

# Structural and Optical Properties of ZnO:Al and ZnO:Cu Nanoparticle Thin Films

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**ABSTRACT----** *Pure and Al- and Cu-doped ZnO nanoparticle thin films were deposited on a glass substrate using the chemical spray pyrolysis technique at 400 °C. X-ray diffraction analysis confirmed the formation of the stable hexagonal wurtzite structure of the ZnO films with crystallite sizes in the range of 21. 72–26. 73 nm. The morphology of the films was studied by atomic force microscopy, which revealed that the films were homogeneous in structure with a surface roughness of 1. 02–4. 47 nm and grain sizes in the range of 101. 33–90. 35 nm; these features depended on the type and concentration of the dopant. The optical characteristics of the films were studied by UV–Vis spectrophotometry at 300–1100 nm, which revealed that the doped and undoped films present high transmittance (>90%) in the visible wavelength range. The direct optical energy gap of the films ranged from 3. 3 eV to 3. 2 eV and also depended on the type and concentration of the dopant.*

**Keywords---** Nanoparticle, ZnO:Al, ZnO:Cu, Structural, Optical, Thin films

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## 1. INTRODUCTION

ZnO nanomaterials are highly versatile materials with excellent mechanical, electrical, magnetic, and chemical sensing properties. ZnO has a wide direct band gap of 3. 37 eV [1], and doped ZnO films have been used in various applications, such as electronic devices, optical devices, and gas sensors [2–4]. Paragnay et al. [5] observed that the surface morphology and electronic defects of ZnO films are strongly dependent on the type and concentration of their dopant atoms.

Pure and doped ZnO films have been investigated for use in gas sensors [5–7]. One of the requirements of gas sensors is low power consumption because the sensor must work reliably and continuously. A material with low resistance has a low driving power when used as a sensor. Appropriate donor doping can produce electronic defects that increase the influence of the partial pressure of oxygen on the conductivity of ZnO films.

In this work, we investigated the structural and optical properties of spray-pyrolyzed ZnO:Al and ZnO:Cu nanoparticle films.

## 2. EXPERIMENTAL

Pure and doped ZnO thin films with 3 vol. %, 5 vol. %, and 7 vol. % Al and Cu were prepared by chemical spray pyrolysis. The films were deposited on micro glass slides that were first cleaned with detergent water and then dipped in acetone. The spray solution was prepared by mixing 0. 1 M aqueous solutions of ZnCl<sub>2</sub>(99% purity) , AlCl<sub>3</sub>·6H<sub>2</sub>O and CuCl<sub>2</sub> at concentrations of 3 vol. %, 5 vol. %, and 7 vol. % using a magnetic stirrer.

The spray solution was then transferred to a hot glass substrate kept at 400 °C using filtered air as the carrier gas flowing at a normalized rate of approximately 3 mL/min. To prevent the substrate from cooling excessively, the prepared solution was sprayed on the substrate for 10 s at 15 s intervals. The films had a uniform thickness averaging 550 nm. The structural properties of the films were determined by X-ray diffraction (XRD, Shimadzu) with CuK $\alpha$  radiation ( $\lambda = 0. 15406$  nm). Film morphologies were analyzed by atomic force microscopy (AFM, CSPM). The optical absorption and transmission spectra of the films were obtained using a UV–Vis spectrophotometer (6800 JENWAY, Germany) within the wavelength range of 300–1100 nm.

### 3. RESULTS AND DISCUSSION

#### 3.1 Structural Properties

The XRD spectra of the as-grown Al- and Cu-doped ZnO films are shown in Figures 1 and 2. The peaks observed clearly matched those in ASTM Card No. 00-001-1136, which reveals that the ZnO thin films exhibit a crystal structure of

the hexagonal wurtzite type with a preferred orientation of (002). No phase corresponding to Al, Cu, or their other compounds were observed in the XRD spectra. Doping affected the peak intensity along these planes. Crystallinity decreased along the (002) plane with increasing Al and Cu doping concentration but improved along the (100), (101), and (102) plane at 5 vol. % Al doping and along the (101) and (102) planes at 5 vol. % Cu doping. These results agree with those reported by Prajapati et al. [7], Wasan et al. [8], and Shampa [9]. Grain size decreased from 26.73 nm to 22.27 nm with 5 vol. % Al doping and 21.7 nm with 5 vol. % Cu doping, as shown in Table 1. The grain size was determined for the main peak at  $2\theta=34.31^\circ$  of the (002) plane using the Debye–Scherrer formula [10]; that the d-spacing of the films changed according to the dopant type, likely because of differences in the ionic radii of  $Zn^{2+}$ ,  $Cu^{2+}$ , and  $Al^{3+}$ , which are equal to 0.074, 0.069, and 0.054 nm respectively. These ionic radii imply that the doping atoms were incorporated into the crystal structure of the ZnO film.

Figures 3, 4, and 5 display AFM images of the pure and Al- and Cu-doped films. The presence of homogeneous grains throughout the films can be clearly observed. The grain size of the ZnO:Al films ranged from 101.33 nm to 97.13 nm, while that of the ZnO:Cu films ranged from 101.33 nm to 90.35 nm; grain sizes depended on the dopant concentration. The grain size, root mean square (RMS), and surface roughness of the films are shown in Table 2. Roughness increased from 1.02 nm for the pure film to 2.05 and 4.47 nm for the films doped with 5 vol. % Al and Cu, respectively. RMS also increased from 1.22 nm for the pure film to 2.74 and 5.19 nm for films doped with 5 vol. % Al and Cu, respectively. These results demonstrate that roughness and RMS increase with decreasing grain size.

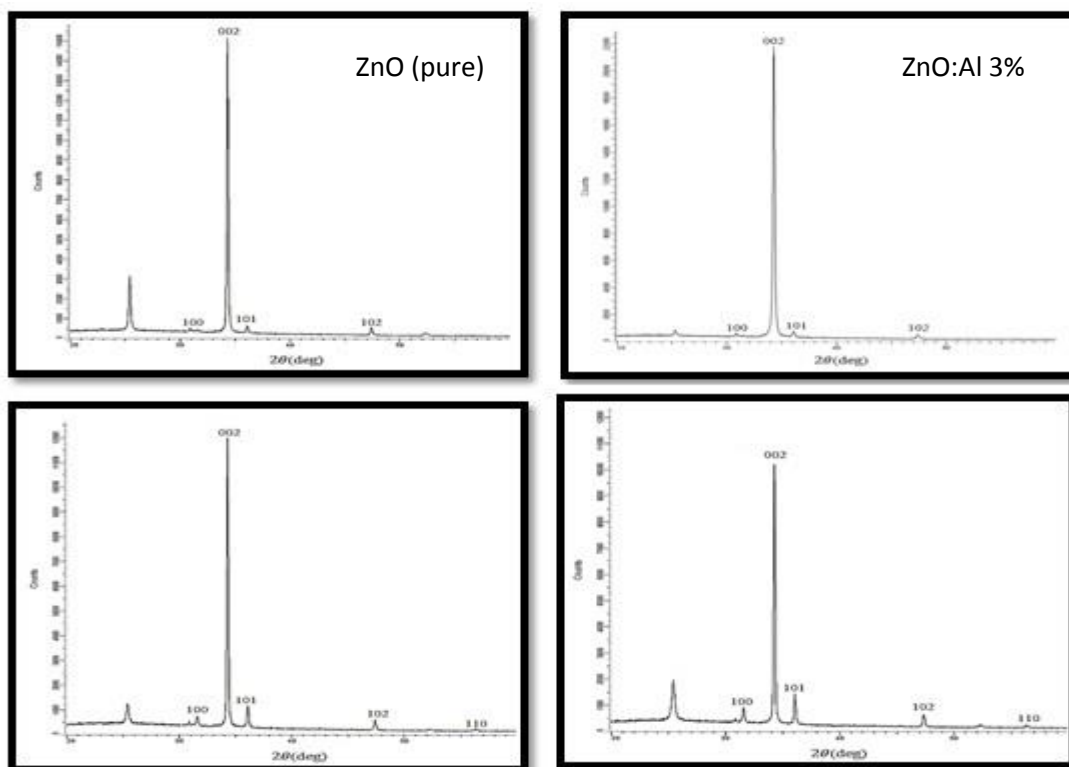
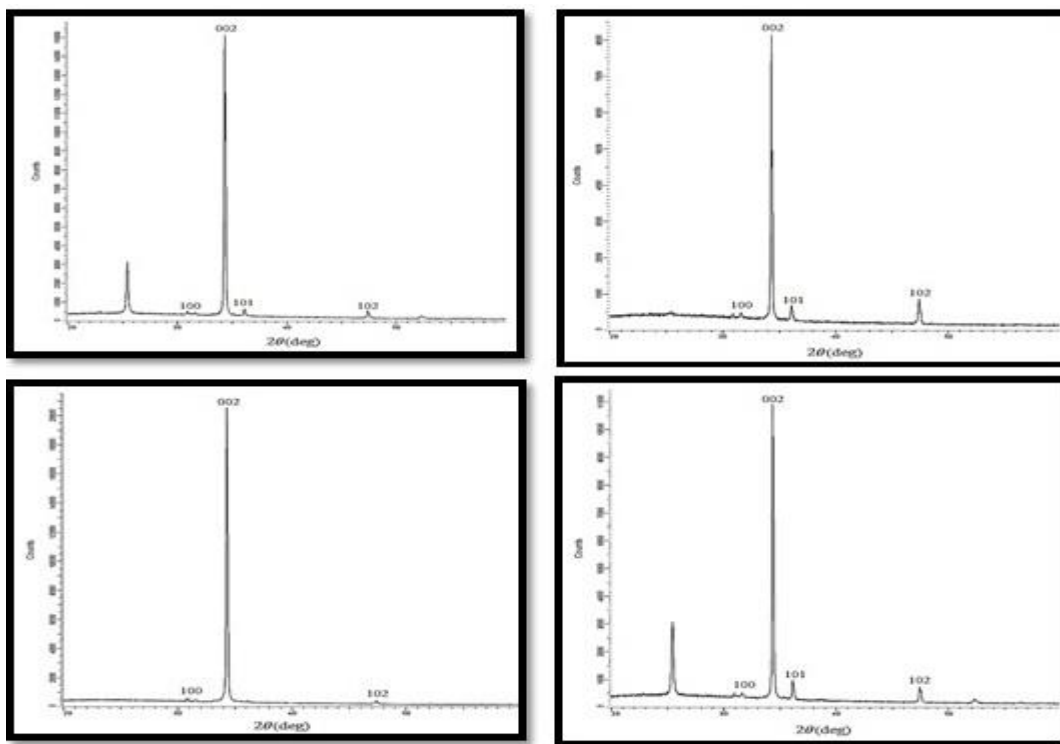


Figure 1: XRD pattern for ZnO:Al thin films



**Figure 2:**XRD pattern for ZnO:Cu thin films

**Table1:**X-Ray diffraction analysis of the Al,Cu doped and undoped ZnO thin films for (002 ) plane

sample	2θ deg.	$d_{hkl}$ Å <sup>o</sup>	Intensity counts)	Crystal size ( nm)
ZnO/ASTM (001-1136)	34. 33	2. 610	—	—
ZnO pure	34. 31	2. 6115	15200	26. 73
ZnO:AL (3%)	34. 28	2. 6137	22000	23. 48
ZnO:AL (5%)	34. 3	2. 6123	12000	22. 27
ZnO:AL (7%)	34. 27	2. 6145	11900	22. 56
ZnO:CU(3%)	34. 315	2. 612	8200	25. 7
ZnO:CU(5%)	34. 36	2. 608	10900	22. 86
ZnO:CU(7%)	34. 32	2. 6108	20500	21. 72

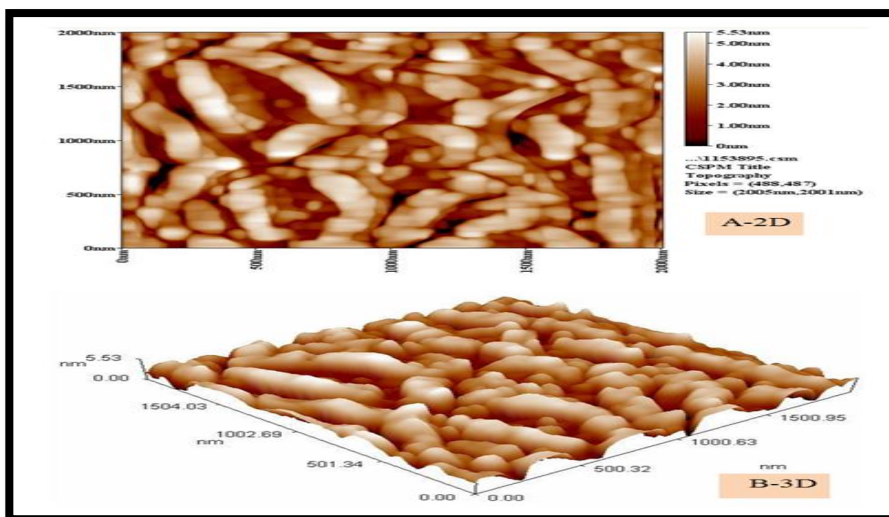


Figure 3: AFM image for pure ZnO

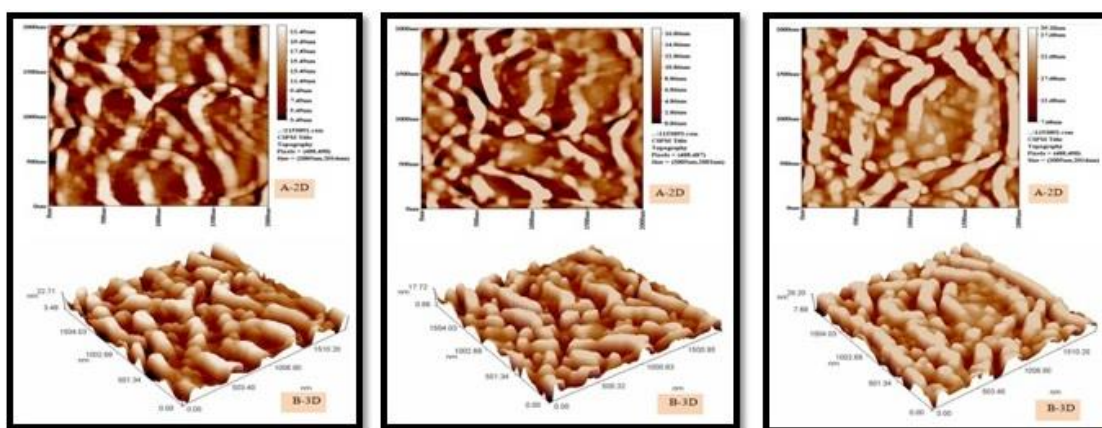


Figure 4: AFM image for ZnO:Al, a(3%), b(5%), c(7%)

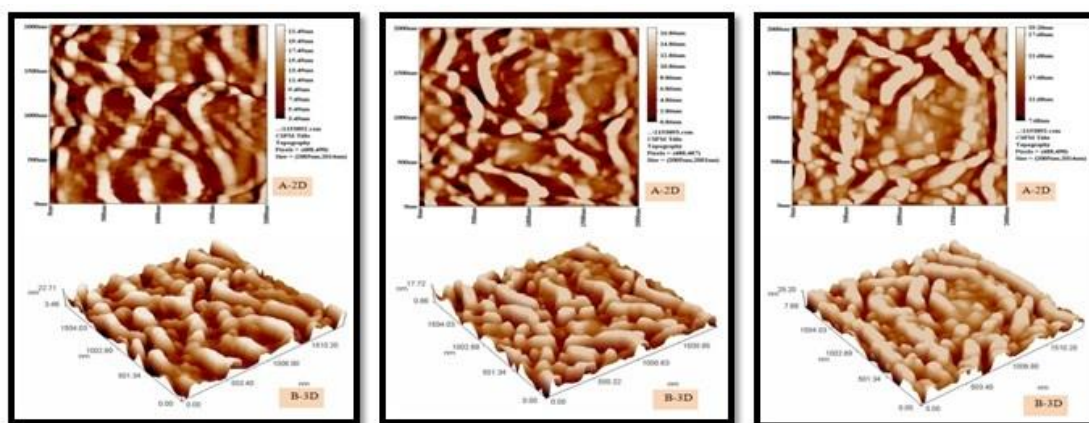
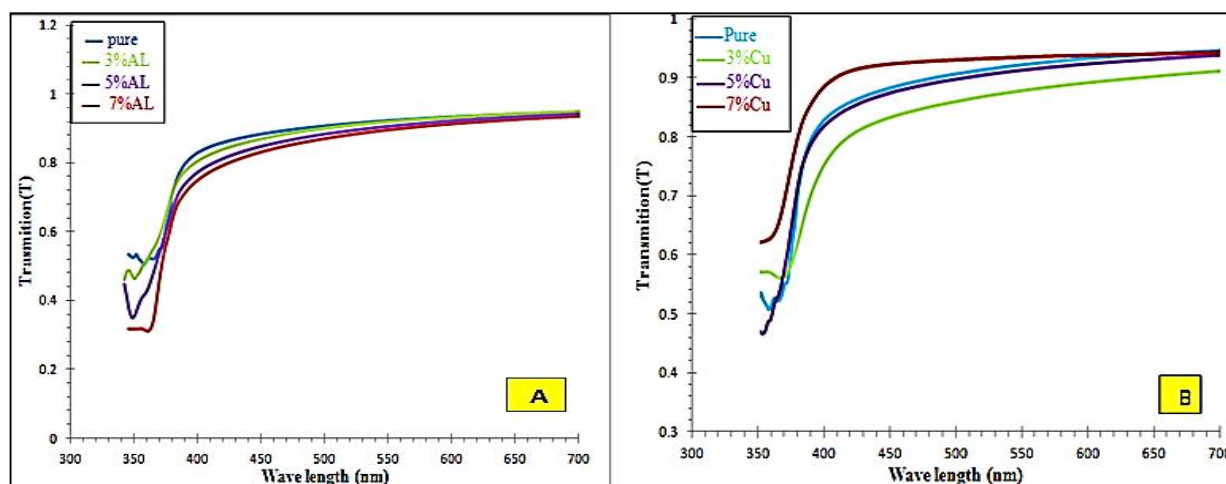


Figure 5: AFM image for ZnO:Cu a(3%), b(5%), c(7%)

**Table 2:**AFM analysis of undoped and Al,Cu doped ZnO thin films

Doping concen.	Roughness Average (nm)		Root mean Square (nm)		Peak-Peak		Grain Size (nm)	
	Al	Cu	Al	Cu	Al	Cu	Al	Cu
3%	1.35	3.74	1.6	4.31	6.71	14.3	97.13	98.55
5%	2.05	4.47	2.74	5.19	11.5	17.8	97.82	93.83
7%	1.85	0.815	2.2	0.974	8.85	18.1	105.65	90.35
0%	1.02		1.22		5.53		101.33	



**Figure 6:** Optical transmission of ZnO thin films doped by A-(Al), B-(Cu)

### 3. 2-Optical properties

Figure 6 presents the transmittance spectra of the undoped and Al- and Cu-doped films as a function of wavelength in the visible region. The pure film showed >90% transmittance, and transmittance increased or decreased depending on the type and concentration of the dopant. Figure 6 illustrates that the transmission of the films decreased to 87% as the Al concentration increased and reached 92% as the Cu concentration increased. Shelke et al. [11] found that transmittance decreases with increasing Sn doping of ZnO. Tsayet al. [12] also found that the transmittance of sol-gel-derived ZnO thin films increases with increasing Sn doping.

The discrepancy in the results of Al and Cu doping may be due to differences in the process parameters of film growth. The increased surface roughness of the films also decreased their transmittance, as evidenced by the results of AFM analysis. Rough surfaces increase optical scattering, which, in turn, reduces optical transmittance.

The optical band gaps of ZnO:Al and ZnO:Cu films are shown in Figure 7 and were compared with the band gap of undoped ZnO as calculated using Tauc's formula for direct band gap semiconductors [13,14]:

$$(\alpha h\nu)^2 = \beta (h\nu - E_g)$$

where  $\alpha$  is the absorption coefficient,  $\beta$  is a constant,  $E_g$  is the optical energy gap,  $\nu$  is the incident photon frequency, and  $h$  is Planck's constant. The energy gap of pure ZnO is equal to 3.3 eV. The  $E_g$  of Al-doped films decreased with increasing Al concentration, reaching 3.25 eV at 5 vol. % and then decreasing to 3.2 eV at 7 vol. %. This result reveals that the absorption edge of the films shifted toward lower energy levels (red shift) when Al is used as a dopant. By comparison, the  $E_g$  of Cu-doped films increased with increasing Cu concentration, reaching 3.26 eV at 7 vol. % as shown in Table 3.

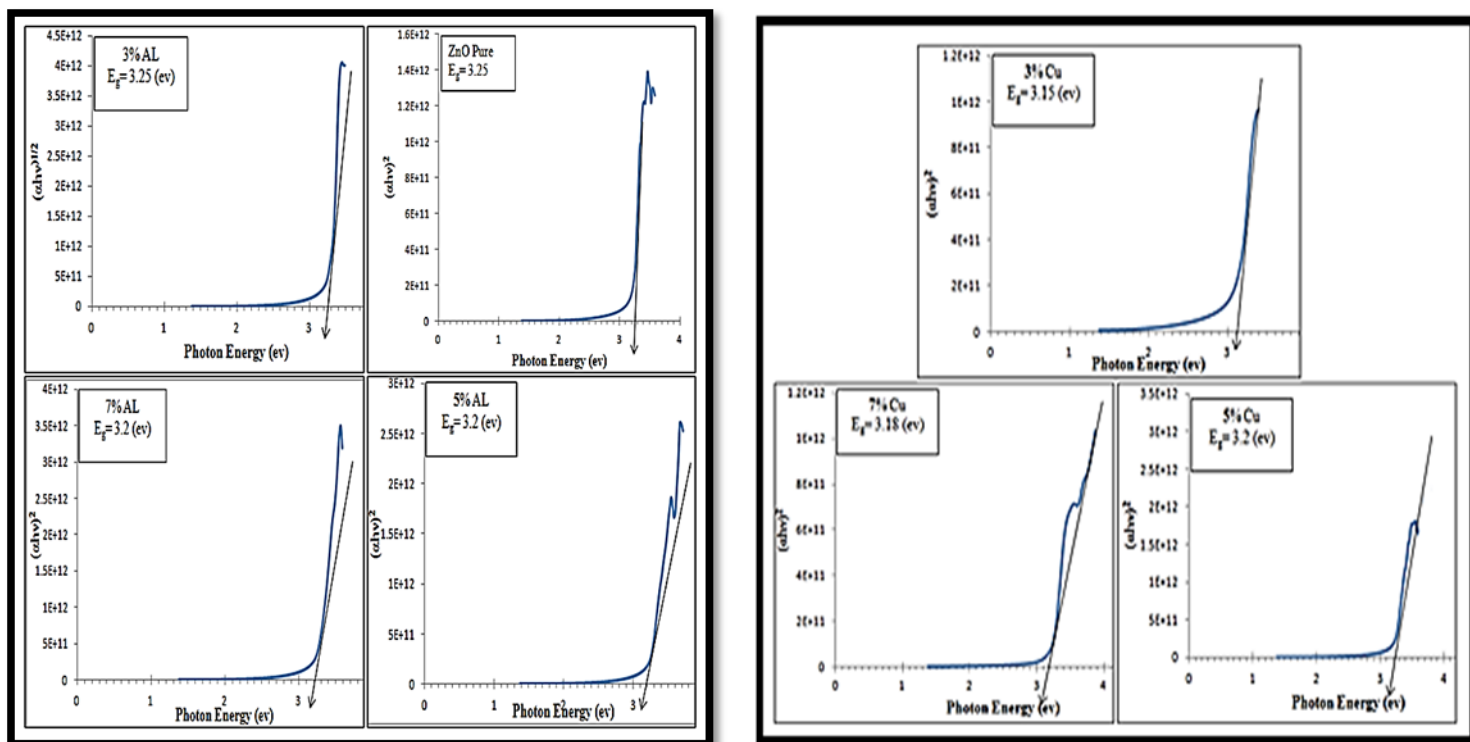


Figure 7: plots of  $(\alpha h\nu)^2$  with  $(h\nu)$  of ZnO:Al,Cu thin films

Table3: The optical energy gap ( $E_g$ ) of pure and doped ZnO thin films

concentration	$E_g$ eV (Al)	$E_g$ eV (Cu)
0%	3.3	3.3
3%	3.29	3.2
5%	3.25	3.25
7%	3.2	3.26

#### 4. CONCLUSIONS

Undoped and Al- and Cu-doped ZnO thin films grown by the chemical spray pyrolysis technique were found to possess a hexagonal wurtzite structure and nanoscale grain sizes that decreased with the doping concentration. Morphological analysis showed that the films were homogeneous in structure and had grain sizes smaller than 100 nm; grain size decreased according to the dopant type and concentration. Optical studies revealed that the films have high transmittance (>90%) that increased or decreased slightly according to the type of dopant used. The undoped film showed a direct band gap equal to 3.3 eV; this value also decreased or increased slightly according to the dopant type and concentration.

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