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LETTER TO THE EDITOR Open Access

Study on the correlation between crystallite size and optical gap energy of doped ZnO thin film

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Abstract

In the present paper, we have studied a new approach to the description of correlation between the optical and structural properties of ZnO thin films with doping levels of Al, Co, and In. The doped zinc oxide thin films were deposited using ultrasonic spray technique on a glass substrate at 350°C. The correlation between structural and optical properties with doping level suggests that the crystallite size of the films is predominantly estimated by the bandgap energy and the concentration of Al, Co, and In. Also, the gap energy of doped films was estimated by the crystallite size and doping level. The measurement in the crystallite size and optical gap energy of doped films with correlation is equal to the experimental data. The minimum error value was estimated in doped ZnO thin films with indium and cobalt. Thus, results indicate that such Co-doped ZnO thin films are chemically purer and have many fewer defects and less disorder, owing to an almost complete chemical decomposition.

Keywords: ZnO; Thin films; Semiconductor doping; Crystallite size; Optical gap energy; Correlation

Findings

Background

Zinc oxide has a wurtzite structure, which is a hexagonal crystal structure (lattice parameter: $a = 0.325$ nm, $c = 0.521$ nm), belonging to the space group P63mc, and is characterized by two interconnecting sublattices of Zn^{2+} and O^{2-}, such that each Zn ion is surrounded by a tetrahedra of O ions and vice versa [1]. ZnO which is one of the most important binary II-VI semiconductor compounds is a natural n-type electrical conductor with a direct energy wide bandgap of 3.37 eV at room temperature and a large exciton binding energy (approximately 60 meV) [2-5].

ZnO thin films can be doped with a variety of semiconductors to meet the demands of several application fields. Stoichiometric ZnO films are highly resistive. Conducting films can be made either by creating oxygen vacancies, which act as donors, or by doping with various dopants such as Ga^{3+}, Mn^{4+}, Al^{3+}, In^{3+}, Co^{2+}, and V^{3+} [6-11]. Many attempts were reported about doped ZnO films, but most of them are related with Al doping. There are several works that use dopants such as Co, In, or Al in ZnO to enhance the optical and electrical conductivity. The doped films can be used for various applications such as transparent electronics, piezoelectronic devices, gas sensors, and the transparent electrode window layer of thin-film solar cells [8-13]. The films (ZnO:Al) are considered to be utmost important materials due to their high conductivity, good transparency, and lower cost.

The aim of this paper is to study the possibility of the correlation between the optical and structural properties of ZnO thin films with doping level. Ramana et al. [14] found that the grain size of V_2O_5 thin films produced by pulsed laser ablation strongly influences their optical characteristics. Bensouyad et al. [15] describe the relation between structural and optical properties of TiO_2: ZnO thin films in a considerate experimental study and controlled the variation of crystallite size by modifying the annealing temperature, film thickness, and doping. Therefore, Cuong Ton-That et al. [16] estimated the direct correlation between the bandgap and crystal structure and suggest that the band edge optical properties of Mn-doped ZnO are predominantly influenced by the amount of Mn atoms substituting Zn on the lattice sites. However, similar works have investigated the dependence of physical properties of a ZnO thin film as a function of parameter conditions such a temperature,

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thickness, oxidizing conditions, nitrogen addition, and doping for characterizing the thin films [17-25].

The aim of our paper is to present a new approach to calculate the crystallite size by the optical gap energy and doping level of a doped ZnO thin film. Also, we have estimated the relationships between the optical gap energy and the crystallite size with doping level of doped ZnO thin films. Detailed calculations are developed from doped ZnO thin films with Al, Co, and In.

Methods and model

The ZnO, ZnO:Al, ZnO:Co, and ZnO:In samples were deposited on glass substrates using ultrasonic spray technique at a temperature of 350°C with 2 min of deposition time. The optical gap energy and crystallite size of the films were measured with doping level. In our papers, we have studied the effect of various parameters such as doping level, growth times, substrate temperature, and annealing temperature of the ZnO thin films [26-31] (see Table 1).

The correlation between the structural and optical properties of doped ZnO thin films was investigated in two parts. First, we studied the optical gap energy and doping level. Second, we estimated a correlation with crystallite size and the doping level for the optical gap energy, wherein ZnO was doped by various elements such Al, Co, and In and the element concentration was changed to get a doping limitation.

The correlation parameters for the crystallite size (G), bandgap energy (E_g), and doping level X_0 of doped ZnO thin films resulted from the following equation:

$$\begin{cases} G_{(*)} = \dfrac{G_{(e)}}{G_{(e)Max}} \\ E_{g(*)} = \dfrac{E_{g(e)}}{E_{g(e)Max}} \\ X_{0(*)} = \dfrac{X_{0(e)}}{X_{0(e)Max}}, \end{cases} \quad (1)$$

where $G_{(e)}$, $E_{g(e)}$, and $X_{0(e)}$ are the experimental data; $G_{(e)Max}$, $E_{g(e)Max}$, and $X_{0(e)Max}$ are maximal experimental values; and $G_{(*)}$, $E_{g(*)}$, and $X_{0(*)}$ are the first values that have been calculated in the correlation relationships.

Table 1 E_g and G of ZnO, ZnO:Al, ZnO:Co, and ZnO:In as a function of Al concentration [26-31]

Doping (%)	ZnO:Al		ZnO:Co		ZnO:In	
	E_g (eV)	G (nm)	E_g (eV)	G (nm)	E_g (eV)	G (nm)
0	3.10	29.76	3.25	33.28	3.25	33.28
1	3.15	17.35	3.295	35.25	-	-
2	3.19	18.93	3.362	55.46	3.158	41.60
3	3.26	32.05	3.30	40.19	3.185	45.78
4	3.13	16.02	-	-	3.066	32.002
5	3.15	14.36	-	-	-	-

E_g, band gap energy; G, crystallite size.

Results

Correlation with crystallite size

The doped ZnO thin films were deposited for the precursor molarity equal to 0.1 M. In this point, the doping level is equal to zero for undoped ZnO thin films. Therefore, we have estimated the relationships between the crystallite size and the bandgap energy with doping level as the following empirical relationships:

$$\begin{cases} G_{(c)} = a \times E_{g(*)}^{\,b} \times X_{0(*)}{}^{c} & \text{if} \quad X_0 > 0 \\ G_{(c)} = 1.4442 \times 10^{-4} \times 6,627^{\,E_{g(*)}} & \text{if} \quad X_0 = 0 \end{cases}, \quad (2)$$

where a, b, and c are empirical constants and depend on the dopant. These parameters are collected in Table 2 and estimated as a function of dopant element. Table 3 present the correlate values.

$$\begin{aligned} &\text{ZnO:Al} \quad G_{(c)} = 0.963 \times E_{g(*)}^{19.67} \times X_{0(*)}{}^{-0.035} \\ &\text{ZnO:Co} \quad G_{(c)} = 1.038 \times E_{g(*)}^{19.32} \times X_{0(*)}{}^{0.092} \\ &\text{ZnO:In} \quad G_{(c)} = 1.227 \times E_{g(*)}^{9.657} \times X_{0(*)}{}^{0.033} \end{aligned}$$

Correlation with optical gap energy

In this part, we have studied the correlation between the optical gap energy and the crystallite size with doping level. The formula studied in the correlation with crystallite size is based on a nonlinear correlation; however, we have chosen the complex equation to correlate the optical gap energy as the following empirical relationships:

$$\begin{cases} E_{g(c)} = \exp\left(a' \times \left(\ln G_{(*)} - \left(b' \times \ln X_{0(*)} + c'\right)\right)\right) \\ \qquad \text{if} \quad X_0 > 0 \\ E_{g(c)} = 0.11365 \ln G_{(*)} + 1.00498 \\ \qquad \text{if} \quad X_0 = 0 \end{cases} \quad (3)$$

Table 2 Variation of empirical constants estimated by Equations 2 and 3 of ZnO:Al, ZnO:Co, and ZnO:In

Empirical constants	Dopant element		
	Al	Co	In
a	0.963	1.038	1.227
a'	0.04978	0.05176	0.03386
b	19.67	19.32	9.657
b'	−0.04295	0.09271	0.7691
c	−0.03524	0.0927	0.0333
c'	−0.02884	0.03759	1.096

Table 3 G and E_g of ZnO:Al, ZnO:Co, and ZnO:In as a function of doping level

Doping (%)	ZnO:Al		ZnO:Co		ZnO:In	
	G_c (nm)	$E_{g(c)}$ (eV)	G_c (nm)	$E_{g(c)}$ (eV)	G_c (nm)	$E_{g(c)}$ (eV)
0	28.48	3.12	31.85	3.260	31.85	3.260
1	16.63	3.156	35.24	3.295	/	/
2	20.80	3.174	55.44	3.362	41.59	3.178
3	31.43	3.261	40.18	3.300	45.77	3.155
4	13.97	3.152	/	/	31.99	3.094
5	15.71	3.137	/	/	/	/

The crystallite size and optical gap energy were estimated by Equations 2 and 3. G, crystallite size; E_g, optical gap energy; G_c, correlate value of crystallite size; $E_{g(c)}$, correlate value of optical gap energy.

where a', b', and c' are empirical constants and depend on the dopant. These parameters are collected in Table 2 and estimated as a function of dopant element.

$$\mathrm{ZnO{:}Al}\quad E_{g(c)} = \exp\left(0.04978 \times \left(\ln G_{(*)} - \left(-0.04295 \times \ln X_{0(*)} - 0.02884\right)\right)\right)$$

$$\mathrm{ZnO{:}Co}\quad E_{g(c)} = \exp\left(0.05176 \times \left(\ln G_{(*)} - \left(0.09271 \times \ln X_{0(*)} + 0.03759\right)\right)\right)$$

$$\mathrm{ZnO{:}In}\quad E_{g(c)} = \exp\left(0.03386 \times \left(\ln G_{(*)} - \left(0.7691 \times \ln X_{0(*)} + 1.096\right)\right)\right)$$

Discussion

In this study, we will show the evolution of the doping level on the crystallite size and optical gap energy. We tried to establish correlations for each model proposed. In our calculations, the crystallite size and optical gap energy of doped ZnO thin films were estimated from Equations 2 and 3; the ZnO films exhibiting single crystals are n-type semiconductors with a high crystallinity.

As shown in Figures 1, 2, and 3, significant correlation was found between the crystallite size and the optical gap values of the doped ZnO thin films as a function of Al, Co, and In concentration, respectively. The increase of the crystallite size has been indicated by the enhancement of the crystallinity and c axis orientation of ZnO thin films by Zhu et al. [25]. The measurement in the crystallite size of doped films by Equation 2 is equal to the experimental data; thus, the error of this correlation is smaller than 13% and can be calculated from the relationship $|(G_{\mathrm{Exp}} - G_{\mathrm{Corr}})/G_{\mathrm{Exp}}| \times 100$. The minimum error value was estimated in the cobalt- and indium-doped ZnO thin films (see Figure 4).

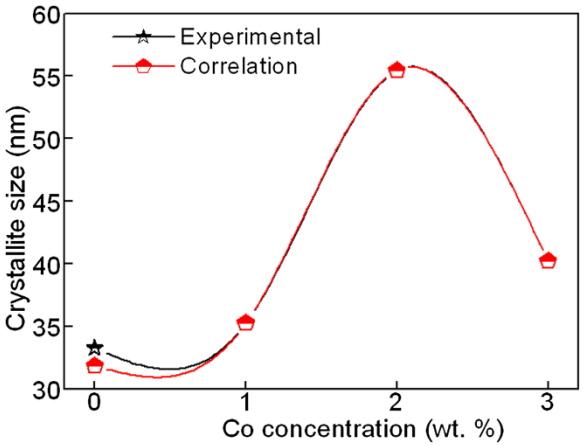

Figure 2 Experimental crystallite size and correlation of ZnO:Co thin films as a function of Co concentration.

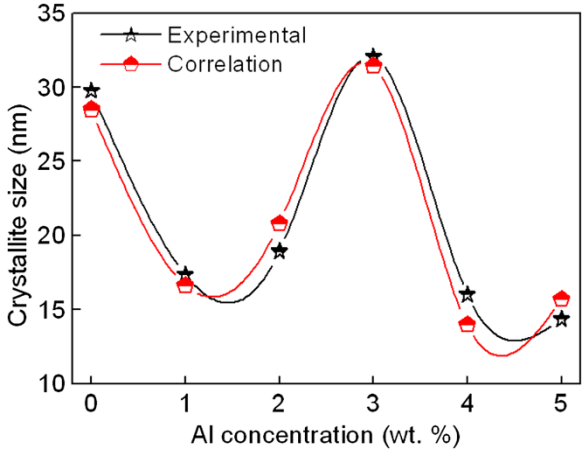

Figure 1 Experimental crystallite size and correlation of ZnO:Al thin films as a function of Al concentration.

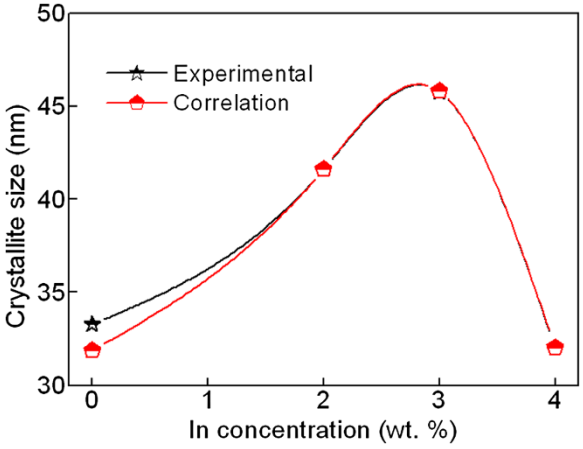

Figure 3 Experimental crystallite size and correlation of ZnO:In thin films as a function of In concentration.

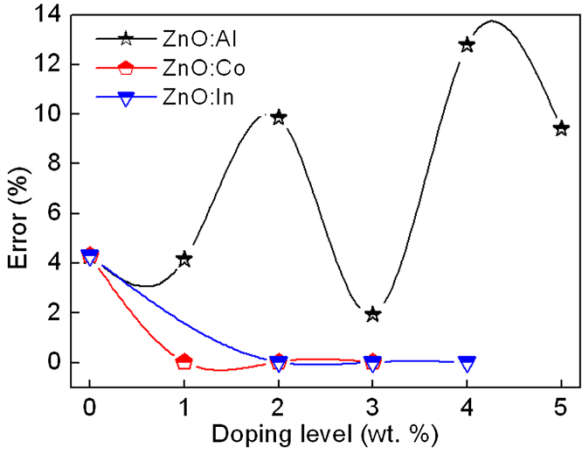

Figure 4 Error variation of crystallite size of doped ZnO thin films as a function of doping level. The error variation was estimated by Equation 2.

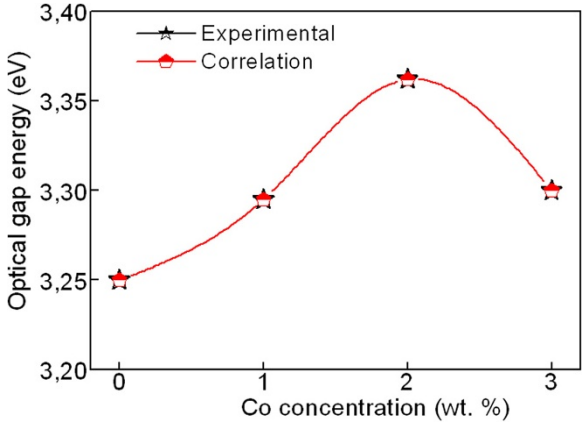

Figure 6 Experimental optical gap energy and correlation of ZnO:Co thin films as a function of Co concentration.

The maximum enhancement of the crystallite size was found to be of minimum error after doping at 3 wt.% (see Figure 4). The amount of Al, Co, and In doping contents achieved in doped ZnO film is 3 wt. %. Based on the experimental and correlation values for the crystallite size that were developed, good agreement was found between the calculated and experimental values.

The variation of optical gap energy with doping level calculated by Equation 3 is shown in Figures 5, 6, and 7 and shows that the optical gap energy can be estimated using crystallite size data by varying the doping level in all films. The final correlation data show that the errors calculated from Equation 3 are smaller than those from Equation 2, as shown in Figure 8. As can be seen, the minimal error is achieved in Co-doped ZnO thin films and limited to 0% in all concentrations.

We know that such ZnO:Co and ZnO:In thin films are chemically purer and have many fewer defects and less disorder, owing to an almost complete chemical decomposition, and contain higher optical bandgap energy; thus, we have obtained a minimum error with crystallite size from Equation 2.

We have estimated the crystallite size and optical bandgap of doped films using various elements such as Al, Co, and In. The element concentration was changed to get a doping limitation. As can be noted, the ZnO thin film considers a higher transition tail width between the conduction band and valence band. From Equation 3, it can be concluded that the optical gap is affected by the crystallite size of undoped and doped ZnO thin films.

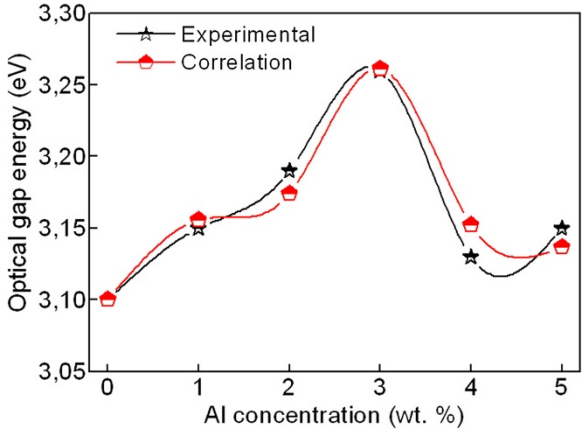

Figure 5 Experimental optical gap energy and correlation of ZnO:Al thin films as a function of Al concentration.

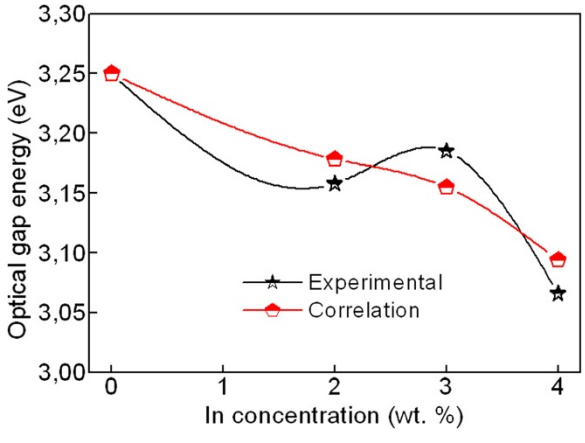

Figure 7 Experimental optical gap energy and correlation of ZnO:In thin films as a function of In concentration.

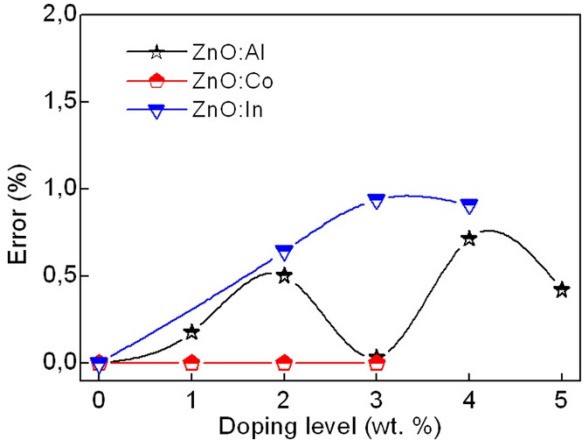

Figure 8 Error variation of optical gap energy of doped ZnO films as function of doping level. The error variation is estimated by Equation 3.

Thus, the correlation between the crystallite size and the bandgap with the doping level was investigated.

Conclusion

In this paper, we have presented a new approach to the description of correlation between crystallite size and optical gap energy with doping levels of Al, Co, and In. The following conclusions can be drawn from the results presented:

- The correlation between the crystallite size and the bandgap with doping levels of Al, Co, and In was investigated.
- The crystallite size of the films is predominantly estimated by the bandgap energy and the concentration of Al, Co, and In. Also, the gap energy of doped films was estimated by the crystallite size and doping level.
- The measurement in the crystallite size and optical gap energy of doped films with correlation is equal to the experimental values.
- The error of correlation of the crystallite size is smaller than 14%; the minimum error achieved for ZnO:Co and ZnO:In is limited to 0%. However, for the correlation of the optical gap energy, the error found is smaller than 2%. Co-doped ZnO films have a minimal error limited to 0%.

Competing interests

The authors declare that they have no competing interests.

Authors' contributions

AA participated in the modeling section. OB and AG participated in the design section. SB participated in the experimental data and performed the statistical analysis. SB, AA, OB, and AG carried out the manuscript preparation. All authors read and approved the final manuscript.

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References

1. Ohtsu, M: Progress in Nano-Electro Optics VII, pp. 73–108. , Tokyo (2002)
2. Zhang, Y, Wu, C, Zheng, Y, Guo, T: Synthesis and efficient field emission characteristics of patterned ZnO nanowires. J. Semicond. **33**, 023001–1 (2012)
3. Zhang, H, Liu, H, Lei, C, Zhou, A, Yuan, C: Low-temperature deposition of transparent conducting Mn–W co-doped ZnO thin films. J. Semicond. **31**, 083005–1 (2010)
4. Benramache, S, Benhaoua, B, Khechai, N, Chabane, F: Elaboration and characterization of ZnO thin films. Matériaux Tech. **100**, 573–580 (2012)
5. Ma, L, Ai, X, Huang, X, Ma, S: Effects of the substrate and oxygen partial pressure on the microstructures and optical properties of Ti-doped ZnO thin films. Superlattice. Microst. **50**, 703–712 (2011)
6. Wang, SK, Lin, TC, Jian, SR, Juang, JY, Jang, JSC, Tseng, JY: Effects of post-annealing on the structural and nanomechanical properties of Ga-doped ZnO thin films deposited on glass substrate by rf-magnetron sputtering. Appl. Surf. Sci. **258**, 1261–1266 (2011)
7. Mazhdi, M, Saydi, J, Karimi, M, Seidi, J, Mazhdi, F: A study on optical, photoluminescence and thermoluminescence properties of ZnO and Mn doped-ZnO nanocrystalline particles. Optik **124**, 4128–4133 (2011)
8. Hafdallah, A, Yanineb, F, Aida, MS, Attaf, N: In doped ZnO thin films. J. Alloys. Compd. **509**, 7267–7270 (2011)
9. Rahmane, S, Djouadi, MA, Aida, MS, Barreau, N, Abdallah, B, Hadj Zoubir, N: Power and pressure effects upon magnetron sputtered aluminum doped ZnO films properties. Thin Solid Films **519**, 5–10 (2010)
10. Van, LH, Hong, MH, Ding, J: Structural and magnetic property of Co-doped ZnO thin films prepared by pulsed laser deposition. J. Alloys. Compd. **449**, 207–209 (2008)
11. Mhamdi, A, Boukhachem, A, Madani, M, Lachheb, H, Boubaker, K, Amlouk, A, Amlouk, M: Study of vanadium doping effects on structural, opto-thermal and optical properties of sprayed ZnO semiconductor layers. Optik **124**, 3764–3770 (2013)
12. Rozati, SM, Akesteh, S: Characterization of ZnO:Al thin films obtained by spray pyrolysis technique. Mater. Charact. **58**, 319–323 (2007)
13. Ma, QB, Ye, ZZ, He, HP, Wang, JR, Zhu, LP, Zhao, BH: Preparation and characterization of transparent conductive ZnO:Ga films by DC reactive magnetron sputtering. Mater. Charact. **59**, 124–129 (2008)
14. Ramana, CV, Smith, RJ, Hussain, OM: Grain size effects on the optical characteristics of pulsed-laser deposited vanadium oxide thin films. Phys. Stat. Sol. A **199**, R4–R6 (2003)
15. Bensouyad, H, Adnane, D, Dehdouh, H, Toubal, B, Brahimi, M, Sedrati, H, Bensaha, R: Correlation between structural and optical propertiesof TiO2: ZnO thin films prepared by sol–gel method. J. Sol–gel Sci. Technol. **59**, 546–552 (2011)
16. Ton-That, C, Foley, M, Phillips, MR, Tsuzuki, T, Smith, Z: Correlation between the structural and optical properties of Mn-doped ZnO nanoparticles. J. Alloys. Compd. **522**, 114–117 (2012)
17. Joshi, B, Ghosh, S, Srivastava, P, Kumar, P, Kanjilal, D: Correlation between electrical transport, microstructure and room temperature ferromagnetism in 200 keV Ni^{2+} ion implanted zinc oxide (ZnO) thin films. Appl. Physica. **107**, 393–400 (2012)
18. Wang, SD, Miyadera, T, Minari, T, Aoyagi, Y, Tsukagoshi, K: Correlation between grain size and device parameters in pentacene thin film transistors. Appl. Phys. Lett. **93**, 043311–1 (2008)
19. Minami, T, Nanto, H, Takata, S: Correlation between film quality and photoluminescence in sputtered ZnO thin films. J. Mater. Sci. **17**, 1364–1368 (1982)

20. Zhu, JJ, Vines, L, Aaltonen, T, Kuznetsov, AY: Correlation between nitrogen and carbon incorporation into MOVPE ZnO at various oxidizing conditions. Microelectronics J. **40**, 232–235 (2009)
21. Deng, R, Zou, Y, Tang, H: Correlation between electrical, optical properties and Ag^{2+} centers of ZnO:Ag thin films. Physica. B. **403**, 2004–2007 (2008)
22. Ajimsha, RS, Das, AK, Singh, BN, Misra, P, Kukreja, LM: Correlation between electrical and optical properties of Cr:ZnO thin films grown by pulsed laser deposition. Physica. B. **406**, 4578–4583 (2011)
23. Gredig, T, Silverstein, EA, Byrne, MP: Height-height correlation function to determine grain size in iron phthalocyanine thin films. J. Phys. Conference Series **417**, 012069–5 (2013)
24. Vollmann, W, Berger, W, Hamann, C, Libera, L: Relations between the morphology and conductivity of thin films of tetrathiofulvalinium-tetracyanoquinodimethane. Thin Solid Films **111**, 7–16 (1984)
25. Asadov, A, Gao, W, Li, Z, Lee, J, Hodgson, M: Correlation between structural and electrical properties of ZnO thin films. Thin Solid Films **476**, 201–205 (2005)
26. Benramache, S, Chabane, F, Benhaoua, B, Lemmadi, F: Influence of growth time on crystalline structure, conductivity and optical properties of ZnO thin films. J. Semicond. **34**, 023001–1 (2013)
27. Gahtar, A, Benramache, S, Benhaoua, B, Chabane, F: Preparation of transparent conducting ZnO:Al films on glass substrates by ultrasonic spray technique. J. Semicond. **34**, 073001–1 (2013)
28. Benramache, S, Benhaoua, B, Bentrah, H: Preparation of transparent conducting of ZnO:Co and ZnO:In thin films by ultrasonic spray method. J. Nanostruct. Chemist. **3**, 1–7 (2013)
29. Benramache, S, Benhaoua, B, Chabane, F: Effect of substrate temperature on the stability of transparent conducting cobalt doped ZnO thin films. J. Semicond. **33**, 093001–1 (2012)
30. Benramache, S, Benhaoua, B: Influence of substrate temperature and cobalt concentration on structural and optical properties of ZnO thin films prepared by ultrasonic spray technique. Superlattice. Microst. **52**, 807–815 (2012)
31. Benramache, S, Benhaoua, B: Influence of annealing temperature on structural and optical properties of ZnO:In thin films prepared by ultrasonic spray technique. Superlattice. Microst. **52**, 1062–1070 (2012)
32. Zhu, BL, Zhao, XZ, Su, FH, Li, GH, Wu, XG, Wu, J, Wu, R: Low temperature annealing effects on the structure and optical properties of ZnO films grown by pulsed laser deposition. Vacuum **84**, 128–130 (2010)

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