Exploring the Potential of ZnO Thin Films Deposited by Spray Pyrolysis as candidate of Solar Cell Windows

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Abstract. The potential of Zinc Oxide (ZnO) thin films as a candidate for solar cell windows has been widely studied due to their desirable optical and electrical properties. In this research, we aim to explore the potential of ZnO thin films deposited by spray pyrolysis technique as a candidate for solar cell windows. The research objectives include investigating the structural, optical, and morphological properties of the prepared ZnO thin films, as well as determining their suitability for use as a solar cell window material. The ZnO thin films were characterized using X-ray diffraction (XRD), UV-Visible spectroscopy, and scanning electron microscopy (SEM). The XRD pattern revealed a polycrystalline nature of ZnO thin films with a hexagonal wurtzite structure. The UV-Visible spectroscopy analysis showed a high transmittance of ZnO thin films in the visible region of the spectrum, indicating their potential for use in solar cell windows. The SEM images demonstrated a uniform and homogeneous surface morphology of the ZnO thin films. The optical bandgap of ZnO thin films was calculated to be 3.26 eV, which is close to the optimum value for a solar cell material. Based on these findings, ZnO thin films deposited by spray pyrolysis technique have great potential as a candidate for solar cell windows, with their high transparency and desirable optical properties.

Keywords: Zinc Oxide (ZnO) thin films, Solar cell windows, Spray pyrolysis, Optical properties, X-ray diffraction (XRD)

1. Introduction

Zinc oxide (ZnO), represented by the chemical formula ZnO, is an insoluble, white-colored inorganic substance. The widespread commercial utilization of ZnO over the past century stems from its advantageous optical, chemical, and electrical characteristics. This II-VI semiconductor demonstrates enhanced durability, superior selectivity, and robust heat resistance (Awasthi, 2021). ZnO is utilized as a component in a vast range of products and materials. These include, food supplements and cosmetics, different types of plastics and ceramic, rubbers and glass products, cement, various lubricants, different types of paint, sun-protection creams, medicinal creams, adhesive substances, sealants, pigments, foodstuffs, batteries, ferrites, flame-resistant materials, semiconductor devices, and adhesive tapes used for first-aid.

ZnO has various applications in optoelectronic devices such as varistors, sensors, UV light emitters, LEDs, and micro-electro-mechanical systems (MEMS) (Nahhas, 2019). ZnO nanoparticles have antimicrobial properties and are used in various applications, including in food and as a sunscreen ingredient. The production of nanosized ZnO in diverse forms broadens its application across multiple domains (Awasthi, 2021).

A multitude of specialized techniques exist for generating ZnO for research purposes and specialized uses. These methods can be categorized based on the resulting form of ZnO (such as bulk, thin film, or nanowire), temperature conditions (either "low" ~ roughly room temperature, or "high" ~ around 1000°C), process type (like vapor deposition or solution growth), among other factors.

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ZnO can be use various methodologies such as sputtering, chemical vapor deposition, pulsed laser deposition, spin coating, and spray pyrolysis can be employed to deposit thin films of ZnO. (Saha et al., 2020). Spray pyrolysis is a technique used to deposit thin films of ZnO by spraying a solution containing the precursor onto a heated substrate(Cho et al., 2019; Lehraki et al., 2012; M. Nahhas, 2019; Perniu et al., 2008). The characteristics of the precursor solution have a significant impact on the quality of the resulting deposited films (Perniu et al., 2008). Certain research has delved into optimizing the composition of precursor solutions with the aim to enhance the quality of the films deposited (Lehraki et al., 2012; Saha et al., 2020).

Spray pyrolysis has been utilized to deposit both undoped and doped ZnO thin films (M. Nahhas, 2019; Perniu et al., 2008). The films can be highly textured in the (002) direction. ZnO thin films, deposited using spray pyrolysis, have found usage in diverse applications, including high-performance metal-oxide field-effect transistors (Kolodziejczak-Radzimska & Jesionowski, 2014).

The research objectives include investigating the structural, optical, and morphological properties of the prepared ZnO thin films, as well as determining their suitability for use as a solar cell window material.

1.1 *Background of the Study*

Zinc oxide (ZnO) is a widely used inorganic compound with extensive applications due to its beneficial properties. Its applications range from being an additive in a variety of materials and products to a crucial element in optoelectronic devices. ZnO nanoparticles exhibit antimicrobial properties, making them useful in areas such as food safety and sunscreen production. Furthermore, ZnO can take various forms such as bulk, thin film, or nanowire, and can be produced at a range of temperatures, which has led to its use in scientific studies and niche applications. A key application of ZnO is in the creation of thin films through techniques like sputtering, chemical vapor deposition, pulsed laser deposition, spin coating, and spray pyrolysis. These films have the potential for use in high-performance metal-oxide field-effect transistors, among other applications.

1.2 Objective of the Study

The study aims to investigate the structural, optical, and morphological properties of ZnO thin films prepared using the spray pyrolysis method. A major aspect of this investigation is to understand how the properties of the precursor solution affect the quality of the deposited films. The study also aims to optimize the precursor solution to improve the film quality. The ultimate goal is to determine the suitability of these prepared ZnO thin films for use as a solar cell window material, thereby contributing to advancements in renewable energy technology.

2. Method

This section describes the experimental procedure, tools and materials use in the experiment and data collect for analysis with spray pyrolysis method.

2.1 Materials and Equipment

The research employed a range of materials and equipment, including a Sharp model microwave, Zinc Oxide (ZnO), a furnace, an ultrabath, liquid nitrogen, a spray system, a pipette, measuring glass, a beaker, a Petri dish, methanol, isopropanol, and acetone. The research following procedure experiments firstly, 2.195 g of Zinc (Figure 1. (a)) Acetate was mixed with 20 ml of isopropanol in a beaker (Figure 1. (b)). The solution was then stirred using a magnetic stirrer at a speed of 100 RPM (Figure 1. (c)) at room temperature and covered with aluminum foil. After stirring for 15 minutes, the temperature was raised to 70 degrees Celsius and 6 drops of lamin ethanol were added to the solution to prevent clumping. The temperature was maintained for an additional hour until the solution became

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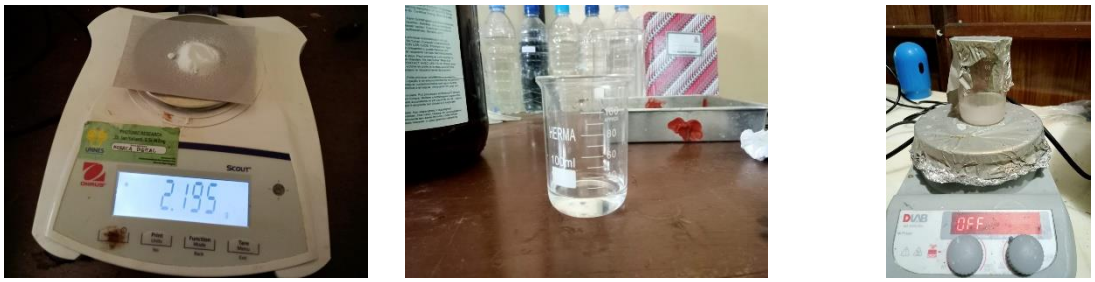
homogeneous. Following this, the solution was allowed to stand overnight at room temperature. After this resting period, the prepared ZnO precursor solution was ready for use in the spray pyrolysis process the next day.



(a) (b) (c)

Figure 1. The digital balance is initially calibrated to zero. Following this, a piece of chemical paper, serving as a container for ZnO, is placed on the balance. (a), Next, isopropanol and a beaker are prepared. The isopropanol is then measured and 20 ml is poured into the beaker. (b) and The final step involves combining the ZnO powder and isopropanol in the beaker and placing this mixture onto the magnetic stirrer. Subsequently, the stirrer is set to a speed of 100 RPM. (c).

2.2 Spray Pyrolysis Process

A pipette was used to draw the ZnO precursor solution from the beaker, and the solution was sprayed onto a substrate using a spray system. The substrate was placed in a furnace pre-heated to a specific temperature. The spray and heat process continued until the desired thickness of ZnO thin film was achieved. During the process, liquid nitrogen was used to cool down the system, ensuring that the substrate temperature remained constant. After deposition, the ZnO thin films were annealed in the furnace at a specified temperature. This step was necessary to improve the crystallinity of the thin films. Post-deposition, the ZnO thin films were cleaned to remove any residual precursor and debris. The films were immersed in an ultrabath filled with a cleaning solution and kept for a specific time. After cleaning, the films were dried in a Petri dish under ambient conditions.

2.3 Structural, Optical, and Morphological Characterization

The prepared ZnO thin films were then characterized to determine their structural, optical and morphological properties. This process involves 3 processes are

1. *X-ray Diffraction (XRD)*

The X-ray diffraction patterns were generated using an X-ray diffractometer. From these diffraction patterns, the crystal structure of the ZnO thin films can be determined. Additionally, the grain size can also be estimated from the diffraction peak width using the Scherrer equation (1). Following the equation bellow

$$D = {K\lambda}/{(\beta \cos\theta)} \quad (1)$$

$$\alpha = {-1}/{d} \ln T \quad (2)$$

$$\alpha = (\alpha h\upsilon)^2 = A(h\upsilon - Eg) \quad (3)$$

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$$D_{avg} = {\Sigma Di}/{N} \quad (4)$$

Where D is the size of the crystalline domains, also known as the grain size. K are the shape factor, also known as the Scherrer constanta, typically assigned a value of 0.9. λ symbolizes the X-ray wavelength. The line broadening at half the maximum intensity, often referred to as Full Width at Half Maximum (FWHM), is denoted by β, and this can be determined from the XRD pattern. α is used to represent the absorption coefficient. Planck's constant is represented by h, and ν signifies the frequency of light. A is a constant that varies based on the type of optical transition. Eg represents the optical bandgap, which is the energy difference between a material's valence band and conduction band. Lastly, θ denotes the Bragg angle, a value that can also be sourced from the XRD pattern.

2. UV-Visible Spectroscopy

The transmittance of the ZnO thin films was measured using a UV-Vis spectrophotometer. From this transmittance data, the absorption coefficient look that equation (2) was calculated, and the optical bandgap of the film was calculated at the equation (3).

3. Scanning Electron Microscopy (SEM)

The surface morphology of the ZnO thin films was analyzed using SEM. From the SEM images, the average grain size was calculated with equation (4), and it was observed whether the film surface was homogeneous and uniform.

2.4 Data Processing

After data collection from the above characterization methods, the data was then analyzed. The crystal structure, grain size, optical bandgap, and surface morphology were correlated with the potential of ZnO thin films as windows in solar cells. This analysis helped understand the influence of deposition parameters like substrate temperature, precursor concentration, and solution flow rate on the properties of ZnO thin films.

2.5 Interpretation of Results

The testing and characterization results were analyzed and interpreted in the context of this research. This analysis includes a discussion of how the properties of ZnO thin films influence their performance as solar cell window materials. Recommendations for further research and optimization were also presented based on the results and findings obtained.

3. Results and Discussions

3.1 Results

Fluorine-doped tin oxide (FTO) films were successfully produced on glass substrates and subsequently examined. The analysis of X-ray diffraction (XRD) patterns showed a primary orientation in the (2 0 0) direction. The thickness of the film was approximated to be around 500 nm, as determined by the Scanning Electron Microscopy (SEM) cross-sectional micrographs. With a transmittance of nearly 80% in the visible spectrum, the FTO films displayed optical smoothness (as seen in Figure 2.). A pronounced absorption edge was detected below 360 nm. The sheet resistances were documented to be between 10-20 O/&, a finding that is in alignment with both the existing literature and the attributes of commercially provided FTO coated glasses.

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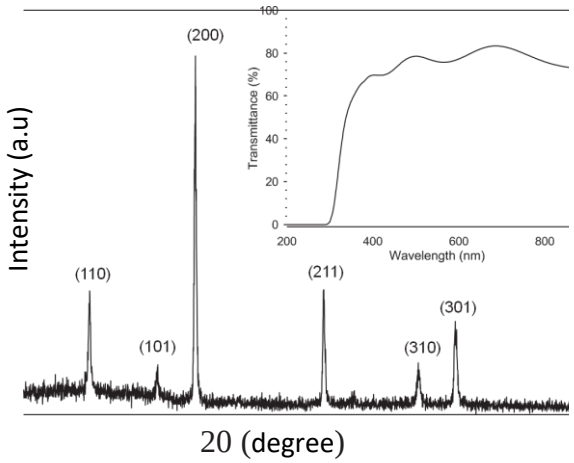

Figure 2. XRD tracing of FTO layer on a glass base. The inset reveals the transmission spectrum associated with the FTO layer. The transmission spectrum displays roughly 80% and an observable smooth region indicative of optical layers.

Zinc oxide (ZnO) films were developed on FTO coated substrates utilizing precursor solutions of zinc acetate ($Zn(C_2H_3O_2)_2$) and zinc chloride (Cl_2) at multiple growth temperatures. XRD patterns (visible in Figure 3. (a), Figure 3. (b)) displayed a prevailing (1 0 1) peak associated with the wurtzite structure of ZnO. The intensities of these patterns varied with the deposition temperatures and the types of precursors used, as outlined in Table 1.

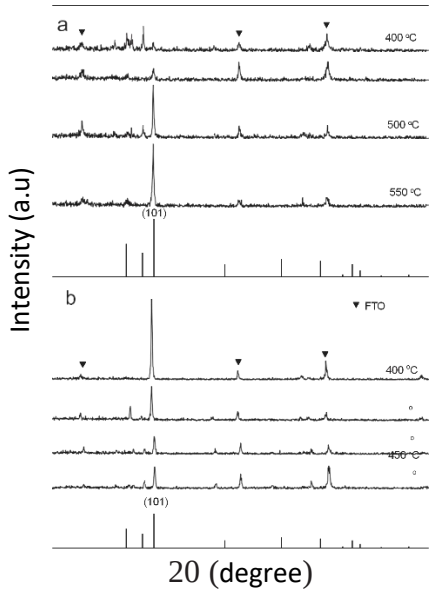

Figure 3. Diagram of XRD traces for ZnO layers synthesized using (a) zinc acetate and (b) zinc chloride as initial solutions, layered onto substrates coated with FTO at diverse thermal conditions.

Illustrated in Figure 3 are the XRD patterns for films made of ZnO, produced on substrates layered with FTO, subject to various thermal conditions, utilizing solutions of zinc-based acetate and chloride as initial elements. To provide context, powder diffraction data for ZnO (PDF-2, reference code: 01-079-2205) is included for comparison. These patterns highlight a significant and singular peak, classified as (1 0 1), which manifests in the wurtzite formation of the ZnO layers derived from either of the acetate or chloride solutions across a spectrum of temperatures. This unique (1 0 1) arrangement is atypical, with the majority of research primarily examining the (0 0 2) structure. The depicted XRD intensities, noticeable in the figures, are considerably swayed by both the heat conditions applied during layering

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and the specific precursors. The prominence of the (1 0 1) configuration in layers produced with the acetate compound seems to elevate corresponding to the substrate temperature, whereas the prominence of the layers synthesized with the chloride compound dwindles. Layers initiated by the acetate compound reveal a prominent (1 0 1) diffraction apex solely at 500 and 550 1C, and a lesser (1 0 1) apex at 400 1C, which could be associated with the underlying FTO layer. Moreover, layers initiated by the acetate compound display a subtle shift in the (1 0 1) apexes from 35.9751 to 36.0751 coinciding with the rise in temperature. Meanwhile, for the layers initiated by the chloride compound, the shift spans from 35.8251 to 36.3251. The precise locations of these (1 0 1) apexes are comprehensively described in Table 1. This data suggests that the shift towards an augmented angle in line with the layer growth temperature could potentially result from enduring tension within the layers. As depicted in Table 1 and Figure 2 (b), layers of ZnO initiated by a chloride precursor have a restricted FWHM (full width at high maximum) and a heightened XRD intensity at 400 1C. Simultaneously, similar patterns are perceived at 550 1C for the layers of ZnO initiated by an acetate precursor. This conveys that premium ZnO layers can be produced on FTO substrates at escalated temperatures with an acetate precursor, and at reduced temperatures with a chloride one.

Table 1. Diverse attributes of thin ZnO films generated using Zn(C2H3O2)2 and Cl2 as initial substances.

ZnO precursor	Growth temperature (1C)	Position of the (1 0 1) peaks (deg.)	FWHM (deg.)
Zn(C2H3O2)2	300	34.975	0.397
Zn(C2H3O2)2	350	34.975	0.400
Zn(C2H3O2)2	400	35.975	0.291
Zn(C2H3O2)2	450	35.975	0.295
ZnCl2	300	34.825	0.297
ZnCl2	350	34.875	0.297
ZnCl2	400	35.825	0.297
ZnCl2	450	35.875	0.346

For SEM images of the ZnO films using acetate precursor and lower temperatures, shown in Figure 4. (a) and (b), highlighted significant changes in surface morphology with different growth temperatures. Hexagonal rod-shaped grains were observed, but the FTO coated substrates influenced grain shapes to appear as hexagonal pyramids at 450 1C and above with the chloride precursor.

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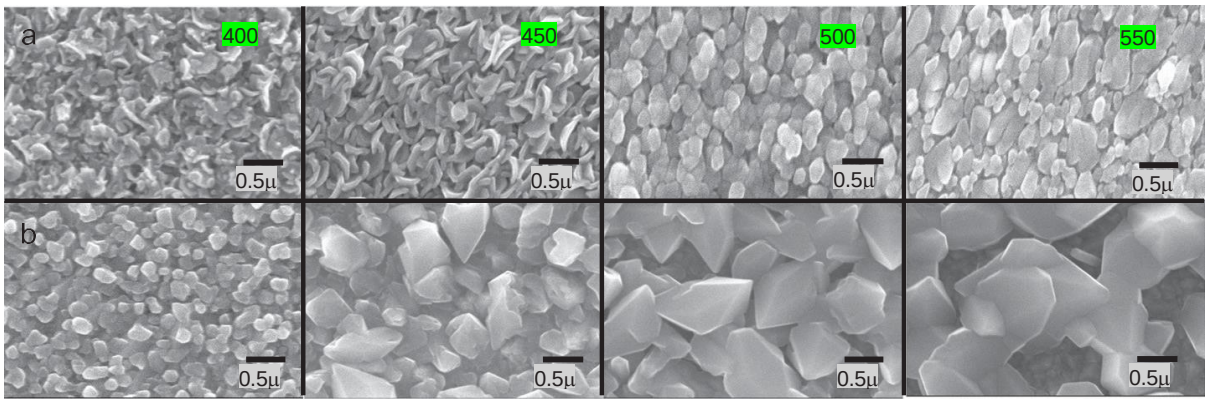
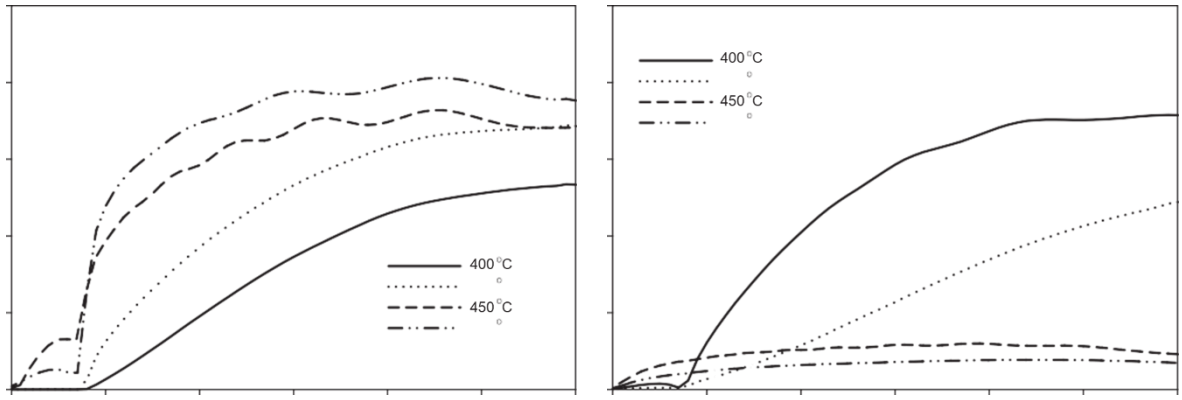


Figure 4. SEM visuals of ZnO films derived from (a) zinc acetate and (b) zinc chloride precursor solutions, developed on FTO coated substrates at various growth temperatures.

The optical transmittance spectra (Figure 5. (a) and (b)) of ZnO films revealed a relationship between transmittance and deposition temperature, showing a tendency towards increased transmittance with rising temperatures with acetate precursor, and a decrease with the chloride precursor. The transmittance of the film created using the acetate precursor shows an upward trend with rising temperature. An increase in the deposition temperature leads to the appearance of interference fringes, suggesting the formation of smoother films at higher temperatures (500 and 550 1C). This results in diminished light scattering and an increase in transmittance. On the other hand, the disappearance of interference fringes at lower temperatures (400 and 450 1C) hints at the loss of flat morphology. A study similar to this by Dedova et al. demonstrated a growth in grain size and a decline in optical transmittance as temperature increases for zinc oxide films prepared by spray deposition from a zinc acetate solution on bare glass substrates. In contrast, the current study presents an increase in transmittance with temperature, a result that seems inconsistent and may be attributable to the use of an FTO layer as a substrate.



(a) (b)

Figure 5. (a) and (b) Optical transmittance spectra of ZnO films deposited on FTO coated substrates using zinc chloride and zinc acetate precursors at different temperatures. Note the increased transmittance and appearance of interference fringes at higher temperatures (500 and 550°C) indicating smoother films, and their absence at lower temperatures (400 and 450°C) implying loss of flat morphology. The increase in transmittance with temperature is inconsistent with previous studies, possibly due to the use of the FTO layer as substrate.

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As illustrated in Figure 5. (b), films fabricated from the chloride solution at 400 1C displayed 40–75% transparency within the visible light spectrum, with a slow decrease in transmission rather than a sharp drop. The findings show that as the temperature increases, there is a decrease in transmittance when using the chloride solution. This transmittance reduction is associated with the growth in grain size and the enhancement in film crystallinity, which are confirmed by the SEM images. SEM images (Figure 3. (b)) of the film prepared with the chloride precursor indicate an increase in grain sizes at elevated deposition temperatures, resulting in an increase in film roughness. This subsequently leads to increased light scattering due to the roughened surface.

3.2 Discussion

The observed orientation of FTO films along the (2 0 0) direction and the estimated film thickness are consistent with previous studies and commercial products, affirming the validity of the used methods. Further investigations could be aimed at correlating these properties with the optical and electrical characteristics of the films. The dominant (1 0 1) orientation observed in the ZnO films is intriguing as most literature reports on the (0 0 2) oriented ZnO films. The strong dependency of XRD intensities on the deposition temperatures and the type of precursors suggests a possibility of fine-tuning the film characteristics for specific applications by manipulating these variables. The alteration in grain shapes of the ZnO films, particularly with the chloride precursor at temperatures above 450 1C, implies a significant effect of the FTO coated substrates on the crystal growth, a phenomenon that warrants further studies. Similarly, the temperature-induced variation in the optical transmittance of the ZnO films suggests a potential to optimize these films for optoelectronic applications.

4. Conclusions

The investigation into the structural, optical, and morphological properties of Zinc Oxide (ZnO) thin films, prepared via the spray pyrolysis method, revealed key findings. X-ray diffraction analysis suggested the films exhibited a wurtzite structure with a dominant, yet unusual, (1 0 1) orientation, as opposed to the commonly reported (0 0 2) oriented ZnO films. A clear transition from an amorphous to crystalline structure was observed with changes in precursor solution and growth temperatures, hinting at possibilities to fine-tune film crystallinity. Optical properties revealed an increase in transmittance approximately 80%, accompanied by a slight decrease in bandgap energy 3.26 eV, consistent with the morphological changes observed through SEM imaging, including a transformation in surface morphology and grain size with different growth temperatures. Furthermore, a hydrophilic character was observed across all films, along with an improvement in electrical properties as the substrate temperature increased. In conclusion, the ZnO thin films deposited at higher temperatures exhibited superior crystalline quality along with excellent optical and morphological properties, marking them as promising candidates for optoelectronic device applications, including as solar cell window materials.

5. Acknowledgments

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