JETIR.ORG ISSN: 2349-5162 | ESTD Year : 2014 | Monthly Issue
JOURNAL OF EMERGING TECHNOLOGIES AND INNOVATIVE RESEARCH (JETIR)
An International Scholarly Open Access, Peer-reviewed, Refereed Journal

Al doped Zinc Oxide Quantum Well based Ethanol Sensor

Rajarshi krishna Nath [1], L. Hitesh Kumar Singha, Arindam Roy, Indira Dey
Department of Physics, Gurucharan University Silchar, Assam, India

Abstract: Al-doped zinc oxide (ZnO:Al) Quantum Wells have been deposited on to the glass substrates under different doping concentrations (0-1.5at%) by spray pyrolysis technique. The structrual, optical & morphological properties of the quantum wells have been investigated and then examined for ethanol sensing. The structural and morphological studies done by XRD & TEM are in good agreement with each other with a minimum variation in size. The response of the quantum well have been studied for all the samples within the concentration range (100 -500)ppm of ethanol in air at various operating temperature (225-350^{0}C). It is observed that incorporation of Al in ZnO enhances the response of the samples to ethanol. A maximum response of (~60%) is observed for 1 at% ZnO:Al quantum well at 300 ^{0}C to 500 ppm of ethanol in air. Further the response & recovery times are found to be decreased with an increase in doping concentration and also at higher operating temperatures.

Key words: ZnO:Al, quantum well, spray pyrolysis, ethanol, sensor.

1. Introduction

The use of sensors has been increasing at an outstanding rate in the last few years and modern world depends highly on the use of sensors for a variety of purposes such as detection of smoke, radiation, gases etc. The use of solid- state gas sensor has been increasing at an outstanding rate for the last few decades due to its use as the chemical sensitivity of semiconductor surfaces to different adsorbed gases. Presence of dopant elements to an appropriate amount can produce various electronic defects, which increase the influence of oxygen partial pressure on the resistivity. Zinc oxide (ZnO) is an important metal-oxide semiconductor for sensing toxic pollutant gases, combustible gases and organic vapours. Doped ZnO quantum wells have numerous attractive applications in electronic and optoelectronic devices such as transparent electrodes, solar cell windows, piezoelectric devices, gas sensors etc. For gas sensing purposes, this material has been investigated in various forms such as single crystals, sintered pellets, thick films, quantum wells as well as heterojunctions. [1-5]. However, quantum wells are more suitable for gas sensing purposes, as the gases are adsorbed on the material surface and the surface reactions occur. This reaction modifies the concentration of charge carrier in the material, giving rise to a change in its electrical property such as resistance/conductance.

Various methods for the synthesis of quantum wells have been developed by several researchers for gas sensing applications. These include chemical vapor deposition, sol-gel process, spray pyrolysis, sputtering etc. Paraguay et al studied the influence of Al, In, Cu, Fe and Sn dopants on the response of thin film/ quantum well ZnO gas sensor to ethanol vapour. [6]. Sahay et al had studied Al-doped zinc oxide thin films/quantum well for liquid petroleum gas (LPG) sensors. [7]. T.Minami. et al have investigated Group III impurity doped zinc oxide thin films/quantum well prepared by RF magnetron sputtering[8]. In this work, we have investigated the structural and morphological properties of Al-doped zinc oxide (ZnO:Al) quantum well prepared by spray pyrolysis technique and finally the sensing behavior of these quantum wells towards ethanol vapour is studied, as ethanol vapour has been one of the most extensively studied vapours for metal oxide gas sensors, particularly due to the need for small practical devices to detect alcohol on the human breath or even to detect leaks in industrial distribution lines.

2. Experimental

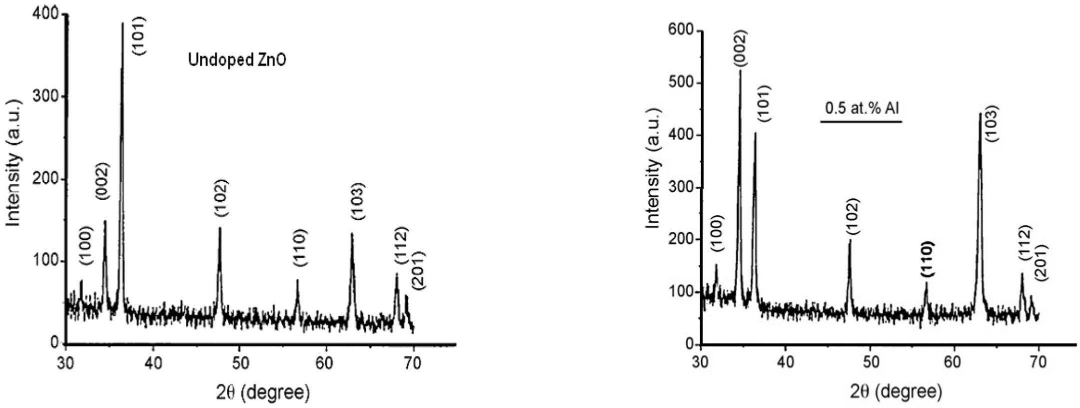
The glass substrates (microscopic slides) prepared in 37.5 mm× 12.5mm × 1.35 mm dimensions are subsequently cleaned in freshly prepared chromic acids, followed by detergent solution and distilled water. The cleaned substrates are placed on hot plate at a constant temperature of $(410 \pm 10)^0$ C. The precursor solution used is of 0.1M concentration of high purity zinc acetate dehydrate (Merck, India) prepared in distilled water. The compound sources of dopants are aluminium chloride. The atomic percentage of dopants in the solution is varied from 0 to 1.5 at%. The atomization of the solution into a spray of fine droplets is carried out by the spray nozzle, with the help of a compressed air as carrier gas. A schematic representation of the typical spray pyrolysis setup, developed in our laboratory and various process parameters for the deposition of quantum well is reported elsewhere [9]. The substrate temperature is monitored using a chromel-alumel thermocouple with the help of a Motwane digital multimeter (Model: 454). During optimization of the process parameters, the substrate temperature has been found to be the most important parameter in quantum well preparation for gas sensing applications. The thickness of the samples is measured by the weight difference method using an electronic high precision balance (Citizen, Model: CY 204) & are found to lie within 200-400nm with an error of ±10%.

. Structural analysis of the films is carried out using a PANalytical X'Pert Pro X-ray diffractometer with CuKα radiation (λ = 1.5418 Å) as an X-ray source at 40kV and 30mA in the scanning angle (2θ) from 30 to 70^0 with a scan speed 0.02^0/ s. The morphological studies are carried out using Transmission Electron Microscope (Model: JEM 1000C X II). High conducting silver paste is used to make ohmic contacts on both the ends of the samples and is dried at a temperature of 150^0C. The film is mounted on a home made two-probe assembly placed into a silica tube, which is inserted coaxially inside a tubular furnace. The electrical resistance of the film is measured before and after exposure to acetone vapour using a Keithley System electrometer (Model: 6514). The sensing characteristics of the film under different concentration levels of ethanol are studied at different operating temperature in the range 225^0C–350^0C. To study sensing properties of the film required volume of ethanol is injected by a micro syringe into the closed silica tube maintained at various temperatures, and subsequently, the decrease in resistance of the samples is monitored till it becomes stationary. Finally, both ends of the tube are opened and the resistance of the samples is allowed to recover the initial value in air.

3. Results and Discussions

A. Structural analysis

Fig. 1 shows the X-ray diffraction patterns of the typical Al-doped ZnO quantum wells.



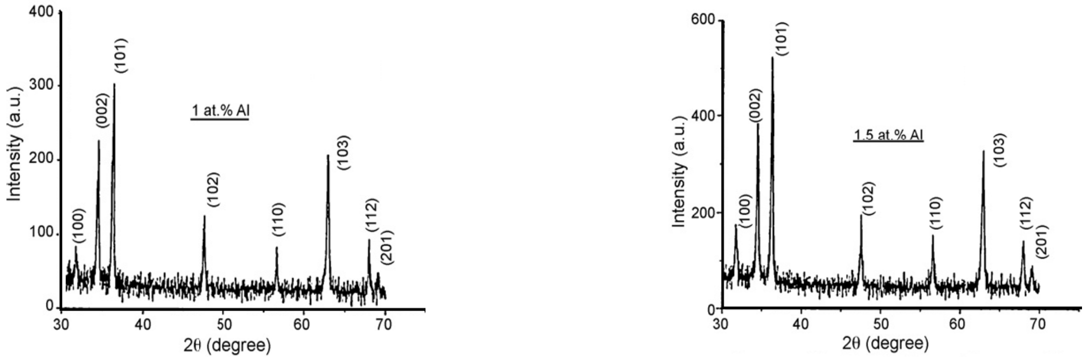


Fig.1. XRD patterns of the typical Al-doped ZnO quantum wells

All the samples are found to be polycrystalline in nature, possessing "hexagonal wurzite" structure as per ICDD reference pattern (01-070-8070). No phase corresponding to aluminum or other aluminum compound is observed in the XRD patterns, which indicates a low level incorporation of Al in ZnO film.[9] The crystallite size of the sample is calculated using Debye-Scherrer equation.

$$D = \frac{0.9\lambda}{W_a \cos\theta} \quad \text{---------(1)}$$

The instrumental broadening is corrected using the following formula

$$W_a = \sqrt{W_o^2 - W_i^2} \quad \text{---------(2)}$$

W_a = actual FWHM, W_o = observed FWHM and W_i = instrumental FWHM (Instrumental broadening supplied)

It is observed that the crystallite size of doped ZnO quantum well is lesser than that of undoped ZnO of similar thickness. This is due to the lesser ionic radius of Al^{3+} ($R_{Al^{3+}}$ = 0.071 nm) which substitutes Zn^{+2} ($R_{Zn^{2+}}$ = 0.074 nm), thereby decreasing the crystallite size. However, crystallite size does not vary systematically with Al dopant concentration, which is attributed to the lattice disorder produced in the samples at higher dopant concentrations due to the difference in their ionic radii.[9]

The relative error in the measurement of crystallite size (D) is given by-

$$\frac{\Delta D}{D} = \frac{\Delta\lambda}{\lambda} + \frac{\Delta W}{W} + \frac{\Delta \cos\theta}{\cos\theta}$$

Where $\Delta\lambda$ = 0.01 Å, ΔW = 0.00001 rad, $\Delta\cos\theta$ = 0.0001

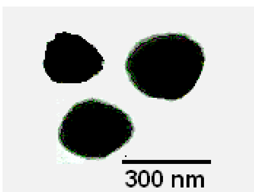
For a particular sample of W = 0.00435 rad, $\cos\theta$ = 0.9573, and λ = 1.54 Å,

The percentage error in D is given by

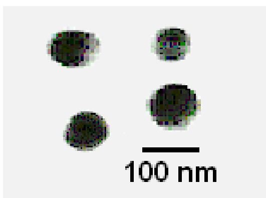
$$\frac{\Delta D}{D} = 0.88\%$$

B. Morphological studies

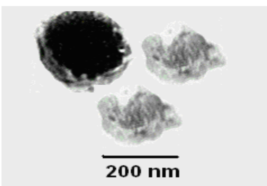
The TEM images of Al-doped ZnO samples are displayed below.



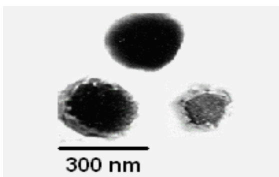
0at%Al-doped ZnO



0.5at% Al-doped ZnO



1 at % Al-doped ZnO



1.5 at% Al-doped ZnO

Fig.2. TEM images of Al-doped ZnO samples

Samples	Crystallite size (nm) (From TEM)	Crystallite size (nm) (From XRD)
Undoped ZnO	270	265
0.5at% ZnO:Al	97	93
1 at % ZnO:Al	257	251
1.5at% ZnO:Al	201	206

Table 1: Crystallite size of Al-doped ZnO samples from TEM & XRD studies

C. Ethanol sensing properties

In this section, the sensing behaviour of ZnO quantum wells towards ethanil vapour and the effects of Al dopants on ethanol sensitivity are explained. The gas sensing measurement is carried out using a static system. The schematic diagram of the static measurement setup used to measure the response of ethanol vapour is shown in fig.3.

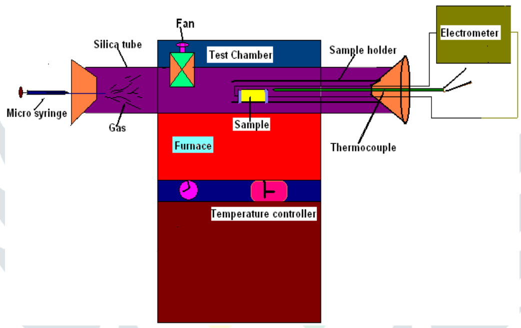
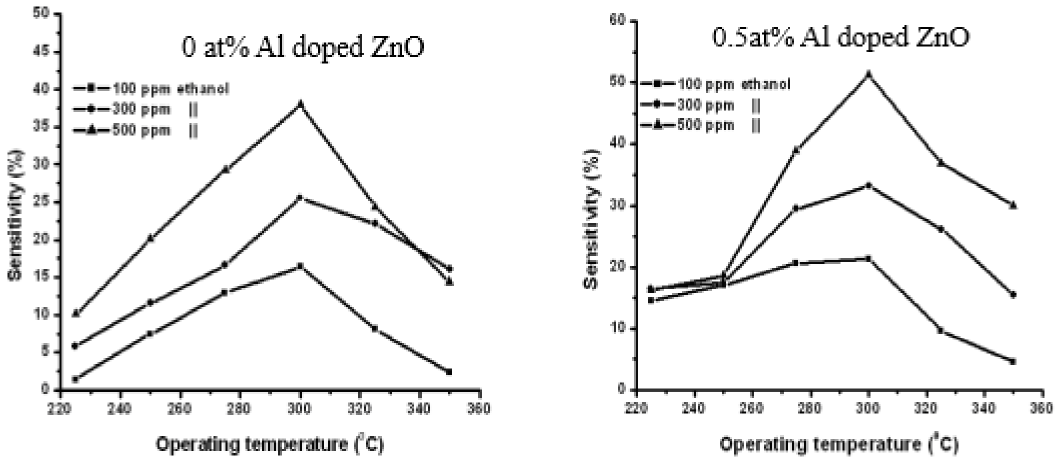


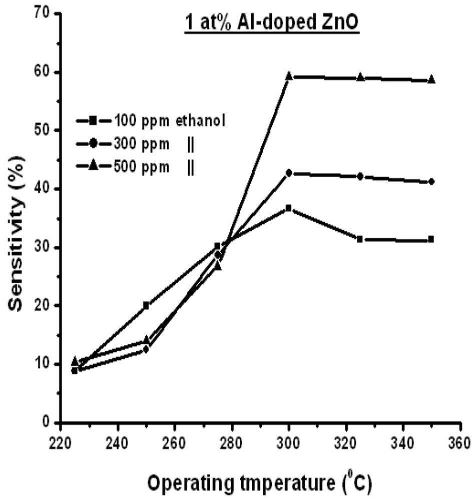
Fig.3. Schematic representation of static measurement setup.

The sensitivity (response) of the quantum is determined using following equation as ethanol possesses the properties of reducing gas [10].

$$S = \frac{(R_a - R_g)}{R_a} \times 100\,\% \quad \text{---------(5)}$$

where R_a = resistance of the film in air, R_g = resistance of the film upon exposure to ethanol. The sensing characteristic of ZnO:Al quantum well as a function of the operating temperature for three different concentrations (100, 300, and 500 ppm) of ethanol is shown in fig.4.





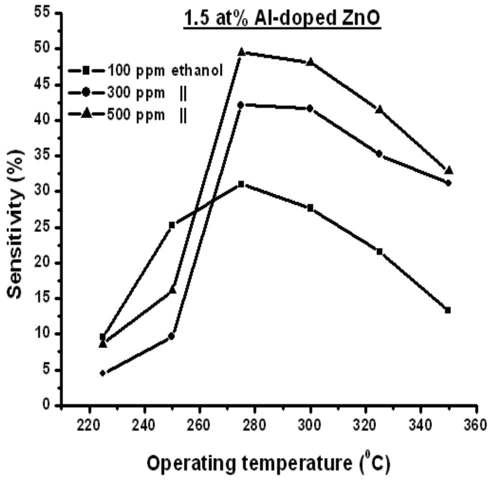


Fig.4.Sensitivity characteristics Al-doped ZnO quantum wells as a function of operating temperature for three different concentrations (100, 300 and 500ppm) of ethanol in air.

It is observed that the sensitivity increases with an increase in ethanol concentration. Further It is observed in the figure that compared to undoped ZnO quantum well, Al-dopant increases the sensitivity of the quantum well towards ethanol vapour. It is reported in the literature that an appropriate donor doping can produce electronic defects, which increase the influence of oxygen partial pressure, thereby increasing the sensitivity [11]. Among all the quantum wells, 1 at% Al-doped ZnO film shows the maximum sensitivity (~60%) at 300 ^{0}C to 500 ppm of ethanol vapour in air. Except 1.5 at% Al-doped ZnO quantum well, all other samples show the peak sensitivity at an operating temperature of 300^{0}C. It indicates that at 300^{0}C, most of the adsorbed oxygen species reacts with the OH group of ethanol vapour [12].
The sensitivity of 0at% Al doped ZnO quantum well as a function of ethanol concentration in air at different operating temperatures is shown in fig.5

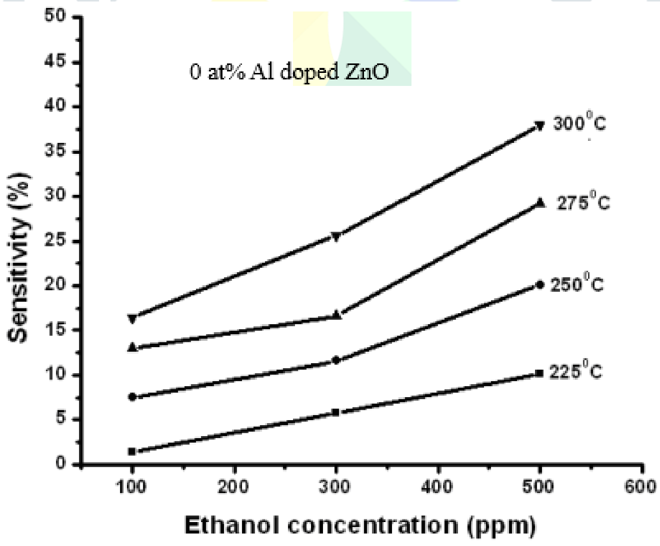


Fig.5. Sensitivity of 0 at% Al doped ZnO quantum well vs ethanol conc at different operating temp.

It is obvious from the above figure that at a particular temperature, the sensitivity shows an increasing trend with an increase in ethanol concentration. At higher concentration of ethanol, the sensitivity increases more rapidly than that at lower concentration. This behavior is attributed to the enhancement of adsorption of atmospheric oxygen on the quantum well surface at higher operating temperature [13]. Similar variation of sensitivity with ethanol concentration has also been observed in case of all the Al-doped ZnO quantum wells.
Fig.6. represents the transient response characteristics of Al-doped ZnO quantum well to 500 ppm of ethanol vapour in air at 300^{0}C.

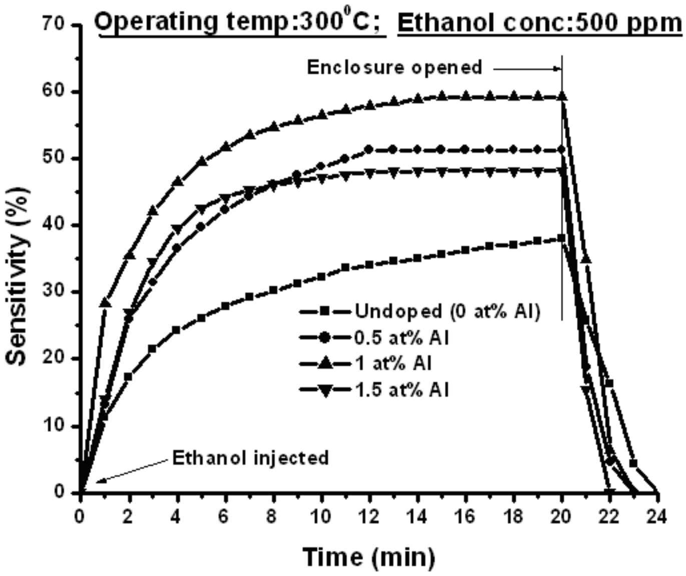


Fig. 6. Transient response characteristics of Al-doped ZnO quantum well to 500ppm of ethanol vapour in air at 300^{0}C.

It is observed in the figure that compared to undoped ZnO, Al doping decreases the response as well as recovery time of the quantum well towards ethanol vapour. This indicates that Al-dopant enhances the adsorption and desorption mechanism. Further, it is observed that all the quantum wells show fast response and recovery to ethanol at higher operating temperatures.

The ethanol-sensing mechanism of the quantum well may be explained as follows. At first, oxygen is chemisorbed on the surface of the quantum well when it is heated in air. During chemisorption, atmospheric oxygen forms ionic species such as O^{2-} and O^{-} which acquire electrons from the conduction band. The temperatures on which sensor studies have been carried out, only O^{-} species reacts with ethanol [13].

The reaction between ethanol vapour and ionic oxygen species can take place by two different ways [13,14].

$$C_2H_5OH\ (gas) + O^{-} \leftrightarrow CH_3CHO + H_2O + e^{-}$$
$$C_2H_5OH\ (gas) \leftrightarrow H + C_2H_5O\ (surface)$$
$$C_2H_5O \leftrightarrow H + CH_3CHO$$
$$CH_3CHO + O\ (bulk) \leftrightarrow CH_3COOH + O\ (vacancies).$$

4. Conclusion

The Al-doped zinc oxide quantum wells prepared by chemical spray pyrolysis technique have been studied for ethanol sensors. The structural analysis indicates a decrease in crystallize size with a small Al dopant concentration. It is observed that compared to undoped ZnO quantum well, Al-doped ZnO quantum wells are highly sensitive to ethanol and the magnitude of response can be varied either by changing the operating temperature or the ethanol concentration. Among the all Al-doped ZnO quantum wells studied in this work, the 1at% Al-doped ZnO quantum well shows the maximum sensitivity (~ 60%) at 300^{0}C to 500 ppm of ethanol in air, whereas in case of undoped ZnO quantum well, the sensitivity is found to be about 35% at the same operating temperature and concentration of ethanol in air. The average response and recovery times are found to be respectively 8 min and 2 min.

Acknowledgment

The authors wish to acknowledge Department of Physics, NIT Silchar, and SUS, Narsingpur, for their assistance in this work.

References.

[1] A. Jones, T.A. Jones, B. Mann, J.G. Griffith, The effect of the physical form of the oxide on the conductivity changes produced by CH4, CO and H2O on ZnO, Sens.Actuators 5 (1984) 75–88.

[2] S. Saito, M. Miyayama, K. Koumoto, H. Yanagida, Gas sensing characteristicsof porous ZnO and Pt/ZnO ceramics, J. Am. Ceram. Soc. 68 (1985) 40–43.

[3] M. Suchea, S. Christoulakis, K. Moschovis, N. Katsarakis, G. Kiriakidis, ZnO transparent thin films for gas sensor applications, Thin Solid Films 515 (2006)551–554.

[4] N. Koshizaki, T. Oyama, Sensing characteristics of ZnO-based NO*x* sensor, Sens.Actuators B 66 (2000) 119–121.

[5] S. Pizzini, N. Butta, D. Narducci, M. Palladino, Thick film ZnO resistive gas sensors, J. Electrochem. Soc. 136 (1989) 1945–1948.

[6] F Paraguay D., M. Miki-Yoshida, J. Morales, J. Solis,W. Estrada L., Influence of Al,In, Cu, Fe and Sn dopants on the response of thin film ZnO gas sensor to ethanolvapour, Thin Solid Films 373 (2000) 137– 140.

[7] P.P. Sahay, R.K.Nath, Sensors and Actuators B: Chemical. vol.133. pp. 222-227, 2008.

[8] T. Minami, H. Sato, H. Nanto, S. Takata, Group III impurity doped zinc oxide thin films prepared by RF magnetron sputtering, Jpn. J. Appl. Phys. (Part 2) 24 (1985)L781–L784

[9] P.P. Sahay, R.K.Nath, Sensors and Actuators B: Chemical. vol.133. pp. 222-227, 2008.

[10] P.P. Sahay, R.K. Nath, Sensors and Actuators B: Chemical. Vol.134,pp.654-659., 2008

[11] F. Paraguay D., M. Miki-Yoshida, J. Morales, J. Morales, J. Solis, W. Estrada., Thin Solid Films 373 (2000) 137-140

[12] Mishra S, Ghanshyam C., Ram N., Singh S., Bajpai R.P., Bedi R.K.; *Bull. Mater. Sci.*, Vol. 25, No. 3, pp. 231-234. 2002.

[13] Sahay P.P., Tewari S., Jha.S, M.Shamsuddin. *Journal of Materials Science* Vol. 40. pp. 4791-4793. 2005.

[14] Mishra S, Ghanshyam C., Ram N., Singh S., Bajpai R.P., Bedi R.K.; *Bull. Mater. Sci.*, Vol. 25, No. 3, pp. 231-234. 2002