Digest Journal of Nanomaterials and Biostructures Vol. 4, No 3, September 2009, p. 511 - 518

GAS SENSITIVITY AND CHARACTERIZATION OF CADMIUM OXIDE (CdO) SEMI CONDUCTING THIN FILM DEPOSITED BY SPRAY PYROLYSIS TECHNIQUE

R. L. MISHRA*, A. K. SHARMA[a], S. G. PRAKASH
Department of Electronics and Communication, University of Allahabad, Allahabad India
[a]*Department of physics Sagar Institute of Technology Barabanki, (U.P) India*

The undoped Cadmium Oxide (CdO) semi conducting transparent thin film is deposited on glass substrate by spray pyrolysis technique using ultrasonic nebulizer. The thickness of the deposited film is of the order 0.1μ. This film having good adhesion with the substrate exhibits sensitivity in gaseous atmosphere like Ethanol, CO, etc. The optical absorption and transmission has been analyzed. The direct energy band gap of CdO thin film (Eg = 2.37 ev) is calculated by plotting graph between (h ν) vs $(\alpha h\nu)^2$. The sensitivity of the CdO film in CO gas is more than Ethanol. The XRD and SEM analysis for its structural and micro-structural characteristic has been preformed .The grain size of deposited film is calculated to be 18.6 nm.

(Received September 15, 2009; accepted September 30, 2009)

Keywords: Transparent CdO thin film, glass substrate, spray pyrolysis and gas sensitivity.

1. Introduction

Thin film technologies play the pivotal role specifically in the field of microelectronics, optical coating, integrated optics and superconductors etc. The changes in chemical and electrical properties by the irradiation of the thin films are utilized for optical and micro machines. By deposition of the oxide films like Sn, Cd, Zn, and alloys by incorporating appropriate doped impurities a range of useful synthetic transparent conductors with about 90 % transparencies in the visible and semi-metallic conductivity have been obtained. Such transparent conductors are being used extensively in thin film solar cells [1-3] and opto electronic devices [4 -5].

Recently, semi-conducting, thin films of various oxide materials like ZnO, SnO_2 and CdO etc. have shown significant results as regard to gas sensing properties [6-9] which is tremendously being used in the field of gas sensors. Numerous techniques are being used to prepare good oxide films. CdO thin film has its own interest particularly in applications like transparent electrodes TCO (transparent conducting oxide), optical switching and optical limitting etc. [10 -12]. CdO thin films have been deposited by spray pyrolysis using cadmium nitrate and cadmium acetate [13,14] as a starting material. In the present work XRD, SEM, optical properties and gas sensitivity have been performed for analysis of the deposited CdO film.

2. Experimental detailes

Spray pyrolysis is essentially a thermal reaction between cluster of liquid / vapor atoms of different chemical species. The spray technique involves spray of solution, usually aqueous, in mist form containing solvable salts of the constituent atoms. Saxena etal. [15-16] has developed

* Corresponding author: ramlalmishraald@rediffmail.com

the detailed and advanced experimental set up of spray pyrolysis technique. Performance of the CdO semi-conducting thin films prepared by spray pyrolysis involves cleaning of substrate, spray rate, and substrate temperature etc. [17].

The preparation of CdO thin film have been done by spray of an aqueous nitrate solution of 0.2 M concentration in double distilled water mixed with the methanol (for the decomposition of the nitrate solution) in the ratio of 3 : 2 onto the glass substrate at deposition temperature of 400 $\pm 10^0$ C. The spray rate was maintained via compressed carrier gas of the order ~ 0.52 ml/min. The nozzle was kept 5 inch apart from the substrate.

The deposited CdO semi-conducting film was taken out from the heater surface after temperature of heater came down to room temperature. Structural analysis of the as deposited CdO film was carried out by using XRD and SEM. Optical analysis was done by UV measurements. The sensitivity of the CdO film has been performed in presence of different gas atmosphere like Ethanol and CO.

3. Results and discussion

3.1 Optical characterization

The absorbance spectra (in the range 340 nm – 640 nm) were recorded using a ultraviolet visible Spectrophotometer (UR-VIS-IR) Shimadzu model no.- 1601.It was used for band gap measurement. The variation of optical (%) transmission with wavelength λ is shown in Fig- 1. The absorption coefficient, α was determined [18] by relation

$$\alpha = (1/d) \times \ln [(1-R_\lambda)^2 / T_\lambda]$$

where, d = is film thickness, R_λ and T_λ are reflection and transmission coefficient respectively at wavelength λ.

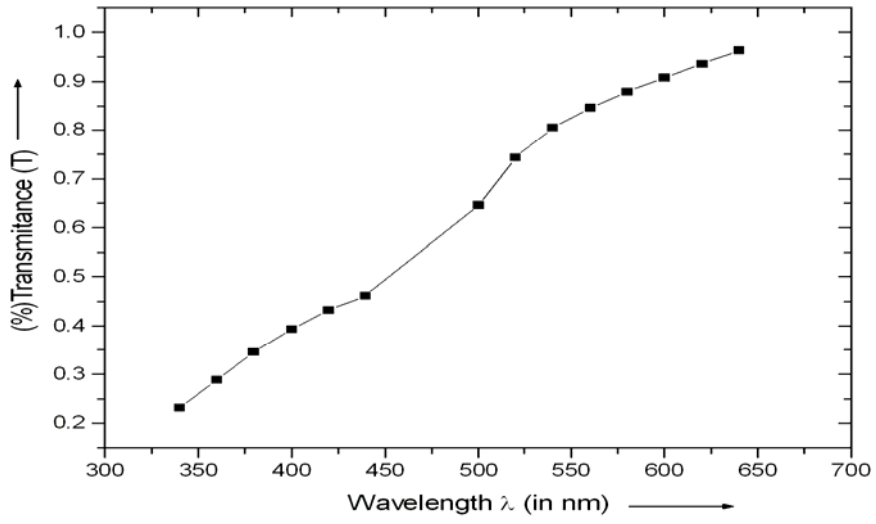

Fig. 1 Variation of optical (%) transmission (T) vs wavelength (λ)

The CdO exhibits direct band gap in the range of 2.3 to 2.5 eV [19]. Band to band transition in oxide films depends on the absorption coefficient α and photon energy by the relation

$$(\alpha h \nu)^2 = A (h\nu - Eg)^{1/2} \quad (1)$$

Where, A is constant hν and E_g is the photon energy and optical band gap energy respectively. The value E_g is calculated out by plotting $(\alpha h \nu)^2$ vs $(h\nu)$ as in Fig-2 . The obtained value, of direct band gap E_g= 2.37 eV, is in good agreement with the reported results for CdO thin films [20, 21]

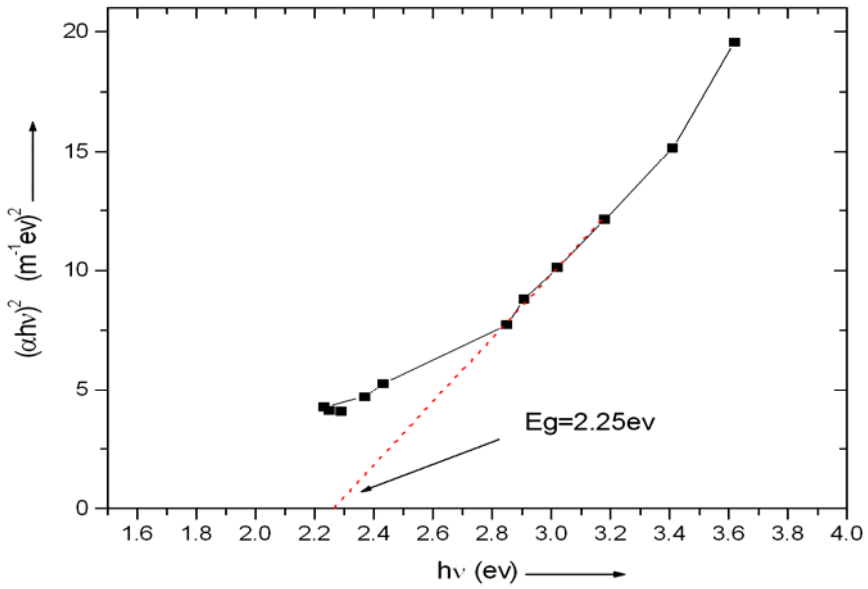

Fig. 2 Plot showing the variation of $(h\nu)$ vs $(\alpha h \nu)^2$ (Eg= 2.25 ev)

3.2 Structural and micro structural analysis of CdO thin film

Structural analyses of the deposited CdO thin film were carried out using CuKα radiation, having wavelength 1.5406 Å. The X-ray diffraction patterns of the film are recorded by using SIEMENS diffrakto meter model – D500, of .2M concentrations deposited on glass substrate at temperature 400±10 ^oC shown in Fig-3. XRD patterns of the film show well-defined peaks (111), (200), (220), and (311) etc. at angle 33.01^o, 38.30^o, 55.28^o, 65.91^o which are well matched with standard JCPDS card No. 75-0594. To obtain more quantitative information, the XRD pattern was analyzed with Gaussian function at Full Width at Half Maxim [FWHM]. The grain size of thin is film determined by the Scherer's formula

$$D = \frac{0.9\,\lambda}{\beta \cos\theta}$$

Where, D = Crystalline grain size
β = FWHM of the observed peak
λ= wave length of the X-ray diffraction
θ = Angle of diffraction

The W-H plot [22] for the ZnO thin film is performed and given in Fig. 4. The origin of strain is related to lattice 'misfit" which in turn depends upon the growing condition of the film. In W-H method following relation is used for the calculation of average crystalline size

$$\beta \cos\theta = \frac{c\lambda}{t} + 2\varepsilon \sin\theta \qquad (2)$$

where β is FWHM in radian, t is the grain size (nm), ε is the strain , λ is the X-ray wavelength and c is the correction factor. For the estimation of micro strain (ε) developed in the thin film we use the following relation [23]

$$\varepsilon = (\beta \cot \theta)/4 \tag{3}$$

where β and ε has their usual significances.

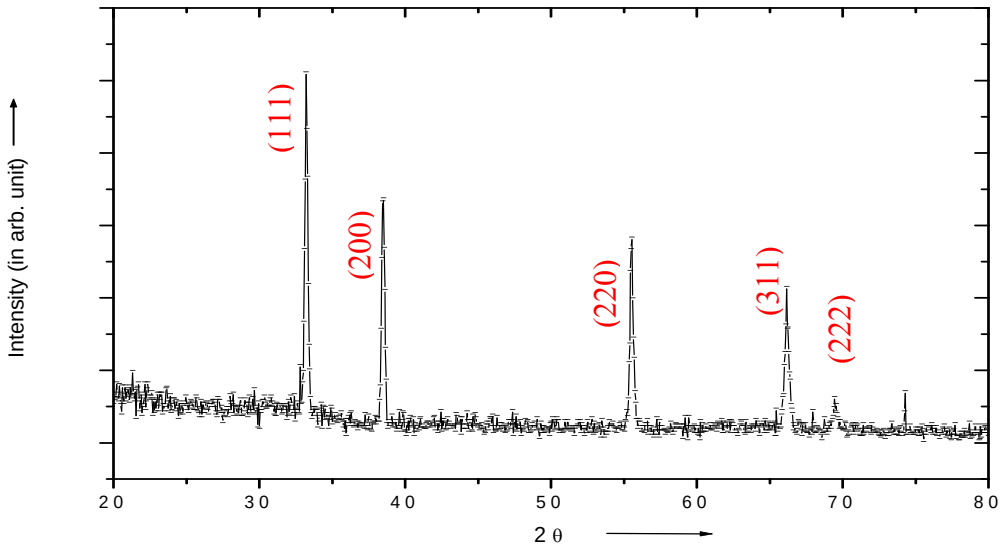

Fig. 3 XRD pattern of as deposited CdO thin film

The average particle size of CdO thin film is obtained 18.6 nm and the micro strain (ε) is .020 .In the process of film formation, it is possible to involve the dislocations. The dislocation density of thin film is given by the Williamoson and Smallmans relation [24]

$$\delta = \frac{n}{t^2} \tag{4}$$

where n is a factor, which is unity and t is grain size. In this film the possible dislocation density is of order 0. 33×10^{12} cm^2 . .

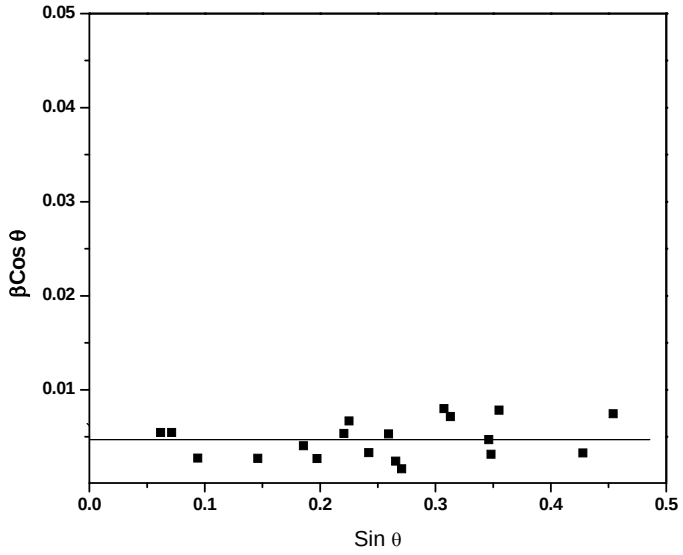

Fig. 4 W- H Plot of CdO thin film.

The average grain size of the deposited CdO thin film is calculated to be 18.6 nm. The sharpness of the peaks show that film has good crystalline nature. The SEM micrograph shows the surface topography of CdO nano- crystalline thin film in Fig. 5 . The film shows the polycrystalline nature and uniform distribution of spherical grains.

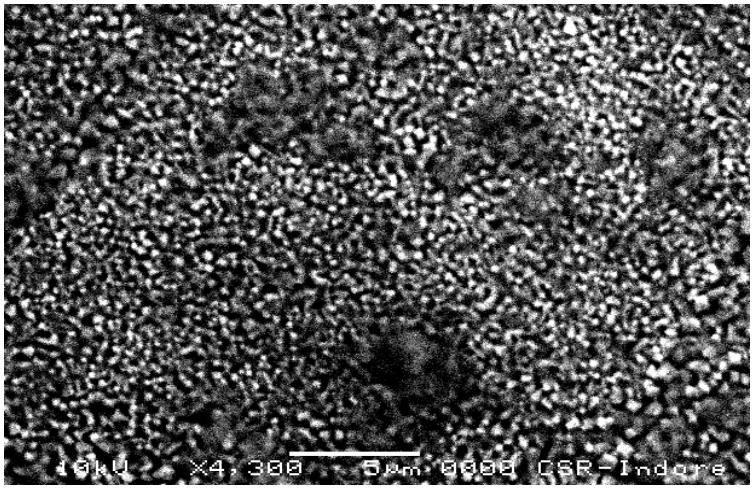

Fig. 5 SEM morphology of deposited CdO thin film

3.3 Gas sensitivity of CdO nano- crystalline thin film:

In this study, the ethanol and CO gas sensing properties of the nano-sized CdO thin film deposited by spray pyrolysies techniques. The sensitivity (S) of the film is defined as the ratio of surface resistance of the film in air (Ra) and gas (Rg)

$$S=\frac{Rair}{Rgas}$$

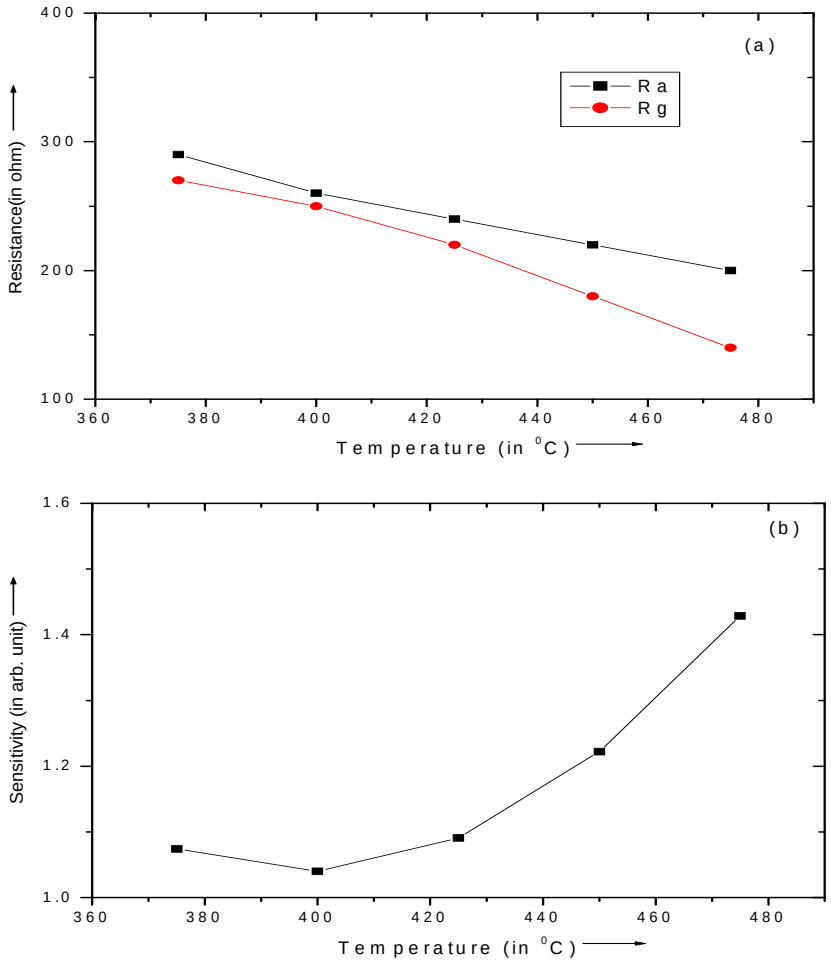

Fig. 6(a) Representing variation of resistance in air (Ra) and in Ethanol atmosphere (Rg) at 100 ppm (b) Representing sensitivity of the CdO thin film in Ethanol gas atmosphere.

The temperature is an important parameter for gas sensing materials and designing of the sensor. The sensing materials have to appropriate temperature to achieve crystallization and structural evaluation .A sufficient degree of crystallinity is required to attain the desired electronic properties necessary for gas sensor application. A number of experiments have been carried out to measure the sensitivity as a function of operating temperature. All the time sensitivity of the sensor element has approximately constant value indicating the repeatability of the sensor. The sensing mechanism of ethanol and CO are quite complex and it proceeds through several intermediate steps. It is based on the changes in the resistance of the CdO, which is controlled by gas species. It is known that a certain amount of oxygen from air is absorbed on the surface of the CdO thin film. The CdO thin film interacts with the oxygen, by transferring the electrons from the conduction band to adsorbed oxygen atoms, resulting into the formation of ionic species such as O_2^- or O^- . The reaction kinematics may be explained by the following reaction.

$$O_2 \text{ (gas)} \Leftrightarrow O_2 \text{ (absorbed)}$$
$$O_2 \text{ (absorbed)} + e^- \Leftrightarrow O_2^-$$
$$O_2^- + e^- \Leftrightarrow 2O^-$$

The electron transfer from the conduction band to the chemisorbed oxygen results into the decreased in the electron concentration. As a consequence, an increase in the resistance of the CdO is observed.

The molecules reducing hydrogen species are bounded to carbon therefore the ethanol and CO dissociates less easily into the reactive reducing compounds on the CdO surface. When the nano-sized CdO thin film exposed to reducing gas like ethanol and CO reacts with the chemisorbed oxygen there by releasing and electron back to the conduction band which decreased the resistance of the CdO. The overall reaction explains as follows.

$$2C_2H_5OH + O_2^{2-} = 2CH_3CHO + 2H_2O + 2e$$
$$2C_2H_5OH + O_2^{-} = 2CH_3CHO + 2H_2O + 1e.$$

The effect of chemisorptions is discussed in details by V. S. Vaishnav et al. [9]. The gas sensitivity of as deposited CdO thin film for Ethanol and CO has been performed at gas concentration 100 ppm in Figs. 6(b) , 7(b) represents the variation in the sensitivity for different range of temperature for Ethanol and CO gas respectively. Figs. 6(a), 7(a) represents the variation of resistance in air and in gas atmosphere with temperature at 100 ppm concentration. It has been observed that the sensitivity of the film is quite large for CO as compared to the Ethanol. The sensitivity of CdO thin film for CO gas is max. at temperature at 273 ^{o}C .

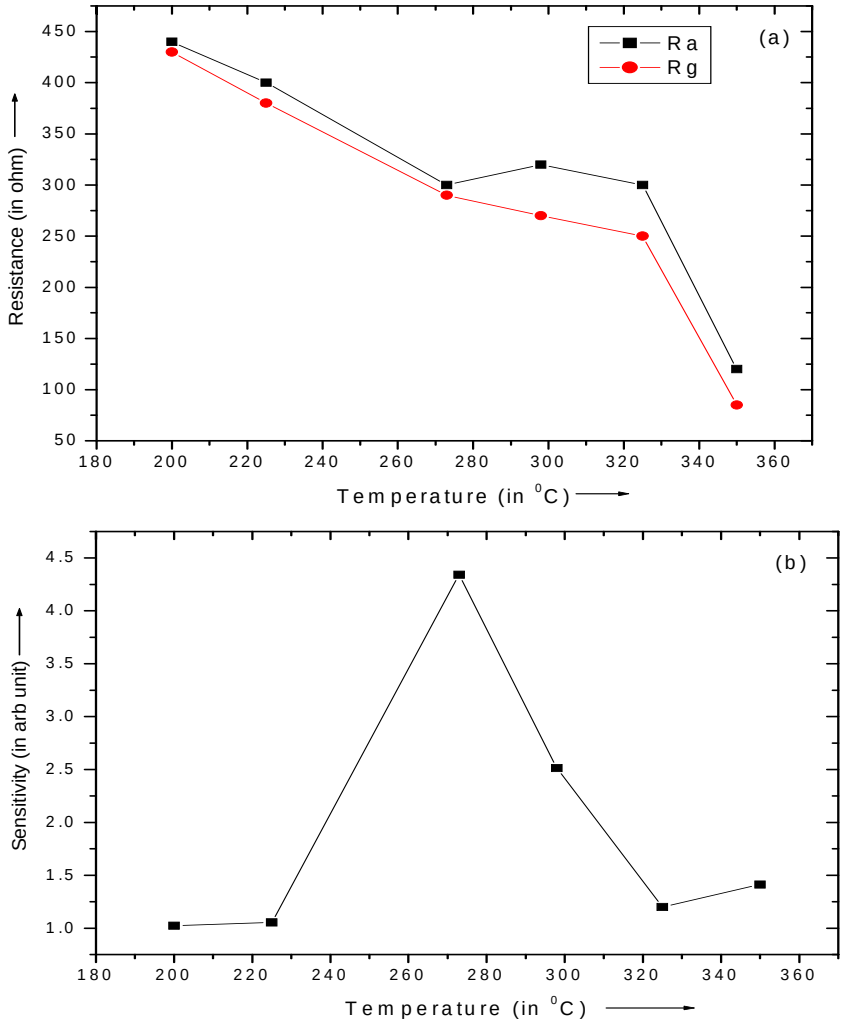

Fig. 7 (a) Representing variation of resistance with air (Ra) and in CO atmosphere (Rg) at 100 ppm (b) Representing sensitivity of the CdO thin film in CO gas atmosphere.

4. Conclusions

The CdO thin film deposited through spray pyrolysis method on glass substrate shows better sensitivity in CO atmosphere at temperature 273^{o}C. The average grain size of CdO thin film has been calculated 18.6nm and direct band gap of 2.37 eV.

Acknowledgements

Author is grateful to Dr. V.R. Reddy for XRD measurements (CSR-INDORE), Dr D. M. Phase for SEM (CSR-INDORE).

References

[1] K. L Chopra, S. Mejor, D K Pandya, Thin Solid Films . **102**, 1 (1983)
[2] S. Ashok, P. P Sharma, S J Fonash, IEEE Trans. on Electron. Devices, **ED-27,** 725 (1980)
[3] O. Gomez Daza, A. Arias-Carbajal Readigos, J. Campos, M. T. S. Nair, P. K. Nair, Modern Phys. Lett. **B ,17**, 609 (2001)
[4] B S Wherret, Semicon. Sci. Technol., **A65**, 6 (1991)
[5] A Renolds, D C Look, B Jagai, Solid State Comm. **99**, 873 (1996)
[6] P R Potil, P S Potil, C D Lokhande, Ind. J. Phys. **226,** 14 (1995)
[7] K Gurumurgan, D Mangalraj, S K Narayandass, C Balasubramanian, in: Proceeding of the Symposium on DAE Solid State Phys. **36**, 326 (1993)
[8] A Arulgnanam, A Balsubramaniam, S Balachandran, in : Proceeding of the conference on the Physics and Technology of Semiconductors and Integrated Circuits. 566 (1992)
[9] M G. Ambia, M N. Eslam, M O. Hakim, Sol. Energy Mat. Sol. Cells. **28**, 103 (1992)
[10] F A Benko, F P Koffyberg, Solid State Comm. **57,** 901 (1996)
[11] Lee W. Tutt, T F Boggess, Prog. Quant. Elecr. **17,** 299 (1993)
[12] F Z Henari, S MacNamara, O Stevenson, J Callagham, D Weldon, W J Blau, Adv. Mater. **5**, 930 (1993)
[13] S. Wng, M Concivera, J. Electroche. Soc. **139**, 3220 (1992)
[14] M D Uplane, P N Kshirsagar, B J Lokhande, C H Bhosale, Mater. Che. Phys. **64,** 75 (2000).
[15] A K Saxena, S S P Arya, B Das, A K Singh, R S Tiwari, O N Srivastav, Solid State Comm. **166,** 163 (1988).
[16] K K Verma, A K Singh, A K Sexena, R S Tiwari, O N Srivastava, Supercondut. Sci. Technol. **5,** 163 (1992)
[17] Y Y Ma, R H Bube, J.Electroche. Soc. **124,** 1430 (1997)
[18] A A Dakhel and F Z Henari , Cryst. Res. Technol.. **38**(11), 979 (2003)
[19] K L Chopra, S R Das, Thin Film Solar Cells, Plenum Press, NewYork (1993).
[20] B J Lockande, M D Uplane, Mater. Res. Technol. **36,** 439 (2001)
[21] A A Dakhel, F Z Henari, Cryst. Res. Technol**. 38,** 979 (2003)
[22] G.K.Willianson and W.H.Hall Acta Metal 1 22 (1983) .
[23] S. Sen , S.K. Halder, S.P. Sen, Gupta, J.Phys. Soc. Japan **38**, 1643 (1975).
[24] D. P. Padiyan, A. Marikini, K. R. Murli, Mat. Chem. And Phys. 78 51 (2002).