Luminescence and electrical resistivity properties of cadmium oxide nanoparticles

Amrut S Lanje^{1*}, Raghumani S Ningthoujam², Satish J Sharma³ & Ramchandra B Pode⁴

¹Department of Electronics, Dr. Ambedkar College, Chandrapur 442 401, India

²Chemistry Division, Bhabha Atomic Research Center, Mumbai 400 085, India

 3 Department of Electronics, R.T.M. Nagpur University, Nagpur 440 033, India

⁴Department of Physics, Kyung Hee University, Seoul 130 701, Korea

*E-mail: amrut.lanje@gmail.com

Received 20 September 2010; revised 6 January 2011; accepted 11 February 2011

Cadmium oxide (CdO) nanoparticles have been prepared by precipitation method using cadmium acetate and ammonia solution. The electrical resistivity (ρ) has been measured at low temperature using four-probe method which is found to be 0.351 Ω-cm at 7 K and 0.264 $Ω$ -cm at 300 K, respectively. The decrease of resistivity with increasing temperature indicates the semiconducting behaviour. The activation energy values are found to be 0.06 meV in temperature range $7-15 \text{ K}$ and 0.6 m meV in 39-152 K from temperature dependent resistivity. Photoluminescence (PL) spectrum shows band edge emission at 395 nm and green emission at 550 nm. Green emission arises from the oxygen vacancy of CdO materials because of recombination of a photo generated hole in valence band with an electron in conduction band.

Keywords: Cadmium oxide, Resistivity, Photoluminescence, Nanoparticles

1 Introduction

 Productions of mono disperse metal oxide nanoparticles have a special interest because it not only increases surface area, but also provides superior electrical conductivity as compared to other morphologies^{1,2}. The brown CdO is, generally, formed by burning of Cd in air. The CdO is insoluble in water and absorbs $CO₂$ from air and can be reduced to the conducting oxides. It is one of the promising candidates for optoelectronics³. Cadmium oxide (CdO), a II-VI *n*-type semiconductor has interesting properties like large band gap, low electrical resistivity and high transmission in the visible region etc; which makes it useful for a wide range of applications such as solar cells, photo transistors, photo diodes, transparent electrodes and gas sensors⁴⁸.

CdO has 2.5 eV direct band gap^{$\overline{9}$} and 1.98 eV indirect band gap¹⁰. The optical transmittance of CdO in the visible region of the spectrum has been reported to be low¹¹. In the present paper, synthesis of CdO nanoparticles has been carried out and their photoluminescence and electrical resistivity properties have been studied.

2 Experimental Details

 In the present work, we have synthesized cadmium oxide (CdO) nanoparticles by simple and low cost

precipitation method using cadmium acetate and ammonium hydroxide as starting materials.

 All chemicals used in the experiment were of analytic reagent (AR) grade. Cadmium acetate was purchased from Glaxo Smith Kline Pharmaceutical Ltd. (99.0%) and ammonia solution 25% GR from Merck, India. All chemicals were used as received without further purification. Deionized water was used during the experiment.

 Cadmium acetate (6.66 g, 0.5 M) was dissolved in 100 ml water and ammonia solution was added to above solution dropwise until *p*H value of about 8 was reached with constant stirring. The white precipitate was formed and it was allowed to settle for 5-6 h and then filtered and washed 3-4 times with water. It was dried at 100°C and then grinded. The resulting powder was calcined at 400°C for 2 h. It turned into yellowish colour which confirmed the formation of CdO. Figure 1 shows the schematic diagram for the preparation of CdO nanoparticles.

$$
(CH3COO)2 Cd·H2O + 2NH4OH \rightarrow Cd(OH)2 + 2H2O + 2CH3COONH4(1)
$$

During calcinations as prepared powder loses H_2O which is as follows:

400°C

$$
Cd(OH)_2 \longrightarrow CdO + H_2O \qquad \qquad \dots (2)
$$

2.1 Characterization techniques

 The powder X-ray diffraction (XRD) was recorded using Philips Holland, XRD system PW 1710 with nickel filtered CuK_α (λ = 1.5405 Å) radiation. The average crystallite size (*t*) has been calculated from the line broadening using the Scherrer's relation: $t = 0.9\lambda$ /*Bcosh*, where, λ is the wavelength of X-ray and *B* is the half maximum line width. Scanning electron microscopy (SEM) was performed by JEOL JSM-5600 and the transmission electron microscopy (TEM) was performed with Tecnai 20 $G²$ under 200 kV. Samples were prepared by dispersing drop of colloid on copper grid, covered with the carbon film and the solvent was evaporated. To record Fourier Transform Infrared (FTIR) spectra, Bomem Hartmann and Braun MB Series Infrared spectrometer was used. CdO powder was crushed with KBr particles (1:5) and pressed into thin pellets. Photoluminescence (PL) measurements were performed by F-4500 FL spectrophotometer with 150 W xenon lamp at room temperature. Powder samples were spread over a glass slide and mounted inside the sample holder. The electrical resistivity of the sample (in the form of pellet) has been carried out using four probe method.

Fig. 1 — Schematic diagram for preparation of CdO nanoparticles

3 Results and Discussion

3.1 XRD study

 XRD pattern of CdO nanoparticles calcined at 400°C is shown in Fig. 2. It confirms a face centered cubic (fcc) structure. Diffraction peaks observed were matched with standard JCPDS data (05-0640) and lattice parameters were calculated using the matched (hkl) values. The lattice parameters is found to be $a = 4.692$ Å and unit cell volume $V = 103.31$ Å³. It is clear from Fig. 2, that all peaks corresponds to fcc structure of CdO and no any other impurity peaks are found, indicating high purity nature of the sample. The peaks are broad due to the nano-size effect. The average crystallite size of CdO nanoparticles is found to be 33 nm using Scherrer's formula.

3.2 FT-IR study

 Figure 3 shows IR spectrum of CdO nanoparticles heated at 400°C. There are O-H stretching (3450 cm^{-1}) and vibration (1660 cm⁻¹) bands in addition to Cd-O band. The broad peak¹² at 620 cm⁻¹ is attributed to CdO. O-H functional group is related to absorption of water during pellet formation 13 .

3.3 Particle morphology study

 Figure 4(a) shows SEM image of CdO nanoparticles heated at 400°C. It shows grain morphology. Some grains are small while some grains are larger. The shape of grain particles is spherical. Figure 4(b) shows TEM image of CdO nanoparticles.

Fig. 2 — (a) XRD pattern of CdO nanoparticles calcined at 400° C and (b) JCPDS file No. 05-0640

Fig. $4 - (a)$ SEM image, (b) TEM image and (c) SAED pattern of CdO nanoparticles

Particle size from TEM is about 30 nm matched with the crystallite size (33 nm) indicating nonagglomeration of crystallites in a particle. Figure 4(c) shows the selected area electron diffraction (SAED) pattern of CdO nanoparticles calcined at 400°C. A cubic pattern of spots shows the highly crystalline nature of CdO.

3.4 Photoluminescence (PL) study

 The room temperature photoluminescence spectra of CdO nanoparticles calcined at 400°C are shown in Fig. 5 after excitation at 250 nm. Three emission peaks are observed at 395 nm (violet), 469 nm (blue) and 550 nm (green) for CdO calcined at 400°C. The peak at 395 nm corresponds to the band-edge emission 14 . The peak at 469 nm is due to artifact. This arises because of Xenon lamp source. The peak at 550 nm arises from the oxygen vacancy of CdO materials because of recombination of a photo generated hole in valence band with an electron in conduction band¹⁵. Similar peaks in spectrum of CdO have been reported by Wu \tilde{et} $al^{16,17}$.

 Figure 6 shows excitation spectra of CdO particles heated at 400°C monitored at 420 nm. It is clearly observed that the band-edge absorption is found at 221 nm (3.4 eV), which is larger than the bulk¹⁸ CdO $(2.5 \text{ eV}).$

3.5 Electrical resistivity measurement

 Figure 7 shows the variation of resistivity with temperature in the range 7-300K. Resistivity is temperature dependent. The resistivity values at 7 and 300 K are found to be 0.351 and 0.264 Ω-cm, respectively. Choi *et al*. ¹⁹ reported high resistivity of CdO ($10^3 \Omega$ -cm) at room temperature. The resistivity decreases with increasing temperature due to increase of electron carriers.

Fig. 5 — Emission spectrum of CdO at 250 nm excitation

Fig. 6 — Excitation spectrum of CdO monitored at 420 nm emission

Fig. 7 — Variation of resistivity (ρ) with temperature (7-300 K) and fit to data of CdO using Arrhenius law is also drawn. Inset shows the ρ versus T^{-1}

 The temperature coefficient of resistivity (TCR) value for CdO is calculated using the relation:

$$
TCR = \frac{1}{\rho_{250}} \left(\frac{\Delta \rho}{\Delta T} \right) \tag{3}
$$

It is found to be -0.0377 K⁻¹ and it is negative. This indicates that the prepared sample is behaving as semiconductor²⁰⁻²⁴. Activation energy (E_a) of CdO nanoparticles is calculated using the equation:

$$
\rho = \rho_0 \exp^{E_a/kT} \tag{4}
$$

where ρ is resistivity, ρ_0 is a parameter, *k* is Boltzmann's constant and *T* is absolute temperature. Fitting to the data is not good using the Eq. (4). Then, we have plotted ln ρ versus. $1/T$, which is shown as inset of Fig. 7. We found two slopes in range 7-15 K and 39-152 K. The former slope gives $E_a = 0.06$ meV and the latter one gives $E_a = 0.6$ meV.

4 Conclusions

 Face centered cubic structure CdO nanoparticles of average size of 33 nm is synthesized. The green emission at 530 nm is observed due to oxygen vacancy of CdO materials because of recombination of a photo generated hole in valence band with an electron in conduction band. The band-edge absorption is found at 221 nm (3.4 eV). The resistivity of CdO is found to be very low 0.351 Ω -cm at 7 K while it is 0.264 Ω-cm at 300 K. Two different activation energy values at different temperature ranges are obtained.

Acknowledgement

 One of authors (ASL) would like to acknowledge financial support from University Grants Commission (UGC), New Delhi, for present research work. The authors are grateful to Dr. Ajay Gupta, Dr N P Lalla, Dr D M Phase and Dr Okram, UGC-DAE Consortium for Scientific Research Center, Indore for providing SEM, TEM and resistivity measurements facilities. Thanks are also extended to Dr R. R. Dahegaonkar for providing laboratory facilities.

References

- 1 Maestre D, Cremades A & Piqueras J, *J Appl Phy*, 97 (2005) 044316.
- 2 Lanje A S, Ningthoujam R S, Sharma S J, Pode R B & Vatsa R K, *Int J Nanotechnol*, **7** (2010) 979.
- 3 Huynh W U, Dittmer J K & Alivisatos A P, *Science*, 295 (2002) 2425.
- 4 Pasquier A D, Chen H & Lu Y, *Appl Phy Lett*, 89 (2006) 253513.
- 5 Ristic M, Popovic S & Music S*, Mater Lett*, 58 (2004) 2494.
- 6 Zou B S, Volkov V V & Wang Z L, *Chem Mater*, 11 (1999) 3037.
- 7 Wang Y W, Liang C H, Wang G Z, Gao T, Wang S X, Fan J C & L D Zhang, *J Mater Sci Lett,* 20 (2001) 687.
- 8 Liu Y K, Yin C R, Wang W Z, Wang Y J & Wang G H, *J Mater Sci Lett,* 21 (2002) 137.
- 9 Gulino A, Compagnini G & Scalisi A A, *Chem Mater,* 15 (2003) 3332.
- 10 Lide D R, *CRC Handbook of Chemistry and Physics*, $(77th)$ edition, CRC Press, Boca Raton), 1996.
- 11 Gurumurugan K, Mangalaraj D, Narayandass S K, Sekar K & Girija Vallabhan C P, *Semicond Sci Tech,* 9 (1994) 1827.
- 12 Gurumurugan K, Mangalaraj D & Narayandass S K, *J Electron Mater*, 25 (1996) 765.
- 13 Gajbhiye N S, Ningthoujam R S, Ahmed A, Panda D K, Umre S S & Sharma S J, *Proc of ASID '06, 8-12 Oct, New Delhi,* 2006, p5.
- 14 Ningthoujam R S, Sudarsan V & Kulshreshtha S K, *J Lumin,* 127 (2007) 747.
- 15 Ningthoujam R S, Lahiri D, Sudarsan V, Poswal H, Kulshreshtha S K, Sharma S M, Bhushan B & Sastry M D, *Mater Res Bull,* 42 (2007) 1293.
- 16 Wu X, Wang R, Zou B, Wang L, Liu S & Xu J, *J Mater Res,* 13 (1998) 604.
- 17 Moumita G & Rao C N R, *Chem Phys Lett*, 393 (2004) 493.
- 18 Wu X, Wang R, Zou B, Wang L, Liu S & Xu J, *J Mater Res,* 13 (1998) 604.
- 19 Choi Y S, Lee C G & Cho S M, *Thin Solid Films*, 289 (1996) 153.
- 20 Yu L, Marshall D, Eshrich T, Narayanan V, Rowell J M, Newman N & Freeman A J, *Phys Rev,* B65 (2002) 245110.
- 21 Ningthoujam R S, Sudhakar N, Rajeev K P & Gajbhiye N S, *J Appl Phys,* 91 (2002) 6051.
- 22 Zasadzinski J, Vaglio R, Rubino G, Gray K E & Russo M, *Phys Rev,* B32, (1985) 2929.
- 23 Gleiter H, *Prog Mater Sci,* 33 (1989) 223.
- 24 Lanje A S, Sharma S J, Pode R B & Ningthoujam R S, *Arch Appl Sci Res*, 2 (2010) 27.