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CdO:Al films deposited by sol–gel process: a study on their structural and optical properties

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Undoped and Al–doped CdO films have been prepared by sol–gel spin–coating method. Effects of Al dopant on the structural and optical properties of CdO film have been investigated. The films were prepared for Al/Cd ratios of 1% and 3%. The crystal structure and orientation of the films have been investigated by X–ray diffraction method. CdO and CdO:Al films have polycrystalline structure with (111) preferential orientation. Al dopant increases the optical transparency of the films in the visible region. The optical absorption study reveals that the direct optical transitions occur in the optical band gap and the films have a direct optical band gap. The optical band gaps of undoped, 1% Al–doped and 3% Al–doped CdO films were found to be 2.476, 2.591 and 2.682 eV, respectively. The optical constants, refractive index, extinction coefficient and optical dielectric constants of these films were determined using transmittance and reflectance spectra. Al doping concentration affects strongly the optical constants of the thin films. The optical constants and optical absorption edge of the CdO thin film can be controlled by Al dopant.

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Keywords: CdO, Sol–gel spin–coating, Optical band gap, Optical constant

1. Introduction

Transparent conducting oxides (TCOs) have long been a subject of various investigations due to its unique physical properties and applications in commercial devices [1, 2]. Among these TCOs, CdO is an important material for the fundamental studies. It is now well conceived that the CdO shows many excellent properties, which make it suitable as a TCO. CdO is an n–type semiconductor with band gap of approximately 2.5 eV [1, 3]. CdO films have been successfully used for many applications, including phototransistors [4], gas sensor [5], solar cells [6], liquid crystal displays, IR detectors and anti reflection coatings [7]. CdO thin films have already been developed by different methods such as sol–gel [3, 8], spray pyrolysis [9], DC magnetron sputtering [10], chemical bath deposition (CBD) method [11], etc. The sol–gel method has several advantages due to its simplicity, easy control of the film composition, safety, low cost of the apparatus and raw materials. Doping of CdO thin films incorporating various elements such as Sn [12], In [13] F [14] and Al [15, 16] have already been studied.

Although aluminum has been used as a suitable dopant for other transparent conducting thin films like ZnO, studies on CdO:Al thin films are less. Maity et al have deposited glass substrate using Al–doped CdO using sol gel method [15]. But in the available literature we don't found data for optical parameters and Wemple–DiDomenico single oscillator model of the Al–doped CdO films. In this paper, we report on the structural and optical properties undoped and Al–doped CdO film films deposited by the sol–gel spin–coating method.

2. Experimental details

Undoped and Al–doped CdO films were deposited onto glass substrates by the sol–gel method using a spin–coating method. The CdO precursor solutions were prepared starting from cadmium acetate dehydrated (CAD, 0.01 mol), methanol (0.46 mol), glycerol (0.02 mol), triethylamine (0.005 mol). At first, the CdO precursor solution was prepared by the following procedure: *i*) the cadmium acetate was dissolved in half of the methanol (0.23 mol for each mol of CAD) at constant magnetic stirring until a transparent solution was obtained. *ii*) the glycerol was added to the solution. *iii*) the triethylamine previously dissolved in the other half of the methanol was also incorporated. The solution was stirred constantly during its preparation. The second, dopant solution was prepared. Aluminum nitrate ($Al(NO_3)_2.9H_2O$), 2-methoxethanol ($C_3H_8O_2$) and monoethanolamine (C_2H_7NO, MEA) were used as a dopant source, solvent and stabilizer, respectively. Aluminium nitrate solutions and CAD of 1 M were mixed together in two different volume proportions 1 and 3%. The procedure was done entirely at room temperature. The obtained mixture was stirred at 60 ^{o}C for 2 h to yield a clear and homogeneous solution, which was then served as the coating source after cooling down to room temperature. The glass substrates were first cleaned by detergent, and then in methanol and acetone each for 10 min by using ultrasonic cleaner. At last, the substrates were rinsed with deionized water and dried with nitrogen. The coating solution was dropped into the glass substrate, which was rotated at 2000 rpm for 30 s using LAURELL WS-400B-6NPP/LITE spin coater. After the spin coating, the film was dried at 110 °C for 10 min in a furnace to evaporate the solvent and to remove organic residuals. This coating/drying procedure was repeated for five times before the film was inserted into a tube furnace and annealed at 300 °C in air for 45 min.

X–ray diffraction (XRD) patterns were obtained with a Rigaku Rint 2200 Series X–Ray Automatic Diffractometer using the CuK_α radiations (λ=1.54059 Å) in the range of 2θ between 20° and 70°. Surface morphology was studied using Zeiss Supra 50VP model scanning electron microscope (SEM). Optical transmittance measurements were recorded with a double beam Shimadzu UV 2450 spectrophotometer with an integrating sphere in the wavelength range 190–900 nm. The thickness of the films were determined with Mettler Toledo MX5 microbalance by using weighing method and found to be about 300 nm.

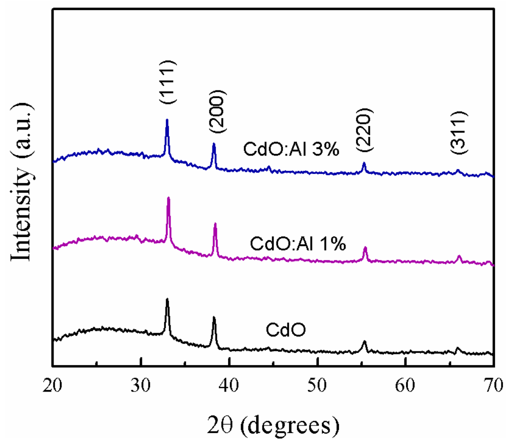


Fig. 1. X–ray diffraction spectra of undoped and Al–doped CdO films.

3. Results and discussion

3.1 Crystal structure of the undoped and Al–doped CdO films

XRD spectra of the undoped and Al–doped CdO films are shown in Fig. 1. These results indicate that all of the films have a polycrystalline structure. For the films, the main characteristic peaks are assigned to the (111), (200), (220) and (311) planes. The relatively stronger intensity of the peak indicates preferential (111) orientation of the films and similar behavior has also been reported by other researchers [15, 16].

The average grain size and strain for the films can be determined using the equation [17],

$$\beta = \frac{\lambda}{D\cos\theta} - \varepsilon_s \tan\theta \qquad (1)$$

where β=FWHM and θ the Bragg angle, D grain size and ε_s is the strain. The plot of $(\beta\cos)/\lambda$ vs. $(\sin\theta)/\lambda$ for the various reflecting planes were plotted. The D and ε_s values were determined from the intercept and slope of this graph and given in Table 1. The preferential growth orientation was determined using a texture coefficient *TC(hkl)* and given in Table 1.

Table 1. Structural parameters of the undoped and Al-doped CdO films.

Film	*D* (nm)	strain	*TC*
CdO	25	2.0×10^{-3}	1.73
CdO: Al 1%	67	4.5×10^{-3}	1.80
CdO: Al 3%	39	1.0×10^{-3}	1.72

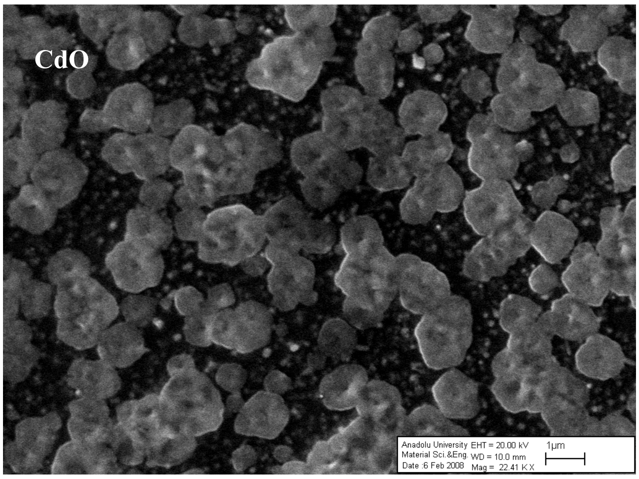
In order to obtain the true value of the lattice constant, we use Nelson-Riley function (*NRF)* defined by the following relation [17]

$$NRF = \frac{1}{2}\left(\frac{\cos^2\theta}{\sin\theta} + \frac{\cos^2\theta}{\theta}\right) \qquad (2)$$

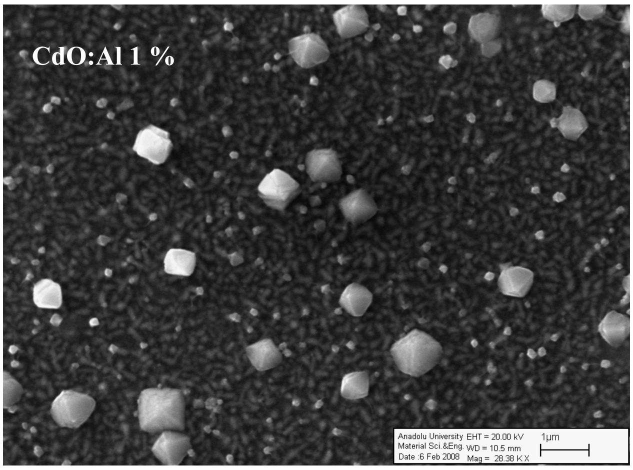
where θ is the Bragg angle. The plot of a vs. *NRF* for the CdO film were plotted and extrapolation to *NRF*=0 yields the true parameter, a_0. The value of a_0 was obtained for the true lattice parameter is given in Table 2, in agreement with previous results [18].

Table 2. D–values, NRF and lattice constant of the undoped and Al-doped CdO films.

(hkl)	CdO			CdO:1%Al			CdO:3%Al		
	d(Å)	*NRF*	*a(Å)*	*d(Å)*	*NRF*	*a(Å)*	*d(Å)*	*NRF*	*a(Å)*
(111)	2.7122	1.647	4.6977	2.7056	1.643	4.6862	2.7154	1.650	4.7032
(200)	2.3470	1.383	4.6940	2.3434	1.381	4.6868	2.3506	1.386	4.7012
(220)	1.6598	0.860	4.6946	1.6577	0.858	4.6887	1.6661	0.861	4.7124
(311)	1.4158	0.658	4.6957	1.4136	0.656	4.6884	1.4163	0.659	4.6973



(a)



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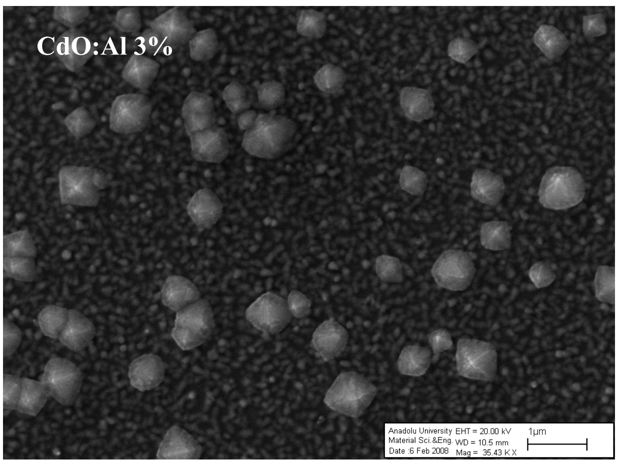


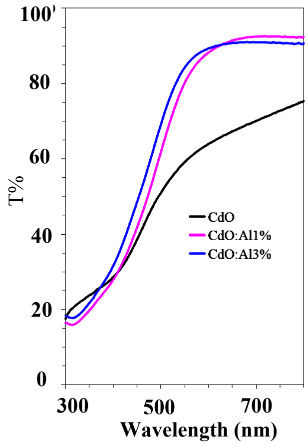
(c)

Fig. 2. SEM micrographs of the undoped and Al–doped CdO films.

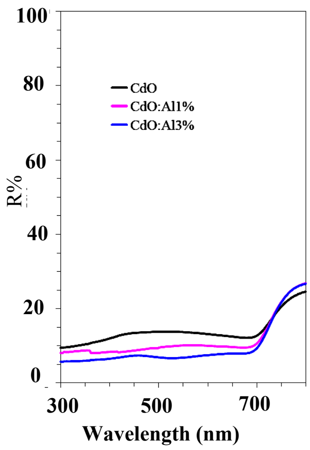
Fig. 2 shows scanning electron micrographs (SEM) of the undoped and Al–doped CdO films. From the first image, it is seen that the particles have rounded shape about 1 m diameter. But the second and third images, the particles shape are like pyramids and the number of pyramids-like particles increased with doping. Furthermore, at the third image, we can see that the pyramids-like shape particles are more homogeneous than the second.

3.2. Optical properties of the undoped and Al–doped CdO films

The transmittance and reflectance spectra of the films are shown in Fig. 3(a) and (b). Al incorporation increases the transmission of the CdO film by doping in the visible region. As seen in Fig. 3(b), the reflectance values of the films in the visible region change with Al dopant.



(a)



(b)

Fig. 3. (a) Transmittance and (b) reflectance spectra of the undoped and Al–doped CdO films.

The optical absorption edge of the films was determined by the optical absorption, which provides explaining features concerning the band structure of the film.The optical absorption edge was analyzed by the following relationship [19],

$$(\alpha h\nu) = A(h\nu - E_g)^{1/2} \quad (3)$$

where A is a constant, $h\nu$ is the photon energy and E_g is the optical band gap. The values of the optical band gap E_g values of the films were obtained from the intercept of $(\alpha h\nu)^2$ versus $h\nu$ curves plotted. Fig. 4 shows the plots of $(\alpha h\nu)^2$ vs. $h\nu$. E_g values are given in Table 3. It is seen that E_g values increase with aluminum dopant. The blue shift in the optical band gaps of the films may be attributed to the band Burstein–Moss effect. This effect is frequently observed in n–type semiconductors. The increase of carrier concentration in doped thin film will cause the Fermi level move into the conduction band. The filling of the conduction band by electrons will generally result in blue shift in the near band edge emission.

Table 3. Optical parameters of the undoped and Al–doped CdO films.

Films	E_g (eV)	E_U (meV)	E_d (eV)	E_0 (eV)	M_{-1}	M_{-3} $(eV)^{-2}$
CdO	2.476	863	10.274	3.957	2.597	0.166
CdO:Al 1%	2.591	392	11.576	5.112	2.264	0.087
CdO:Al 3%	2.682	389	6.196	4.559	1.359	0.065

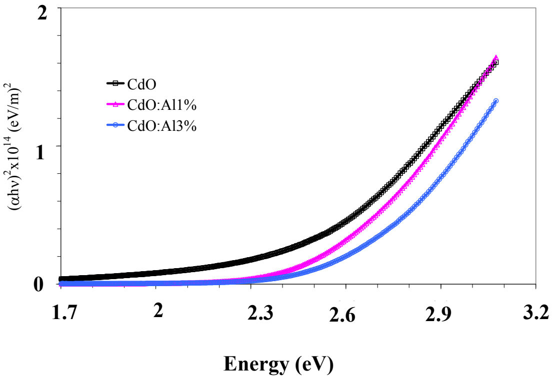


Fig. 4. The plots of $(\alpha h\upsilon)^2$ vs. photon energy of the undoped and Al–doped CdO films.

The width of the localized states available in the optical band gap of the films affects the optical band gap structure and optical transitions and it is called as Urbach tail, which is related directly to a similar exponential tail for the density of states of either one of the two band edges [20]. The Urbach tail of the films can be determined by the following relation [21],

$$\alpha = \alpha_o \exp(E / E_U) \tag{4}$$

where E is the photon energy, α_o is constant and E_U is the Urbach energy which refers the width of the exponential absorption edge. Fig. 5 shows the variation of $ln\alpha$ vs. photon energy for the films. This behavior corresponds primarily to optical transitions between occupied states in the valence band tail to unoccupied states at the conduction band edge.

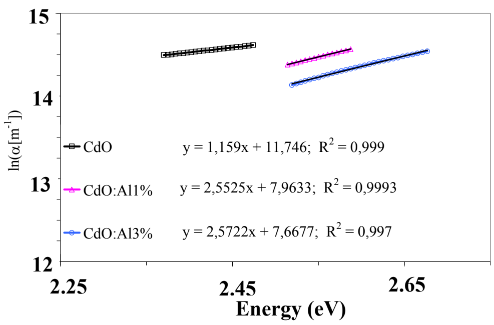


Fig. 5. The plots of $ln\alpha$ vs. photon energy of the undoped and Al–doped CdO films.

The E_U value was calculated from the slope of Fig. 5 using relationship,

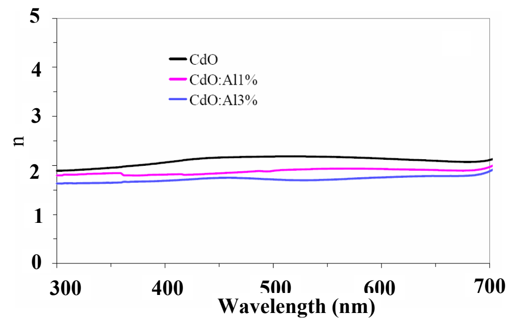
$$E_U = \left(\frac{d(ln\alpha)}{d(h\nu)} \right)^{-1} \tag{5}$$

The obtained E_U values are given in Table 3. Urbach energy values of the films decrease with increasing aluminum dopant. The E_U values change inversely with optical band gaps of the films.

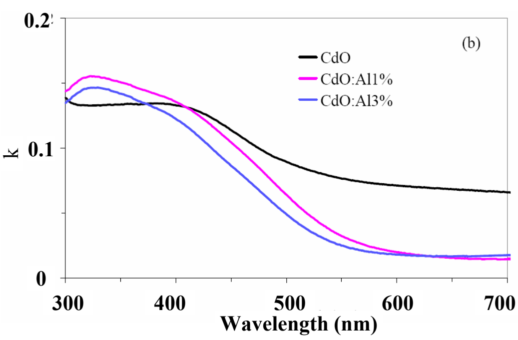
The refractive index dispersion plays an important role in the research for optical materials. Because, it is a significant factor in optical communication and in designing devices for spectral dispersion. The refractive index of the films can be determined by the following relation [22],

$$n = \left(\frac{1+R}{1-R} \right) + \sqrt{\frac{4R}{(1-R)^2} - k^2} \tag{6}$$

where k ($k=\alpha\lambda/4\pi$) is the extinction coefficient. The refractive index values of the films were calculated using Eq (6) where k ($k=\alpha\lambda/4\pi$) is the extinction coefficient. The refractive index values of the films were calculated using Eq (6).



(a)



(b)

Fig. 6. Variation of refractive index (a) and extinction coefficients (b) of the undoped and Al–doped CdO films.

As shown in Fig. 6(a), the refractive index dependence of wavelength was plotted. Fig. 6(b) shows the plots of extinction coefficient vs. wavelength for the films. After 400 nm, the extinction coefficient changes strongly with Al dopant due to the structural changes in the films. As seen in plotted figure of refractive index, the refractive index decreases with Al dopant.

The dispersion of refractive index below the inter-band absorption edge according to the Wemple-DiDomenico single oscillator model [23] is given as follow:

$$n^2 = 1 + \frac{E_d E_o}{E_o^2 - (h\nu)^2} \tag{7}$$

where E_o and E_d are the single–oscillator energy and dispersion energy parameter, respectively. By plotting $(n^2-1)^{-1}$ vs. $(h\nu)^2$ and fitting the data, a straight line is obtained as shown in Fig. 7. E_o and E_d are determined directly from the gradient, $(n^2-1)^{-1}$ and the intercept (E_o/E_d), on the vertical axis [23]. The obtained E_o and E_d values suggest that the single–oscillator model is valid for the films. The values of E_o and E_d for the films are given in Table 3. E_o values of the films increase with increasing Al dopant and oscillator energy change with Al dopant.

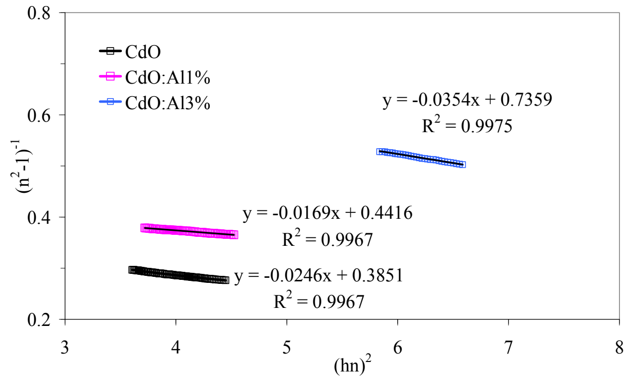


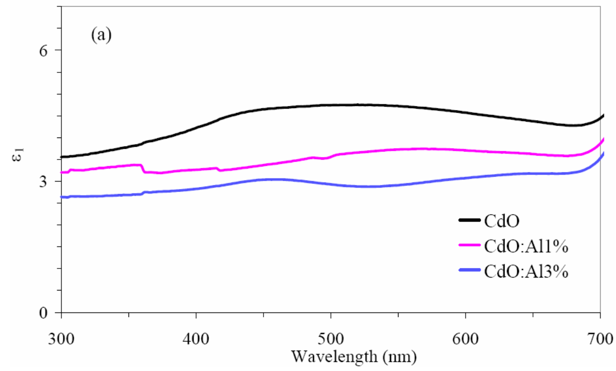
Fig 7. Plot of $(n^2\text{-}1)^{-1}$ vs. $(h\nu)^2$ of the undoped and Al–doped CdO films.

The fundamental electron excitation spectrum of the films was described by means of a frequency dependent of the complex electronic dielectric constant. Real and imaginary parts of the dielectric constant are related to the n and k values. The ε_1 and ε_2 values were calculated using the formulas [24],

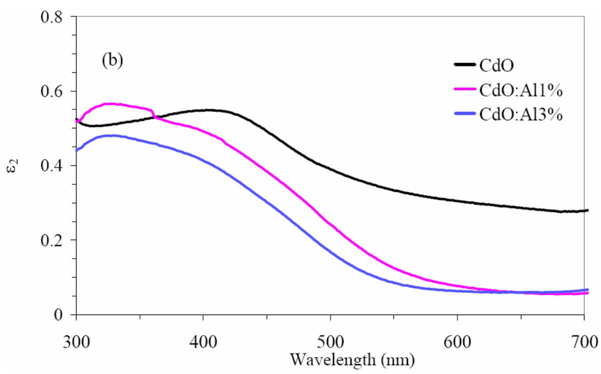
$$\varepsilon_1 = n^2 - k^2 \tag{8}$$

$$\varepsilon_2 = 2nk \tag{9}$$

Fig. 8 shows ε_1 and ε_2 values dependence on the wavelength. The ε_1 and ε_2 values of the films change with wavelength and Al dopant. Al dopant decreases both the real part and imaginary part of the dielectric constant of the films.



(a)



(b)

Fig. 8. Variation of real (a) and imaginary (b) parts of the dielectric constants of the undoped and Al–doped CdO films.

The M_{-1} and M_{-3} moments of the optical spectra can be obtained from the following relations [25]

$$E_o^2 = \frac{M_{-1}}{M_{-3}}, \qquad E_d^2 = \frac{M^3_{-1}}{M_{-3}} \tag{10}$$

The obtained values are given in Table 3. The M_{-1} and M_{-3} moments of the films decrease with increasing Al dopant due to the electronic changes in the optical band and oscillator parameters of the films.

4. Conclusions

The undoped and Al–doped CdO films were deposited by sol–gel spin–coating method. The structural and optical properties of the CdO film were influenced by Al doping. XRD results showed films have (111) preferred orientation. The optical band gap values were found to decrease from 2.476 to 2.682 eV with Al doping. The optical constants, refractive index, extinction coefficient and optical dielectric constants, of these films were determined using transmittance and reflectance spectra. Al doping concentration affects the optical parameters of the thin films.

Acknowledgements

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References

[1] D. M. Carballeda-Galicia, R. Castanedo-Perez, O. Jimenez-Sandoval, S. Jimenez-Sandoval, G. Torres-Delgado, C. I. Zuniga-Romero, Thin Solid Films **371**, 105 (2000).
[2] Y. Caglar, S. Ilican, M. Caglar, Eur. Phys. J. B **58**, 251 (2007).
[3] J. Santos-Cruz, G. Torres-Delgado, R. Castanedo-Perez, S. Jimenez- Sandoval, J. Marquez-Marin, O. Zelaya-Angel, Sol. Energy **80**, 142 (2006).
[4] L. M. Su, N. Grote, F. Schmitt, Electron. Lett. **20**, 716 (1984).
[5] R. R. Salunkhe, C. D. Lokhande, Sensors and Actuators B **129**, 345 (2008).
[6] T. L. Chu, S. C. Shirley, J. Electron. Mat. **19**, 1002 (1990).
[7] I. M. Ocampo, A. M. Ferandez, P. J. Sabastian, Semicond. Sci. Technol. **8**, 750 (1993).
[8] S. Aksoy, Y. Caglar, S. Ilican, M. Caglar, Int. J. Hyd. Energ. (2008), in press.
[9] C. H. Bhosale, A. V. Kambale, A. V. Kokate, K. Y. Rajpure, Materials Science and Engineering B **122**, 67 (2005).
[10] Q. Zhou, Z. Ji, B. Hu, C. Chen, L. Zhao, C. Wang, Mater. Lett. **61**, 531 (2007).
[11] D. S. Dhawale, A. M. More, S. S. Latthe, K. Y. Rajpure, C. D. Lokhande, App. Sur. Sci. **254**, 3269 (2008).
[12] L. R. de León-Gutiérrez, J. J. Cayente-Romero, J. M. Peza-Tapia, E. Barrera-Calva, J. C. Martínez-Flores, M. Ortega-López, Mat. Lett. **60**, 3866 (2006).
[13] R. K. Gupta, K. Ghosh, R. Patel, S. R. Mishra, P. K. Kahol, Mater. Lett. **62**, 3373 (2008).
[14] R. J. Deokate, S. M. Pawar, A. V. Moholkar, V. S. Sawant, C. A. Pawar, C. H. Bhosale, K. Y. Rajpure, App. Sur. Sci. **254**, 2187 (2008).
[15] R. Maity, K. K. Chattopadhyay, Sol. Energ. Mater. Sol. Cell **90**, 597 (2006).
[16] B. Saha, S. Das, K. K. Chattopadhyay, Sol. Energ. Mater. Sol. C. **91**, 1692 **(**2007).
[17] K. Gurumurugan, D. Mangalaraj, Sa. K. Narayandass, J. Electron. Mater. **25**, 765 (1996).
[18] K. Gurumurugan, D. Mangalaraj, Sa.K. Narayandass, K. Sekar, C. P. Girija Vallabhan, Semicond. Sci. Technol. **9**, 1827 (1994).
[19] J. I. Pankove, Optical Processes in Semiconductors, Prentice-Hall Inc., Englewoord Cliffs, NJ, 1971.
[20] G. D. Cody, J. Non-Cryst. Solids **141**, 3 (1992).
[21] F. Urbach, Phys Rev. **92**, 1324 (1953).
[22] N. A Subrahamanyam, A textbook of Optics, 9^{th} ed.: Brj. Laboratory, Delhi, India, 1977.
[23] M. DiDomenico, S. H. Wemple, J. Appl. Phys. **40**, 720 (1969).
[24] T. S. Moss, G. J. Burrell, B. Ellis, Semiconductor Opto-Electronics, Wiley, New York, 1973.
[25] S. H. Wemple, M. DiDomenico, Phys. Rev. Lett. **23**, 1156 (1969) .

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