

## STRUCTURAL AND SURFACE MORPHOLOGICAL INVESTIGATION OF FORMATION STAGES OF HIGHLY (002) ORIENTED ZnO FILMS ON GLASS SUBSTRATES BY SPRAY PYROLYSIS METHOD

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ZnO thin films were coated on amorphous glass substrate at various temperatures in the range 160-500 °C by spray pyrolysis method. The as deposited films were characterised by using XRD and SEM. Wurtzite phase of ZnO was formed at a substrate temperature of 400 °C, highly oriented (002) phase was developed with respect to increase of substrate temperature from 450 to 500 °C. Morphological and growth mode of these films were analyzed with respect to structural orientation of films from wurtzite to highly (002) oriented phase. Present study reveals that substrate temperature was one of the important parameters which determine the crystalline quality, population of defects, grain size, orientation and morphology of the films.

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### 1. Introduction

Transparent electrically conducting oxide films are widely used for variety of applications including electrodes for flat panel displays, light emitting devices, solar cells, gas sensors and heat mirror etc [1-3]. Zinc oxide (ZnO) is a unique material which exhibits excellent optical, physical and chemical properties useful for the advancement of technology in the areas of optoelectronics, optics, piezoelectric sensors, transducers, resonators, spintronics, biomedical sciences, catalytic chemistry and solar energy harvesting devices etc. [4]. It has three different crystalline forms, viz. wurtzite, zinc blende and graphitic structure depending upon its occurrence and synthesis procedure. Among these structures, wurtzite phase in hexagonal system is more stable which crystallizes in space group  $P63mc$  with lattice parameters  $a = 3.296$  and  $c = 5.2065 \text{ \AA}$  [5]. Zinc blende phase in cubic system is a meta stable phase, it crystallizes in space group ( $F\bar{4}3m$ ) with unit cell length of  $4.580 \text{ \AA}$  (JCPDS- 65-2880)[6-7]. The graphitic structure is thermodynamically the most favourable for thinner films which likely to form thin films nanowires or plates [8]. The lattice parameters of wurtzite phase of ZnO are similar to that of GaN and is promising one for replacing GaN for optoelectronic applications[9]. Interestingly, ZnO exhibit the most splendid and abundant configurations of nanostructures that one material can form [10]. Nano crystalline ZnO thin film materials with different size morphology etc. are hot topic of research for the past several years and wide variety of deposition techniques are being used by the investigators [11]. Among the different thin film deposition methods, spray pyrolysis is a cost effective one for depositing ZnO in large area [12-15]. Several researchers exploited this method of ZnO thin film deposition under different deposition conditions on substrates like glass, quartz, alumina, sapphire and silica, and on flexible substrates [15-17]. It is evident from previous studies that, crystallographic growth orientation of polycrystalline ZnO thin film can be tuned by changing deposition parameters such

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as substrate temperature, molarity of the precursor solution, chemical nature of the precursor and deposition rate etc [13,17]. The variations in afore said coating parameters influence the formation of the micro structure of nano materials as nano crystallites, nano amorphous grains or as nano cluster agglomerates. Usually grains are the basic components of thin films, the physical as well as optical properties of spray pyrolytically deposited grains will change with respect to morphology, size, growth orientation and concentration of various types of defects. ZnO with (002) phase is potential for device applications in broadband UV photo detectors with high tunable wavelength, acoustic optic devices, piezoelectric surfaces etc. Previously, zinc acetate precursor solution was used by the researchers for the deposition of (002) preferential oriented ZnO thin films [3,18-21]. In the present work a systematic investigation is carried out to understand the evolution of highly (002) oriented growth in spray pyrolytically coated ZnO thin films at a spray rate of 12 ml/minute on glass substrate at various temperatures using zinc acetate as a precursor solution in order to get vital information for developing ZnO based devices.

## 2. Experimental

Zinc oxide (ZnO) thin films were deposited on glass substrates by spray pyrolysis technique. The substrates were placed over the temperature controllable oven in air atmosphere. The precursor solution (0.1M) was prepared by dissolving zinc acetate (AR) in hydroethanolic (1:1 ratio) mixture. The solution was sprayed on glass substrate by using air as spraying gas with the aid of an atomizer attached to an air compressor at a spray rate of 12 ml/min. The substrate to atomizer nozzle distance was adjusted to 40 cm so as to have homogenous spraying over the substrate surface. The spraying process was carried out for a period of 60 s. The films were deposited at different substrate temperatures viz. at 160 °C (Sample A), 400 °C (Sample B), 425 °C (Sample C), 450 °C (Sample D), 475 °C (Sample E) and 500 °C (Sample F). The as deposited films were allowed to natural cooling at about 6 hrs. by keeping over the coating system in air atmosphere. X-ray diffraction pattern of the films in the 2θ region 20-60 ° were recorded by using Philips 1830 X-ray diffraction spectrometer with CuKα radiation (1.5406 Å). The SEM of the films was taken by using JEOL JSM 5600 LW electron microscope.

## 3. Results and discussion

ZnO obtained from the most of the deposition procedures including spray pyrolysis are wurtzite phase in hexagonal crystalline system[13,22]. It is an ionic crystal with a non-centro symmetry which is described schematically as a number of alternating planes composed of 4-fold tetrahedral coordinated O<sup>2-</sup> and Zn<sup>2+</sup> ions, stacked alternately along the c-axis [5]. The lattice constants can be obtained from the following expression [23-25].

$$1/d_{hkl}^2 = (4/3)(h^2+hk+k^2)/a^2 + l^2/c^2 \quad (1)$$

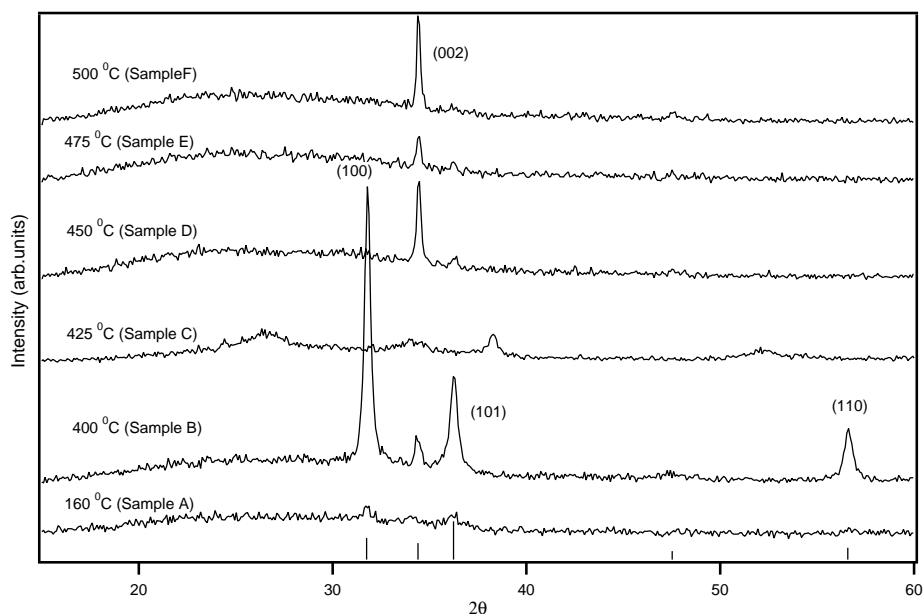
For the (100) orientation the lattice constant 'a' is calculated by the relation ,  $a = \lambda/\sqrt{3}\sin \theta$  where 'θ' is the diffracting angle corresponding to the (100) peak and for the (002) orientation the lattice constant 'c' is calculated by the relation  $c = \lambda/\sin \theta$  [24]. Further, the average grain size of spherical nanocrystallites in thin films can be calculated by Sherrer equation which is as follows[1]

$$D = 0.9\lambda/\beta\cos\theta \quad (2)$$

where 'λ', the wave length of X-ray used, 'β' the full width half maximum (FWHM) peak corresponds to 2θ value.

The diffraction pattern of the sample deposited at 160 °C (sample A) shows very weak diffraction peaks and are observed corresponds to 2θ values at 31.80° (100), 33.97° (002), 37.39° (101) and 56.62° (110) (Fig.1.). In this deposition, temperature energy provided by substrate is not sufficient

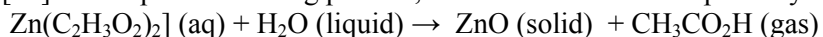
to decompose the precursor solution and consequent oxidation of ZnO to form good crystalline structures. The precursor solution, zinc acetate is likely to decompose almost completely at around 280 °C and forms ZnO [26-28]. So the deposition temperature is raised to 400 °C and experiment is repeated in identical conditions [13]. Good polycrystalline ZnO thin films are formed as one can see from the XRD pattern of this sample (Fig. 1.).



*Fig. 1. XRD of ZnO thin films deposited on glass substrates by spray pyrolysis at different deposition temperatures.*

Well defined X-ray diffraction peaks are observed correspond to  $2\theta$  values  $31.8^\circ$  (100),  $34.41^\circ$  (002),  $36.23^\circ$  (101),  $56.12^\circ$  (110) which can be indexed to wurtzite phase of ZnO, JCPDS No.36-1451[13]. Usually, ZnO in thin film prefer to grow in (002) orientation due to low surface energy of formation [13,29]. But this sample shows an initial growth orientation along (100) plane, and is having maximum intensity which is 95% more intense than that of (002) oriented peak. The unit cell parameters of this sample is evaluated from the diffraction pattern and is found to be  $a = 3.249\text{Å}$ , and  $c = 5.206\text{Å}$  units. Slight modifications in lattice parameters compared to that of bulk ZnO is usually expected in nano structured thin films with two dimensional growths. For real crystal, the calculated values of 'a' and 'c' are the same as that of bulk ZnO which are based as different crystalline planes. However the presence of large number of vacant lattice sites and local lattice disorders may lead to obvious reduction in intensities of XRD peaks (Fig. 1.) attributed to destroyed periodicities in crystal planes [30]. XRD pattern of sample C shows a broad feature with peak around  $26.32^\circ$ , which may be originated from glass and other one is at  $34.113^\circ$  (002). For the sample deposited at  $450^\circ\text{C}$  (Sample D), the X-ray diffraction peak at  $2\theta$  value corresponding (002) phase gains intensity which is nearly 150 % higher than that of sample B. Intensity of (002) peak become more prominent in Sample E, and shows an enhancement of the order of 66 % than that of sample B. But for sample prepared at  $500^\circ\text{C}$  (002) peak also gains 3 % intensity as compared to that Sample E and appears at a  $2\theta$  value of  $34.4^\circ$  [13]. The texture coefficient of this sample is almost unity which clearly suggests that high c-axis orientation [31].

In spray pyrolysis thin film coating process, impinging molecules from the precursor solution undergo endothermic reaction on substrate surface. Temperature of the substrate surface plays an important role in the morphological development of the thin film during the deposition process[32]. In the present coating process, the thin film formation pathway is as follows.



On spraying a mist of zinc acetate with low spray rate (viz.12 ml per minute) on the surface of the heated substrate, the smaller droplets, immediately decompose as compared to larger

droplets and the solid state ZnO will start to nucleate provided other growth conditions are favourable. The higher rate of spraying on the substrate surface leads the accumulation of large amount of precursor on the substrate surface which will evaporate and decompose slowly, and forms large and micro sized structures on the substrate [17]. Generally, crystalline lattice mismatched substrate surfaces or amorphous substrates like glass are not favorable for crystalline type film growth. In this regard, amorphous glass substrates can be considered as amorphous SiO<sub>2</sub> surface in which Si-Si distance is about 3.08 Å and is less than “a” of bulk ZnO (3.25 Å) and hence a lattice mismatch[33]. On the other hand, ZnO crystalline film growth on amorphous glass substrate requires large formation energy especially at the first stage of growth i.e. just before the ZnO ultra thin layer covers the surface of the glass substrate. Thus crystallization is difficult in lower substrate temperature. As a result amorphous layer or poor crystalline grains will grows which is in agreement with poor crystalline films obtained in sample A [34]. The coating time in the present work is 60 s, and a few seconds after starting spray process, some nanocrystallites are likely to deposit as dots on the substrate surface. The initially deposited nanocrystalline dots will act as growth centers for further island type growth mode which will leads to the formation of initial ultra thin layer on substrate surface.

The temperature of the substrate also provides the energy for the formation of crystalline grains. The most likely initial growth at low temperature has to be island formation from nucleation sites as reported by Zhang *et al.*[31,35]. In thin film growth, the structure of substrates and its chemical nature is important in determining the growth mode. If the affinity of the amorphous glass substrate to deposited crystalline particles is weak as in the present case, islands will grow three-dimensionally to minimize the particle-substrate interaction, which is in Volmer-Weber growth mode[36]. ZnO islands are not densely packed in the early stages of growth. Such variation in morphologies is expected due to comparatively lower temperature of the substrate (400 °C). Oxygen is generally present as background impurity which can easily diffuse in to the crystal lattice during the deposition of nanocrystalline ZnO films at various substrate temperatures by spray pyrolysis method. The oxygen impurities are absorbed at the grain boundaries in the first stage of growth and then on the surface of thin films. Thus oxygen impurities can alter the structure and grain size of constituent nanocrystallites consequently morphology and light emitting properties of thin films as reported[13].

Optical as well as physical properties of nanocrystalline thin films to a certain extent depend on the morphology of constituent particles or grains. The morphology of the nanocrystals in thin films, on the substrate surface depends on the super saturation condition of the growth solution. The samples deposited at different substrate temperatures possibly have different ranges of super saturation and growth morphologies [37,38]. The higher substrate temperatures favour the rapid evaporation of droplets from the zinc acetate mist [17]. So, early super saturation condition may achieve on the substrate surface of samples B to F and oxidation process as compared to that of deposited at lower substrate temperatures. Further, substrate temperature controls the nature of mobility of the adsorbed atoms which eventually determines the structural development of the film. Substrate temperature is different in each case and hence the ad atom mobility as a result morphology of the grains is expected to change with variations in ad atom mobility. Surface with low ad atom mobility encourages the formation of amorphous or randomly oriented crystallite structures. These films possess low density of particle in surface, sometimes porous in nature with rough surface texture. Shunichi H.M *et al.* observed that surface of crystallized polycrystalline ZnO film is rough, especially which deposited at lower substrate temperature since the crystal plane grows randomly [34]. In the present study, the SEM image (Sample B) shows (Fig.2.(a)) large number of flakes like morphological structures with random distribution and is having more surface roughness [13,39].

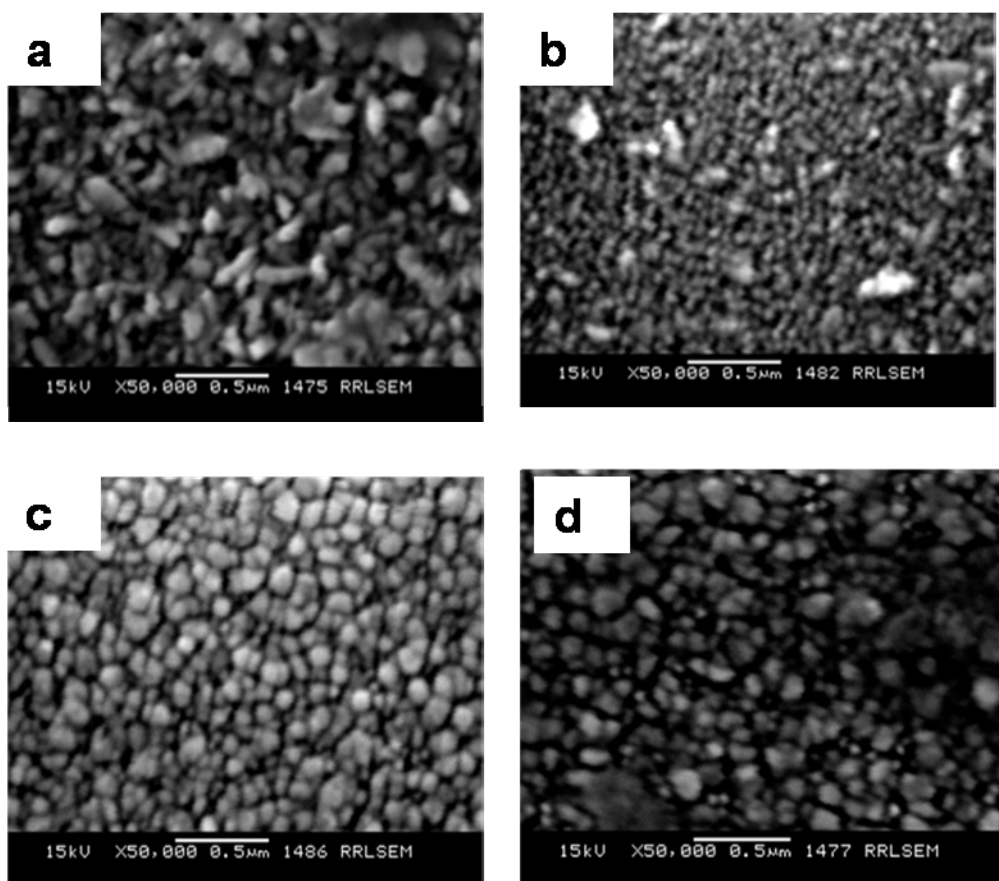


Fig. 2. SEM images of ZnO thin films deposited on glass substrates by spray pyrolysis at (a) 400, (b) 425, (c) 475 and (d) 500 °C.

The shape and morphology of grains also depends on interfacial energy of the system[13]. Spherical shape has the minimum interfacial energy and generally nanocrystallites have a tendency to form spherical grains[23]. The nucleation with various orientations can be formed at the initial stage of the deposition and each nucleus competes to grow, but only nuclei having fastest growth rate can survive. High substrate temperatures promote higher rate of ad atom mobility and re-evaporation of poorly combined structures. This leads to a high-density smooth layer of well-oriented crystallites. In the present study also this is evidenced by the nucleation and growth pattern of the films with the increase of substrate temperature. It is usually expected that on spraying smaller molecules will initiate the nucleation process on the substrate surface and later more molecules are attached to this smaller crystallites. As time grows during deposition, more and more molecules will attach on the surface of the previously grown structure and this will leads to the formation of small aggregates of islands. Further spraying on the surface of these aggregate structures, large sized particles will be formed. From the SEM micrographs, one can see that grains approaches approximately spherical shape, when the substrate temperature is 475 °C (Fig. 2.(c)). The sample deposited at 500 °C also shows high orientation and most of the granules show almost round in shape morphology (Fig.2.d)[13]. This observation indicates that adjacent particles segregate to grow with spherical morphology in order to maintain low interfacial energy and also orient in a particular crystalline plane viz. (002) which leads to Ostwald ripening[40,20]. In this case, most stable close-packed plane, namely the c-axis oriented layer, grows in accordance with Bravais's law or Wulff's theorem as reported by Hayamizua *et al.*[34]. Further, the rate of oxidation is also detrimental in determining the crystalline size. The grain size is expected to increase with increasing temperature and deposition time as a result of more oxidation. In the present study the coating time is kept constant (60 s). The observed sharp nature of the X-ray diffraction peaks of the sample prepared at higher temperature indicates the increased grain size as result of segregation of smaller particles[13] (Fig. 1).

The amorphous nature of the substrate introduces strain on as deposited films, [40] The strain in the film can be evaluated by the formulae,

$$\varepsilon = \frac{c - c_0}{c_0}$$

where 'c' is the lattice constant of the film and  $c_0$  in that for the bulk. The in-plane strain introduced by substrate is compressive, as a result diffraction angles of coated material (ZnO) may shift slightly towards low angle side which is in agreement with XRD pattern of present samples (Fig.1.) [41].

We calculated the stress parallel to the film surface by using the following relation.

$$\text{Stress in the film} = \frac{2c_{13}^2 - c_{33}(c_{11} + c_{12})}{2c_{13}} \times \left( \frac{c - c_0}{c_0} \right)$$

Here

$$c_{11} = 208.8 \text{ GPa}$$

$$c_{33} = 213.8 \text{ GPa}$$

$$c_{12} = 119.7 \text{ GPa}$$

$c_{13} = 104.2 \text{ GPa}$  are constants reported by Hwang *et al.* [42,43]. By substituting all the constants the stress can be written as  $(-453.6 \times 10^9) \times \text{strain of the film}$ . (Table. 1)

Table. 1. Lattice constant(c), grain size and stress of ZnO thin films grown on glass substrates at various substrate temperatures by spray pyrolysis method.

Substrate temperature ( $^{\circ}\text{C}$ )	Unit cell parameter 'c' in $\text{\AA}^{\circ}$	FWHM (in radians)	Strain	Stress $\times 10^9 \text{ Nm}^{-1}$	Particle size (nm)
400 (B) [13]	5.213	0.403	-0.001248	0.5662	20
425 (C)	5.199	0.457	0.00144	-0.653	19
450 (D)	5.2077	0.252	-0.00023	0.1044	33
475 (E)	5.2067	0.280	0.0000192	-0.00870	30
500 (F) [13]	5.199	0.242	0.000038	-0.0174	31

While considering strain on the films, shows a negative value in the case of (002) oriented films which indicate that the lattice constant 'c' is elongated as compared to that of unstressed ZnO films. Once a free surface exists, there exists missing bonds of the atoms on the surface. At relatively higher substrate temperatures the concentration of the missing bonds increases so that there is a tendency for the surface to rearrange, in order to increase the bonding with respect to deposition temperature. The bi axial strain thus formed will lead to a particular orientation for the film and hence (002) orientation of the film is occurring while increasing temperature of the substrates [44]. The population of defect concentration may vary especially with respect to deposition temperatures [13,30]. Crystalline strain will affect the crystal quality of films. The positive stress indicates the biaxial stress is tensile; negative stress indicates, the biaxial stress is compressive. Stress and strain of the films shows both positive and negative values due to variations in concentration of different types of defects in films as revealed by the photoluminescence spectrum of the samples reported previously[13,45].

#### 4. Conclusions

Wurtzite phase of ZnO can be coated on glass substrate by providing temperature above the decomposition temperature of precursor salt. Higher substrate temperature in the range 450-500  $^{\circ}\text{C}$  will favours the formation of technologically important highly (002) orientated wurtzite phase ZnO films on glass substrates. Substrate temperature is identified to be one of the important factors which controls the crystalline quality, growth orientation, morphology, grain size,

population of defects, stress, strain and hence physical as well as optical properties of thin films grown by spray pyrolysis method.

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### References

- [1] T. David, S. Goldsmith, R.L.Boxman, *J.Phys.D:Appl.Phys.***38**, 2407 (2005).
- [2] Y.H.Zhang, J. Liu, T. Liu, L.P You, X.G.Li, *J.Cryst. Growth.* **285**, 541-548 (2005).
- [3] B. J.Lokhande, P.S Patil, M.D. Uplane, *Mat.Lett.* **57**, 573 (2002).
- [4] D.C.Look, D.C Reynolds, C.W.Litton, R.L Jones, D.B .Eason, G.Cantwell, *Appl. Phys. Lett.* **81**, 1830 (2002).
- [5] Z. L. Wang, *J.Phys.Cond.Mat.* **16**, R829 (2004).
- [6] S-M. Zhou, H-C. Gong, B.Zhang, Z-L. Du, X-T.Zhang and S-X. Wu, *Nanotechnology.***19**,175303 (2008).
- [7] R. Liu, A.A.Vertegel, E.W Bohannan, T.A Sorenson, J.A Switzer, *Chem. Mat.***13**,508 (2001).
- [8] C. L.Freeman, F.Claeyssens, N.L. Allan, *Phy. Rev. Lett.* **96**,066102, (2006).
- [9] A.Toshimitsu, S.Koji, M.Katsumi, *J.Vac.Sci.Tech. B*, **18**, 1406 (2000).
- [10] L.Dai ,X.L.Chen, W.J.Wang, T.Zhou , B.Q. Hu, *J.Phys.Condens.Matt.* **15**, 2221 (2003).
- [11] S.Singh, P.Thiyagarajan, K.M.Kant, D.Anita,S.Thirupathiah, N. Rama, M.B.Tiwari, M.S.Kottaisamy, R.Rao, *J. Phys. D :Appl .Phys.* **40**,6312(2007).
- [12] K.Krunks, V.Bijakina.O.Mikli, T.Varema. E.Mellikov, *Physica Scripta.* **T79**,209 (1999).
- [13] M.J.Bushiri, V.Gopakumar, V.K.Vaidyan, *Surf. Rev.Lett.* **15**,551(2008).
- [14] E.Bacaksiz, S.Aksu,S.Yilmaz, M.Parlak, M. Altunbaş, *Thin Solid films*, **518**,4078 (2010).
- [15] B.Godbole, N.Badera, S.B.Shrivastav,V.Ganesan, *J. Inst. Soc.India.* **39**,42(2009).
- [16] Y.L.Shi, J.Wang, H.L.Li, *Appl.Phys.A*, **79**, 1797(2004).
- [17] M.J.Bushiri, S.Agouram, C.Reig, M.C.M-Tomás, J.J.Hortelano, V.M.-Sanjosé, *Phys. Procedia.* **8**, 14 (2010).
- [18] J.L.V.Heerden, R.Swanepoel, *Thin Solid Films.* **299**,72(1997).
- [19] F.Paraguay.D,W. Estrada L, D.R. Acosta N, E. Andrade, M. Miki-Yoshida, *Thin Solid films.***350**,192 (1999).
- [20] C.Gumus, O.M.Ozkendir, K.H.Ufuktepe, *J.Opto electro.Adv Mat.* **8**,299(2006).
- [21] B.Joseph, P.K.Manoj,V.K.Vaidyan, *Cer. Int.* **32**,487-493(2006).
- [22] T.Takao, M. Lutz, E.P Sotiris, *J.Nanoparticle.Res.***4**, 337(2002).
- [23] Z.W.Chen, J.K.L. Lai, C.H.Shek, *Phys.Rev.B.* **70**, 165314,(2004).
- [24] F.K.Shan, B.I.Kim,G.X.Liu, Z.F.Liu, J.Y.Sohn, W.J Lee, B.C Shin, Y. S. Yu, *J. Appl Phys.* **95**,4772(2004).
- [25] C. Kittel, Wiley Eastern Ltd, (5<sup>th</sup> edition) (1983).
- [26] C-C. Lin, Y.Y.Li, *Mater.Chem. Phys.***113**,334-337 (2009).
- [27] T.Maruyama, J .Shionoya, *J.Mat.Sci.Lett.***11**,170 (1992).
- [28] S.Xin, Z. Zhengiun, Yuquan W, Z. Minmin, *J. Phys. D Appl. Phys.***38**,3934(2005).
- [29] J-L.Zhao,X-M. Li, S.Zhang, C.Yang, X-D.Gao, W-D. Yu, *J.Mat.Res.***21**,2185, (2006).
- [30] R.Lamber, S.Wetjen, N.I. Jaeger, *Phys. Rev.B.* **51**,10968(1995).
- [31] H.Z.Zhang, X.C.Sun, R.M .Wang, D.P.Yu, *J.Crys.Growth.* **269**,464(2004).
- [32] B.S .Li, Y.C Liu, Z.Z.Zhi. D.Z Shen, J.Y Zhang, Y.M. Lu, X.W.Fan, X.G.Kong, *J.Vac.Sci.Technol A.***20**, 1779(2002).
- [33] M. Benoit, S. Ispas, P.Jund, and R.Jullien, *The Europ.Phy.J.B* **13**,631 (2000).
- [34] S.Hayamizu, H.Tabata, H.Tanaka and T.Kawai, *J. Appl. Phys.* **80**,787, (1996).
- [35] W.Yapin, H.Z .Xian, X.Fuchun, S.Z. L.Jungyong, *Nanotechnology.***20**, 325709(2009).
- [36] R. Koch, D.Hu, A.K Das, *Phy. Rev.Lett.***94**, 146101(2005).

- [37] S. Agouram, M.J. Bushiri, D.N. Montenegro, C. Reig, M.C. Martinez-Tomas and V. Munoz-Sanjose, *J. Nanoscience and Nanotechnology*. **12**, 6792(2012).
- [38] B. D. Yao, Y.F. Chan, N. Wang, *Appl. Phys. Lett.* **81**, 757(2002).
- [39] S. Im, B.J. Jin, S. Yi, *J. Appl. Phys.* **87**, 4558 (2000).
- [40] K. M. Kiyofumi, K. Shoji, *Thin Solid Films*. **515**, 8632, (2007).
- [41] Y.H. Zhang, J. Liu, T. Liu, L.P. You, X.G. Li, *J. Crystal Growth*. **285**, 541 (2005).
- [42] K-SHwang, Y-S. Jeon, B-A. Kang, K. Nishio, T. Tsuchiya, J-H An, B-H. Kim, *J. Kor. Phy. Soc.* **46**, 521 (2005).
- [43] C. Li, X.C. Li, P.X. Yan, E.M. Chong, Y. Liu, G.H. Yue, *Appl. Sur. Sci.* **253**, 4000(2007).
- [44] Z. Lixin, H. Hanchen, *Appl. Phys. Lett.* **90**, 023115 (2007).
- [45] V. Gopakumar, Ph.D. Thesis Univ. Kerala, 2011.