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Research Article

Synthesis and Characterization of Calcium-Doped Zinc Oxide Thin Films: Structural and Optical Properties

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Abstract

Calcium-doped zinc oxide (ZnO: Ca) thin films were synthesised by the chemical bath deposition (CBD) technique and investigated to determine the influence of calcium incorporation on their structural and optical properties. Zinc nitrate hexahydrate was used as the zinc precursor, diethanolamine as a complexing agent, and ammonia to adjust the alkaline bath conditions. Calcium nitrate was introduced to obtain nominal Ca concentrations of 1%, 2%, and 3%. The deposited films were characterised by X-ray diffraction (XRD), ultraviolet–visible (UV–Vis) spectroscopy, and photoluminescence (PL). XRD analysis showed that the films retained the hexagonal wurtzite structure of ZnO. The crystallite/grain size estimated from the dominant (101) reflection decreased from 20.38 nm for undoped ZnO to 19.56, 17.76, and 18.01 nm for 1%, 2%, and 3% Ca-doped films, respectively. The optical band gap values were 3.65, 3.72, 3.79, and 3.70 eV for 0%, 1%, 2%, and 3% Ca, respectively. Photoluminescence measurements under different excitation wavelengths showed violet to near-ultraviolet emission, with a general shift toward shorter wavelengths as Ca concentration increased. The findings indicate that controlled Ca incorporation can modify crystallite size, optical band gap, and luminescence behaviour, making ZnO: Ca thin films promising for ultraviolet and blue-light optoelectronic applications.

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KEYWORDS: calcium-doped zinc oxide, ZnO thin films, chemical bath deposition, X-ray diffraction, optical band gap, photoluminescence.

1. INTRODUCTION

Zinc oxide (ZnO) is a wide-band-gap II–VI semiconductor that has attracted considerable attention because of its optical, electrical, piezoelectric, chemical, and thermal properties. Its hexagonal wurtzite structure, relatively large exciton binding energy, and strong ultraviolet response make it useful for optoelectronic devices, sensors, solar cells, photodetectors, light-emitting devices, and transparent conducting applications. At the nanoscale, ZnO exhibits size-dependent properties, allowing its structural and optical characteristics to be modified through synthesis conditions and controlled incorporation of dopants.

Thin-film deposition is particularly important for integrating ZnO into functional devices. Chemical bath deposition is an inexpensive, low-temperature solution-based approach capable of producing adherent and relatively uniform films over large areas. The deposition process is sensitive to precursor concentration, complexing-agent concentration, pH, bath temperature, deposition time, and post-deposition annealing. These parameters influence nucleation, crystallite growth, defect formation, and consequently the optical response of the resulting films.

Doping is an effective strategy for tuning the properties of ZnO. Calcium incorporation is of particular interest because it can alter lattice parameters, crystallite dimensions, defect populations, and optical transitions. Previous investigations have reported changes in band gap and blue/violet luminescence in Ca-doped ZnO materials. The present study therefore examines Ca-doped ZnO thin films prepared by CBD, focusing on the relationship between Ca concentration and structural, optical absorption, and photoluminescence characteristics.

2. OBJECTIVES

- To synthesize undoped and Ca-doped ZnO thin films by the chemical bath deposition technique.
- To investigate the structural characteristics of the films using X-ray diffraction.
- To determine the optical band gap from UV–Vi's absorption measurements and Tauc analysis.
- To examine the photoluminescence behavior of the films under different excitation wavelengths.
- To evaluate the influence of Ca concentration on crystallite size, band gap, and emission characteristics.

3. MATERIALS AND METHODS

Film Preparation

ZnO thin films were deposited on cleaned glass substrates using the chemical bath deposition method. Zinc nitrate hexahydrate [Zn (NO3)2·6H2O] was used as the zinc precursor and diethanolamine (DEA) as the complexing agent. The glass substrates were cleaned sequentially with nitric acid, methanol, and deionized water, followed by ultrasonic cleaning and drying in a hot-air oven.

For the deposition bath, 0.2 M zinc nitrate was dissolved in 40 mL distilled water, followed by addition of 1.5 M DEA. A 25% ammonia solution was added dropwise, approximately 5–5.5 mL, until a clear solution was obtained. The bath was continuously stirred to ensure homogeneity, and the measured pH was approximately 12. The glass substrate was immersed at an inclined angle. The bath was heated for approximately 1 hour; the final bath temperature was reported as approximately 74 °C. After deposition, the coated substrates were rinsed with hot distilled water, dried, and annealed at 300 °C for 1 hour. Ca doping was achieved by introducing calcium nitrate into the zinc nitrate bath at nominal concentrations of 1%, 2%, and 3%.

Structural Characterization

The crystal structure of the films was examined using a Rigaku MiniFlex 600 X-ray diffractometer with Cu Kα radiation (λ = 1.5406 Å), scanning over 2θ = 25°–75°. Diffraction peaks were indexed by comparison with standard reference data. Crystallite size was estimated from the full width at half maximum of the intense (101) reflection using the Debye–Scherrer approach. Lattice parameters, c/a ratio, dislocation density, microstrain, residual stress, Zn–O bond length, and unit-cell volume were also evaluated from the XRD data.

Optical Characterization

UV–Vi's absorption spectra were recorded over 200–1000 nm. Optical band gaps were estimated from Tauc plots by extrapolating the linear portion of the absorption edge to the energy axis. Photoluminescence measurements were performed using excitation wavelengths of 270, 325, and 350 nm to evaluate emission behavior and the influence of Ca incorporation on the optical transitions.

4. RESULTS

Structural Properties

All investigated films exhibited the hexagonal wurtzite structure characteristic of ZnO. For undoped ZnO, diffraction peaks at approximately 31.76°, 34.40°, 36.26°, 47.48°, 56.72°, 62.89°, 68.00°, and 69.22° were assigned to the (100), (002), (101), (102), (110), (103), (112), and (201) planes, respectively. The Ca-doped films retained the ZnO wurtzite phase, indicating that the investigated Ca concentrations did not produce a detectable secondary crystalline phase under the experimental conditions.

The crystallite size decreased from 20.38 nm for undoped ZnO to 19.56 nm at 1% Ca and 17.76 nm at 2% Ca. At 3% Ca, the estimated value increased slightly to 18.01 nm. The overall reduction in crystallite size with Ca incorporation suggests that Ca affects nucleation and crystal growth during film formation. The lattice parameters remained close to the characteristic values of hexagonal ZnO, while small variations in lattice constants and c/a ratios indicate modest lattice distortion associated with Ca incorporation.

Table 1

Sample	Ca (%)	Grain/Crystallite size (nm)	a (Å)	c (Å)	Band gap (eV)
Pure ZnO	0	20.38	3.2507	5.2099	3.65
Ca-doped ZnO	1	19.56	3.2527	5.2099	3.72
Ca-doped ZnO	2	17.76	3.2507	5.2099	3.79
Ca-doped ZnO	3	18.01	3.2527	5.2069	3.70

Summary of structural and optical parameters of the prepared ZnO: Ca thin films.

Optical Absorption and Band Gap

The UV–Vi's spectra revealed strong absorption in the near-ultraviolet region. The absorption maxima were approximately 307.94 nm for pure ZnO, 304.68 nm for 1% Ca, 304.22 nm for 2% Ca, and 305.15 nm for 3% Ca. The corresponding Tauc-derived optical band gaps were 3.65, 3.72, 3.79, and 3.70 eV, respectively. The maximum band gap occurred at 2% Ca, coinciding with the smallest estimated crystallite size. This behavior is consistent with a size-dependent modification of the electronic structure, although the non-monotonic decrease at 3% Ca indicates that factors beyond crystallite size, including defect states and dopant-related electronic effects, may also contribute.

Photoluminescence

The PL spectra consisted primarily of violet to near-ultraviolet emission. Under 270 nm excitation, emission maxima were reported at 391.96, 393.93, 393.03, and 373.03 nm for 0%, 1%, 2%, and 3% Ca, respectively. Under 325 nm excitation, the corresponding values were 391.06, 391.96, 391.96, and 361.07 nm. Under 350 nm excitation, the reported maxima were 389.07, 391.96, 388, and 380 nm. Overall, increasing Ca concentration was associated with a shift of emission toward shorter wavelengths, particularly at the higher doping level. The results suggest that Ca incorporation modifies defect-related and near-band-edge recombination pathways. The reported quenching at 1% Ca also indicates that the relationship between dopant concentration and emission intensity is not strictly linear and may depend on the balance between radiative and nonradiative defect-related recombination.

5. DISCUSSION

The combined structural and optical results demonstrate that Ca incorporation modifies ZnO thin films without destroying the parent hexagonal wurtzite structure. The reduction in crystallite size up to 2% Ca is accompanied by an increase in optical band gap from 3.65 to 3.79 eV. This correlation supports the possibility of size-related quantum confinement and altered defect populations contributing to the optical shift. However, the slight increase in crystallite size and decrease in band gap at 3% Ca indicate that the effect of Ca is concentration-dependent and may involve competing mechanisms.

The persistence of the wurtzite phase across the investigated compositions is significant for device-oriented applications because the structural framework responsible for ZnO's optical and piezoelectric behaviour is retained. Small changes in lattice constants and c/a ratios suggest that Ca incorporation produces only limited structural distortion at the studied concentrations. The increase in dislocation density and microstrain up to 2% Ca is consistent with increased lattice imperfections, while the 3% sample shows a modest reduction relative to the 2% sample.

The optical results are particularly relevant to ultraviolet optoelectronics. The band gap values above that of bulk ZnO and the observed violet/near-ultraviolet PL indicate that the films can be engineered for short-wavelength emission and detection. The progressive movement of PL peaks toward shorter wavelengths with increasing Ca concentration provides evidence of a Ca-dependent blue shift. Nevertheless, the present study would benefit from additional measurements, including compositional verification by energy-dispersive X-ray spectroscopy, surface morphology by scanning electron microscopy or atomic force microscopy, electrical conductivity and carrier concentration measurements, and systematic uncertainty analysis. Such measurements would help distinguish the effects of Ca substitution from changes in oxygen-vacancy concentration and other intrinsic defects.

6. CONCLUSION

Ca-doped ZnO thin films with nominal Ca concentrations of 0%, 1%, 2%, and 3% were successfully prepared by chemical bath deposition and characterized using XRD, UV–Vis spectroscopy, and photoluminescence. All samples retained the hexagonal wurtzite structure. The estimated crystallite size generally decreased with Ca incorporation, reaching a minimum of 17.76 nm at 2% Ca. The optical band gap increased from 3.65 eV for undoped ZnO to a maximum of 3.79 eV at 2% Ca before decreasing slightly at 3% Ca. PL measurements showed violet to near-ultraviolet emission and a concentration-dependent shift toward shorter wavelengths. These results demonstrate that controlled Ca doping is an effective route for tailoring the structural and optical properties of ZnO thin films. The enhanced band gap and blue-shifted luminescence suggest potential for ultraviolet and blue-light optoelectronic devices, while further compositional, morphological, and electrical studies are recommended to establish structure–property relationships more rigorously.

Future Research Directions

- Verify Ca incorporation and chemical composition using EDS/XPS and quantify the actual dopant concentration.
- Investigate surface morphology and roughness using SEM and AFM.
- Study electrical resistivity, carrier concentration, and mobility as functions of Ca concentration.

- Examine the influence of annealing temperature and time on phase stability, crystallinity, and optical response.
- Explore Ca-doped ZnO as a transparent electrode and active layer for UV photodetectors, solar cells, and blue/UV optoelectronic devices.

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Ackinsa Manuel is associated with the Department of Physics, Nirmalagiri College, Kuthuparamba, Nirmalagiri, Kerala, India. Their academic interests encompass physics education and scientific research. Dedicated to advancing knowledge through teaching and scholarly activities, they contribute to higher education by promoting scientific inquiry, innovation, and academic excellence in the field of physics.