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A REVIEW ON GROWTH AND STRUCTURAL PROPERTIES OF ZNO NANOSTRUCTURES

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ABSTRACT

Zinc oxide nano structures are versatile nano material with a wide range of applications in optoelectronic, sensor technology, transducers and biomedical services. A controlled growth mechanism is required for commercial usages of ZnO nanostructures. This work reviews different growth mechanism and structural properties of ZnO nanostructures for novel applications. This work is focused on getting better understanding about the role of various growth parameters for tuning the structural and morphological properties of zinc oxide nanostructures.

Keywords: Growth Mechanism, Lattice Parameters, Ph, SEM, XRD.

I. INTRODUCTION

The keystone of modern electronic industry is metal oxide nano structure. They have been used widely in fabrication of photovoltaic, optoelectronic and photonic devices. In last few decades, zinc oxide nano materials have received broad attention due to their numerous structural and optical properties suited for various technological applications. Among all metal oxide nano structures, zinc oxide nano material has become of particular interest to scientist for their surprising optoelectronic and magnetic properties. The strong piezoelectronic and pyroelectronic properties are observed in ZnO nanostructures because of the lack of a centre of symmetry in wurtzite structure combined with large electro-mechanical coupling. It is a versatile functional material and it has diverse group of growth morphologies. ZnOnano structures are obtained in the form of nano rods, nano combs, nano wires, nano belts, nano springs, nano flowers etc. The different synthesis procedures, structural optical properties and the potential applications of ZnOnano structures will be reviewed in this work (1-3).

Zinc oxide is a wide band gap (3.37 eV) material with high exciton binding energy of 60 meV. This high exciton binding energy of ZnO material would allow for excitonic transitions even at room temperature. It could results for high radiative recombination efficiency for spontaneous emission as well as Zinc oxide can be made highly conductive by the method of doping and it is transparent to visible light. Zinc oxide nano materials fulfill the demand of new technological world because of its fundamental properties such as larger band gap, higher electron mobility as well as higher break down field strength. Some fundamental aspects of ZnOnano structures about their growth mechanism, structural and optical properties will be explained in this work (4-6).

1.1 Growth of ZnO Nanostructures:s

It is very important to study the different growth mechanism for the synthesis of Zinc oxide nano structures and investigate their properties. Different growth methods such as hydrothermal method, vapor-phase transport, pulsed laser deposition, chemical vapor deposition, electro chemical deposition etc. have been used for production of zinc oxide nano particles. The structural, optical and electrical properties of ZnOnano materials can be improved by controlled synthesis procedure. Zinc oxide nano structures were prepared by Sadraei R using very simple synthesis procedure. Zinc sulfate heptahydrate '$ZnSO_4$ $(H_2O)_7$' and Ammonium hydroxide 'NH_4OH' were used as precursors for the synthesis of ZnOnano structures. Zinc sulfate heptahydrate (2.9386 ml) solutions were prepared in 100 ml of deionized water. The solutions of Zinc sulfate (25 ml) and Ammonium hydroxide (25 ml) were stirred at the temperature about 50^0 to 60^0 c. The final precipitates were obtained after drying the samples at 60^0 c in an oven(7).

H. S. Hassan et al. synthesized and characterized ZnOnano structures for gas sensor application. Zinc chloride '$ZnCl_2$' solutions of 0.1 M concentration were prepared by adding 4 gm of $ZnCl_2$ in 250 ml of distilled water. The pH of the solution was maintained at 9 by adding NH_3OH to the solution. The solutions were stirred for the growth of ZnOnano structures. For preparation of 1%, 5% and 10% wt indium doped ZnO, an equivalent amount of indium chlorides were added to the solution. The mixture solutions were stirred for another 24 hours at 80^0 C temperatureand In-doped ZnOnano structures were obtained(8).

T. Naz et al. have reported the synthesis of ZnOnano structures via coprecipitation of $Zn(NO_3)_{2.}$ $2H_2O$ in 2-aminoethanol under different growth conditions. For this synthesis, the solution of 2- aminoethanol of 20 ml were placed in a 250 ml round bottom flask and $Zn(NO_3)_{2.}$ $6H_2O$ (4.15 gm, 14 mmol) were added into it. The mixtures were dissolved by using ultra sound sonication to obtain a clear solution. Then liquid NH_3 (10ml) was added to the solution and pH of the mixture was maintained at 11.2. The reaction temperatures were varied between 60^0 C to 94^0C,while growth time was varied in the range of 15 to 120 minutes(9).

The green synthesis of ZnOnano tubes were explained by A. Oudhia et al. They have reported a simple synthesis procedure of ZnOnano structures using Neem leaf extract for bio medical application. Zinc Acetate solutions of 0.5 M were prepared in ethanol and water mixture (1:3 ratio). The pH of the solution was maintained at 11 by addition of NaOH. Finally, the Neem extract solution and equal amount of prepared zinc acetate solutions were mixed and stirred for one hour at 60^0 C- 70^0 C temperature. The precipitates were filtered and washed by ethanol for several times. The zinc oxide nanostructures were obtained (10).

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S. Sagadvan et al. have reported the preparation and characterization of zinc oxide nano fluids. They have used all chemical of analytical reagent grade and one step solvo-thermal method was used for preparation of Zinc oxide nano particles. One solution of Zinc Acetate dehydrate was prepared in methanol and another solution of potassium hydroxide was prepared by dissolving potassium hydroxide in methanol. Both of the solutions were mixed and allowed to stirred for 2 hour at 52^0 C. The nano particles of ZnO were settled at the bottom and these precipitates were washed, dried for further use (11).

1.2 Structural Properties of ZnO Nanostructures

The quantum size effect of ZnOnano structures will lead to new structural and optical properties of the material. In the nano meter range, the quantum size effect becomes dominant which redefines the properties of the prepared nano structures. A. Mansouri et al. have studied the variation in structural and optical properties of ZnOnano structures prepared by aqueous chemical growth. The zinc oxide nano structures were prepared by mixing equal amount of $Zn(NO_3)_2$. $6H_2O$ (zinc nitrate Hexahydrate) and $C_6H_{12}OH$ (Hexametheneetramine) as precursors under constant stirring. The role of pH in aqueous chemical method was well explained. Bruker AXSD8 Advanced X- ray diffraction analyzer (CuKα) was employed for analysis of synthesized nano structures at pH7 and pH8. They have found single phase nano structures with wurtzite hexagonal structures. They have suggested the poor crystal quality for large value of pH. The morphologies of prepared ZnO nanostructures were characterized by CamScan MV 2300 Scanning Electron Microscope (SEM) for different values of pH. Different shapes of prepared nano structures were observed for changing the pH of the growth solution between 7 and 12. The morphology of ZnO nanostructures were presented by them at pH= 7 and pH= 8 as shown in the figure 1.

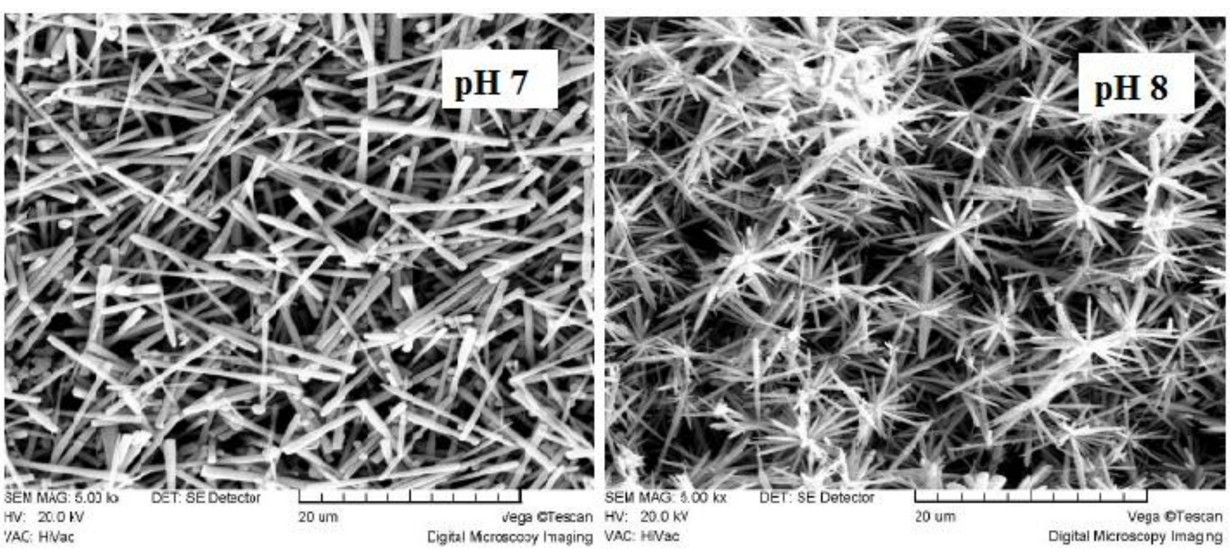

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Fig 1: SEM images of ZnO Nanostructures at pH (Nano wires) and pH 8 (Nano flowers) (Reproduced from Ref.12)

ZnOnano wires grown under pH7 were seen with random distribution of length 2- 10 µm and diameter 150- 300 nm. At higher pH (12) value at the growth reaction, the morphology of ZnOnano wires were changed to ZnO flowers of length 2-4 µm and diameter 150- 500 nm. The thermal degradation of Hexamethylenetramine (HMT) released hydroxyl ions and indicated the formation of ZnOnano structures. These hydroxyl ions were reacted with Zn^{2+} ions to form ZnOnano structures as given below

$6(CH_2)_6N_4 + 6H_2O \leftarrow\text{-------}\rightarrow NH_3 + HCHO$ …………………………..(1)

$NH_{3\,+}\;\; H_2O \leftarrow\text{------}\rightarrow OH^{-} + \;NH_4^{+}$ ……………………………………..(2)

$H_2O + ZnO_{(s)}$ ----------------$\rightarrow Zn(OH)_2 \leftarrow\text{-----}\rightarrow Zn^{2} + OH^{-2}$ …………...(3)

They have observed that the concentration of OH^- or the values of pH have played a dominant role in growth kinetics of ZnOnano structures (12).

S. Y. Pung et al. have successfully synthesized and characterized the Cu doped ZnOnano rods by using sol-gel method. They have used zinc nitrate tetrahydrate, methenamine and cupric acetate monohydrate as precursors. The effect of Cu doping on morphology, crystallinity and optical properties of ZnOnano rods were studied by them. The crystalline phase of the prepared samples were determined by Bruker Advanced X- ray D8 (CuKα) and found as wurzite structure (JCPDS Card No. 00- 001- 1136). The morphology of the samples were examined by Field Emision Scanning Electron Microscope (Zeiss Supra 35 VP) attached with an energy with an energy dispersive spectroscope. The SEM images were recorded by them as given below

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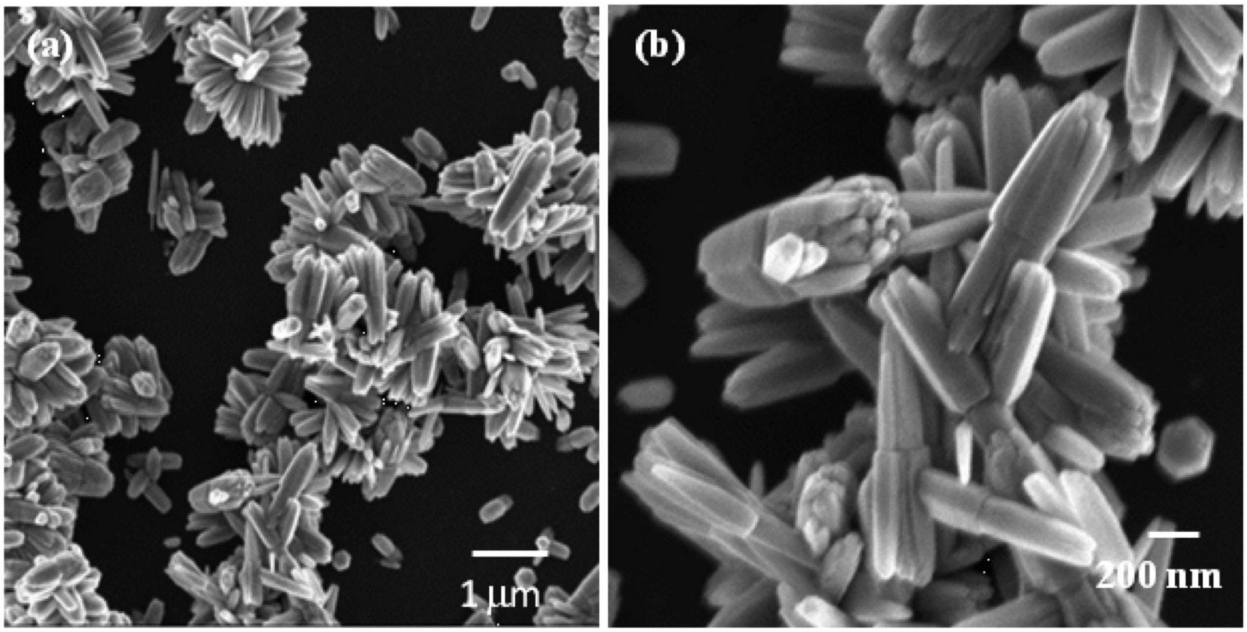

Fig 2: SEM images of ZnO Nanostructures (a) 10 kX (b) 30 kX (Reproduced from Ref.12)

Agglomeration of ZnOnano rods were observed in Fig 2 (a)while in Fig 2 (b) the ZnOnano rods were composed of a twin rod structure. They have explained that the agglomeration could be attributed to the secondary nucleation which was occurred on the surface of some nano rods. Again ZnOnano rods were formed by two smaller nano rods as shown in the Fig 2 (b). The polar surfaces of ZnOnano rods might be responsible for these structures. They have made a graphical presentation for the incorporation of Cu^{2+} ions into the ZnO crystal and the effect on the lattice parameters ‘a’ and ‘c’ as shown in fig 3.

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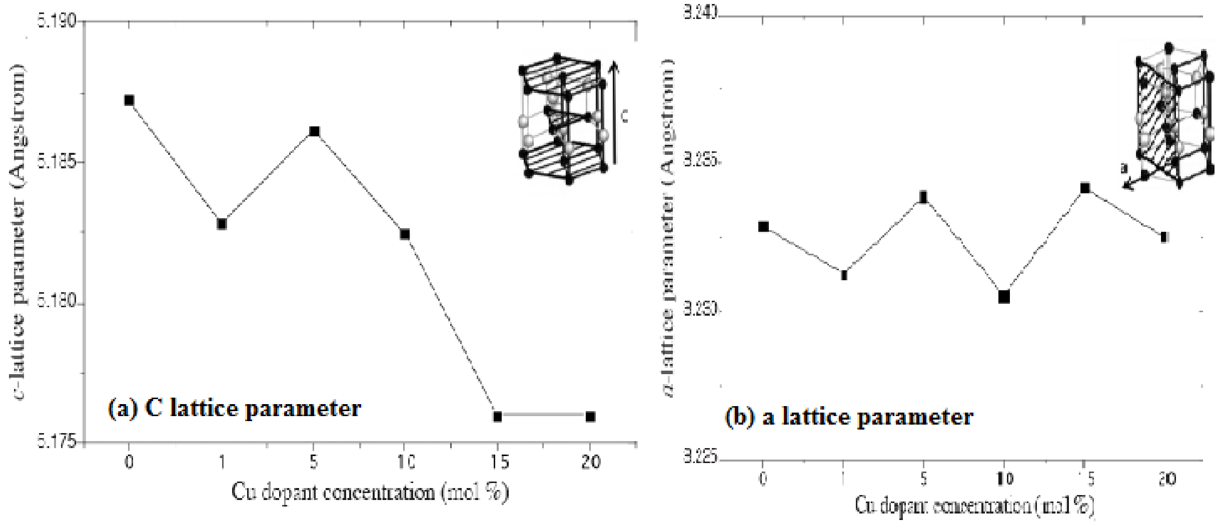

Fig 3: Variation of Lattice parameters of ZnO Nanostructures on different Cu dopant concentrations (a) C-lattice parameter (b) a-lattice parameter (Reproduced from Ref. 13)

The acculmulation effect of Cu^{2+} ions to reduce the C- lattice parameter of ZnO was more significant than that of lattice parameter ‘a’. They have mentioned that the rods like structures of ZnO particles were retained on increasing of Cu dopant concentration also. The homogenous nucleation was more dominant than heterogeneous nucleation for the growth of Cu doped ZnOnano rods in sol-gel synthesis method. But the length of Cu doped ZnOnano rods were decreased with higher concentration of Cu dopant (13).

The optical-structural properties of ZnO thin films were reported by Z. R. Khan et al. by using sol- gel method. The ZnO nanostructures were prepared by using Zinc Acetate dehydrate ‘$Zn(CH_3COO)_2$. $2H_2O$ in a 2- methoxyethanal $(CH_3)_2$ CHOH and monoethanolamine ‘MEA:$H_2NCH_2CH_2OH$ solution. PanalyticalDiffractometer PW3710 with CuKα radiation was used for phase identification of the prepared samples. The typical hexagonal wurtzite structures were found in XRD diffraction pattern. The prepared films were oriented along C- axis and a strong preferential growth was observed along (002) plane of ZnOnano structures. The crystalline grain sizes were calculated by using the Scherer formula as mentioned below

$$D=\frac{K\lambda}{\beta cos\theta} \quad ....(4)$$

In the equation K= 0.94 (a constant), λ was the wavelength used (λ = 1.54 A^0) and β was used for the full width at half maximum of (002) peak of their XRD pattern. The Bragg angle 2θ was around 34.44 and the average value grain size was calculated as 20 nm (14). The XRD pattern of their work is shown in Fig. 4.

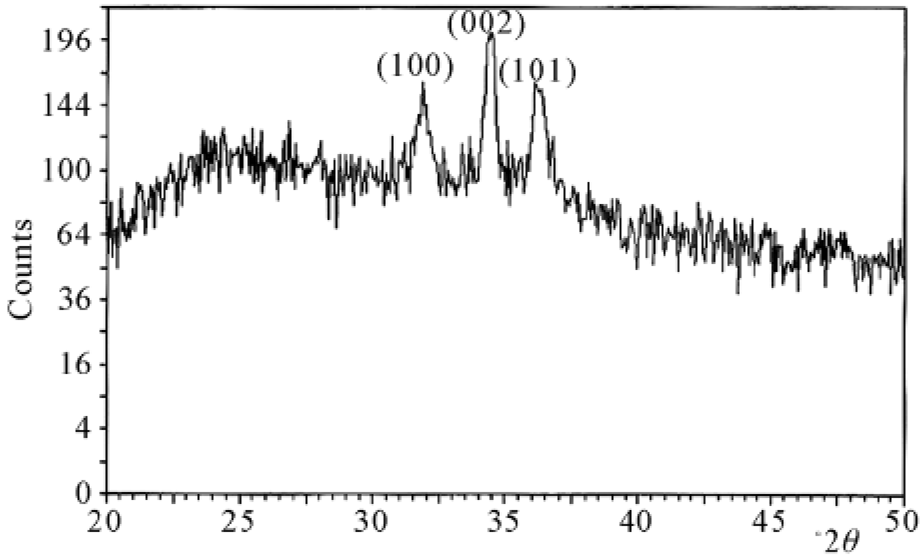

Fig 4: XRD pattern of ZnO Nanostructures (Reproduced from Ref.14)

They have estimated the dislocation density (δ) of the prepared sample by using the following equation.

$\delta = 1/D^2$……………………………………..(5)

The strain (ε) of the thin film was estimated by using the following equation.

$\varepsilon = \frac{\beta cos\theta}{4}$ .... (6)

They have evaluated the structural parameters of the synthesized ZnO nanostructure as shown in Table 1.

Planes	Interplanar Spacing A^0 d(002)	FWHM(β) (002) X 10^{-3} rad	Grain Sizes D (nm)	δ (X10^{14}) (lines/m^2)	ε (X 10^{-3})
(100)	2.8095	8.37	18	30.86	2.01
(002)	2.6016	6.28	24	17.36	1.49
(101)	2.4764	8.37	18	30.86	1.98

Table 1: Structural parameters of ZnO nanostructures in thin film (Reproduced from Ref.14)

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Scientists around the world are focusing on the tuning of structural properties of nano material without altering their chemical composition. This review work provides on study of different growth mechanism adopted by different workers for structural and morphological properties utilization of ZnOnano structures. Many authors have reported the structural change of ZnOnano particles depending on growth mechanism and parameters. The main objective of this review work is restricted to extracting a comprehensive picture of structural properties of ZnOnano structure regarding their different shapes, surface morphology, grain sizes and lattice parameters only. This interrelation between structural morphology and quantum size confinement's effects were also discussed. Chemical methods, hydro thermal methods and sol- gel procedures are found as popular synthesis methods for workers. Since these methods provided versatile and efficient path for synthesizing ZnOnano particles. It was found that the size and shape of nano materials can be controlled by adjusting the concentration of precursors, reaction time and temperature of the growth process. The different growth mechanism and correlated structural properties of ZnOnano structures have various applications in nano size electronics, optoelectronic devices and sensor applications. These growth procedures provided efficient technique for tuning the structural properties of ZnOnano particles for future applications.

REFERENCES

1. Rai P, Yu Y-T Citrate-assisted hydrothermal synthesis ofsingle crystalline ZnO nanoparticles for gas sensor application.Sens Actuators B Chem 173:58–65, (2012).
2. Veriansyah B, Kim J-D, Min BK et al Continuous synthesis of surface-modified zinc oxide nanoparticles in supercritical methanol. J Supercrit Fluids 52:76–83(2010).
3. T. Dietl, H. Ohno, F. Matsukura, J. Cibert and D. Ferrand, "Zener Model Description of Ferromagnetism in Zinc- Blende Magnetic Semiconductors," *Science*, Vol. 287, No. 5455, pp. 1019-1022 (2000).
4. C. D. Pemmaraju, R. Hanafin, T. Archer, H. B. Braun, S. Sanvito, Impurity-ion pair induced high-temperature ferromagnetismin co-doped zno, Phys. Rev. B 78 054428(2008).
5. Sundaresan, R. Bhargavi, N. Rangarajan, U. Siddesh and C.N. R. Rao "Ferromagnetism as a universal feature of nanoparticles of the otherwise nonmagnetic oxides", Physical review B 74, 161306(R) (2006)
6. . Dietl, H. Ohno, F. Matsukura, J.Cibert, D. Ferrand "Zener model description of ferromagnetism in zinc blende magnetic semiconductors", Science, 287, 1019(2000)
7. Sadraei R,A Simple Method for Preparation of Nano-sized ZnO, Research & Reviews: Journal of Chemistry, Vol.5,No.2, p.45-49,(2016).
8. H. Shokry Hassan, A.B. Kashyout, I. Morsi, A.A.A. Nasser,Ibrahim Ali, Synthesis, characterization and fabrication of gas sensor devices using ZnO and ZnO:Innanomaterials, BeniSuef University Journal of Basic and Applied Sciences, Vol.3, p.216-221, (2014).

IJARSE
ISSN (O) 2319 - 8354
ISSN (P) 2319 - 8346

9. TehminaNaz , Adeel Afzal, Humaira M. Siddiqi, Javeed Akhtar , Amir Habib, Mateusz Banski , ArturPodhorodecki, 2-Aminoethanol-mediated wet chemical synthesis of ZnO Nanostructures, ApplNanosci, DOI 10.1007/s13204-014-0334-1, 2014
10. Anjali Oudhia, Pragya Kulkarni and Savita Sharma, Green Synthesis of ZnO Nanotubes for Bioapplications, International Journal of Advanced Engineering Research and Studies,Vol.1.p.280-281,(2015).
11. Suresh Sagadevan, SenthilShanmugam, A Study of Preparation, Structural, Optical, and Thermal Conductivity Properties of Zinc Oxide Nanofluids, Nanomedicine& Nanotechnology, S6: 003. doi:10.4172/2157-7439.S6-003, 2015.
12. A. Mansouri, A.R. Akbari,Role of pH in Aqueous Chemical Growth of ZnO Nanostructures, Proceedings of the 4th International Conference on Nanostructures (ICNS4) 12-14 March, 2012, Kish Island, I.R. Iran
13. S.Y. Pung, C.S. Ong, K. MohdIsha&M.H. Othman, Synthesis and Characterization of Cu-doped ZnONanorods, SainsMalaysiana 43(2),p.273–281, (2014).
14. Ziaul Raza Khan, MohdShoeb Khan, Mohammad Zulfequar, MohdShahid Khan, Optical and Structural Properties of ZnO Thin Films Fabricated by Sol-Gel Method, Materials Sciences and Applications, 2, p. 340-345, (2011).