



Band Gap shift in Template Synthesised CdSe Nanowires on Thermal Annealing

Ranjeet Singh,

Associate Professor in Physics

Govt College for Women, Panchkula- 134109, India

ABSTRACT

Synthesis and characterization of one-dimensional nanostructures have attracted attention primarily due to their potential myriad applications in different fields including magnetic, electronic and optical devices. There are various techniques used in the fabrication of one-dimensional structures but template synthesis is an elegant, versatile and economic method for synthesizing variety of these one dimensional nanostructures, and so on. Highly ordered CdSe nanowires each having 200 nm diameters were synthesised into the pores of anodic alumina membrane (AAM) template by using direct chemical deposition method. The nanowires were deposited using cadmium acetate as a Cd^{2+} ion source and sodium selenosulfate as Se^{2-} ion source. The nanowires were characterized by Scanning Electron Microscope SEM and UV-Vis spectrophotometer to see surface morphology and optical band gap respectively. The as-deposited CdSe nanowires embedded in AAM are red in colour and having optical band gap 2.25eV. The embedded nanowires were thermally annealed in air at 673 K for 5 h and effect of annealing on optical band gap studied. After annealing optical band gap shows a red-shift of 0.45 eV

Keyword: CdSe Nanowires, Anodic Alumina Membrane (AAM), Scanning Electron Microscope (SEM), Optical Band Gap

INTRODUCTION

Over a decade, much attention has been paid toward synthesis and characterization of one dimensional nanostructures mainly due to their unique magnetic, electronic and optical properties and their potential myriad applications in different fields including magnetic, electronic and optical devices [1–6]. There are various techniques used in the fabrication of one dimensional structures but template synthesis is an elegant, versatile and economic method for synthesizing variety of these nanostructures including metal, semiconductors, hetero-junctions, conducting polymers, carbon nanotubes (CNT's) etc [5–15]. CdSe is one of the II–IV semiconductors and because of high photosensitivity it has been widely used in photoconductive devices [16–19]. CdSe nanowires have been fabricated by direct current (dc) as well as alternating current (ac) electrodeposition into the pores of Anodic Alumina Membrane (AAM) using CdSO_4 and Se dissolved in DMSO (dimethyl sulfoxide) at high temperature [20,21]. CdSe nanowires also have been fabricated through the pores of AAM from alkaline solution containing CdSO_4 and SeO_2 by electrodeposition at room temperature [22]. Highly precise conditions like concentration, pH and cathodic potential are required to have good stoichiometry ratio for Cd and Se. We report here a non-galvanic method (chemical method) for preparing an ordered and crystalline (ensembled from nanoparticles) array of CdSe nanowires at room temperature using AAM as template which is sandwiched in a two-compartment cell [28]. CdSO_4 complexed with tartaric acid (TA) is employed as Cd^{2+} source and Na_2SeSO_3 in the presence of OH^- ions employed as Se^{2-} source. Electron microscopy, and UV–Vis characterization were performed for morphological and optical band gap study respectively.

EXPERIMENTAL

All the chemical reagents used were RA grade and without further purification. CdSO_4 , Na_2SO_3 and Se powder were from s.d.fine-Chem Ltd. Mumbai, India, and all solutions were prepared in de-ionized water. AAM anodisc-21 (Whatman, UK) with pore diameter 200nm was used as template. For the deposition of CdSe nanowires, anodisc is sandwiched in a two-compartment cell. 50mM solution of CdSO_4 complexed with TA was filled in one compartment and 50mM solution of Na_2SeSO_3 with a pH value 12, adjusted by KOH, was filled in other compartment. Na_2SeSO_3 aqueous solution (0.5M) was prepared by refluxing 0.05 mol Se powder in 100 ml Na_2SO_3 aqueous solution (1.00M) for 3 hours [23]. After filling the cell, it was left for 12 hours at room temperature so that CdSe nanowires are formed inside the pores of AAM. The sample is annealed at a temperature of 400°C for 5 hour. The morphological of CdSe nanowires was examined by SEM by first liberating them from the matrix by dissolving AAO template in 1M NaOH solution at 25°C for 1hour followed by subsequent washing. The cleaned and dried samples were mounted on special designed aluminum stubs with the help of the two way adhesive tape, coated with a layer of gold using JEOL, FINE SPUTTER JFC-1100 sputter coater and viewed under JEOL, JSM 6100 SEM. The optical absorption spectra of un-annealed and annealed sample were recorded within the range 300-850 nm using Syntronics UV-Vis spectrophotometer:119.

RESULTS AND DISCUSSIONS

In one of the compartments of cell, the cationic precursor solution, $[\text{Cd}(\text{Tartaric Acid})]^{2+}$ complex releases Cd^{2+} ions while in the other compartment of cell, the anionic precursor solution Na_2SeSO_3 hydrolyses in the presence of OH^- ions to give Se^{2-} . In the pores of AAM, Cd^{2+} combine with Se^{2-} to give CdSe precipitate. When the cell is left for adequate time (here 12 hours), the above process continues till the pores are completely filled with the CdSe . This results into the formation of CdSe nanowires.

Figure.1 shows SEM images of CdSe nanowires. It can be seen that diameter of nanowires is about 200nm that closely corresponds to the diameter of pores of template used and also all the CdSe nanowires are oriented and the length, diameter and direction of growth of CdSe are quite uniform which is due to the confined growth of nanowires in the ordered pores of AAM template.

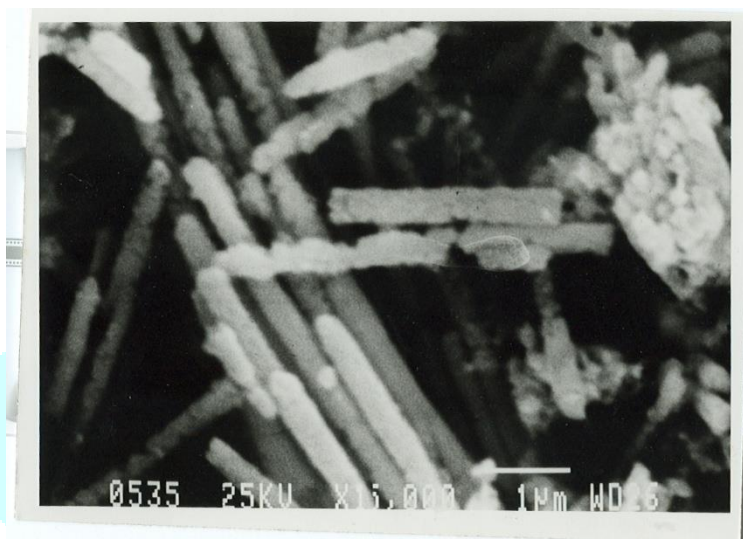


Figure1. SEM image of annealed CdSe nanowires each having diameter of 200 nm.

Figure 2 & 3 show the UV-Vis absorption spectrum of un-annealed and annealed nanowires respectively. The optical band gap of CdSe nanowires is estimated from UV-Vis absorption spectrum and Tauc plot [19,25]. The optical band gap of un-annealed sample obtained from this fit is 2.25eV, which is greater than standard band gap (1.7eV) for bulk [26] showing a blue shift of 0.55eV in band gap. The blue shift in band gap is due to quantum confinement effect [27, 28]. It is known that the size quantization is because of the localization of electrons and holes in the semiconductor nanocrystallites of nanosize in the range of 30-100Å which causes a change in electronic band structure and hence an optical band gap as compared with that of the bulk. Similar blue shift in band gap value is reported by Kale et al [25] in case of thin films. Murray et al [24] also reported band shift in case of nanocrystallites of CdSe . The optical band gap for thermally annealed sample is 1.8 eV which is nearer to bulk value. Hence on thermal annealing, the optical band gap shows a red-shift of 0.45 eV.

CONCLUSION

CdSe nanowires are template synthesized in the pores of AAM using non galvanic(chemical) method at room temperature. The SEM analysis shows that nanowires are highly ordered and uniform in diameter. From the optical absorption spectrum and Tauc plot, the band gap of CdSe nanowires were measured for un-annealed as well as for annealed sample. The optical band gap shows red shift on thermal annealing the CdSe nanowires. The mechanism of the grown nanowires is also demonstrated. This method can be possibly used in the synthesis of other chalcogenides also.

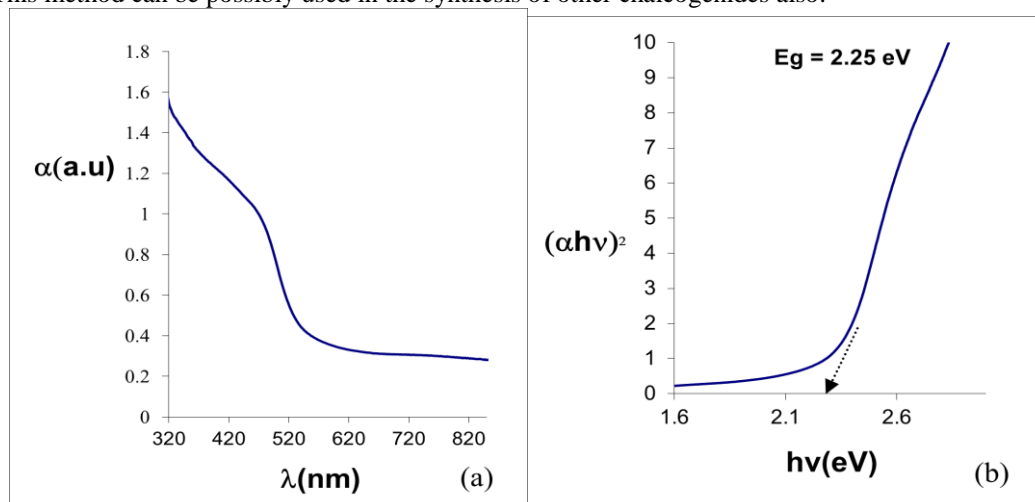


Figure 2: UV-Vis spectra and Tauc plot for un-annealed CdSe nanowires.

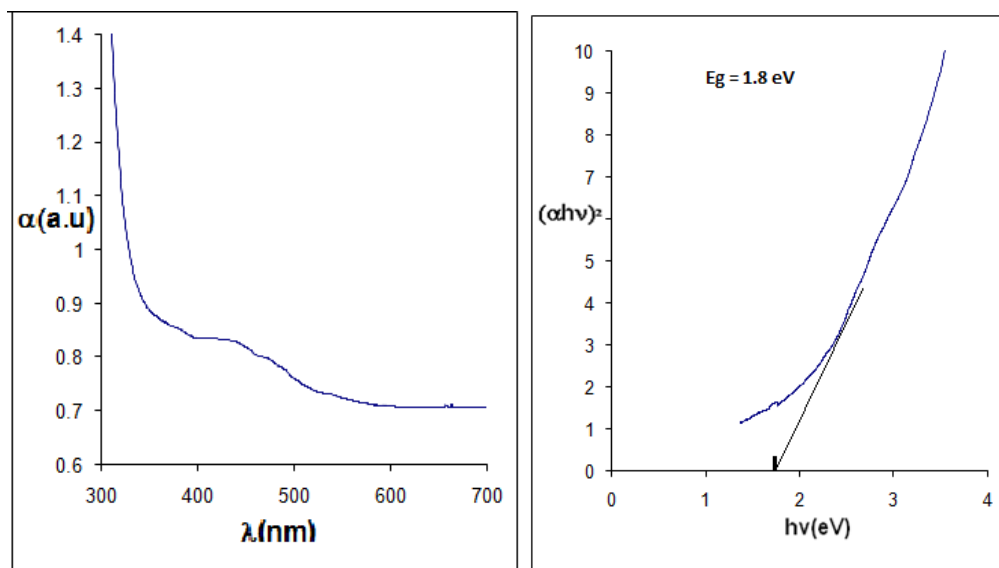


Figure 3: UV-Visible spectra and Tauc plot for annealed CdSe nanowires

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REFERENCES

- [1] K. Liu, K. Nagodawithana, P. C. Searson, C. L. Chien, *Phys. Rev. B* **51** (1995) 7381.
- [2] W. Fritzsche, K. J. Bohm, E. Unger, J. M. Kohler, *Appl. Phys. Lett.* **75** (1999) 2854.
- [3] Y. Kondo, K. Takayanagi, *Science* **289** (2000) 606.
- [4] X. Duan, C. M. Lieber, *Adv. Mater.* **12** (2000) 298.
- [5] CR Martin, *Science* **266** (1994) 1961.
- [6] S.K.Chakarvarti and J. Vetter, *Radiat. Meas.* **29(2)** (1998) 149
- [7] A.Huczko, *Appl. Phys. A* **70** (2000) 365
- [8] SK Chakarvarti, *Proceedings of SPIE*, Vol. **6172** (2006) p. 61720G1, San Diego, California, USA.
- [9] A Blondel, B. Ddoudin, J. -Ph. Ansermet, *J. Magn. Magn. Mater.* **165** (1997) 34.
- [10] G.S. Cheng, S.H.Chen, X.G.Zho, Y.Q. Mao, L.D. Zhang, *Mat. Sci. and Engg.* **A286** (2000) 165.
- [11] D.J. Pena, J.K. Mbindyo, A.J. Carado, T.E. Mallouk, C.D. Keating, B. Razavi, T.S. Mayer, *J. Phys. Chem. B* **106** (2002) 7458.
- [12] Tatsuya Iwasaki, Taiko Motoi, Tohru Den, *Appl. Phys. Lett.* **75** (1999) 2044.
- [13] U. Lunz, M. Keim, G. Reuscher, K. Schull, A. Waag, G. Landwehr, *J. Appl. Phys.* **80** (1996) 6329.
- [14] Rajesh Kumar, Vijay Kumar and S.K.Chakarvarti, *J. Mat. Sci Lett.* **40** (2005) 3523.
- [15] Ranjeet Singh, *International Journal of Creative Research Thoughts* **10** (2022) 1341
- [16] Brue LE, *J Chem. Phys.* **80** (1984) 4403.
- [17] Alivisatos AP, Harris TD, Carroll PJ, Stiegerwald ML, Brus LE, *J Chem. Phys.* **90** (1989) 3463
- [18] Gutierrez M T, Ortega J, *J. Electrochem. Soc.* **136** (1989) 2316
- [19] G.V. Parkash, R.Singh, A. Kumar, R. K. Mishra, *Material Letters* **60** (2006) 1744.
- [20] Dongsheng Xu, Dapeng Chen, Yajie Xu, Xuesong Shi, Guolin Guo, Linlin Gui, Youqi Tang, *Pure Appl. Chem.* **72** (1,2) (2000) 127.
- [21] D.Routkoyitch, A.A. Tager, J. Haruyama, D.Almawlawi, M. Moskorvits, J.M. Xu, *IEEE Trans. Electron Devices* **43** (1996) 1646.
- [22] X.S. Peng, J. Zhang, X.F. Wang, Y.W. Wang, I.X. Zhao, G.W. Meng, L.D. Zhang, *Chem. Phys. Letters* **343** (2001) 470.

[23] Xiao-Dong Ma, Xue-Feng Qian, Zie Yin, Zi-Kang Zhu, *J. Mater. Chem.***12** (2002) 663

[24] C.B. Murray, D.J. Norris, M.G. Bawendi, *J. Am. Chem. Soc.* **115** (1993) 8706

[25] RB Kale, SD Sartale, BK Chougule, CD Lokhande, *Semi. Sci. Techol.* **19** (2004) 980

[26] HM Pathan, CD Lokhande, *Bull. Mater. Sci.* **27**, No.2 (2004) p.85

[27] M. Li, J.C. Li, *Material Letters* **60** (2006) 2526.

[28] Ranjeet Singh, Rajesh Kumar, S K Chakarvarti, *Materials Letters*, **62** (2008) 874.

