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SPRAY PYROLYSIS GROWTH OF ZnSnO THIN FILMS: STRUCTURAL AND MORPHOLOGICAL ANALYSIS

CREȘTEREA FILMELOR SUBȚIRI DE ZnSnO PRIN SPRAY PIROLIZĂ: ANALIZA STRUCTURALĂ ȘI MORFOLOGICĂ

Vadim MORARI[1] e-mail: vadim.morari@iien.utm.md ORCID ID: 0000-0003-3625-251X

Emil V. RUSU[2] e-mail: emil.rusu@iien.utm.md ORCID ID: 0000-0001-9010-492

[1,2]IIEN „D. Ghițu”, Technical University of Moldova

Abstract: *Zinc tin oxide (ZnSnO) thin films were synthesized at different deposition times via spray pyrolysis to investigate the effect of film thickness on structural and morphological properties. SEM surface and cross-sectional measurements showed that with increasing deposition time the film thickness increased from 80 nm (3 min) to 320 nm (10 min). At the same time, the surface morphology evolved from uniform, compact layers with smaller crystallites to denser structures with larger grains. This transition was attributed to the competition between nucleation and growth during film formation. XRD analysis confirmed the coexistence of Zn_2SnO_4 and SnO_2 phases in all samples. With increasing thickness, the relative intensity of Zn_2SnO_4 peaks increased while SnO_2 peaks decreased, indicating preferential stabilization of Zn_2SnO_4 in thicker films. In particular, the (110) peak of SnO_2 diminished, whereas the (220) peak of Zn_2SnO_4 became more pronounced, evidencing progressive phase transformation. These results indicate a clear correlation between deposition time, film thickness, crystallite size, and phase composition, while the optical transparency decreases from 84% to 72% as the thickness increases from 80 nm to 320 nm.*

Keywords: *Films thickness, SEM, Transmittance, XRD pattern, ZnSnO.*

1. INTRODUCTION

Oxide thin films represent a wide class of functional materials with remarkable optical, electrical, and catalytic properties. They are widely applied in optoelectronic devices, solar cells [1], sensors [2], and protective coatings [3], due to their stability and tunable characteristics. The ability to engineer band gap [4], conductivity [5], and surface morphology [6] makes oxide films highly adaptable for next-generation technologies. Recent studies highlight their role in transparent electronics [7], UV detectors [8], and flexible devices [9]. Therefore, the development of oxide-based thin films remains a key research direction in modern materials science. Among these materials, ZnSnO (zinc–tin–oxide) has emerged as a promising candidate due to its favorable semiconductor [10] behavior and environmental stability.

The presence of both Zn and Sn cations allows tailoring of electronic structure and crystallinity, enabling applications in transparent conducting oxides and thin-film transistors. ZnSnO thin films also exhibit high optical transmittance in the visible range combined with controllable electrical conductivity [11]. Such properties make them suitable for integration into energy conversion devices [12], gas sensors [13], and optoelectronic systems [14]. As a result, ZnSnO continues to attract growing attention as a versatile oxide material with technological potential. There are many deposition techniques for fabricating ZnSnO thin films, such as pulsed laser deposition [15], molecular beam epitaxy [16], and magnetron sputtering [17], which usually require sophisticated equipment and high cost.

In contrast, spray pyrolysis is a simple, low-cost, and scalable method that enables the growth of uniform thin films with controllable composition and morphology [18]. In this work ZnSnO thin films were deposited using the spray pyrolysis technique for different durations to investigate the influence of deposition time on their morphology, thickness, and structural properties.

2. MATERIALS AND METHODS

ZnSnO thin films were deposited via the spray pyrolysis technique. A precursor solution was prepared by dissolving 0.25 M zinc nitrate [$Zn(NO_3)_2$] and 0.25 M tin chloride [$SnCl_4$] in ethanol [C_2H_5OH]. The solutions were mixed in a Zn2:1Sn molar ratio using an ultrasonic bath for 30 minutes at 50 - 60 °C prior to deposition. The resulting solution was sprayed onto n-Si (100) substrates, using oxygen gas (O_2) as the carrier with an outlet pressure of 0.05 Bar. During deposition, the substrate temperature was maintained between at 480 °C, while the spray nozzle-to-substrate distance was fixed at 4 cm to ensure uniform droplet distribution. Film thickness was controlled by the precursor injection rate (0.5 ml/min) and the deposition time, which varied between 3 and 10 minutes. Prior to deposition, the Si substrates were cleaned sequentially with acetone, ethanol, and deionized water, followed by drying in nitrogen gas. After deposition, the films were annealed in air at 500 °C for 1 hour to improve crystallinity and eliminate residual organic species. The structural and morphological properties of the films were subsequently characterized using X-ray diffraction (XRD) and scanning electron microscopy (SEM).

3. RESULTS AND DISCUSSIONS

ZnSnO thin films were prepared by spray pyrolysis technique at different deposition times (3, 5, 7 and 10 min) to examine their morphological and structural variations. Surface SEM images were analyzed to correlate structural evolution with the growth process. SEM images of the films grown at different deposition times are shown in Figure 1. At a deposition time of 3 minutes (Figure 1 a), the film exhibited a smooth and relatively uniform morphology with clearly distinguishable crystallites.

The average thickness measured in cross-section was about 80 nm, indicating the formation of a thin and compact initial layer. When the deposition time increased to 5 minutes (Figure 1 b), the thickness reached 150 nm and the surface became slightly more textured, showing the development of grain boundaries. For the sample deposited for 7 minutes (Figure 1c), the film thickness increased to 250 nm, accompanied by a visible increase in crystallite size. The SEM micrographs revealed a denser and more ordered structure, suggesting that the accelerated growth rate promotes the coalescence of larger grains. At a deposition time of 10 minutes (Figure 1d), the ZnSnO layer reached 320 nm, and the surface morphology became even clearer. The crystallites appeared larger, and the film showed a more ordered structure compared to shorter deposition times. This trend indicates that longer deposition not only favors thickness growth but also stimulates an increase in crystallite size. The increase in crystallite size with increasing thickness can be attributed to the competition between nucleation and growth processes. At short deposition times, crystallites have more space to grow laterally, forming smaller grains. As deposition continues, the film becomes denser, limiting the lateral expansion of grains and resulting in larger crystallite sizes.

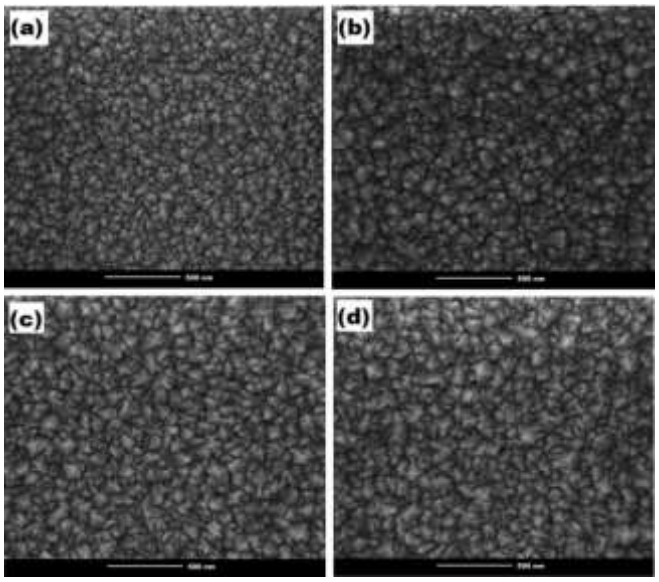


Figure 1. SEM images of ZnSnO thin films deposited by spray pyrolysis method for different times: a) 3 min, b) 5 min, c) 7 min, and d) 10 min.

This structural evolution plays a crucial role in determining the optical and electrical properties of ZnSnO films. Therefore, achieving an optimal balance between film thickness and crystal ordering is crucial for the practical implementation of these films and the enhancement of device performance. Overall, SEM analysis demonstrates that thin ZnSnO films evolve from ordered layers with low thickness to ordered nanostructures with high thickness and larger crystallites. These findings highlight the strong dependence of microstructural properties on deposition time, which must be carefully controlled for targeted applications. The XRD patterns (Figure 2) reveal the coexistence of two crystalline phases, Zn_2SnO_4 and SnO_2, for all deposition times. With increasing deposition time, and consequently increasing film thickness, the diffraction peaks corresponding to Zn_2SnO_4 become more intense, indicating an enhancement of its crystallinity and preferential growth. In contrast, the relative intensity of the SnO_2 peaks decreases, suggesting that the prolonged deposition favors the formation and stabilization of the Zn_2SnO_4 phase at the expense of SnO_2. This structural evolution highlights a phase transformation tendency driven by film thickness and growth dynamics.

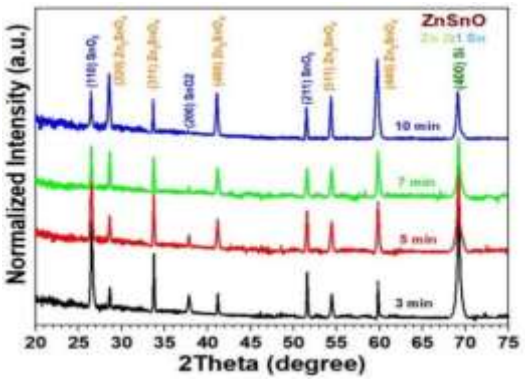


Figure 2. XRD patterns of ZnSnO thin films deposited by spray pyrolysis method at different times: a) 3 min, b) 5 min, c) 7 min, and d) 10 min.

Figure 3 displays the (110) and (220) diffraction peaks, where it can be clearly seen that, as the film thickness increases, the intensity of the (110) peak associated with the SnO_2 phase decreases, whereas the intensity of the (220) peak corresponding to the Zn_2SnO_4 phase increases. With increasing thickness, the diffusion and intermixing of Zn and Sn atoms become more pronounced, which promotes the stabilization of the ternary Zn_2SnO_4 phase. At the same time, the reduction of SnO_2 peak intensity suggests that excess Sn is gradually incorporated into the spinel lattice, leading to improved phase homogeneity in thicker films. This behavior indicates a progressive suppression of the SnO_2 phase and a preferential crystallization of Zn_2SnO_4 in thicker films.

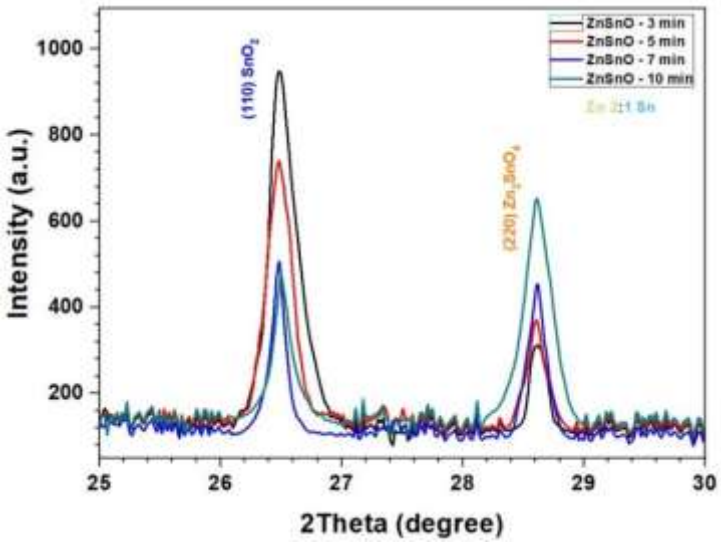


Figure 3. Magnified XRD patterns highlighting the (110) and (220) diffraction peaks of ZnSnO thin films by spray pyrolysis method at different deposition times.

To highlight the optical transparency of these films, given the previously discussed variations in thickness, figure 4 presents the optical transmittance spectra as a function of photon energy (eV) for thin ZnSnO films deposited at different times (3, 5, and 10 minutes). All samples exhibit a high level of transparency in the visible region, with average transmittance values of approximately 84%, 75%, and 72%, respectively. As the deposition time increases, a slight decrease in transmittance is observed, which can be attributed to the increased film thickness leading to enhanced light scattering and absorption processes within the material. The transmittance spectra display a similar shape for all samples, with a sharp absorption edge appearing around 3.7–3.8 eV. The position of this edge remains essentially unchanged regardless of deposition time, indicating that the optical band gap of the ZnSnO films is not significantly affected by thickness variations. This stability in the absorption edge suggests good compositional uniformity and consistent film quality across the investigated samples. Overall, the high transmittance and stable optical behavior confirm the suitability of ZnSnO films for use in optoelectronic and photovoltaic applications, such as transparent electrodes or window layers in solar cells.

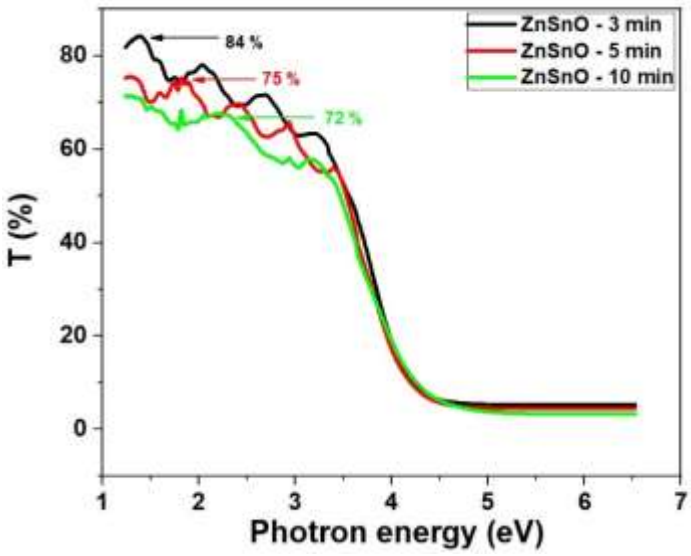


Figure 4. Transmittance spectra of ZnSnO thin films deposited by spray pyrolysis method obtained at different times: 3 min, 5 min, 10 min.

4. CONCLUSIONS

ZnSnO thin films deposited at different times exhibited a clear dependence of their structural and morphological properties on film thickness. SEM observations showed that as the deposition time increased, the films grew from 80 nm to 320 nm, while their surface morphology evolved from relatively uniform layers with larger crystallites to denser but more disordered structures with smaller grains. This microstructural change was attributed to the competition between nucleation and growth processes during film formation. XRD analysis revealed the coexistence of Zn_2SnO_4 and SnO_2 phases in all samples, with a noticeable shift in phase balance as the thickness increased. The intensity of Zn_2SnO_4 diffraction peaks became stronger, while the peaks of SnO_2 gradually diminished, indicating a preferential stabilization of the Zn_2SnO_4 phase in thicker films. This transformation suggests that prolonged deposition enhances the interdiffusion of Zn and Sn atoms, resulting in improved phase homogeneity. A clear correlation is observed between deposition time, film thickness, crystallite size, and phase composition, with optical transparency decreasing from 84% to 72% as the thickness increases from 80 nm to 320 nm. Overall, the study demonstrates that deposition time is a critical parameter for controlling the microstructure and phase composition of ZnSnO thin films, providing valuable guidance for their optimization in optoelectronic applications.

REFERENCES:

1. RABISANKAR, D., MAHENDER, P., KUMAR, S., ANKUR, S. Preparation of ZnO layer for solar cell application. In: *Materials Today: Proceedings* 2021, Vol. 41, Part 2, pp. 161-164. https://doi.org/-10.1016/j.matpr.2020.08.448.
2. KUMAR, R., MAMTA, K. R., SINGH, V.N. SnO_2-Based NO_2 Gas Sensor with Outstanding Sensing Performance at Room Temperature. In: *Micromachines* 2023, 14, 728. https://doi.org/10.3390/mi140-40728.

3. WORSLEY, M., SMULDERS, V., MEI, B. Controlled Synthesis of Chromium-Oxide-Based Protective Layers on Pt: Influence of Layer Thickness on Selectivity. In: *Catalysts* 2022, 12, 1077. https://-doi.org/10.3390/catal12101077.
4. MORARI, V., RUSU, E. V., URSAKI, V. V., NIELSCH, K., TIGINYANU I. M. Aerosol spray deposited wurtzite ZnMgO alloy films with MgO nanocrystalline inclusions. In: *IFMBE Proceedings – Springer Nature Switzerland AG* 2022, Vol. 87, p. 32-39. https://doi.org/10.1007/978-3-030-92328-0_5.
5. WANG, Y., ZHANG, H., ZHANG, X., ZHOU, Z., WANG, L. Tuning Electrical and Optical Properties of SnO_2 Thin Films by Dual-Doping Al and Sb. In: *Coatings* 2025, 15, 669. https://doi.org/10.3390/-coatings15060669.
6. IZYDORCZYK, W., IZYDORCZYK, J. Structure, Surface Morphology, Chemical Composition, and Sensing Properties of SnO_2 Thin Films in an Oxidizing Atmosphere. In: *Sensors* 2021, 21, 5741. https://doi.org/10.3390/s21175741
7. PATEL, J., SHARME, R. K., QUIJADA, M. A., RANA, M. M. A Review of Transparent Conducting Films (TCFs): Prospective ITO and AZO Deposition Methods and Applications. In: *Nanomaterials* 2024, 14, 2013. https://doi.org/10.3390/nano14242013
8. MORARI, V., URSAKI, V. V., RUSU, E V., ZALAMAI, V. V., COLPO, P., TIGINYANU, I. M. Spin-Coating and Aerosol Spray Pyrolysis Processed $Zn_{1-x}Mg_xO$ Films for UV Detector Applications. In: *Nanomaterials* 2022, Vol. 12, Issue 18, 3209. https://doi.org/10.3390/nano12183209.
9. SHUANGYUAN, L., XIAOFEI, X., JIE, J. Flexible transparent ITO thin film with high conductivity and high-temperature resistance. In: *Ceramics International* 2024, Vol. 50, Issue 22, Part C, p. 47649-47654. https://doi.org/10.1016/j.ceramint.2024.09.110.
10. Pan, W., Zhang, G., Liu, X., Song, K., Ning, L., Li, S., Chen, L., Zhang, X., Huang, T., Yang, H., et al. Achieving High Performance of ZnSnO Thin-Film Transistor via Homojunction Strategy. In: *Micromachines* 2023, 14, 2144. https://doi.org/10.3390/mi14122144
11. DRIDI, R., MRABET, C., LABIDI, A., MAHDHI, N., AMLOUK, A., AMLOUK, M. Electrical conductivity of Zn_2SnO_4 thin films along with wettability and EtOH-sensing. In: *Journal of Alloys and Compounds* 2017, Vol 708, p. 769-779. https://doi.org/10.1016/j.jallcom.2017.03.055.
12. JAE, Y. C., et all. Atomic-layer-deposited ZnSnO buffer layers for kesterite solar cells: Impact of Zn/(Zn+Sn) ratio on device performance. In: *Journal of Alloys and Compounds* 2022, Vol. 895, Part 2, 162651. https://doi.org/10.1016/j.jallcom.2021.162651.
13. JIAXIN, D., WEIMIN, S., QUANBI, Z., GANG, Z., XINZHEN, W. Facile synthesis of nano-porous $ZnSnO_3$ cubes for excellent gas sensing properties toward n-butanol. In: *Ceramics International* 2025. ISSN 0272-8842. https://doi.org/10.1016/j.ceramint.2025.08.274.
14. GUO, L., WANG, Q., WANG, C., CHU, X., HAO, Y., CHI, Y., YANG, X. Effect of Ga Doping on the Stability and Optoelectronic Properties of ZnSnO Thin Film Transistor. In: *Micromachines* 2024, 15, 1445. https://doi.org/10.3390/mi15121445.
15. HONGYAN, Z., BIAO, Z., RONGRONG, C., XINYU, H., et all. High-performance solar-blind photodetectors based on Ta-doped $ZnSnO_3$ single crystal thin films. In: *Journal of Alloys and Compounds* 2024, Vol. 997, 174854. https://doi.org/10.1016/j.jallcom.2024.174854.

16. HIROYA, M., KOHEI, F., ATSUSHI, T. High-mobility field-effect transistor based on crystalline $ZnSnO_3$ thin films. In: *AIP Advances* 2018, Vol. 8, 5, 055327. https://doi.org/10.1063/1.5034403
17. SHIQIAN, D., TAO, W., RAN, L., et all. Preparation and electrical properties of N-doped ZnSnO thin film transistors. In: *Journal of Alloys and Compounds* 2018, Vol. 745, p. 256-261. https://doi.-org/10.1016/j.jallcom.2018.02.198.
18. MORARI, V., MONAICO, E. I., MONAICO, E. V., RUSU, E V., URSAKI, V. V. Interrelationships Between Topology and Wettability of Nanostructured Composite Wide Bandgap Metal Oxide Films Prepared by Spray Pyrolysis. In: *Applied Sciences* 2025, Vol. 15, 5, 2381. https://doi.org/10.3390/ap-p15052381.

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