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Characterization and gas sensitivity of cadmium oxide thin films prepared by thermal evaporation technique

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Abstract: Cadmium oxide CdO thin films were deposited by thermal evaporation technique at different substrate temperatures on glass substrates. The XRD analysis shows that CdO films are amorphous and transform to polycrystalline with cubic structure when deposited at 448K and annealed at 573K. The direct energy band gap of CdO thin film decreases with increases of substrate temperature, while at an annealing temperature of 573K the energy gap increases. The results were explained on the biases of structural disordered intruding by the effect of Ts. Other optical constants, such as refractive index, extinction coefficient, dielectric constant were also studied. The response of the films to sense H2 gas has been investigated and they exhibited a maximum sensitivity of 6%. The response time to immediate injection and removal of a certain amount of gas were measured.

Keywords: CdO thin film, optical and structural properties, semiconductor oxide, transparent thin films, wide band gap materials, TCO gas sensors.

1 Introduction

The availability of the raw materials and economics of the deposition method are significant factors in choosing the most appropriate Transparent Conducting Oxides (TCO) material. CdO is regarded as a material with many attractive properties such large energy band gap, high transmission coefficient in visible spectral domain, remarkable luminescence characteristics etc. Bulk CdO is an n-type broad band gap (2.3 eV) semiconductor, with an indirect band gap of 1.36 eV [1]. It has wide range of applications as solar cells, windows, flat panel display, photo transistors etc. It was experimentally established that structural, electrical and optical properties are very sensitive to the film structure and deposition conditions [2-8]. Such transparent conductors are being used extensively in thin film solar cells [9-11] and optoelectronic devices [12, 13]. CdO films can be fabricated by means of a number of techniques such as sputtering [14], chemical vapor deposition (CVD) [15], spray pyrolysis [16], thermal evaporation [17] and sol gel [18].

Thin films of various oxide materials like ZnO, SnO_2 and CdO etc. have shown significant results as regard to gas sensing properties [19-22] which is tremendously being used in the field of gas sensors. The sensing mechanism is based on the changes in the resistance of the film which is controlled by gas species. The sensitivity (S) of the film is defined as the ratio of surface resistance of the film in air (R_{air}) and gas (R_{gas}). The temperature is an important parameter for gas sensing materials and designing of the sensor. A sufficient degree of crystallinity is required to attain the desired electronic properties necessary for gas sensor application. Gas sensors using transparent CdO semiconductors to detect different gases at relatively low operating temperature have been extensively reported [23-25].

Unfortunately, the CdO sensors are not sensitive to only one but many kinds of reducing gases. However, sensing mechanisms of these gas sensors have not been fully understood and further investigations are required to determine the microstructure characteristics of the sensors. The present study

determines the effect of substrate temperatures on the structural, optical properties of as deposited films. The variations of the sensitivity of the fabricated sensors have been speculated to be due to the microstructure of the films, mainly the porosity.

2 Experimental

Thermal evaporation technique (Edwards E306A coating system) was used to prepare CdO films. The CdO material was placed in a molybdenum boat in a vacuum chamber at a pressure of $2x10^{-6}$ torr, The glass substrate was cleaned by using detergent water to remove any oil or dust that might be attached to the surface of the substrate, and then they were rubbed gently under tap for 15 minutes, after that, they were placed in a clean beaker containing distilled water and then rinsed in ultrasonic unit for 15 minutes and repeated by replacing the distilled water with pure alcohol solution which reacts with contamination such as grease and some oxides. The slides eventually were dried by air blowing and wiped with soft paper.

All the films were prepared with a constant deposition rate of 1.25 nm/sec at different substrate temperatures (398, 423 and 448 K), and annealed at a temperature 573 K. The film were taken from the coating system and kept in the vacuum desiccators until the measurements were made. The crystallinity of the films was determined by X-ray diffractometer (Rigaku Model RAD II A with Cu-K_α radiation (λ =1.541 Å) with Current= 20 mA, Voltage = 40 KV and Scanning speed =5 cm/min). Optical transmittance was measured by UV-VIS single beam spectrophotometer (ELICO-159) in the wavelength range (200-800nm) to calculate the energy gap and the other optical constants.

3 Results and Discussions

3.1 Structural Properties

The XRD pattern for films deposited at substrate temperatures 398, 423 and 448K showed that they are amorphous. By annealing the same samples to 573K the transformation from amorphous to polycrystalline structure takes place. The XRD patterns for these annealed CdO films are presented in Fig. 1.

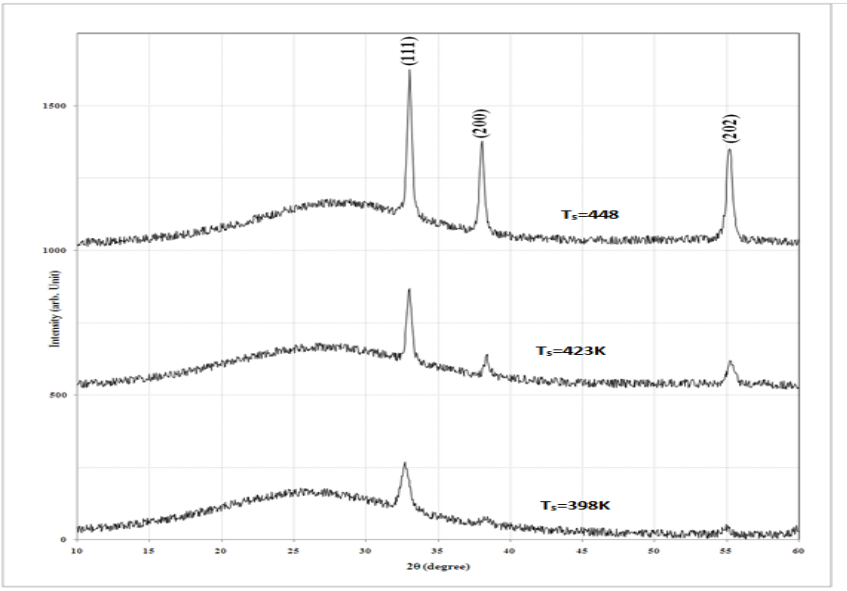

Figure.1 XRD for CdO thin films at different substrate temperatures after annealed at 573K

Several peaks of cubic face-centered CdO corresponding to (111), (200) and (202) planes with a_0 = 4.6953 A˚ can be seen in the figure and have been compared with standard X-ray diffraction data file (JCPDS file No. 75-0594) [26]. The information on the grain size of the deposited films has been obtained using Scherer's formula and shows that, as the substrate temperature increases, the grain size also increases after

annealing to 573 K. The interplaner spacing (d) corresponding to XRD peaks, and JCPDS card have been compared as shown in Table 1.

Table (1) comparison between experimental and standard d_{hkl}, I/I_o and hkl of CdO films deposited at 448K and annealed 573 K [26]

T_s (K)	2θ Exp. (degree)	d_{hkl} Exp. (Å)	Int. (arb.unit)	Grain size (Å)	d_{hkl} std. (Å)	(hkl)
398	32.969	2.715	158.3	120.518	2.711	111
	38.300	2.348	25.3	132.032	2.348	200
	55.000	1.668	20.4	150.820	1.660	202
423	33.017	2.711	251.2	195.135	2.711	111
	38.400	2.342	62.1	188.674	2.348	200
	55.300	1.660	72.545	147.491	1.660	202
448	33.031	2.710	499.1	216.825	2.711	111
	38.047	2.363	314.6	209.658	2.348	200
	55.200	1.663	312.8	173.944	1.660	202

3.2 Optical Properties

3.2.1 Transmission spectra

Optical study of CdO film was carried out in the wavelength range 400–800 nm at room temperature for the films deposited on glass substrate. Transmittance spectra recorded for CdO films deposited at different substrate temperature (398, 423 and 448K) as a function of wavelength are shown in fig.2a. The plots show a narrow range of variation with increase in substrate temperatures. The film deposited with higher substrate temperatures shows higher transmittance compared to others. Fig.2b shows the transmittance spectra of the same samples shown in figure 2a after annealed at 573 K. The transmission is seen to increase after annealing due to the increase in crystallite size observed from the x-ray diffraction data shown in table 1. In previous studies on pure and doped-CdO films deposited by e-beam [27,28], it was noted that these films have a high optical transmittance (>80%) in the visible region and polycrystalline structure. Moreover, Xiu *et al* [29] studied CdO as a buffer layer to improve the structural properties of ZnO films and using a thin buffer layer of CdO to enhance some physical properties of ITO films.

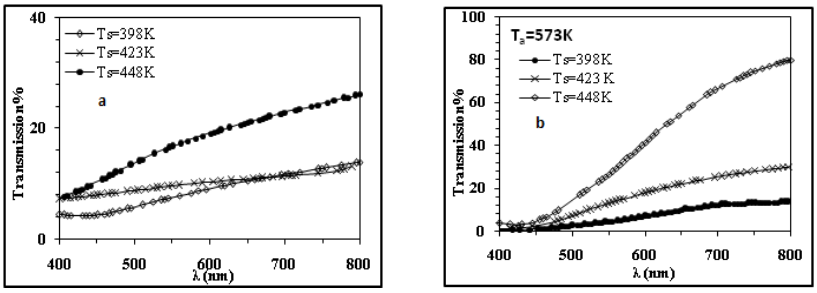

Figure.2 The transmittance spectrum of CdO thin films at **a**)-different T_s **b**)-after annealed to 573 K

3.3.2 Absorption Coefficient

The dependence of the absorption coefficient on the wavelength for different substrate temperatures (T_s) and for annealed film at 573 K is shown in Fig.3a and fig.3b respectively.

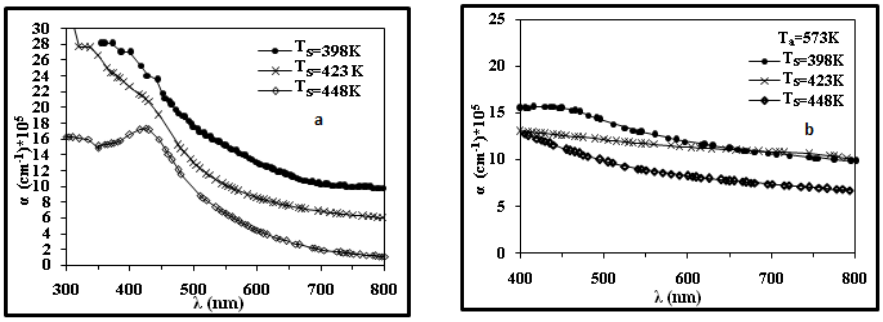

Figure. 3 Absorption coefficients of CdO thin film at a)-different T_s and b)-T_a=573K

In the shorter wavelengths, the absorption coefficient α exhibits high values which means that there is a large probability of the allowed direct transition, and then α decreases with increasing of wavelength. Also we can notice from these figures that α in general decreases with the increase of T_s, this is due to the increasing of energy gap with Ts.

3.3.3 Optical Band Gap

The optical energy gap values (E_g) for CdO films have been determined by using Tauc equation $\alpha h\upsilon = B'\left(h\upsilon - E_g\right)^r$ [12]. This is used to find the type of the optical transition by plotting the relations $(\alpha h\upsilon)^{1/2}$,$(\alpha h\upsilon)^{1/3}$,$(\alpha h\upsilon)^{2/3}$,and $(\alpha h\upsilon)^2$ versus photon energy ($h\upsilon$). It is found that the relation for r=1/2 yields linear dependence, which describes the allowed direct transition. E_g is then determined by the extrapolation of the portion at (α =0) as shown in fig.4a and fig.4b for as deposited films at different substrate temperatures and for annealed films. The value of the optical energy gap decreases with increasing T_s for all samples and this may be due to the increasing grain size and the decrease in defect states near the bands and this in turn decreased the value of E_g. The optical band gap was found to increase after heat treatment; this may explained on the basis of the fact that the heat treatment made CdO samples more transparent or less absorbing to the incident light.

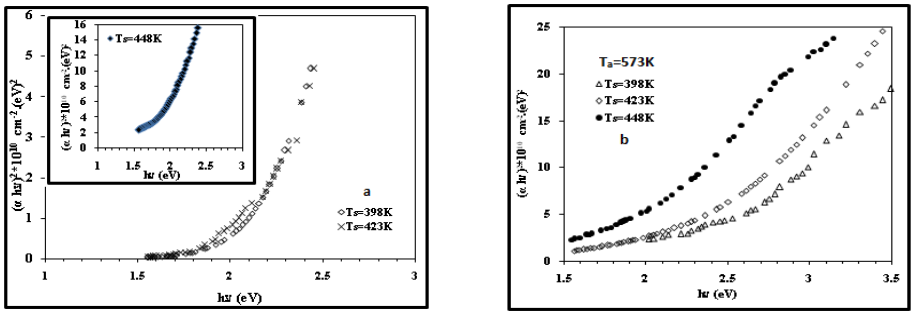

Figure.4 variation of$(\alpha h\upsilon)^2$ versus photon energy ($h\upsilon$) for CdO thin film at **a**)-different T_s **b**)- annealed to T_a=573K

3.3.4 Optical Constants

Fig.5 shows the variation of extinction coefficient (k) of the as deposited and annealed films. We know that the extinction coefficient depends mainly on absorption coefficient according to the relation ($k= \alpha\lambda/4\pi$); for this reason, we notice the increasing of extinction coefficient with increasing photon energy because the increasing of absorption coefficient. This means that direct electronic transition happens in these films. The behavior of extinction coefficient (k) is nearly similar to the corresponding absorption coefficient and we can see that the value of k increased with increasing T_s.

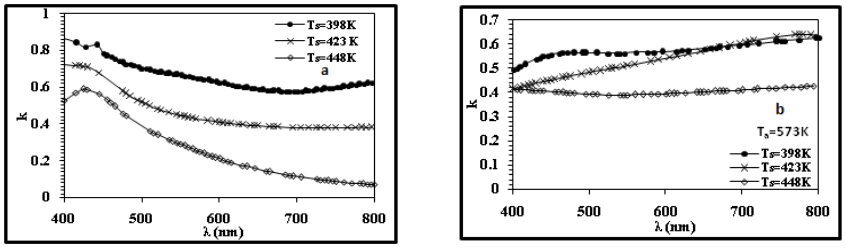

Figure.5 variation of extinction coefficient (k) with wave length for CdO thin films at a) - different Ts **b**) - at T_a=573K

The variation of the refractive indexes with wavelength in the range 400–800 nm, for as deposited and annealed films are shown in Fig. 6. We can notice from these figures that the refractive index, in general decreases slightly with annealing temperature (T_a=573K. This behavior is due to the increment in energy gap which is maybe due to the increased grain size and decrease of the defect density which means decreasing of the reflection. Also we can see from this figure that the refractive index decreases with the increasing of the wavelength of the incident photon.

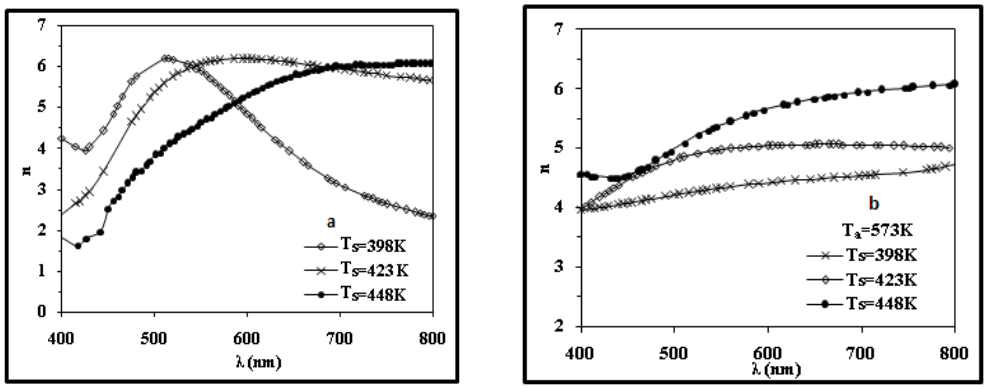

Figure.6 variation of refractive index with the wave length for CdO thin films at **a**)-different T_s **b**)-at T_a=573K

The variation of the real and imaginary parts of the dielectric constant values versus wavelength are shown in fig.7 and 8 for the as deposited and annealed films. It is found that ε_1 and ε_2 decrease with increasing substrate temperatures. The variation of the real part of dielectric constant ε_1 depends on the value of the refractive index. By contrast, the imaginary part of the dielectric constant ε_2 depends mainly on the extinction coefficient values which are related to the variation of absorption coefficient.

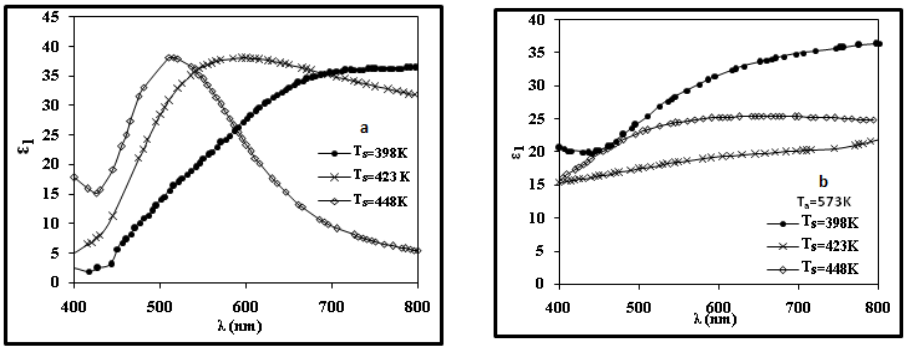

Figure.7 The variation of ε_1 with the wave length for CdO thin films at a)-different T_s and b)-T_a=573K

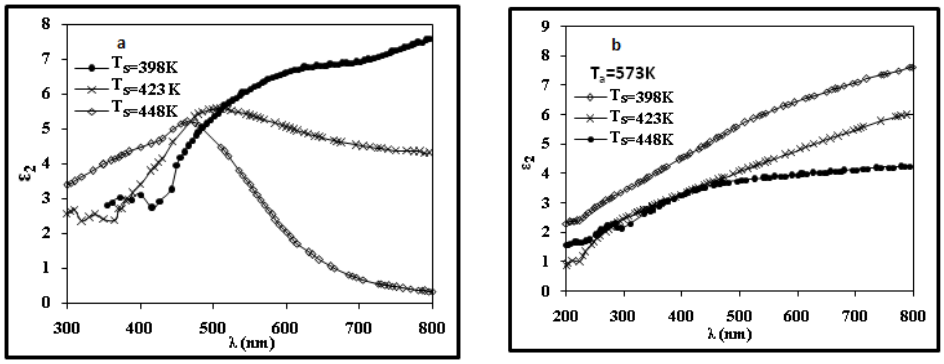

Figure.8 The variation of ε_1 with the wave length for CdO thin films at a)- different T_s and b)- T_a=573K

The variation in the optical constants is summarized in table 2.

Table 2 energy gap, extinction coefficient, refractive index and real and imaginary part of dielectric constant

T_a (K)	T_s (K)	E_g (eV)	k	n	ε_1	ε_2
As deposited	398	1.90	0.39	4.33	18.5	2.11
	423	1.88	0.51	4.97	24.2	3.66
	448	1.8	0.56	5.4	28.5	3.45
Annealed at 573 K	398	2.42	0.44	4.6	21	6.2
	423	2.34	0.29	5.8	34	3.4
	448	1.95	0.66	6	36	5.4

4 Gas sensor

The response time (defined as the interval within which the peak intensity has reached to its maximum value and calculates from $t_{res.}$ =Abs ($t_{G90\%}$-t_{Gair})) is taken as the time the sensor requires to achieve 90% of the conductance change upon the step introduction of the analyze gas at the sensor. Likewise, the recovery time is taken as the time the sensor requires to achieve 90% of the conductance change upon the step interruption of the analyze gas at the sensor. The sensitivity of the metal oxide semiconductor sensor is mainly determined by the interaction between the target gas and the surface of the sensor. The greater the surface area of the materials, the stronger is the interaction between the adsorbed gases and the sensor surface, i.e. the higher the gas sensing sensitivity.

The test carried out at operating temperature of 473K and 10 V bias voltages with 3 and 6% of Hydrogen in air for thermally evaporated CdO gas sensor, fabricated with the film deposited at 448K and annealed to 573K. The changes in sensitivity versus H_2 concentration of the CdO gas sensors are shown in Fig.9. The sensitivity of the CdO gas sensor increased as the H_2 gas concentration was increased from 3% to 6% and it dropped rapidly when the H_2 gas was removed, indicating that the gas sensor has a good response for different H_2 concentrations. This result was consistent with the conclusion for the dominance of operation temperature for the response time.

The results indicate 20% efficiency for Hydrogen concentration of 3%. The response time to immediate injection and removal of a certain amount of gas was measured. The results are independent of the amount of injected gas onto the surface. A value of 21 s was measured for the response time of the thermally evaporated CdO gas sensor and then a time of 32 s was obtained for its recovery (at 3%H_2), while at (6%H_2) the response time become18 s and the recovery time 40 s. This fast response time could be due to a

high porosity of the film that causes the adsorbed gas acting as donors to induce an accumulator layer at a very high rate. Electron microscopy studies are underway to confirm this.

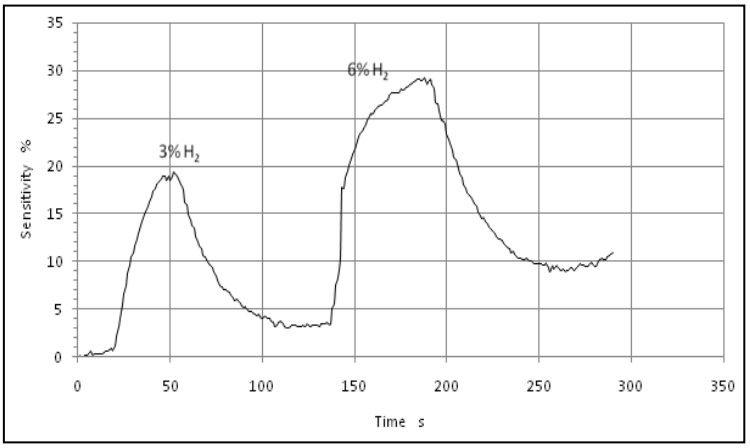

Figure.9 Transient sensitivity s% at 473K temperature and for 3 and 6% H_2 gas mixing ratio

5 Conclusions

CdO films have been deposited by thermal evaporation technique at different substrate temperatures and the films were annealed at 573K. The XRD tests of these films showed that the structure of as deposited films is amorphous and transformed to polycrystalline after annealing at 573K and exhibited cubic structure. The energy gap decrease whiles the refractive index (n), extinction coefficient (k) increase with increasing substrate temperatures.

The fabrication of cadmium oxide gas sensor using thermal evaporation has been reported. The change in sensitivity of the thermally evaporated CdO in response to hydrogen was evaluated. The variations of the sensitivity of the fabricated sensors have been speculated to be due to the microstructure of the films, mainly the porosity. Furthermore the sensitivity of the gas sensor also increased as the concentration of H_2 gas was increased. The sensitivity as well as the response time was improved by increasing the concentration. The maximum sensitivity in this study was obtained for 6% H_2 concentration.

References

[1] K. Gurumurugan, D. Mangalaraj and Sa. K. Narayandass, J. Cyst. Growth, 147,355(1995).
[2] R. S. Rusu and G. I. Rusu, J. of Optoelectronics and Advanced Materials 7, 1511 (2005).
[3] Dong Ju Seo, J. of the Korean Physical Society, 45, 1575 (2004).
[4] D. M. Carballeda-Galicia, R. Castanedo-Perez, O. Jimenez- Sandoval, G. Tores-Delgado and C. I. Zuniga-Romero, Thin Solid Films 371,105 (2000).
[5] B. J. Lockande and M. D. Uplane, Mater. Res. Bull. 36, 439 (2001).
[6] A. A. Dakhel and F. Z. Henari, Cyst. Res. Technol. 38, 979 (2003).
[7] R.L.Mishra, A.K.Sharma and S.G.Prakash, J. of Nanomaterials and Biostructures, 4, 511 (2009).
[8] K.Gurumurugan, D.Mangalraj and S.K.Narayanandas, Thin Solid Films, 251, 7 (1994).
[9] K. L Chopra, S. Major and D K Pandya, Thin Solid Films 102, 1(1983).
[10] S. Ashok, P. P Sharma and S J Fonash, IEEE Trans. on Electron. Devices, ED-27, 725 (1980).
[11] O. Gomez Daza, A. Arias-Carbajal Readigos, J. Campos, M. T. S. Nair and P. K. Nair, *Semicond. Sci. Technol.* 15, 1022 (2000).
[12] Adachi Sadao, Numerical Data and Graphical Information (Hardcover, ISBN 978-0-7923-8567-7(1999) 736).
[13] A. Renolds, D. C. Look and B. Jagai, Solid State Comm. 99, 873 (1996).
[14] L.I.Popova, S.K. Andreev, V.K. Gurorguev and E.B. Manolov, Proceedings of the 20th international, IEEE Conference on Microelectronics 2, 581 (1995).
[15] K.B.Sundaram and G.K. Bhagara, J. Phys.D: Appl.Phys. 14, 333 (1981).
[16] G.Gordillo, L.C.Moreno, W.Dela Cruz and P. Teheran, Thin Solid Films 252, 61 (1994).
[17] A.Salehi and M. Gholizade, Sensors Actuators B: Chemical 89, 173 (2003).
[18] C.Cobianu, C.Saraniu, P.Ciciliano, S. Caponoe, M. Utrianien and L.Ninisto, Sensors Actuators B 77, 496 (2001).
[19] R. S. Rusu and G. I. Rusua, J. of Optoelectronics and Advanced Materials. 7, 823 (2005).

[20] K. Gurumurgan, D. Mangalraj, S. K. Narayandass and C. Balasubramanian, Phys. Status Solidi (a), 143, 85 (1994).
[21] P. A. Radi, A. G. Brito-Madurro, J. M. Madurro and N. O. Dantas, Braz. J. Phys.36, 412 (2006).
[22] K.Nomura, H.Shiozawa, T.T akada, H. Reuter and E. Richter, J. Mater.Sci.8, 301 (1997).
[23] M G. Ambia, M N. Eslam and M O. Hakim, Sol. Energy Mat. Sol. Cells, 28, 103 (1992).
[24] Hussein Abdel-Hafez Mohamed and Hazem Mahmoud Ali, Sci. and Technol. Adv. Mater. 9, 025016,(9pp) (2008).
[25] M.Mahaboob Beevia, M.Anusuyab, V.Saravananc and IACSIT Member, International J. of Chemical Engineering and Applications, 1, 151 (2010).
[26] JCPDS powder diffraction file No. 96-101-1052
[27] H. A Mohamed, H M Ali, S. H Mohamed and M M Abd El-Raheem, *Eur. Phys. J. Appl. Phys.* 34, 7 (2006).
[28] H M Ali, H A Mohamed, M M Wakkad and M F Hasaneen, Jpn. J. Appl. Phys. 48, 1101 (2009).
[29] F X Xiu, Z Yang,D. T. Zhao, J. L. Liu, K. A. Alim, A. A. Balandin, M. E. Itkis and R.C. Haddon,*J. Electron. Mater.* 35, 691(2006).