SEM and AFM Characterizing the Roots Morphology of a ZnO(Sn) Thin Film Deposited on a Silicon Substrate by a Sol-Gel Spin Coating Process

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Abstract :

ZnO(Sn) thin films were deposited on Silicon substrates by coating prepared sols with varying amounts of Zn(CH3COO)2·2H2O and SnCl2, SnCl4 (0, 1, 2, and 5%). The films were characterized using X-ray diffractometer (XRD), scanning electron microscopy (SEM), and UV-Vis spectrophotometer. The XRD spectra indicated the presence of a wurtzite hexagonal structure in all the thin films prepared. SEM images revealed root-like morphology on the surface of thin films, with the shortest root diameter measuring between 0.15-0.35 m. The identification of the elements present in the samples was carried out by energy dispersive X-ray spectroscopy (EDX).

Keywords : Solgel; ZnO; deep coating ; scanning electron microscopy(SEM); X-ray diffractometer XRD; energy dispersive X-ray spectroscopy EDX ; rootlike morphology.

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1-Introduction:

Zinc oxide (ZnO) is an important material in modern technology with a wide range of applications as a semiconductor, with a wide bandgap and high electron mobility [1-2], in an optoelectronic ZnO is transparent in the visible region of the electromagnetic spectrum and has a high refractive index, It's also a promising material for sensor applications due to its sensitivity to various environmental parameters such as temperature, humidity and gases[3], ZnO has demonstrated antimicrobial activity, which makes it useful in various applications, including medical implants, food packaging and textiles, and energy storage[4,5]. It is being investigated as an electrode material for energy storage devices such as batteries and supercapacitors due to its high specific surface area and electrochemical strength [3,6].

ZnO thin films have been produced by various techniques, including reactive sputtering, spray pyrolysis, zinc oxidation, electrodeposition, pulsed laser deposition , chemical vapor deposition (CVD), and the sol-gel method [7-16].

The sol-gel technique has emerged as a promising processing method because of its simplicity and high efficiency in preparing thin, transparent, homogeneous oxide films with numerous multicomponent compositions on various substrates. The low cost and the possibility of modifying the refractive index and film thickness by varying the synthesis parameters make it particularly advantageous[8,11-19].

2. Materials and Method:

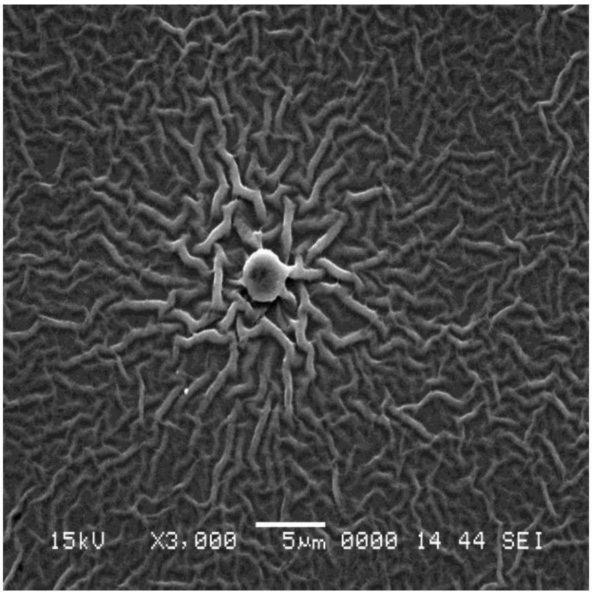
ZnO and ZnO(Sn) thin films were synthesized by the sol-gel spin coating method. As a starting material, zinc acetate dihydrate (Zn(CH3COO)2·2H2O) was dissolved in 2-propanol with a concentration of 0.5 mol L^{-1}. Monoethanolamine (MEA) was wisely dropped into the solution and stirred at room temperature at 70 C for 30 min. For doped films, Slinicium chloroacetate (SnCl2·9H2O) was added to the solution with a molar percentage, fixed at 0, 1, 2, 3, and 4% moles and were then denoted as ZnO, ZS1, ZS2, ZS3, and ZS4, respectively. The precursor solution was deposited onto a silicon substrate by spin coating, annealed at a temperature in a convolution oven of 350° C, and left for 1 h.

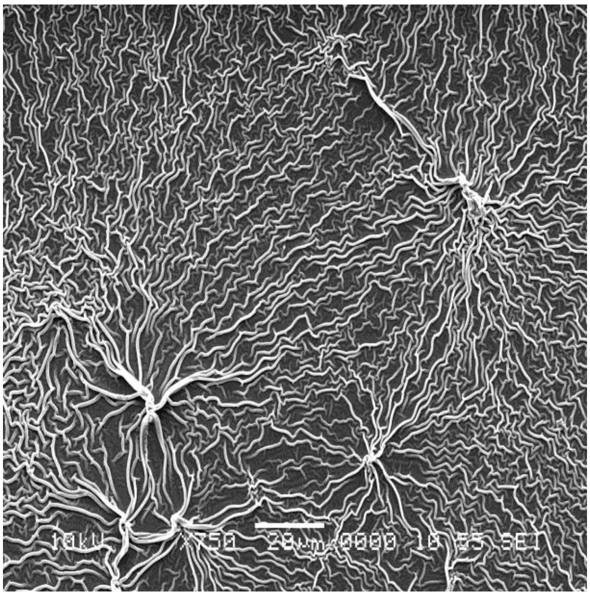
The sol-gel method is a widely used technique for preparing thin films, including ZnO (zinc oxide) thin films. It involves preparing the sol by dissolving the zinc precursor in a solvent, stabilizing it with a stabilizing agent, and depositing it onto the substrate using techniques like spin coating, dip coating, or spray coating. After deposition, the substrate undergoes an annealing process, heating it at a specific temperature in a controlled atmosphere to remove solvent and form a solid ZnO film. Additional post-annealing treatments, such as rapid thermal annealing or laser annealing, can be applied to improve the crystallinity and properties of the ZnO thin film.

It's important to note that the specific details of the sol-gel process, such as the concentration of precursors, solvent, pH, deposition technique, and annealing conditions, may vary depending on the desired properties and application of the ZnO thin film. Optimization and characterization of the thin film properties, such as crystal structure, thickness, and morphology, can be performed using techniques like X-ray diffraction (XRD), scanning electron microscopy (SEM), and optical measurements.

Sol-gel spin coating was used to create thin films of ZnO and ZnO(Sn). Starting with a 0.5 mol L^{-1} concentration of 2-propanol, zinc acetate dihydrate (Zn(CH3COO)22H2O) was dissolved therein. The solution was carefully added, and monoethanolamine (MEA) was agitated for 30 minutes at room temperature at 70 C. SnCl29H2O was added to the solution at molar concentrations of 0, 1, 2, 3, and 4% moles to create doped films, which were subsequently designated as ZnO, ZS1, ZS2, ZS3, and ZS4, respectively. Spin coating was used to deposit the precursor solution onto a silicon substrate, and it was then annealed for one hour at 350° C in a convection oven.

Prior to the deposition, the silicon substrate is (111) Si wafers (p-boron 0.01-0.1 Ω⁄cm), 335-405 μm thick, on SILTRONIX substrates. The Si samples were cleaned with organic solutions and etched with a dilute buffered 10% HF solution to remove the native oxide on the Si surface prior to being loaded into the spin-coating system. The prepared thin films were characterized by X-ray diffraction (XRD) using Shimadzu Maxima 7000 (Cu-K□ wavelength: 1.5405A). The detectionangles were ranging from 2□ = 10 to 90 degree. The morphology of the thin films was revealed using scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDX), which measures the energy of the emitted X-rays and identifies the elements present in the sample. Atomic force microscopy (AFM) was used to characterize the nanoparticles.





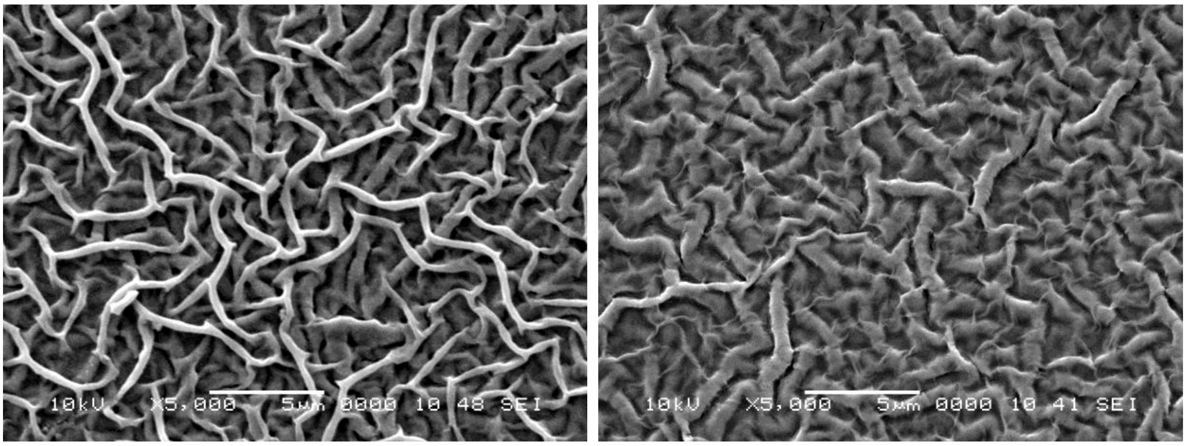


Figure 1: Highly Magnified SEM Image of Zinc Oxide (ZnO) Layer with Wavy Morphology and Root-Like Structures.

3-Results and Discussion

3-1. Scanning Electron Microscope characterization (SEM)

The image provided shows a highly magnified view of a zinc oxide (ZnO) layer, likely taken with a scanning electron microscope (SEM) given the SEI (Secondary Electron Imaging) label.

The morphology of the ZnO layer shows a distinct wavy or wrinkled appearance, which may be due to the following reasons to the specific conditions during the sol-gel synthesis or to post-synthesis treatments, such as annealing. These morphologies can affect properties such as surface area and, in the case of ZnO, photocatalytic activity. The structures appear to be relatively uniform in width and distribution across the surface. Our recommendation is the implementation of a standardized synthesis and deposition process.

The image includes a scale bar indicating a 5µm width at 5,000x magnification, which allows for an understanding of the relative size of the to understand the relative size of the fine structures.

SEM examination of all prepared samples revealed that the films have a root-like morphology. In addition, it was observed that all roots terminate in a spherical knot, with multiple knots observed in one sample. The diameters of the roots vary, but on average they are in the range of 120 nanometers to 310 nanometers. According to reference [1], "Heri Sutanto" explains that the layer of crystalline grains was formed during the deposition process on a glass substrate.

There is a different temperature for the first and other layers that affect how they interact with each other. In a process called radical formation, many molecules combine with other molecules to form a long structure of zinc oxide[1].

It should be noted that the properties of ZnO can potentially have an effect on its morphology. For example, a structure with waviness or porosity can increase the surface area, which is advantageous for a variety of applications such as gas sensors, photocatalysts, or solar cells, which depend on interactions with the material surface for their functionality.

3-2. Atomic Force Microscopy (AFM) and Energy dispersive X-ray spectroscopy (EDS) characterization.

EDAX ZAF QUANTIFICATION STANDARDLESS

Element	*Wt %*	*At %*
O K	34.00	42.72
ZnK	63.44	55.46
SiK	02.56	01.83

Table 1: Table summarizing the spectrum spectroscopy (EDS)

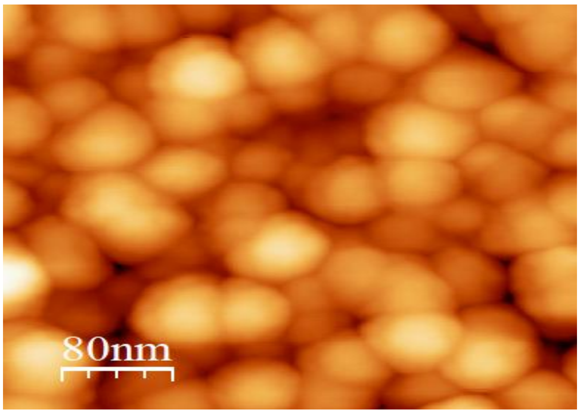


figure 2 : AFM Images of ZnO Thin Films on p-Si Substrates Prepared with Different SnCl2 and SnCl4 Concentrations

To study the variation in morphologies of ZnO thin films deposited on p-Si substrates using a solution prepared with different amounts of SnCl2, SnCl4, atomic force microscopy (AFM) was performed. AFM images showing nanometer-sized particles with diameters ranging from 20 to 100 nm are shown in Figure 2.

Along with the SEM images, energy dispersive X-ray spectroscopy (EDS) table 1 spectra of the ZnO:Sn films were obtained (Figure S2). Although signals from Zn, O, and Sn elements were seen in the spectrum, the atomic ratios of Sn were different than expected. This may be due to the loss of Sn during the high temperature annealing process, which leads to the formation of cracks and voids on the surface.

3-2. Structural analysis XRD characterization.

The XRD patterns of ZnO:Sn thin films on a silicon substrate show well-matched diffraction peaks, with three main peaks indexed to (100), (002), and (101) planes. The addition of SnCl2 to sol shifts the peaks towards lower angles, indicating an increase in interplanar distance. The most intensive peaks belong to the (002) plane, with preferential orientation along the c-axis perpendicular to the substrate.

No other peaks associated with Sn phases were detected. Three key peaks at approximately 2θ ~ 31°, 34°, and 36° were assigned to planes (100), (002), and (101), respectively [17-21].

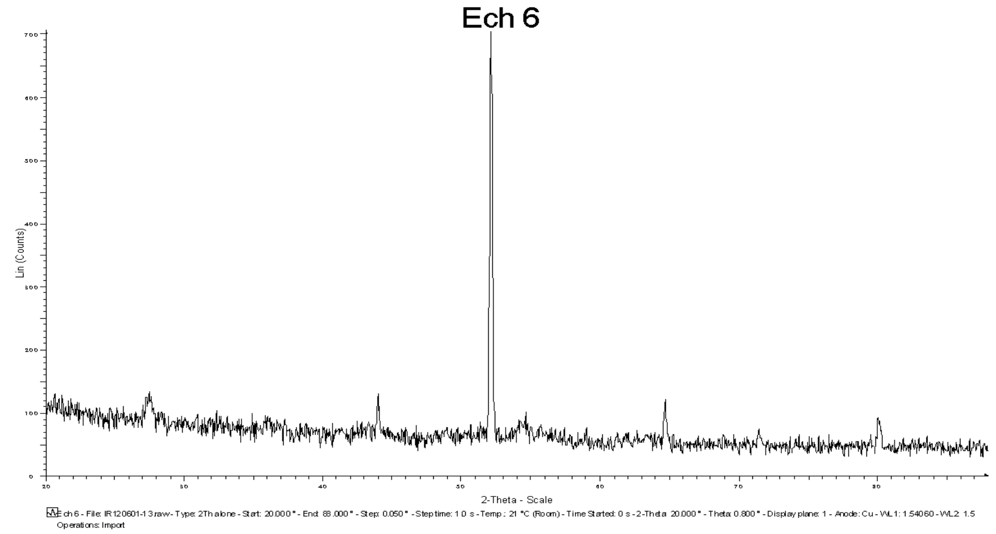


Figure 3 : XRD patterns of ZnO:Sn films

4-Conclusion :

The paper describes the synthesis and characterization of ZnO and ZnO(Sn) thin films using the sol-gel spin coating method. Different concentrations of zinc acetate dihydrate and SnCl2 were used as precursors, and the films were deposited on silicon substrates and annealed to form solid ZnO films. The study underscores the importance of sol-gel processes in thin film preparation, emphasizing parameters like precursor concentration, solvent, pH, deposition technique, and annealing conditions.

SEM analysis of the ZnO layer reveals a unique morphology with root-like structures, suggesting potential applications in gas sensors and photocatalysts for solar cells. Standardized synthesis and deposition processes are recommended for consistent results. AFM images show nanometer-sized particles in ZnO thin films on p-Si substrates prepared with different SnCl2 and SnCl4 concentrations. EDS analysis confirms the presence of oxygen, zinc, and silicon elements. High-temperature annealing leads to the loss of Sn, resulting in cracks and voids, affecting atomic ratios in the spectrum. XRD patterns of ZnO:Sn thin films exhibit well-matched diffraction peaks, with the addition of SnCl2 shifting peaks to lower angles, indicating increased interplanar spacing and a preferred orientation along the c axis[24-34].

In conclusion, the sol-gel spin coating method proves effective in synthesizing ZnO and ZnO(Sn) thin films with controlled properties. Standardization is recommended for consistent results. The study contributes insights into the structural and morphological aspects of these thin films, suggesting potential applications in various technological fields.

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