CdO Thin Films Fabricated by a Simplified Spray Technique Using Perfume Atomizer with Different Molar Concentrations of Cadmium Acetate for Optoelectronic Applications

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Abstract

Highly transparent and conducting cadmium oxide thin films were deposited on glass substrates by a simplified spray technique using perfume atomizer. The films were prepared with different molar concentrations of cadmium acetate. The effect of molar concentration on the structural, morphological, optical and electrical properties was studied. XRD analysis showed that the films exhibit cubic crystal structure with (1 1 1) preferred orientation. With higher solution concentration, the orientation changes to (2 0 0) plane. A slight angle shift of 0.03º to 0.22º for the (1 1 1) peak and a shift of 0.003º to 0.015º for the (2 0 0) peak was observed in the films as the molar concentration changes from 0.025M – 0.1M. The film surface modifies, with grains taking different forms with increased molar concentration.

Keywords

Crystal structure; X-ray diffraction; Optical properties; Electrical properties; Band gap energy

Introduction

Transparent conducting oxides (TCOs) such as cadmium oxide, zinc oxide, indium oxide, tin oxide, etc. have been widely studied because of their use in optoelectronic devices. Due to their optical and electrical properties, TCOs are used for photovoltaic solar cells, phototransistors, liquid crystal displays, optical heaters, gas sensors, transparent electrodes and other optoelectronic devices [1]. Among these TCOs, cadmium oxide (CdO) has attracted considerable attention to various applications such as solar cells, photodiodes [2] phototransistors [3], liquid crystal displays, IR detectors and antireflection coatings [4] due to its low electrical resistivity, high carrier concentration and high optical transmittance in the visible region of the spectrum. CdO is an n-type semiconductor having band gap between 2.2 and 2.7 eV [5]. The high conductivity of undoped CdO film is due to defects of oxygen vacancies and cadmium interstitials [6]. CdO thin films have been prepared using various physical as well as chemical deposition methods [7-9]. Among the chemical methods, spray pyrolysis is applicable for large area film formation.

Film properties can be tuned depending on the spray parameters such as spray rate, substrate temperature, spray nozzle distance, solution concentration and volume of the sprayed solution. Lokhande et al.[10] have studied the properties of sprayed CdO thin films deposited through non-aqueous medium. Influence of post-thermal annealing on the properties of sprayed CdO thin films has been studied by Vigil et al.[11]. In the present work, a simplified spray technique using perfume atomizer is adopted to coat CdO thin films with different molar concentrations of the precursor salt. The effect of precursor molar concentration on the structural, morphological, optical and electrical properties of the films was investigated.

Experimental details

CdO thin films were grown on glass substrates by simplified spray technique using perfume atomizer, with various precursor molar concentrations of cadmium acetate dihydrate (0.025M, 0.05M, 0.075M and 0.1M) under optimized conditions (Table 1). Before spraying, the glass substrates were cleaned by a mild soap solution, washed thoroughly with distilled water and then with boiled water. Finally it was degreased in alcohol vapor. The thickness of the CdO films was measured by a gravimetric weight difference method in terms of the weight of CdO deposited on the glass substrate per unit area (gm/cm^2), since the accurate measurement of CdO film thickness was not possible due to the rough morphology and porosity of the film [12]. To study the structural property, X-ray diffraction (XRD) patterns were obtained with a Philips (PRO Analytical) diffractometer with a CuKα (λ = 1.54060 Å) target. The surface morphological study was accomplished using a scanning electron microscope (SEM) JEOL JSM – 6360. The electrical resistivity of the films was measured by dc four point probe method. The optical absorption spectra of the films were measured by Hitachi UV-vis-NIR spectrophotometer, in the 300 - 1200 nm wavelength range, with glass substrate as a reference.

Table 1 Optimized deposition conditions

Substrate temperature	400º C
Distance between substrate and perfume atomizer	28 cm
Spray angle	45º
Spray time during each cycle	5 sec
Time interval between successive spray	2 sec
Solvent used	Deionized water
Volume sprayed	50 ml

Results and discussion

CdO film formation mechanism and thickness measurement

The mechanism of CdO film formation by the simplified spray technique using perfume atomizer can be enlightened as follows: Aqueous solution of cadmium acetate with different molar concentrations

(0.025M, 0.05M, 0.075M and 0.1M) when sprayed over glass substrates kept at 400ºC, pyrolytic decomposition takes place resulting in the formation of orange colored CdO films. The thickness of CdO films coated with different molar concentrations was calculated using gravimetric weight difference method in terms of the weight of CdO deposited on glass substrates per unit area. The factors affecting the growth phenomena of spray deposited CdO films are substrate temperature, volume of the spraying solution, concentration of the precursor salt used. Variation of the weight of CdO deposited and film thickness with precursor molar concentration is shown in Fig.1. It is observed that film thickness increases with molar concentration which might be due to the increased amount of mass being deposited on the substrates as precursor concentration increases. The terminated thickness, at which the highest amount of CdO was deposited on the substrate, was 0.001 gm/cm^2 for 0.1M concentration.
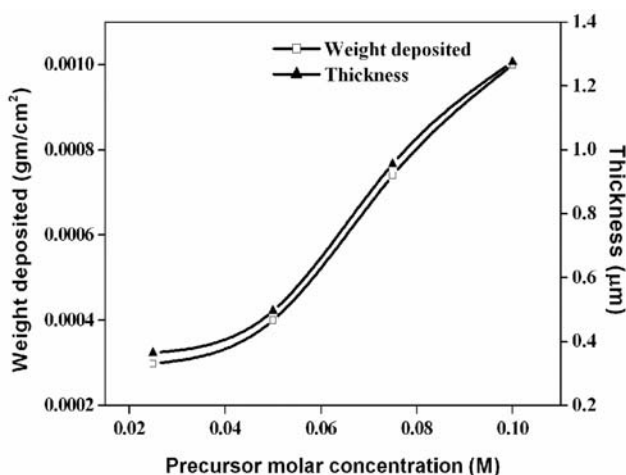

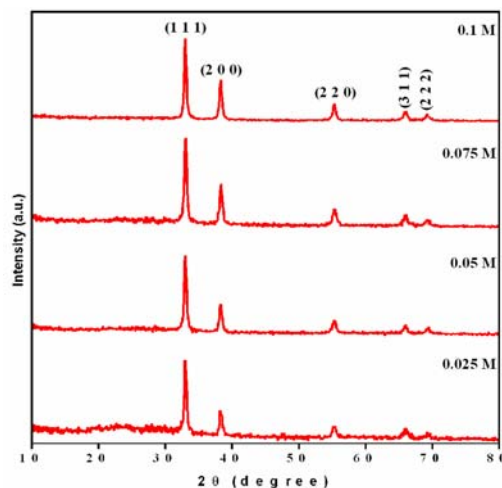Fig. 1 Variation of weight of CdO deposited and film thickness with precursor molar concentration

Fig. 2 XRD patterns of CdO films grown with different precursor molar concentrations

Structural Characterization

Fig. 2 shows the X-ray diffraction patterns of CdO films grown with different precursor molar concentrations by the simplified spray technique. The observed diffraction patterns indicate the polycrystalline nature of the CdO with cubic structure on the basis of JCPDS card No:75-0592.
The peaks observed at 2θ = 32, 39, 54, 68, 69ºC are associated with (1 1 1), (2 0 0), (2 2 0), (3 1 1) and (2 2 2) planes respectively. The absence of impurity peaks suggests the high purity of the cadmium oxide. Fig. 3 shows the variation of preferential orientation factor f(1 1 1) and f(2 0 0) with precursor molar concentration. It is seen that films grown with precursor molar concentration upto 0.05M showed (1 1 1) preferred orientation and the orientation changes to (2 0 0) plane for molar concentration greater than 0.05M. The Bragg position for strong reflections like (1 1 1) direction was 33.017º, 33.011º, 33.042º and 33.007ºC respectively for CdO films with concentrations 0.025M, 0.05M, 0.075M and 0.1M. A slight

angle shift estimated at 0.03 – 0.22º was observed for the (1 1 1) peak as precursor molar concentration increases. Similarly for (2 0 0) peak, the Bragg position was 38.31º, 38.301º, 38.351º and 38.298º respectively for CdO films with concentrations 0.025M, 0.05M, 0.075M and 0.1M. An angle shift of 0.003º to 0.015º was observed for the (2 0 0) peak as precursor molar concentration increases. Therefore, though the substrate temperature is same, the film formation mechanism and hence the crystallinity and orientation changes with precursor molar concentration.

The crystallite size D is calculated using Scherrer's formula [13].

$$D = \frac{0.9\lambda}{\beta\cos\theta} \qquad (1)$$

Where β is the broadening of diffraction line measured at half of its maximum intensity (radians) FWHM and λ is the X-ray wavelength (1.5406Å). Fig. 4 shows the variation of crystallite size and FWHM (β) along the (1 1 1) plane with precursor molar concentration. The intensity of (1 1 1) plane has been found to be increased with precursor molar concentration up to 0.075M and then decreases for higher concentration. The crystallite size associated to the (1 1 1) direction was found to decrease from 23 nm to a minimum of about 19.72 nm for CdO film coated with 0.075M. Above that concentration, the crystallite size increases which might be due to the decreased intensity of (1 1 1) plane obtained for the film coated with 0.1M. The calculated values of microstructural parameters such as lattice constant 'a', strain 'ε', dislocation density 'δ' and the number of crystallites per unit area 'N' of (1 1 1) plane of the CdO films are presented in Table 2.The deviation in the lattice parameter values of the CdO films coated with different precursor molar concentrations might be due to the small shift in 2θ in (1 1 1) diffraction towards higher Bragg angle.
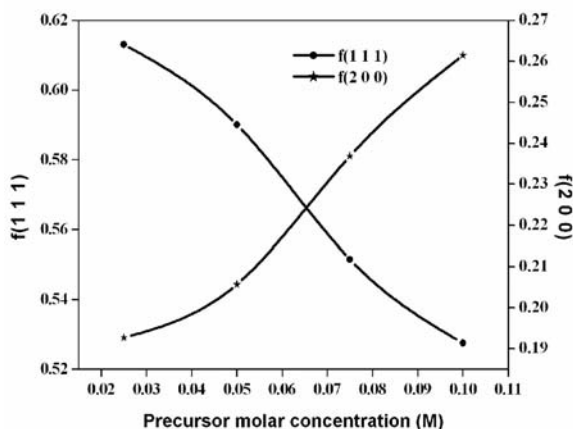

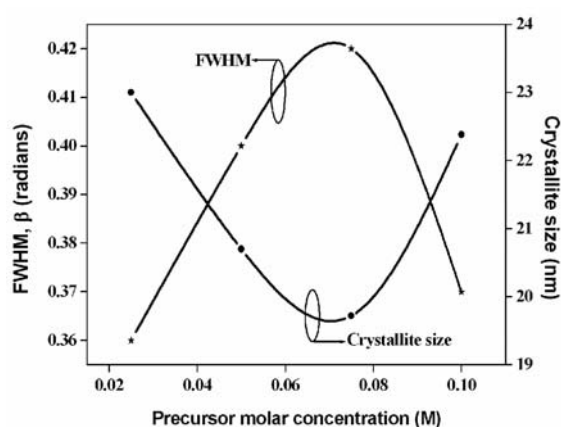Fig. 3 Variation of f(1 1 1) and f(2 0 0) with precursor molar concentration

Fig. 4 Variation of FWHM and crystallite size with precursor molar concentration

Table 2 Structural parameters of CdO films coated with different solution concentration

Precursor molar concentration (M)	Lattice parameter, a (Å)		Crystallite size, D (nm)	Strain, ε x 10^{-3}	Dislocation density, δ x 10^{15} lines/m^2	Number of crystallites, N x 10^{16}
	Calculated	Standard*				
0.025	4.695		23	5.3	1.89	2.999
0.05	4.696	4.694	20.7	5.89	2.33	5.59
0.075	4.690		19.72	6.185	2.571	1.246
0.1	4.697		22.38	5.44	1.996	1.137

*JCPDS 75-0592

Morphological studies

Fig. 5 shows the surface morphology of CdO films coated with different molar concentrations of cadmium acetate. The SEM micrographs take different forms with increase in precursor molar concentration. Clusters of closely packed spherical grains with small empty sites were observed for the film coated with 0.025M. The surface modifies and resembles the shape of cauliflower with well defined grain boundaries for the film coated with 0.05M. This structure has a great importance due to its high specific surface area and potential applications in various fields [14]..
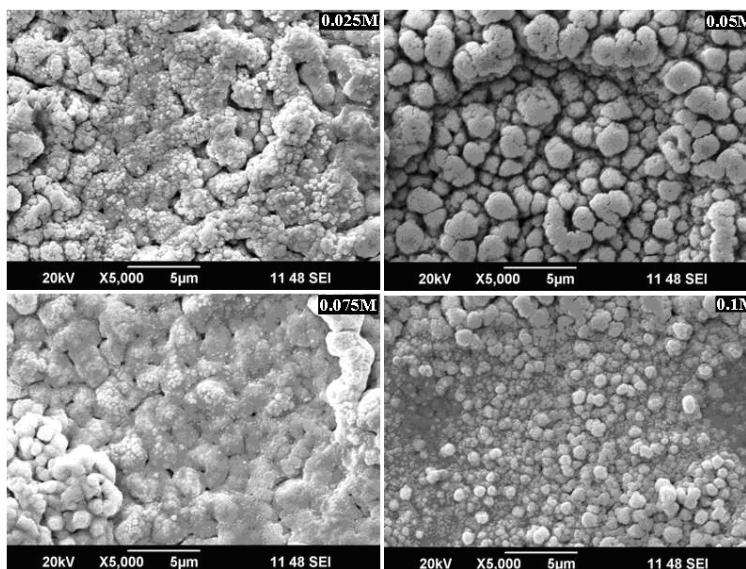

Fig. 5 SEM images of CdO films coated with different precursor molar concentrations

With further increases in solution concentration to 0.075M interconnected chains of spherical grains with no porous space in between was observed throughout the surface. White colored patches were found on the film surface. The surface modifies and tightly packed spherical grains with well defined boundaries were found distributed uniformly throughout the entire surface for the film coated with 0.1M precursor concentration. The film looks more continuous without any cracks or holes which are identification of

improved crystallinity as evident from the XRD analysis. Thus the entire film surface modifies with grains taking different forms as the precursor molar concentration varies from 0.025 to 0.1

Optical studies

Fig.6 depicts the transmittance of CdO films within the wavelength range 300-1200nm. The transmittance of cadmium oxide is expected to depend mainly on three factors: i) oxygen deficiency, ii) surface roughness (surface scattering reduces the transmission, which in turn depends on the crystallite size), and iii) impurity centers. It is observed from the figure, that the optical transmittance decreases with precursor molar concentration. The low transmittance value obtained for the film coated with 0.1M is due to increased surface roughness which acts to decrease the effective mean free path through increased surface scattering. The direct optical band bap (E_g) is expressed as [15]:

$$\alpha h\gamma = \left(h\gamma - E_g\right)^{\frac{1}{2}} \qquad (2)$$

where α is the absorption coefficient, γ is the photon frequency and h is Planck's constant. The optical band gap is estimated from the transmission spectra by extrapolating the linear part of the plot of $(\alpha h\gamma)^2$ versus $h\gamma$ to $\alpha = 0$ as sketched in Fig.7. The optical band gap increased from 2.14 to 2.35 eV with the increase in precursor molar concentration. The increase in the band gap may be due to the decrease in carrier concentration. Such a shift in the band gap towards high energy side was observed with decrease of carrier concentration in sputtered films [16].
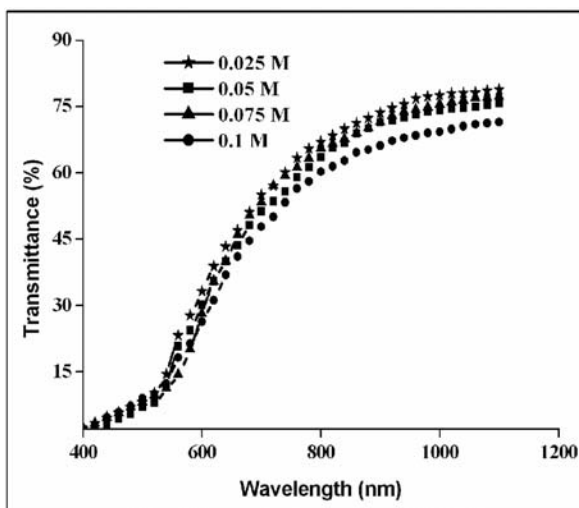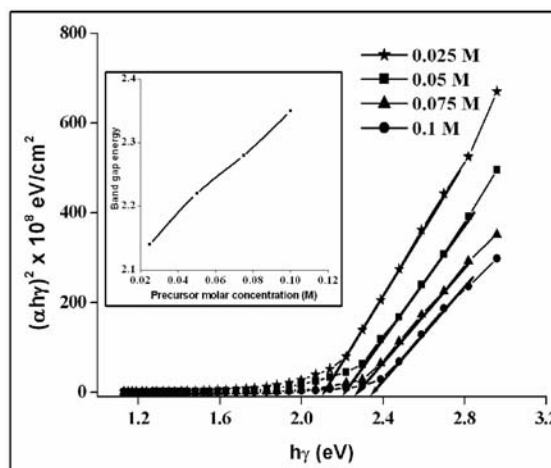

Fig. 6 Transmittance spectra of CdO films

Fig. 7 $(\alpha h\gamma)^2$ versus $h\gamma$ graph. Inset shows the variation of band gap energy with precursor molar concentration

PL studies

The analysis of photoluminescence spectroscopy at room temperature reveals various peaks as shown in the figure. PL spectroscopy can be used to determine the band gap of semiconductors since the most common radiative transition in the semiconductor occurs between states at the bottom of the conduction band and the top of the valence band [17]. Fig. 8 shows the PL spectra of the CdO films

prepared by the simplified spray technique at 400ºC with 0.05 and 0.1 precursor molar concentrations. The PL spectra are consisted of VIS emission peak centered around 434 nm which corresponds to violet region of electromagnetic spectrum. This emission might be attributed to the combination of the electrons from the conduction band and holes from the valence band. The peaks observed at 495 nm (2.51 eV) and 521 nm (2.39 eV) ranged in the green region may be ascribed to defect centers. The peak at 495 nm is attributed to the excitonic transition which is size-dependent and excitation wavelength-independent in certain wavelength range, whereas the peak at 521 nm may be ascribed to the deep trap emission and surface-state emission that is less size dependent[18]. Similar ranges of PL peak positions have been reported in the literature[19].
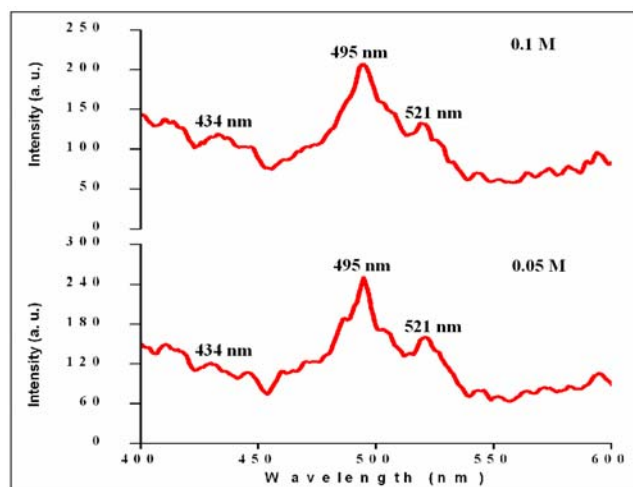

Fig. 8 PL spectra of CdO films coated with 0.05M and 0.1M concentrations
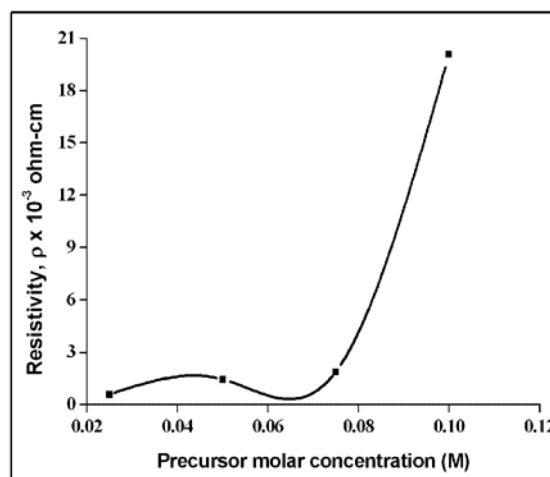

Fig. 9 Variation of electrical resistivity of CdO films with precursor molar concentration

Electrical studies

Pure CdO is an n-type degenerate semiconductor with high electrical conductivity even without any extrinsic doping. The oxygen vacancies and Cd interstitials are responsible for high electrical conductivity of undoped CdO thin films[20]. The electrical measurements were carried out by four probe measurement system. The electrical resistance R at room temperature was calculated by using the eqn[21]:

$R = k\dfrac{V}{I}$ where k is a constant found to be 4.53, V is the applied voltage and I is the intensity of dc current. Fig. 9 shows the variation of electrical resistivity of the films with precursor molar concentration. The resistivity value increases from 0.58 x 10^{-3}Ω-cm to 20.08 x 10^{-3}Ω-cm as the precursor molar concentration increases from 0.025 to 0.1. The resistivity value obtained here exactly matches with the value obtained by Subramanyam et al.[22]. Films become more resistive at higher molar concentration, which may be due to large terminal thickness. The increment in mass deposited at higher molar concentration might have produced lower layers with CdO and upper layers consist of cadmium acetate

due to incomplete thermal decomposition, which induces more resistivity in the samples coated with higher molar concentrations. The increase in resistivity with CdO precursor molar concentration is related to the decrease in free carrier concentration, which may be associated with the removal of oxygen vacancies and the formation of grain boundaries acting as trap sites foe free electrons[23]. This fact is well supported from the SEM images, which showed that film coated with 0.1M concentration consists of tightly peaked spherical grains throughout the surface favoring the decreases in carrier mobility and increased resistivity of the film.

Elemental analysis

The EDAX spectra of the CdO films fabricated by the simplified spray technique with different precursor molar concentrations are shown in Fig. 10. All the films contain the elements Cd and O as deposited components. The atomic ratio compositions of Cd and O in the films are given in the inset of Fig. 10. The Cd/O ratio of all the films are close to stoichiometric except for the film coated with 0.1 M concentration. This might be due to the presence of cadmium acetate on the upper surface of the film due to incomplete thermal decomposition. The very low value of Cd/O ratio obtained for the film coated with 0.1 M concentration strongly favors the high resistivity value obtained for that film.
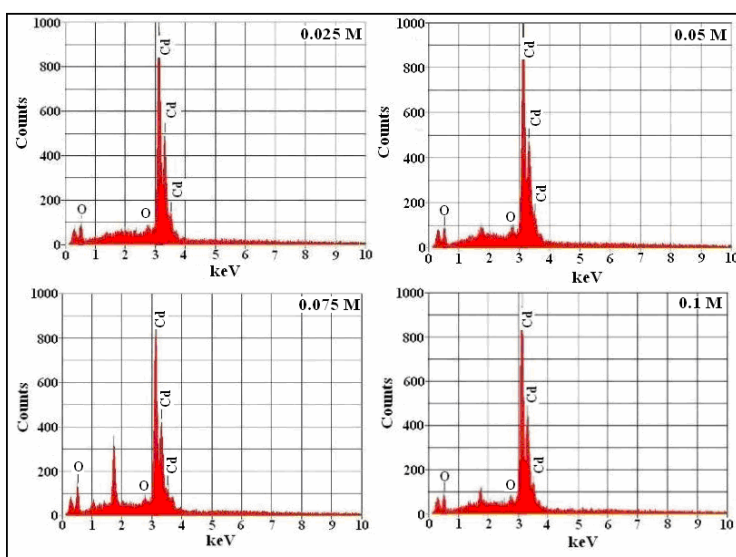

Fig. 10 EDAX spectra of CdO films fabricated by the simplified spray technique with different precursor molar concentrations

Conclusions

Transparent conducting CdO thin films with low resistivity were fabricated at 400ºC by employing a simplified spray technique using perfume atomizer with different precursor molar concentrations. The films have polycrystalline structure with preferential orientation along the (1 1 1) plane. The electrical resistivity increases with increase in precursor molar concentration. All the films exhibit resistivity in the order of 10^{-3} ohm-cm. The optical transmittance in the visible range is > 70 %

and the optical band increases from 2.14 eV to 2.35 eV as the precursor molar concentration increases from 0.025 to 0.1. The films were found to have good physical properties desirable for solar cell and other optoelectronic applications.

Acknowledgements

References

1]. R.K.Gupta, K.Ghosh,R.Patel,S.R.Mishra,P.K.Kahol, *Mater.Lett.,* 2008, 62, 4103-4105.

2]. B.Saha, S.Das, K.K.Chattopadhyay, *Sol.Energy Mater.Sol.Cells.,* 2007, 91, 1692-1697.

3]. L.M.Su, N.Grote, F.Schmitt, *Electron. Lett.* ,1984, 20, 716.

4]. A.R.Balu, V.S. Nagarethinam, M. Suganya, N. Arunkumar, G. Selvan, J. Electron Devices, 2012, 12, 739 – 749.

5]. A.A.Dakhel, *Semicond.Sci.Tech.,* 2008, 23 ,055017.

6]. Z.Zhao, D.L.Morel, C.S.Ferekides, *Thin Solid Films*, 2002, 413, 203.

7]. D.Ma, Z.Ye, L.Wang, J.Huang, B.Zhao, *Mater.Lett.,* 2004, 58,128.

8]. G.Phatak, R.Lal, *Thin Solid Films* ., 1994, 245, 17.

9]. C.H.Bhosale, A.V.Kambale, A.V.Kokate, K.R.Rajpure, *Mater.Sci.Eng.,* 2005, B 122, 67-71.

10]. B.J.Lokhande, P.S.Patil, M.D.Uplane, *Mater.Chem.Phys.,* 2004, 84, 238-242.

11]. O.Vigil, F.Cruz, G.Santana, L.Vaillant, A.M.Acevedo, G.C.Puente, *Appl.Surf.Sci.,* 2000, 161, 27-34.

12]. B.O.Park, C.D.Lokhande, H.S.Park, K.D.Jung, O.S.Joo, *Mater.Chem.Phys.,* 2004, 87,59.

13]. P.Scherrer, *Gottinger Nachrichtes.,* 1918, 2, 98.

14]. H.X.Ren, X.J.Huang, O.Yarimaga, Y.K.Choi, N.Gu, *J.colloid. Interface.Sci.,* 2009, 334, 103-107.

15]. J.I.Pankove, Optical processes in semiconductors, *Prentice – hall Inc., Englewood cliffs, MJ,* 1971, pp 34-42.

16]. K.Tanaka, A.Kunioka, Y.Sakai, *Jpn.J.Appl.Phys.,* 1969, 8, 681.

17]. Nese Kavasoglu, A.Sertap Kavasoglu, Sener oktik, *J.Phys.Chem.Solids.,* 2009, 70, 521-526.

18]. W.Dong, C.Zhu, *opt.Mater.,* 2003, 22, 227.

19]. N.Ueda, H.Maeda, H.Hosono, H.Kawazoe, *J.Appl.Phys.,* 1998, 84, 6174-6177.

20]. Y.Dou, T.Fishlock, R.G.Egdell, *Phys.Rev.,* 1997, B 55, 13381.

21]. R.Legros, les semiconductors, *Eyrolles (Ed.),*vol.1,1974.

22]. T.K.Subramanyam, B.Srinivasulu Naidu, S.Uthanna, *Appl.Surf.Sci.* 20011, 69-170, 529-534.

23]. I.H.Kim, J.H.Ko, D.Kim, K.S.Lee, T.S.Lee, J.H.Jeong, B.Cheong, Y.J.Back, W.M.Kim, *thin Solid Films.,* 2006, 515, 2475.