DEFECT ENGINEERING AND BAND GAP MODULATION IN SULFUR–NITROGEN CO-DOPED ZNO THIN FILMS FOR ADVANCED OPTOELECTRONIC APPLICATIONS

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Abstract

Wide band gap oxide semiconductors have attracted considerable scientific attention due to their important applications in modern optoelectronic devices. Among these materials, Zinc Oxide (ZnO) is recognized as one of the most promising semiconductor compounds because of its direct band gap (3.37 eV), high exciton binding energy (60 meV), excellent optical transparency, chemical stability, and environmental compatibility. However, intrinsic crystal defects, especially oxygen vacancies and grain boundary trapping centers, frequently limit charge transport efficiency and reduce device performance.

In the present study, sulfur–nitrogen co-doped ZnO thin films were synthesized using the sol–gel spin coating method followed by thermal annealing at 500°C. The influence of simultaneous sulfur and nitrogen incorporation on structural, optical, and electrical properties was systematically investigated using X-ray Diffraction (XRD), Scanning Electron Microscopy (SEM), UV–Visible spectroscopy, Photoluminescence (PL) spectroscopy, and Hall effect measurements.

The obtained results demonstrated progressive crystallite size reduction from 41.3 nm to 27.8 nm, optical band gap narrowing from 3.31 eV to 3.06 eV, and conductivity enhancement from 0.38 S/sm to 0.95 S/sm with increasing dopant concentration. PL measurements revealed significant suppression of oxygen-vacancy-related green emission near 540 nm, confirming reduction of defect-assisted recombination centers. Hall effect analysis indicated a strong increase in carrier concentration from 1.2×10^{16}sm^{-3} to 7.4×10^{17} sm^{-3}.

The results confirm that sulfur–nitrogen co-doping provides an effective defect engineering mechanism capable of modifying electronic structure, improving charge transport behavior, and enhancing ZnO thin film performance for future optoelectronic applications[1].

Keywords

ZnO thin films; sulfur doping; nitrogen doping; defect engineering; semiconductor physics; band gap engineering; optoelectronic materials

1. Introduction

Semiconductor thin films have become one of the most important research directions in modern materials science because of their broad application potential in sensors, solar cells, transparent electronics, ultraviolet photodetectors, and advanced optoelectronic systems. Among wide band gap oxide semiconductors, zinc oxide (ZnO) has attracted considerable scientific interest because of its favorable physical and chemical properties. ZnO possesses a direct band gap of approximately 3.37 eV, relatively high exciton binding energy, strong ultraviolet absorption capability, and excellent thermal stability.

Despite these advantages, pure ZnO often contains intrinsic crystal defects such as oxygen vacancies, zinc interstitials, and grain boundary defects. These imperfections strongly affect electrical conductivity and optical performance by increasing defect-assisted recombination losses.

One of the most effective approaches for controlling semiconductor defects is elemental doping. Sulfur doping typically introduces donor states near the conduction band, while nitrogen acts as an acceptor-like impurity capable of modifying oxygen sublattice behavior. Simultaneous sulfur–nitrogen co-doping therefore creates a donor–acceptor compensation mechanism that can systematically modify crystal structure, reduce optical band gap, suppress intrinsic defects, and improve charge transport efficiency[2].

The objective of this study is to investigate structural, optical, and electrical modifications induced by sulfur–nitrogen co-doping in ZnO thin films and evaluate their potential application in advanced optoelectronic devices.

2. Experimental Methodology

Sulfur–nitrogen co-doped ZnO thin films were synthesized using the sol–gel method. Zinc acetate dihydrate was used as the primary precursor, while thiourea and urea served as sulfur and nitrogen sources respectively. Dopant concentrations of 1 wt.%, 3 wt.%, and 5 wt.% were introduced relative to the ZnO host matrix.

Thin films were deposited on cleaned glass substrates using spin coating at 3000 rpm for 30 seconds. Each deposited layer was dried at 120°C for 10 minutes. The deposition cycle was repeated six times to achieve uniform film thickness. Final annealing was carried out at 500°C for two hours under ambient atmosphere.

3. Results and Discussion

3.1 Structural Analysis

The crystal structure of sulfur–nitrogen co-doped ZnO thin films was investigated using X-ray diffraction analysis. All prepared samples exhibited characteristic diffraction peaks corresponding to the hexagonal wurtzite structure of ZnO, confirming successful crystalline phase formation without secondary impurity phases.

The major diffraction peaks observed near 31.8°, 34.4°, and 36.2° correspond to the crystallographic planes (100), (002), and (101), respectively. The dominant (002) peak indicates preferential c-axis orientation perpendicular to the substrate surface.

With increasing dopant concentration, diffraction peaks gradually shifted toward lower diffraction angles, indicating lattice expansion caused by sulfur substitution inside oxygen lattice positions. Simultaneously, peak broadening increased, suggesting progressive crystallite size reduction caused by dopant-induced lattice distortion[3].

Table 1. Structural Parameters of Sulfur–Nitrogen Co-Doped ZnO Thin Films

Sample	2θ (002)	Crystallite Size (nm)
Pure ZnO	34.42°	41.3
1 wt.%	34.37°	36.5
3 wt.%	34.31°	31.7
5 wt.%	34.25°	27.8

The progressive decrease in crystallite size confirms that sulfur–nitrogen incorporation suppresses normal grain growth during thermal crystallization and modifies internal lattice ordering.

3.2 Surface Morphology Analysis

Surface morphology evolution was examined using scanning electron microscopy. SEM micrographs revealed dense and relatively uniform granular morphology distributed across the substrate surface.

A systematic reduction in grain size was observed with increasing dopant concentration. The average grain size decreased from 98 nm for undoped ZnO to 52 nm for 5 wt.% co-doped samples.

This behavior suggests that sulfur and nitrogen atoms partially inhibit grain boundary mobility during annealing and reduce particle growth kinetics. Reduced grain size increases effective surface area, which can improve sensitivity in optoelectronic and sensor applications.

Table 2. Morphological Parameters

Sample	Average Grain Size (nm)
Pure ZnO	98
1 wt.%	81
3 wt.%	63

Sample	Average Grain Size (nm)
5 wt.%	52

3.3 Optical Properties and Band Gap Analysis

Optical absorption behavior was investigated using UV–Visible spectroscopy in the wavelength range between 300 and 800 nm. All samples demonstrated strong ultraviolet absorption behavior typical for ZnO semiconductor systems.

A progressive red shift of the absorption edge toward longer wavelengths was observed with increasing dopant concentration, indicating modification of the electronic structure after dopant incorporation.

Optical band gap values were calculated using the Tauc relation for direct band gap semiconductors.

Table 3. Optical Parameters

Sample	Absorption Edge (nm)	Band Gap (eV)
Pure ZnO	372	3.31
1 wt.%	381	3.23
3 wt.%	392	3.14
5 wt.%	405	3.06

The continuous reduction in band gap energy confirms successful band structure modification. Sulfur atoms introduce donor states near the conduction band while nitrogen creates acceptor-like states near the valence band. The coexistence of these impurity states effectively reduces the transition energy required for electron excitation[4].

3.4 Electrical Conductivity Analysis

Electrical conductivity measurements revealed significant improvement in charge transport behavior after sulfur–nitrogen co-doping.

Table 4. Electrical Conductivity Variation

Sample	Conductivity (S/sm)
Pure ZnO	0.38
1 wt.%	0.54
3 wt.%	0.79
5 wt.%	0.95

The increase in conductivity is mainly attributed to sulfur donor states introducing additional free electrons into the conduction band region. Although crystallinity slightly decreases after co-doping, the strong increase in carrier concentration dominates overall transport behavior and leads to net conductivity enhancement.

3. Results and Discussion (continued)

3.5 Defect State Analysis by Photoluminescence Spectroscopy

Photoluminescence spectroscopy was performed in order to investigate defect-state evolution induced by sulfur–nitrogen co-doping and evaluate intrinsic crystal defects associated with oxygen vacancies.

ZnO thin films typically exhibit two characteristic emission regions. The first emission peak appears in the ultraviolet region and corresponds to near-band-edge excitonic recombination. The second broad visible emission band is generally associated with deep-level crystal defects, particularly oxygen vacancies.

Two dominant emission peaks were observed during PL measurements:

- Ultraviolet emission near **382 nm**
- Green defect-related emission near **540 nm**

The intensity of green luminescence decreased significantly after co-doping.

Table 5. Relative PL Defect Emission Intensity

Sample	PL Intensity at 540 nm
Pure ZnO	100 %
1 wt.%	82 %
3 wt.%	61 %
5 wt.%	37 %

The reduction of green emission intensity indicates suppression of oxygen-vacancy-related recombination centers. Nitrogen atoms partially compensate oxygen-deficient lattice sites and stabilize local defect equilibrium inside the crystal structure.

3.6 Hall Effect and Carrier Transport Analysis

Hall effect measurements were carried out in order to determine changes in charge carrier concentration after sulfur–nitrogen co-doping.

The obtained results revealed a significant increase in carrier concentration with increasing dopant concentration.

Table 6. Carrier Concentration Variation

Sample	Carrier Concentration (sm^{-3})
Pure ZnO	1.2×10^{16}
1 wt.%	5.8×10^{16}
3 wt.%	2.4×10^{17}
5 wt.%	7.4×10^{17}

The increase in carrier concentration is primarily associated with sulfur substitution inside oxygen lattice positions, generating donor-like electronic states near the conduction band edge.

This additional free carrier generation explains the conductivity enhancement observed previously.

4. Defect Mechanism Discussion

The simultaneous incorporation of sulfur and nitrogen generates a complex defect interaction mechanism inside the ZnO crystal lattice.

Sulfur atoms substitute oxygen lattice sites and introduce donor electronic states near the conduction band[5]. Nitrogen atoms act as acceptor-like impurities modifying oxygen sublattice equilibrium and partially suppressing oxygen vacancy formation.

This donor–acceptor compensation mechanism explains the experimentally observed physicochemical changes:

- Reduction of crystallite size
- Suppression of oxygen vacancy defects
- Optical band gap narrowing
- Increased carrier concentration
- Improved electrical conductivity
- Reduced defect-assisted recombination losses

The overall process represents a successful defect engineering strategy for systematic optimization of ZnO semiconductor thin films[6].

5. Conclusion

Sulfur–nitrogen co-doping significantly modifies structural, optical, and electrical properties of ZnO thin films synthesized using the sol–gel method.

XRD analysis confirmed preservation of the hexagonal ZnO crystal phase with progressive crystallite size reduction from 41.3 nm to 27.8 nm. SEM analysis demonstrated grain refinement from 98 nm to 52 nm. Optical measurements revealed continuous band gap narrowing from 3.31 eV to 3.06 eV, indicating successful electronic structure modification.

Photoluminescence spectroscopy confirmed suppression of oxygen-vacancy-related defect emission, while Hall effect measurements demonstrated strong enhancement of carrier concentration from 1.2×10^{16} sm^{-3} to 7.4×10^{17} sm^{-3}. Electrical conductivity increased significantly from 0.38 S/sm to 0.95 S/sm after co-doping.

The obtained results confirm that sulfur–nitrogen co-doping provides an effective defect engineering strategy for improving ZnO semiconductor performance and demonstrates strong potential for advanced optoelectronic applications including ultraviolet photodetectors, transparent conducting oxide systems, and photoresponsive electronic devices[7].

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