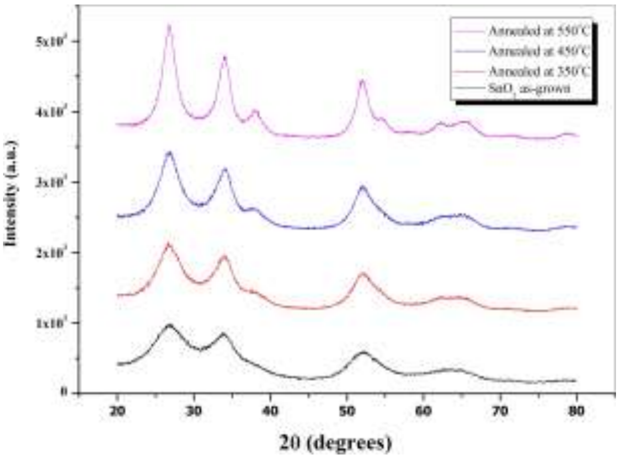

Figure 8. *XRD patterns of as annealed at different temperatures and as grown SnO_2 thin films*

The band gap values of SnO_2 thin films were derived by the Tauc plots shown in Figures 9, 10, 11, and 12. It was found that as the annealing temperature increased, the band gap values decreased. The situation showed an expected decrease in band gap values as the annealing temperature increased [13]. The calculated band gap values of SnO_2 thin film samples that were grown, and annealed at 350, 450, and 550 °C were 3.54, 3.48, 3.44, and 3.24 eV, respectively. All calculated values of the band gap energy fall within the range of the band gap energy of tin dioxide [14].

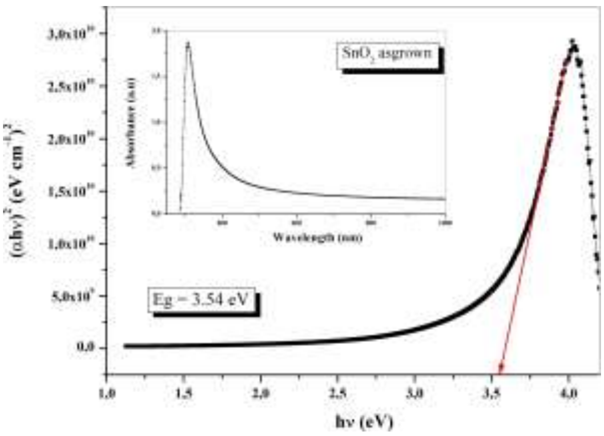

Figure 9. *Band gap value of as-grown SnO_2*

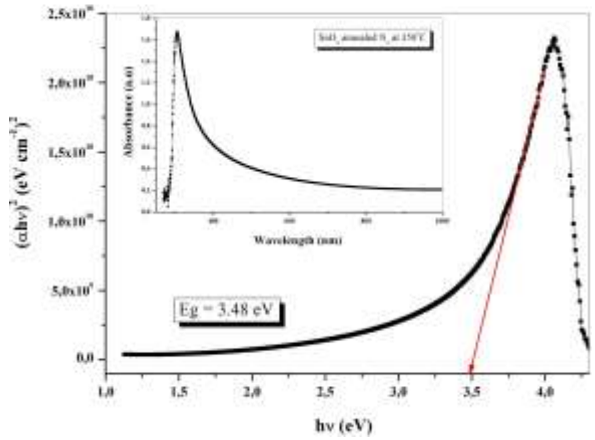

Figure 10. *Band gap value of SnO_2 annealed at 350°C*

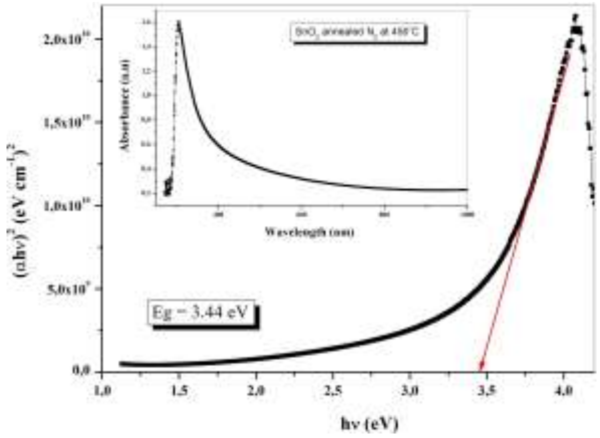

Figure 11. *Band gap value of SnO_2 annealed at 450°C*

The surface roughness parameters of the fabricated SnO_2 films were investigated because of their importance in gas sensor applications [15]. This part of the study was carried out using ez-AFM Nanomagnetics device. Each of the samples was scanned in an area of 10×10 μm^2. AFM images of SnO_2 as grown, annealed at 350, 450, and 550 °C were taken as can be seen in Figures 13, 14, 15 and 16.

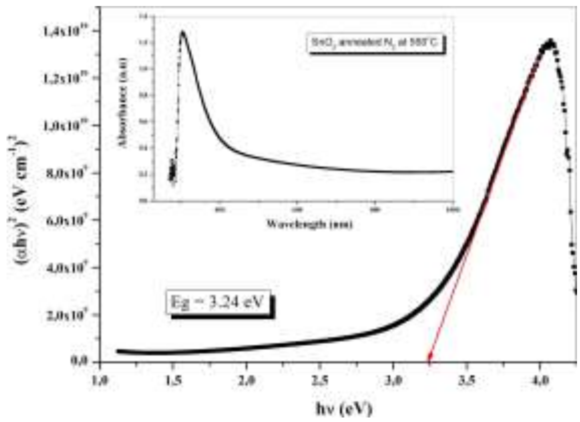

Figure 12. *Band gap value of SnO_2 annealed at 550°C*

It was found that as the annealing temperature increased, the films' surface roughness increased. Using the AFM analysis, the surface roughness parameter Ra of every sample was determined. It was found to be 84 nm for as-grown SnO_2 thin film, 103, 135, and 169 nm for SnO_2 thin films that were annealed at 350, 450, and 550 °C, respectively.

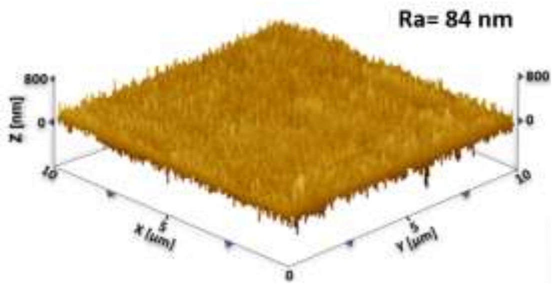

Figure 13. *3D AFM image and roughness value of as grown SnO_2*

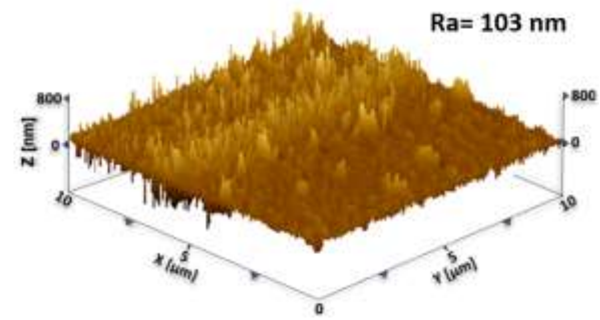

Figure 14. *3D AFM image and roughness value of SnO_2 annealed at 350 °C*

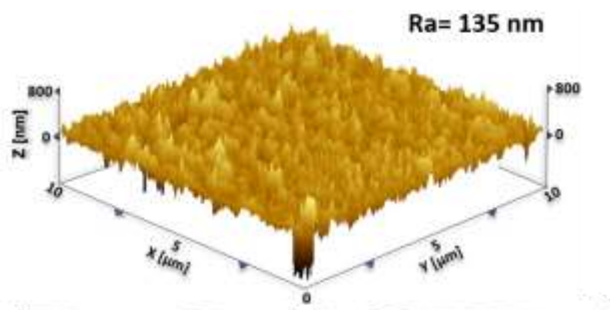

Figure 15. *3D AFM image and roughness value of SnO_2 annealed at 450 °C*

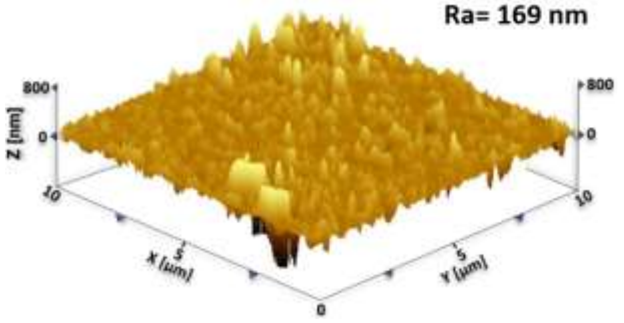

Figure 16. *3D AFM image and roughness value of SnO_2 annealed at 550 °C*

4. Conclusions

SnO_2 thin films were successfully produced using an efficient and inexpensive spraying method (airbrush). The surface characteristics and crystal structure of the generated film were investigated. It was evident from the XRD analysis results that the crystallinity increased with an increase in the annealing temperature in nitrogen atmosphere. Every thin film's crystal structure was identified in the tetragonal structure (PDF 00-041-1445). The SEM images demonstrated the presence of cracks in the structure. Cracks result from the overlapping rings, which are the edges of the micro sized droplets. Uniform growth of each thin film on the glass substrate was seen in the SEM images. By using the AFM analysis, the average surface roughness parameters of each sample are 84 nm for as-grown SnO_2 films and 103, 135, and 169 nm for SnO_2 films that had been annealed at 350, 450, and 550 °C, respectively. The produced tin dioxide thin film can be used in gas-sensor applications. More research is needed to fully understand the annealing process effect in nitrogen atmosphere. In addition, more research is required to understand this inexpensive deposition technique, which may eventually contribute to more affordable production of sensors in general and gas sensors in particular.

Author Statements:

Ethical approval: The conducted research is not related to either human or animal use.

Conflict of interest: The author declares that there is no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Data availability statement: The data that supports the findings of this study are available on request from the corresponding author.

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