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Tunability of ZnO Optical Band on Varying Zn^{2+} Concentration

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Abstract *- **Zinc oxide (ZnO) film is grown by utilizing Ammonium Zincate precursor through Successive Ionic Layer Adsorption and Reaction (SILAR). SILAR processes involves subsequent dipping cycles in cationic and anionic solution under suitable reaction conditions, which facilitates the controlled homogeneous film growth. Significance change in physical properties on change in concentration and dipping cycles, are analyzed by XRD, SEM, Profilometer and UV-Vis spectroscopy. Absence of additional peaks other than ZnO phase in diffraction pattern confirm the phase purity. In addition, observed strong peak intense imports well crystalline nature even at this low reaction temperature. Particularly the film grown with 0.05 molarity has its preferred orientation along (002) plane. Indicates that the grown is predominantly along c-axis as hexagonal structure oriented in perpendicular direction to substrate surface. SEM morphology, the porous particles and small islands of agglomeration are observed for high molarity films. In agreement with the physic observation the 0.05 molarity film show high transmittance (wavelength range 350-800nm) and low transmittance near fundamental absorption.***

Keywords - ZnO, SILAR, Molarity, Ammonium Zincate precursor.

I INTRODUCTION

Zinc Oxide (ZnO) well known n-type semiconducting material, investigated for decades owing to wide and tunable optical band gap. Wide band gap deserves ZnO in choice of optoelectronic device exploits UV to Visible region; also in energy sector as solar cell window [1]. Size confinement provides tunablity in optical band gap, this put researchers in exploring ZnO in form of thin film using Sputtering, Spray Pyrolysis, Sol-Gel, Chemical Bath Deposition (CBD), Chemical Vapor Deposition (CVD), etc [1-5]. Successive Ionic Layer Adsorption and Precipitation Reaction (SILAR) method has unique advantage as large area film deposition with homogeneity, cost effective and user-friendly synthesis route [6,7]. SILAR also provides films with controlled thickness invariant to substrate surface.

SILAR process with cycle of subsequent dipping in cationic and anionic solutions at appropriate temperature results in uniform film growth and strikes to desired thickness. SILAR reaction was first referred as multiple chemical dipping techniques by Ristov et al.[8]. Since, the process induces film formation through precipitation reaction between the adsorbed ion and counter-ion to form merely as a single layer; Nicolau et al. [9] accredited the reaction as SILAR. Microstructure morphological variation on films surface due to variation in reaction conditions, such as temperature, pH environment, etc., were reported.

As highlighted above, the main objective to carry out the series of rinsing are to remove the additional ions in the diffusion layer and loosely adhered solid particles. Therefore, parameters related to the rinsing procedure such as rinsing time, mode, temperature, etc., will exert significant effects on the growth rate and homogeneity of the film. Here, zinc oxide was grown as a thin film on microscopic glass substrate by SILAR, with optimized reaction conditions. Physical properties of the grown films are studied by suitable characterization techniques, such as thickness by Stylus Profilometer, XRD to confirm the phase purity, SEM surface morphology and UV optical absorption analysis.

II EXPERIMENTAL

ZnO thin films with different molarity (0.05, 0.075, 0.1M) of Zn^{2+} source were grown on the glass substrate by SILAR method. Hydrophilic property was established on the substrate surface by pre-cleaning process, which involves sequence of rinsing in HCl solution, deionized water and followed by rinsing in (1:1) ethanol and acetone mixed solution and dried in air atmosphere [5].

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Analytical grade reagents of $ZnSO_4 \cdot 7H_2O$ (99.7 %) and NH_4OH (25%) were used to prepare the Zinc ammonium complex $[Zn\ (NH_3)_4]^{2+}$ which was then served as Zinc cationic precursor solution (11pH) for the deposition of ZnO films. NH_4OH was slowly added to $ZnSO_4 \cdot 7H_2O$ solution under constant stirring, until the white precipitate turns to clear solution (i.e. $ZnSO_4 \cdot 7H_2O$ changes to $[Zn\ (NH_3)_4]^{2+}$). Double Distilled (DD) water maintained at 95 °C was used as anionic precursor.

ZnO thin film was deposited on the cleaned glass substrate by dipping in the above cationic and anionic solution in cycle as elaborated below:

(i) The pre-cleaned substrate was dipped in the cationic solution of Zinc ammonium complex for 10 s to establish the formation of $Zn(OH)_2$.

$$ZnSO_4 + 2NH_3 \cdot H_2O \Rightarrow Zn(OH)_2 + (NH_4)_2 SO_4$$

(ii) 20 s rinsing in DD water and followed by 30 s sonicated at room temperature for effective removal of SO_4^{2-} counter ion and loosely bounded $Zn(OH)_2$ grains.

$$Zn(OH)_2 + 4NH_3 \cdot H_2O \Rightarrow [\ Zn(NH_3)_4\ ]^{2+} + 2OH^- + 4H_2O$$

(iii) Subsequent dipping on anionic solution of DD water at 95 °C for 10 s to initiate the ZnO formation.

$$[Zn\ (NH_3)_4]^{2+} + 4H_20 \Rightarrow Zn(OH)_2 + 4NH^{4+} + 2OH^-$$

$$Zn(OH)_2 \Rightarrow ZnO + H_2O$$

(iv) ZnO formation initiated film was rinsed in DD water for 15 s to remove loosely adhered ZnO particles and unreacted $Zn(OH)_2$ grains. This dipping cycle was end with final drying for 10 s in air atmosphere before starting the next deposition cycle.

After completing the required number of deposition cycles the substrate was heated at 220 °C for 30 min in air to improve crystallinity.

The grown ZnO films are subjected to suitable characterization, to determine the physical property and optical efficiency. Phase confirmation of the fabricated films was carried out in Rigaku (Miniflex-300) X-Ray Diffractometer working with Cu-Kα source and Ni filter to restrict Cu-Kβ rays. Diffraction pattern was recorded between 2θ values of 30° to 65° at scan speed of 10° per min. Surface morphology was observed by Tescon (Japan) Scanning Electron Microscope working with Vega TC software. Optical transmittance spectra in the wavelength range of 300–1100 nm were measured by using UV-Vis-NIR Spectrophotometer (Shimadzu Ltd., UV-3101PC, Japan). Film thickness measurements were carried out by Stylus Profilometer (SJ MITUTOYO 301).

III - RESULTS AND DISCUSSION

XRD pattern of grown ZnO thin films with different molarity (0.05M, 0.075M, 0.1M for 20 Cy) of precursor solution and dipping cycles (30 Cy and 40 Cy) for 0.05M alone, is shown in Fig.1 with corresponding JCPDS (79-2205) standard. Observed peak positions are in well overlap with standard (JCPDS 79-2205) pattern and also the absence of any additional peaks confirms the phase purity. The grown phase pure ZnO film shows hexagonal (wurtzite) structure with P63mc space group. The strongest peaks observed in-between 30° to 37° representing the preferential planes orientation of the film along (100), (002) and (101), which also confirms the polycrystalline nature [5,11]. Increase in peak intensity with increase in precursor molarity owing to growth particle size, which was specified well by the reduction in peak broadening. Such trends for different morality and dipping cycles are expressively correlated in the Table 1 [5].

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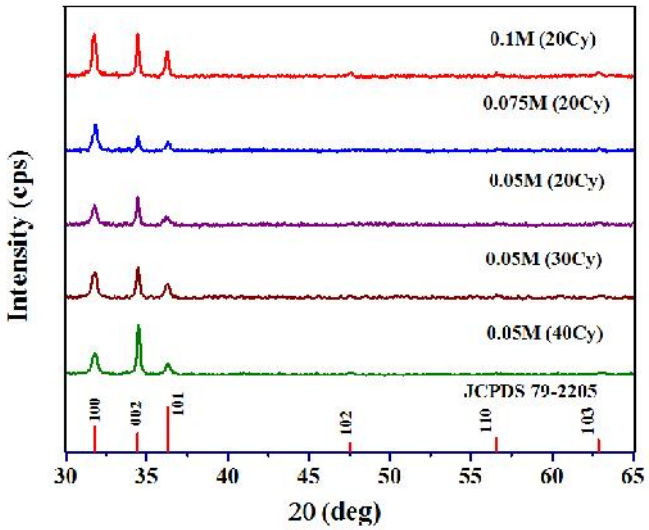

Fig. 1 XRD phase identification for the grown ZnO with different molarity and dipping

Table 1
Calculated Lattice parameter from the XRD pattern

Sample	Unit Cell Parameter (Å)		Crystalline Size (Å)
	a	c	
JCPDS 79-2205	3.2501	5.2071	---
0.1M (20 Cy)	3.2501	5.2070	496
0.075M (20 Cy)	3.2478	5.2037	445
0.05M (20 Cy)	3.2499	5.2058	370
0.05M (30 Cy)	3.2500	5.2068	319
0.05M (40 Cy)	3.2499	5.2045	343

XRD peak intensity increases with increase in dipping cycle for same molarity, indicates increase in particles density (film thickness) also influences in peak intensity. The strongest peak at 34.5° in 0.05M film for all different dipping, refers the preferable oriented (002) plane, thus the hexagonal structure shows the c-axis oriented perpendicular to the substrate. According to "Survival of the fastest" model at first few cycles of deposition nucleation will start with various possible orientations, but each nucleus competes the growth only on the orientation of nuclei having the fastest growth rate. Concurrence, in the grown ZnO hexagonal system achieved orientation in c-axis [5,10].

Surface morphology of the grown phase pure ZnO films was shown in Fig. 2. Homogenous particle distribution and uniform film surface, evidence that the pre-cleaning process with HCL solution improves the hydrophilic nature and reduces the water-glass contact angle to promote the uniform film formation. Upon increasing the Zinc concentration the spherical particle grains also larges the size and form islands with cluster of smaller crystals. Also supports the identification of higher in particle density upon increasing the morality, as indicated by increase in XRD peak intensity [12].

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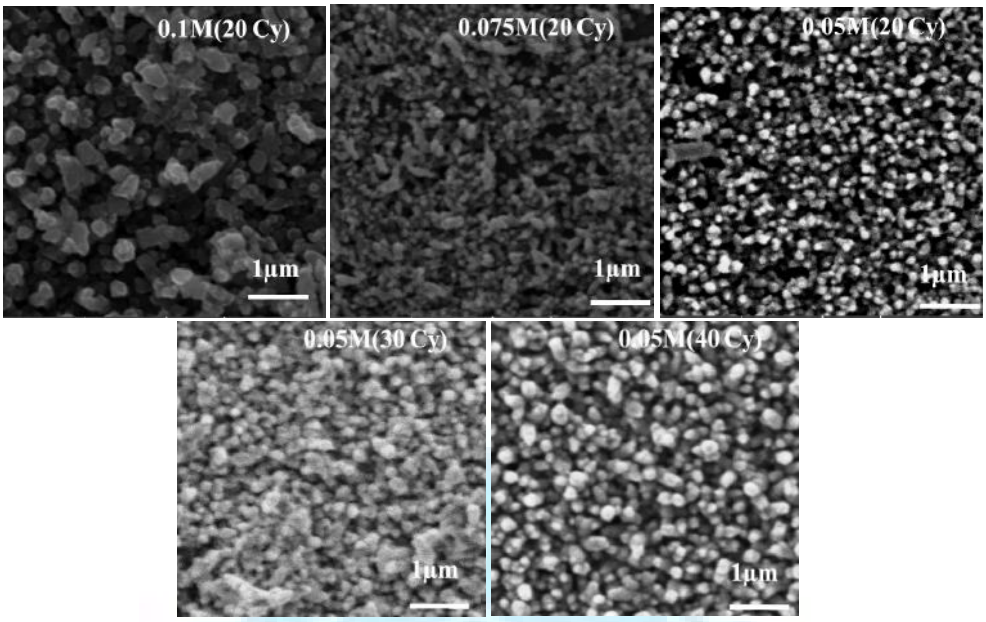

Fig. 2 - SEM surface topography and particle morphology of the grown ZnO flims

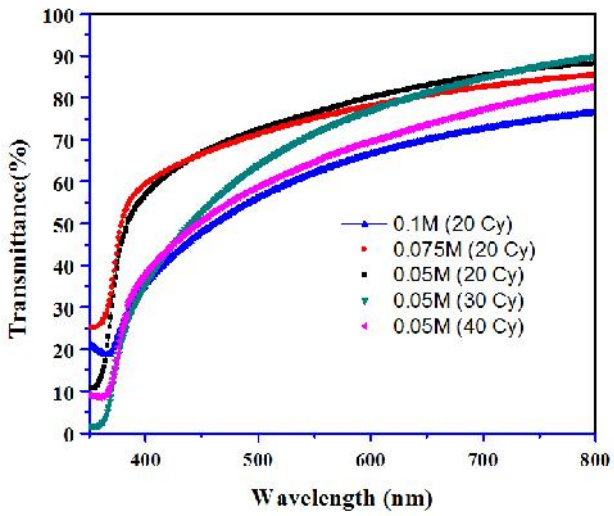

Fig. 3 Optical Transmittance of the grown films by UV-Vis spectroscopy

Transmittance (%T) of the fabricated ZnO thin films analyzed with UV-Vis Spectroscopy was shown in Fig. 3. UV spectra reveal that the increase in molarity decreases the optical transparence of the ZnO films. Increase in film thickness can be a reason, but change in morality will highly lead to change in carrier concentration. Tuac's relationship employed to determine the optical band gap, by using the absorption coefficient (α) and photon energy (hv) [13,14]

$$\alpha h\nu = A(h\nu - E_g)^n$$

Where, n = 1/2 for direct allowed transitions and n = 2 for allowed indirect transitions.

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Table 2

Film Thickness and observed Optical parameters

Sample	Film Thickness (nm)	Transmittance (%)	Band Gap (eV)
0.1M (20 Cy)	842	79	3.07
0.075M (20 Cy)	426	85	3.16
0.05M (20 Cy)	326	88	3.28
0.05M (30 Cy)	435	86	3.27
0.05M (40 Cy)	547	83	3.23

As molarity increases, carrier concentration and conductivity of the film increases with decrease in band gap, well compared in Table 2 [15,16]. Further, the transmittance edge was seen to be shifted slightly towards higher wavelength (red shift) as the zinc concentration was increased. This shift indicates decrease in band gap, which can be attributed to increase in grain size with zinc concentration.

IV - CONCLUSIONS

Homogeneously distributed and hexagonally structure ZnO films were deposited on glass substrate by SILAR method using ambient reaction condition. Phase purity with polycrystalline nature and ‘c’ axis preference orientation for 0.05M was confirmed by X-Ray diffraction. Spherical grain distribution and increase in agglomeration upon increase in concentration was observed in SEM topography. Increase in molarity increases the particle density and carrier concentration, which influence the change in optical direct band gap of 3.07 to 3.28 eV.

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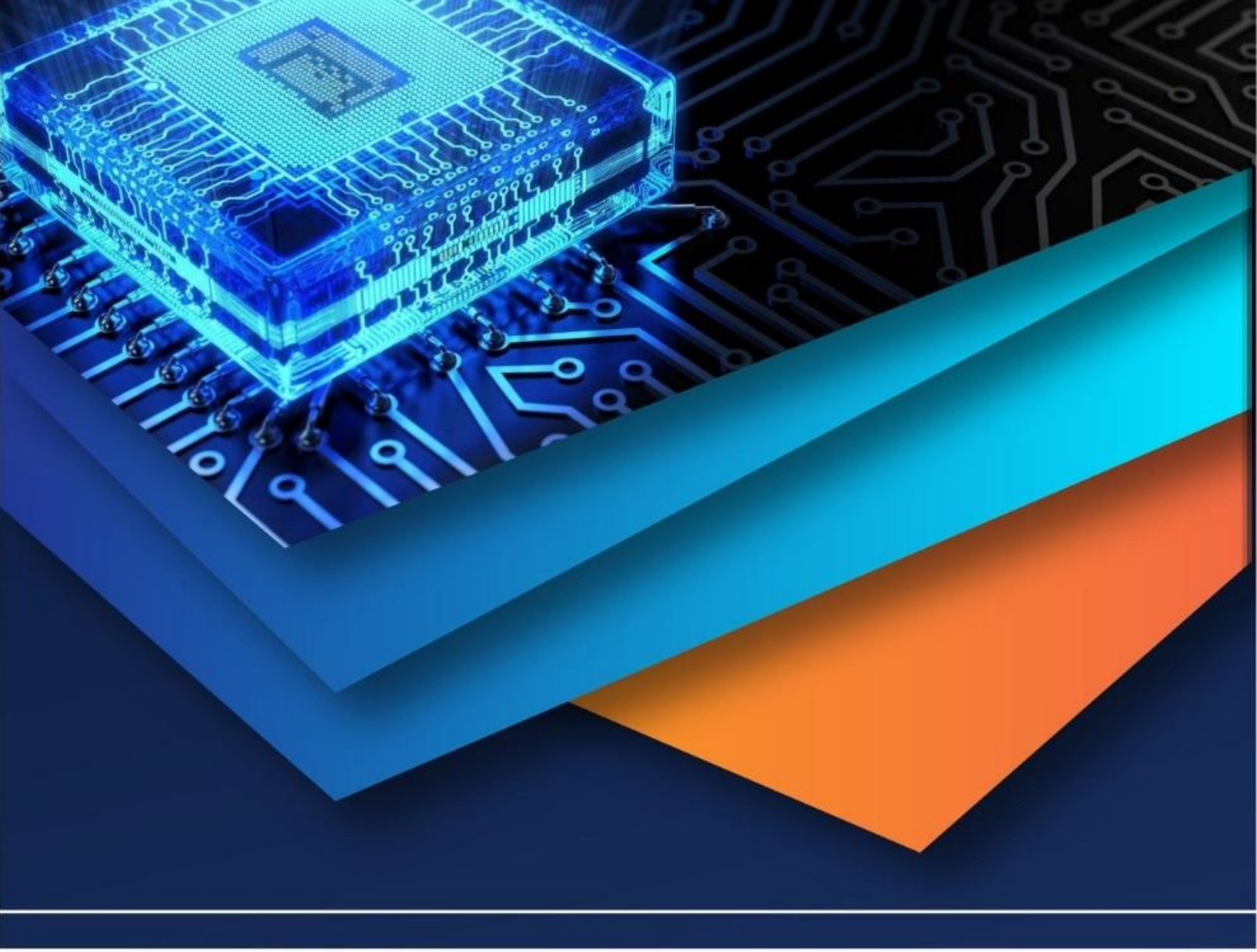
REFERENCES

[1] T. Manami, H. Nanto and S. Takata, Highly Conductive and Transparent Aluminum Doped Zinc Oxide Thin Films Prepared by RF Magnetron Sputtering, Jpn. J. Appl. Phys., 23, (1984), No.5, p.L280.
[2] L. Wang, Z. Xu, F. Zhang, et al., Structure, optical, and magnetic properties of Mn-doped ZnO films prepared by sputtering, Int. J. Miner. Metall. Mater., 17 (2010) No.4, p.475.
[3] E. Fortunato, V. Assunçao, A. Goncalves, et al., High quality conductive gallium-doped zinc oxide films deposited at room temperature, Thin Solid Films, 451(2004), p.443.
[4] M. Khana and M. Islam, Deposition and characterization of molybdenum thin films using dc-plasma magnetron sputtering, Semicond., 47(2013) No. 12, p.1610.
[5] M. Öztas, and M. Bedir, Thickness dependence of structural, electrical and optical properties of sprayed ZnO:Cu films, Thin Solid Films, 516(2008), No.8, p.1703.
[6] G. Xiangdong, L. Xiaomin and Y. Weidong, Preparation and Characterization of Highly Oriented ZnO Film by Ultrasonic Assisted SILAR Method, J. Wuhan. Univ. Technol. Mater. Sci. Ed., 20(2005), No.3, p.23.

ISSN: 2321-9653

International Journal for Research in Applied Science & Engineering Technology(IJRASET)

[7] C.V. Hernandez, F.N.J. Garcia, J.F. Jurado, V.H. Granada, Comparison of ZnO thin films deposited by three different SILAR processes, Microelectronics J., 39(2008), No.11, p.1349.
[8] M. Ristov, G.J. Sinadinovski, I. Grozdanov and M. Mitreski, Chemical deposition of ZnO films, Thin Solid Films, 149(1987), No.1, p.65.
[9] Y.F. Nicolau and J.C. Menard, Solution growth of ZnS, CdS and $Zn_{1-x}CdxS$ thin films by the successive ionic-layer adsorption and reaction process; growth mechanism, J. Cryst. Growth, 92(1988), No.1, p. 128.
[10] A. Van Der Drift, Evolutionary Selection, A Principle Governing Growth Orientation in Vapour-Deposited Layers, Philips Res. Rep., 22(1967), p. 267.
[11] Tatyana Gutul, Emil Rusu, Nadejda Condur, Veaceslav Ursaki, Evgenii Goncearenco and Paulina Vlazan, Preparation of poly(N-vinylpyrrolidone)-stabilized ZnO colloid nanoparticles, Beilstein J. Nanotechnol. 2014, 5, 402–406.
[12] M. Karunakaran, R. Chandramohan, S. Gomathi, et al., Morphological Tailoring of Thin Films Prepared by Low Cost SILAR Method, Int. J. Pharm. Sci. Res., 2(2013), No.4, p. 1752.
[13]J. Tauc, Amorphous and Liquid Semiconductors, Edited by J. Tauc , Plenum Press, London and New York, 1974, p. 159.
[14] E. A. David and N. F. Mott, Conduction in non-crystalline systems v. conductivity, optical absorption and photoconductivity in amorphous semiconductors, Phil. Mag., 22 (1970), No.179, p. 903.
[15] C. Guillen and J. Herrero, Optical, electrical and structural characteristics of Al:ZnO thin films with various thicknesses deposited by DC sputtering at room temperature and annealed in air or vacuum, Vacuum 84(2010), No.7, p. 924.
[16] S. Benramache, O. Belahssen, A. Guettaf, and A. Arif, Correlation between electrical conductivity-optical band gap energy and precursor molarities ultrasonic spray deposition of ZnO thin films, J. Semicond., 34 (2013), No. 11, p.113001.



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