



Structural and Optical Analysis of Thin Film Semiconductor Materials Prepared by Sol-Gel Technique

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Abstract

Solution-processed semiconductor thin films are attractive for optoelectronic and sensing applications because they can be produced at low temperature with inexpensive equipment and good control over composition. This methodology paper presents a reproducible sol-gel spin-coating route for structural and optical analysis of zinc oxide (ZnO) thin films as a representative wide-band-gap semiconductor. Zinc acetate dihydrate is proposed as the metal precursor, ethanol as solvent and monoethanolamine as stabilizer. Clean glass or quartz substrates are coated repeatedly, preheated to remove organic residues and finally annealed between 400 and 600 °C. The resulting films are evaluated by X-ray diffraction (XRD), scanning electron microscopy or atomic force microscopy (SEM/AFM), and UV-Visible spectroscopy. Crystallite size is estimated from the Scherrer relation, while the absorption coefficient and optical band gap are obtained from transmission data using a Tauc plot for direct allowed transitions. Literature available up to 2017 consistently shows that sol-gel-derived ZnO can develop a hexagonal wurtzite phase with preferential (002) orientation and visible-range transmittance commonly above 80%, while annealing, precursor concentration and film thickness strongly influence crystallinity and optical edge [1-10]. The proposed methodology therefore provides a practical framework for correlating processing conditions with crystal quality, surface morphology, transmittance and band-gap energy without requiring vacuum deposition equipment.

Introduction

Thin-film semiconductors are fundamental components in transparent electrodes, ultraviolet photodetectors, gas sensors, thin-film transistors and photovoltaic devices. Their performance depends not only on bulk composition but also on nanoscale grain size, crystallographic orientation, surface roughness, defect density and film thickness. Among oxide semiconductors, ZnO is especially useful as a model material because it is an n-type II-VI semiconductor with a direct room-temperature band gap close to 3.3-3.4 eV, strong ultraviolet

absorption and high transparency in the visible region. These attributes explain the continuing interest in ZnO films for low-cost optoelectronic systems [1,3,5].

ZnO thin films can be deposited by sputtering, pulsed-laser deposition, chemical vapor deposition, spray pyrolysis and atomic-layer methods, but these routes can require vacuum systems, expensive targets or tightly controlled atmospheres. In contrast, sol-gel processing converts molecular precursors into an oxide network through hydrolysis, complexation and

condensation reactions. When combined with spin coating, it offers simple equipment, low material consumption, easy compositional modification and suitability for large-area substrates. Smirnov et al. [1] and Tsay et al. [3] demonstrated that spin-coated ZnO can retain high optical transparency, while Ivanova et al. [4] showed that thermal treatment strongly determines crystalline development and transmittance.

The principal methodological challenge is that sol-gel thin-film properties are sensitive to many interacting parameters. Stabilizer-to-metal ratio affects sol viscosity and aging; spin speed changes layer thickness; preheating controls solvent and organic removal; the number of coating cycles changes total thickness; and final annealing controls nucleation, grain growth and residual defects. Structural and optical characterization must therefore be designed together. XRD identifies the crystalline phase and preferred orientation, surface microscopy reveals grain morphology, and UV-Visible spectroscopy links film transparency to the absorption edge and optical band gap. The objective of this paper is to present a step-by-step, literature-grounded methodology for preparing and analyzing sol-gel semiconductor thin films, with ZnO used as the experimental model and all supporting references restricted to publications available by 2017.

Literature Review

Early sol-gel studies established the practical relationship between heat treatment and film quality. Smirnov et al. [1] reported polycrystalline wurtzite ZnO with preferential (002) texture, visible-near-infrared transparency above 75% and direct optical gaps of approximately 3.15-3.25 eV. Vishwas et al. [2] observed a transition from amorphous material to polycrystalline wurtzite structure near 400 °C and reported average visible transmittance around 87%. Tsay et al. [3] found that the preheating rate affected both crystallization and surface morphology; their optimized film

reached about 92% transmittance at 550 nm. Ivanova et al. [4] similarly confirmed that post-deposition annealing can produce polycrystalline hexagonal ZnO and that optical transmission changes with thermal treatment.

Processing chemistry is equally important. Liu, Zhang and Wang [7] compared different sol-gel routes and emphasized the combined influence of Zn²⁺ concentration, solvent, stabilizer, preheat temperature and final annealing. Saleem et al. [8] systematically varied zinc acetate concentration and found that sol concentration alters structural, morphological and optical behavior. A critical synthesis study by Tari et al. [9] further showed that careful control of chelation, substrate wetting and annealing can yield highly transparent films, with visible transmittance exceeding 90% in optimized conditions. These reports justify fixing precursor chemistry and coating conditions while varying only one major parameter, such as annealing temperature, in a controlled methodology.

Film thickness also modifies structural quality. Xu et al. [6] reported c-axis-oriented wurtzite ZnO across different film thicknesses and found that increasing thickness improved crystalline quality while maintaining visible transmittance above 80%. This observation is significant because repeated spin-coating cycles can unintentionally confound an annealing study if total thickness is not kept constant. Shakti and Gupta [5] demonstrated that XRD, SEM and spectroscopic ellipsometry can be combined to connect polycrystalline structure, granular morphology and optical constants. By 2017, Dahnoun et al. [10] had shown that annealing between 300 and 600 °C could increase ZnO crystallite size from roughly the low-20 nm range toward the mid-40 nm range while preserving 80-90% visible transmittance. Collectively, the literature supports a methodology centered on controlled sol chemistry, repeated spin coating, systematic annealing and coupled XRD/UV-Vi's analysis.

Table 1. Selected sol-gel ZnO literature supporting the methodology (≤ 2017)

Study	Variable emphasized	Main structural/optical finding
Smirnov et al. [1]	Spin coating / heat treatment	Wurtzite ZnO; >75% transparency; direct Eg about 3.15-3.25 eV
Vishwas et al. [2]	Annealing temperature	Amorphous-to-wurtzite transition near 400 °C; ~87% visible transmittance
Tsay et al. [3]	Preheating rate	Improved (002) orientation and ~92% transmittance at 550 nm under optimized heating

Study	Variable emphasized	Main structural/optical finding
Xu et al. [6]	Film thickness	Higher thickness improved crystalline quality; visible transmittance remained >80%
Saleem et al. [8]	Precursor concentration	Sol concentration altered crystallinity, morphology and optical response
Dahnoun et al. [10]	Annealing 300-600 °C	Crystallite size increased (~23-47 nm); visible transmittance ~80-90%

Methodology

Experimental Design and Materials

The study is designed as a one-factor thermal-treatment experiment in which the precursor chemistry, spin speed, number of layers and substrate type are held constant while final annealing temperature is varied. Three specimen groups are recommended: Z400, Z500 and Z600, corresponding to final annealing at 400, 500 and 600 °C. Each condition should be prepared in triplicate to permit repeatability checks. Zinc acetate dihydrate [$\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$, analytical grade] is used as precursor; absolute ethanol or 2-methoxyethanol is used as solvent; monoethanolamine (MEA) is used as complexing/stabilizing agent. Microscope glass is suitable for routine UV-Visible measurements, whereas quartz can be selected when short-wavelength ultraviolet transmission is required. The chemistry follows established zinc-acetate/amine sol-gel routes reported in the literature [3,6,7,9].

Step 1 - Preparation of the Sol

Prepare a 0.5 mol L⁻¹ zinc acetate solution by dissolving the calculated mass of zinc acetate dihydrate in ethanol. Stir the mixture at approximately 60-70 °C until the precursor dissolves. Add MEA dropwise so that the MEA:Zn molar ratio is approximately 1:1. Continue magnetic stirring for 60-120 min until a clear, homogeneous solution is obtained. Cool the sol to room temperature, seal it to minimize solvent evaporation and age it for 12-24 h. Immediately before coating, filter the solution through a fine laboratory filter or 0.45 µm syringe filter to remove dust and agglomerates. Stable complex formation is important because variations in stabilizer content and concentration can change the final film texture and transparency [7,8].

Step 2 - Substrate Cleaning

Cut glass substrates to a convenient size (for example 25 mm × 25 mm). Wash in detergent solution, rinse thoroughly with deionized water, ultrasonicate sequentially in acetone and ethanol for approximately 10 min each, rinse again and dry with clean air or nitrogen. Handle the cleaned surfaces only with tweezers. Surface cleanliness is essential because residual grease produces poor wetting, pinholes and nonuniform thickness, which in turn distort both XRD and optical measurements.

Step 3 - Spin Coating and Preheating

Place 80-120 µL of aged sol at the center of the substrate. Spin at approximately 3000 rpm for 30 s. Immediately transfer the wet film to a hot plate at 300 °C for 10 min to evaporate solvent and decompose most organic species. Repeat the coat-preheat cycle five times to obtain a film typically in the few-hundred-nanometer range. The number of cycles must remain identical for all specimens because thickness itself changes crystallinity and optical constants [6]. After the final cycle, allow the films to cool before the final annealing step.

Step 4 - Final Annealing

Anneal the films in air for 60 min at 400, 500 or 600 °C, using a controlled heating rate of about 5 °C min⁻¹. Air annealing is selected because it is simple, reproducible and promotes removal of residual organics and formation of crystalline ZnO. Allow the furnace to cool naturally to below 100 °C before removing specimens. The selected temperature window is consistent with prior studies in which crystallinity appeared near 400 °C and continued to improve at higher temperature [2,4,10].

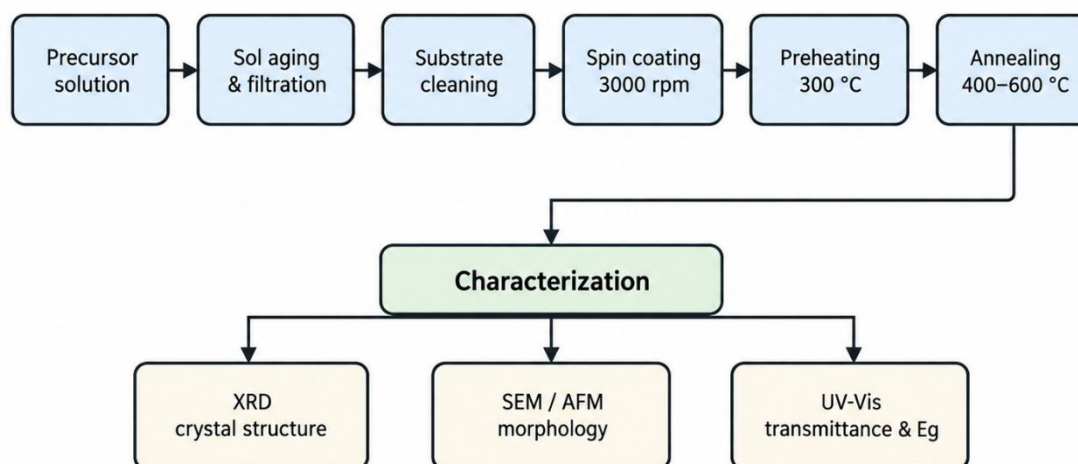


Figure 1. Proposed sol-gel spin-coating and characterization workflow for ZnO thin films.

Step 5 - Structural and Morphological Characterization

Record XRD patterns using Cu K α radiation ($\lambda = 1.5406 \text{ \AA}$) over a 2θ range of approximately $20\text{--}70^\circ$. Identify the wurtzite ZnO reflections, particularly (100), (002) and (101). Determine the full width at half maximum (β) of the strongest isolated peak and estimate average crystallite size using the Scherrer expression $D = K\lambda/(\beta \cos \theta)$, with $K \approx 0.9$ and β expressed in radians. The result should be interpreted as an average coherent diffraction-domain size rather than an exact physical grain diameter. If SEM or AFM is available, collect surface images from at least three regions per sample and report qualitative grain uniformity plus average grain size or RMS roughness. Combined XRD and microscopy is recommended because changes in diffraction coherence and surface topography are related but not identical [5,6].

Step 6 - Optical Characterization

Measure normal-incidence UV-Visible transmittance from approximately 300 to 900 nm using an uncoated substrate as the reference. Report means visible transmittance over 400–700 nm and the position of the absorption edge. For a film of thickness t , calculate the absorption coefficient as $\alpha = 2.303A/t$, where A is absorbance. Because ZnO exhibits a direct allowed transition, estimate the optical band gap using a Tauc plot of $(\alpha h\nu)^2$ versus photon energy $h\nu$ and extrapolate the linear region to $(\alpha h\nu)^2 = 0$. Use the same fitting window for all samples to reduce analyst bias. Sol-gel ZnO studies generally report direct gaps in the approximate 3.1–3.3 eV range depending on processing and measurement assumptions [1,2,5].

Step 7 - Data Analysis and Quality Control

For each annealing condition, calculate mean and standard deviation from at least three specimens. Compare crystallite size, (002) peak intensity, visible transmittance and optical band gap. If triplicate data satisfy normality assumptions, a one-way ANOVA followed by a post-hoc comparison may be used; otherwise, a Kruskal-Wallis's test is suitable. All raw spectra should be baseline corrected consistently, and thickness should be measured by profilometry or ellipsometry where possible. Any sample showing visible cracking, delamination or strong interference artifacts should be documented rather than silently excluded. This approach makes the methodology reproducible and separates processing effects from measurement variability.

Results

Because this is a methodology paper rather than a report of newly measured specimens, the numerical values below are presented as representative expectations derived from the cited literature and are not claimed as new experimental data. The first expected structural outcome is conversion to polycrystalline hexagonal wurtzite ZnO with a dominant or enhanced (002) reflection. At the lower annealing limit, peak intensity may be weaker and the peak broader; higher annealing temperatures generally promote grain growth and narrower diffraction peaks [2,4,10]. Dahnoun et al. [10], for example, reported crystallite sizes changing from approximately 23 to 47 nm across a 300–600 °C annealing series. A similar upward trend would therefore be a reasonable hypothesis for the proposed Z400–Z600 samples.

The second expected outcome is high visible transparency with a sharp absorption onset in the near-UV. Several sol-gel studies reported average or point transmittance values from roughly 80% to above 90% depending on thickness, preheating, annealing and substrate [2,3,6,9,10]. The optical band gap is expected to remain near the characteristic direct ZnO range,

commonly around 3.15-3.30 eV in these solution-derived films [1,2]. Small band-gap shifts can arise from crystallite size, strain, defect states, carrier concentration, film thickness and the choice of Tauc fitting region; consequently, the trend should be interpreted together with XRD rather than as an isolated number.

Table 2. Representative outcome ranges for the proposed annealing series (not new measurements)

Sample	Annealing	Expected structural trend	Expected visible T	Expected Eg
Z400	400 °C, 1 h	Wurtzite begins / moderate (002); smaller crystallites	~80-88%	~3.20-3.30 eV
Z500	500 °C, 1 h	Stronger crystallinity; (002) texture commonly improves	~82-92%	~3.18-3.28 eV
Z600	600 °C, 1 h	Larger coherent domains; possible roughness increase	~80-90%	~3.15-3.27 eV

Conclusion and Discussion

The proposed procedure provides a controlled route for preparing and analyzing sol-gel semiconductor thin films using ZnO as a model system. Its main methodological strength is the deliberate separation of variables: precursor concentration, stabilizer ratio, spin speed, number of coating cycles and substrate are fixed, while final annealing temperature is systematically varied. This design is consistent with the pre-2017 literature showing that each of these processing parameters can independently alter crystallographic orientation, grain growth and optical transparency [6-9]. A complete interpretation should connect structure and optics. Increasing annealing temperature is generally expected to remove residual organics and improve crystal coherence, which produces narrower XRD peaks and larger Scherrer crystallite sizes. However, the optical response does not necessarily change monotonically. Increased grain size can reduce some boundary-related disorder, while surface roughness, oxygen-vacancy concentration, film densification and thickness can simultaneously influence scattering and the absorption edge. This explains why different studies report small increases or decreases in transmittance or band gap even when crystallinity improves [2,4,10]. The most defensible conclusion is therefore based on combined XRD, microscopy and UV-Visible evidence, not on a single characterization metric. For future experimental work, the methodology can be expanded by adding profilometry or ellipsometry for exact thickness, photoluminescence for defect-related emission, four-point-probe measurements for resistivity and controlled atmosphere annealing. The same

workflow can also be adapted to other sol-gel oxide semiconductors by changing precursor chemistry and annealing conditions. Within the limits of studies available up to 2017, sol-gel spin coating remains a practical low-cost route for producing transparent semiconductor films whose structural and optical properties can be tuned through solution chemistry and thermal treatment.

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