

Low-temperature technology to create photovoltaic cells solar energy

M.A. Jafarov*, S.A. Mamedova, E.F. Nasirov

Baku State University, Department of Physics, 23 Z. Xalilov st., Baku Az 1148, Azerbaijan
email: maarif.jafarov@mail.ru

Abstract

In this work a novel chemical reduction method at room temperature is described to synthesize nanocrystalline ZnS, CdS, $Zn_xCd_{1-x}S$. The method is cheap and cost effective. The grown nanoparticles are characterized by XRD, TEM, EDX, UV-VIS absorption and PL study. CdS formation is supported by the systematic splitting of x-ray diffraction peak at lower angle and the peaks are identified. ZnS peaks are also identified comparing with ICDD data. EDX analysis shows two other phases $Zn_{0.8}Cd_{0.2}S$, $Zn_{0.5}Cd_{0.5}S$. The particle sizes are in the range 4-8 nm. The band gap changes with change of composition. Also at each composition the band gap is greater compared to bulk band gap. This indicates quantum confinement takes place. The band gap energy of nanoparticles can be tuned to a lower energy by increasing the Cd content, indicating the formation of the alloyed nanoparticles. PL peak shifts towards higher wavelength as Cd content increases. The peak corresponds to transition associated with surface state.

Keywords: $Zn_xCd_{1-x}S$; nanoparticles; structural properties; optical properties; photoluminescence.

Received: 19 november 2022

Accepted: 9 december 2022

Published: 26 december 2022

1. Introduction

The synthesis and characterization of semiconductor nanoparticles have attracted much interest because of their novel properties as a consequence of the large number of surface atoms and the three-dimensional confinement of the electrons [1-7]. Altering the size of the particles alters the degree of the confinement of the electrons and affects the electronic structure of the solid, especially the band gap edges. Among a variety of semiconductor materials, the binary metal chalcogenides of group II-VI have been extensively studied [1-6]. For example, nanocrystalline thin films of ZnS and CdS are attractive materials in photoconducting cells and optoelectronic devices such as solar cells and photodetectors [7-10].

Alloying of semiconductors is one of the simplest techniques used for tailoring the energy band gap, lattice parameter, electronic and optical properties generally in alloys; the lattice parameter varies linearly with composition and follows the Vegard's law. Among the different ternary II-VI semi-conductors, $Zn_xCd_{1-x}S$ has been widely used as a wide band gap material in heterojunction solar cells, photoconductive devices, high-density optical recording and for blue or even ultraviolet laser diodes.

In this paper, we report a novel chemical reduction route to synthesize ZnS, CdS and $Zn_xCd_{1-x}S$ nanocrystals at room temperature.

2. Experiments

Typically, an appropriate amount of sulfur powder was added to a flask containing 50 mL of tetrahydrofuran (THF). After being stirred using magnetic stirrer for 5 min, the mixture becomes a colorless transparent solution. A stoichiometric amount of $ZnCl_2$ was added to the flask and a black suspension formed upon stirring. After the addition of $NaBH_4$, the suspension turned light green. After the mixture was stirred for 3 h, a white precipitate formed. Then the precipitate was centrifuged and dried at room temperature. The sample is now ready for characterization. For the preparation of nanocrystalline CdS, the process was the same as above except that anhydrous $CdCl_2$ was used instead of $ZnCl_2$. For the preparation of $Zn_xCd_{1-x}S$ stoichiometric anhydrous $ZnCl_2$ and $CdCl_2$ powders were used according to the molar ratios in the target compounds $Zn_{0.7}Cd_{0.3}S$, $Zn_{0.5}Cd_{0.5}S$. The X-ray powder diffraction (XRD) was obtained using a Rigaku MiniFlex-II X-ray Diffractometer using $CuK\alpha$ radiation. Transmission electron microscope (TEM) images were obtained using the JEOL JEM-200 TEM operated at 200 kV. UV-VIS absorption spectra were recorded using a Shimadzu Pharmaspec-1700 spectrophotometer with a 1-cm quartz cell at room temperature. Colloid solutions in ethanol were prepared ultrasonically for the UV-VIS and the photoluminescence (PL) measurements. The Photoluminescence of ZnS, CdS and $Zn_xCd_{1-x}S$ nanoparticles were measured using Perkin Elmer LS 55 Fluorescence Spectrometer.

3. Results and discussion

Figure 1 shows the x-ray diffraction peaks of the as prepared ZnS, CdS and different $Zn_xCd_{1-x}S$ samples. Samples are taken in the powder form and the measured angle is within 20-60 degree. Results show well defined peaks in each case and the peak positions gradually change with composition of the samples. All XRD patterns show obvious size broadening effect. In case of CdS the half width of the first peak is maximum indicating that particle size is minimum which is also confirmed by TEM pattern. For CdS the XRD pattern can be indexed as a wurtzite phase structure with strongly characteristic (100), (002), (101), (102), (110), (103) and (112) peaks, while for ZnS XRD pattern mainly reflects its zinblende character [(111), (220) and (311) peaks] with some wurtzite character [such as the existance of a vague (103)], which indicates either that the ZnS particles have a zinblende structure with some wurtzite stacking faults or that most particles have a zinblende structure with others having a wurtzite structure. As for the $Zn_xCd_{1-x}S$ nanocrystals the diffraction peaks in the XRD patterns gradually shift to larger angels and a phase transition from wurtzite to zinblende occurs with an increase of Zn content. This continuous peak shifting of the nanocrystals also indicates that there is no phase separation or separated nucleation of ZnS or CdS in the $Zn_xCd_{1-x}S$ nanocrystals.

Samples are well dispersed in ethanol by ultrasonification and it is placed on the carbon coated grid for TEM measurement. Figure 2 (a, b, c,d) shows TEM pattern of the as prepared samples. The particle size is measured in each case from the photograph.

TEM analysis indicates that the particles are in the nano range for different samples. Particle size for ZnS is found to be 4 nm. Particle size gradually increases with increase of Cd content. But in case of CdS particle size is reduced. Also from TED pattern it is

observed that in case of CdS diffraction dots predominates ring. Hence CdS nanoparticles show single crystallinity. Other three phases show polycrystalline nature. EDX analysis show the composition of the obtained material. There is difference of the target material and the obtained material for the composition $Zn_{0.8}Cd_{0.2}S$. Optical absorption of the dispersed samples are taken using a spectrophotometer and the data is recorded in the range of 200-900 nm. Figure 3 displays the absorption spectra of the different samples. Optical absorption coefficient (α) is calculated at each wave length.

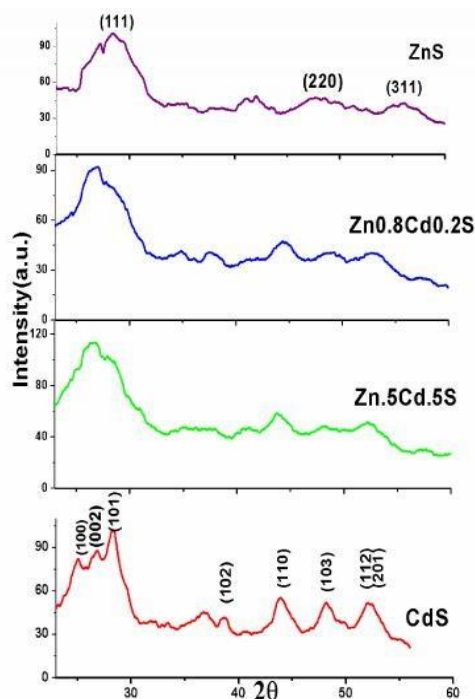


Figure 1. The XRD pattern of the as prepared samples

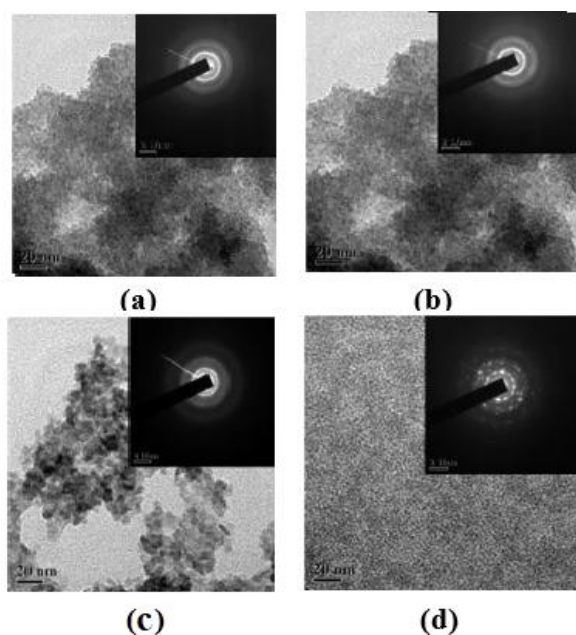


Figure 2. The TEM pattern of as synthesized (a) ZnS (b) $Zn_{0.8}Cd_{0.2}S$ (c) $Zn_{0.5}Cd_{0.5}S$ (d) CdS

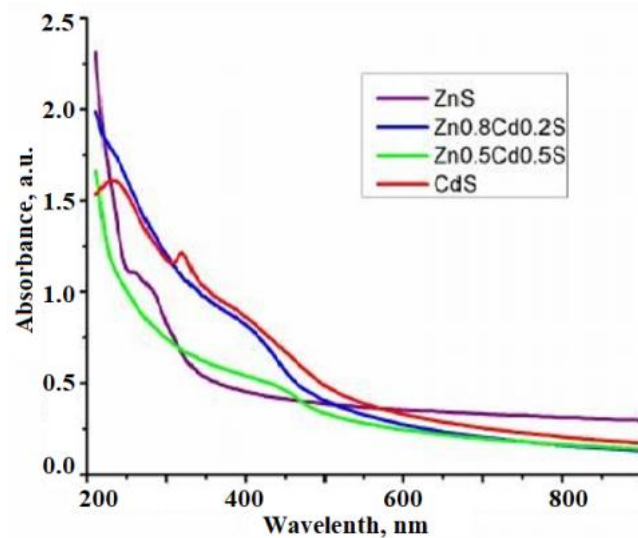


Figure 3. Optical absorption spectra of different samples

Figure 4 shows the plot of $(\alpha h\nu)^2$ vs. energy ($h\nu$) and it is used to determine band gap in each case.

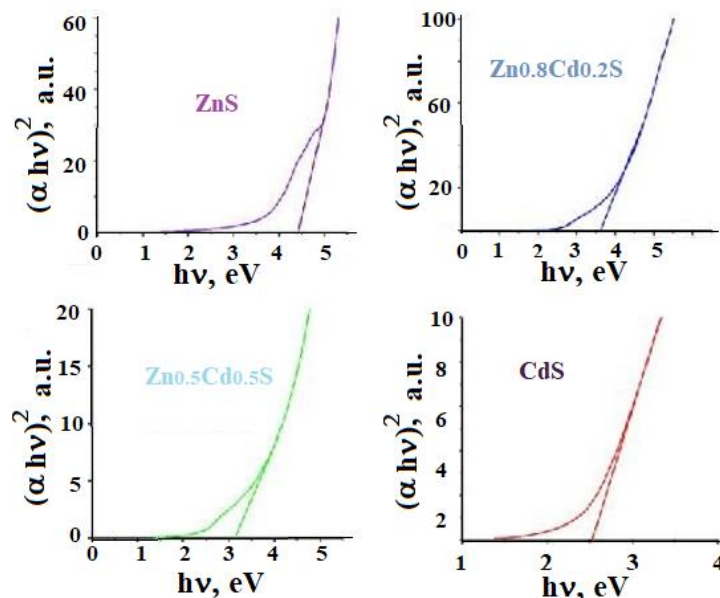


Figure 4. The band gap determination curve for different samples

From the optical absorption study it is found that the band gap of $Zn_xCd_{1-x}S$ are decreases with increase of Cd content and are close to the band gap determined by [8] and [9]. The decrease of band gap is attributed to the increase of particle size as well as the stoichiometric variation of Cd with respect to Zn. But in each sample band gap is found to be greater than the bulk band gap. This clearly indicates quantum confinement takes place in each sample.

Figure 5 displays the PL spectra of the samples dispersed in ethanol. PL peaks are shifted to higher wavelength as Cd content increases.

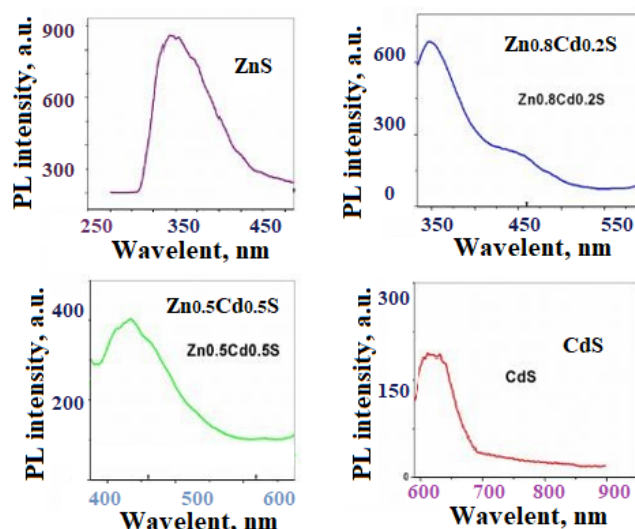


Figure 5. The photoluminescence spectra of as-synthesized samples

Target material	Obtained material	PL peak (nm)	Particle size (nm)	Band GAP (eV)
ZnS	ZnS	320	4	4.46
Zn 0.7 Cd 0.3 S	Zn 0.8 Cd 0.2 S	348	5.4	3.59
Zn 0.5 Cd 0.5 S	Zn 0.5 Cd 0.5 S	435	8.0	3.11
CdS	CdS	621	4.5	2.54

Table 1. Summarisation table

4. Conclusion

The above results reveal that ZnS, CdS and $Zn_xCd_{1-x}S$ nanoparticles are successfully obtained at room temperature and the compositions have been controlled. It is observed that by changing the ratio of $ZnCl_2$, $CdCl_2$ in the reactants the two phases $Zn_{0.8}Cd_{0.2}S$ and $Zn_{0.5}Cd_{0.5}S$ are obtained. The control of the composition of $Zn_xCd_{1-x}S$ nanoparticles may lead to the development of ideal materials for short wavelength diode laser applications.

References

1. I.A. Kariper, C. Gümüş, E. Güneri, F. Göde, Journal of Physics: Conference Series **326** (2011).
2. I.A. Kariper, E. Güneri, T. Özpozan, F. Göde, C. Gümüş **129** (2011) 183.
3. I.A. Kariper, C. Gümüş, E. Güneri, F. Göde, Chalcogenide Letters **12** (2012) 11.
4. Z.Qi.J. Deng, Y. Zhang, Q. Liao, Y. Huang, Nanotechnology **18**(47) (2007) 475603.
5. I.O. Oladeji, L. Chow, Thin Solid Films **474**(1) (2005) 77.
6. X. Wang, Z. Xie, H. Huang, Z. Liu, D. Chen, G. Shen, Journal of Materials Chemistry. **22**(14) (2012) 6845.
7. Y. Liang, H. Liang, X. Xiao, S. Hark, Journal of Materials Chemistry **22**(3) (2012) 1199.
8. C.S. Pathak, M.K. Mandal, V. Agarwala, Superlattices and Microstructures **58** (2013) 135.
9. K. Nagamani, M.V. Reddy, Y. Lingappa, K.T. Ramakrishna, R.W. Miles, International J. of Optoelectronic Engineering **2** (2012) 1.