

Synopsis

The investigation of nanomaterials has gained immense interest due to the fact that it fills the gap between bulk solid and atoms/molecules thus improving our understanding of fundamental properties. Detailed studies on the physical properties of semiconductor nanostructures would help to resolve the challenges that semiconductor technology faces today. As a result of increased interest in this area, semiconductor nanostructures have emerged during the last decade as one of the major technology drivers because of the role they are expected to play in next generation electronic and optoelectronic systems. Up to date, many achievements have been reported in this field, which were a joint effort of material scientists, physicists, chemists and biologists. However, it is imperative to do more studies on the dependence of the properties of nanomaterials on their size, shape and inherent defects as the current understanding about these relationships still remains incomplete.

Semiconductor nanomaterials have been the centre of attention in the field of nanotechnology during the past decade. As the size of the material approaches its exciton-Bohr radius, their physical properties varies remarkably from bulk counterparts. This property has been the heart of low-dimensional research and applications for the last few decades. Among semiconductor nanomaterials, wide-bandgap II–VI semiconductor nanostructures are the most vital materials for high-performance optoelectronics devices such as light-emitting diodes and laser diodes operating in the blue or ultraviolet spectral range. Their high ionicity makes them ideal candidates for high electro-optical and

electromechanical coupling. ZnS and CdS are two of the most important II-VI semiconductors which are widely used as a phosphorescence and fluorescence material in video display screens, gas sensors, optical/UV detectors and solar cells. By controlling their size, shape or chemical compositions, the electronic and optical properties can be manipulated. It is this versatility of CdS and ZnS nanostructures which makes them the most attractive semiconductors for technological applications. Furthermore, synthesis of these nanostructures is easy as compared with III-V semiconductors due to which nanostructures of various sizes and shapes can be developed easily in the labs to meet the specific applications.

Until recently, scientists have only been interested in studying the role of quantum confinement (size) effects in modifying the physical properties of nanomaterials. The importance of surface related phenomena were not fully realized by the scientific world. Surface defects had been considered as a burden and they were removed completely to make it easy to predict the properties. However, as the semiconductor research labs started working on very small (<10 nm) nanoparticles, the importance of surface defects became more evident. Various anomalies have been observed in the properties of semiconductor nanomaterials, recently. Some of the most important of them are the observation of room temperature ferromagnetism in undoped and transition metal doped semiconductors, giant magneto-resistance in TM doped II-VI semiconductors, enhanced dielectric constant, inconsistent values of e-p coupling strength and luminescence quenching. These newly observed properties have mainly been ascribed to the increased surface defect density in un-passivated nanomaterials. As a consequence of the increased

surface to volume ratio, the defect density becomes significantly high at a critical particle size which drastically changes the properties of material. This provides a more efficient method for tuning the physical properties compared to particle size and doping based tuning. However, to realize this, it is necessary to conduct a detailed study on how size and surface effects influence the properties of nanomaterials.

This thesis gives a detailed description of the work done on the synthesis, structural, optical, dielectric and transport properties of nanorods and nanoparticles of CdS and ZnS. The samples have been characterized using X-ray diffraction (XRD), Scanning electron microscopy (SEM), High resolution transmission electron spectroscopy (HR-TEM), Energy dispersive spectroscopy (EDS), Electron spin resonance (ESR), photoluminescence spectroscopy, UV-Visible spectroscopy, Raman spectroscopy, electrical transport studies and dielectric spectroscopy. A comparison of the properties of nanorods and nanoparticles has been done in order to study how the dimensionality of the material influences the properties in nano-regime. This thesis presents a description of the studies conducted to understand the interplay of surface and size effects in redefining the properties of the nanostructures. It also provides answers to certain anomalies like contradictory nature of e-p coupling constant, huge dielectric constant, enhanced electrical conduction and thermal instability observed in semiconductor nanostructures.

This thesis spreads across seven chapters. A general introduction to size and surface effects in nanomaterials is given in chapter 1. This chapter begins with a summary of the fundamentals of semiconductor nanostructures which is followed by a detailed discussion on the recent trends and gap areas. This underlines the motivation of work. After this, a

short description of the various synthesis techniques used for the production of nanomaterials is given. An outline of the characterization techniques used in this work is also added followed by an overview of the thesis.

Chapter 2 explains the synthesis and structural characterization of nanoparticles and nanorods of CdS and ZnS. A detailed description of hydrothermal method and how it is employed to prepare the aforementioned nanostructures have been included. The chapter narrates the use of XRD technique to obtain information about the lattice constants, average crystallite size and micro-strain of the samples. The details of morphology of the samples obtained from SEM and TEM studies are also added. The studies have revealed that average particle sizes of all the samples are less than 40 nm - the size-regime in which surface effects becomes vital. EDS analysis has suggested the possible existence of Cd/Zn rich surface layers in the samples. The highlight of this chapter is the development of a model for the low temperature phase transformation from hexagonal to cubic phase observed in CdS nanoparticles. This model has been developed by taking in to account the concept of dislocations. The chapter also discusses how inherent tensile/compressive strains originate in the samples.

Chapter 3 deals with the optical absorption and emission properties of the samples. It describes how bandgap energies of the nanoparticles and nanorods of CdS and ZnS are determined experimentally as well as theoretically. The anomalous widening of bandgap observed in these samples has been attributed to lattice defect-induced strain. This chapter also discusses the disappearance of band to band/ exciton recombination peaks in the samples and its reappearance on annealing which are explained on the basis of

variations in surface defect densities. A careful analysis of the defect related transitions, which are found to dominate the emission spectra, gives important information regarding the mechanisms of optical processes in these samples. Details of the studies performed on the modifications observed in the optical absorption and emission spectra of CdS nanoparticles due to annealing induced phase transformation have been given. This sheds light in to the concept of defect induced tuning of properties. In a nutshell, the chapter adds a neat description of some of the anomalies in the optical and absorption spectra of nanomaterials and their possible origins. The studies presented in this chapter deconvolutes the contribution to optical spectra by lattice strain and quantum confinement effect thus succeeds to a great extend in gathering information about the mechanisms that leads to various deviations in the optical behavior of nanomaterials.

The Raman spectroscopic studies of CdS and ZnS nanorods and nanoparticles are discussed in chapter 4. The shift in Raman spectrum has been carefully studied to extract information about the size and surface effects in the samples. Analysis of the shift and broadening of Raman modes based on Gaussian confinement model is explained in this chapter. A comparison between the experimental and theoretical values of electron-phonon (e-p) coupling strength is presented followed by novel phenomenological model based on which the contradictory nature of e-p coupling strength observed in nanomaterials is explained.

Chapter 5 is devoted to describe the dielectric properties of nanoparticles and nanorods of CdS and ZnS. In this chapter it is established that in nanostructures with

defective surface, the dielectric relaxation is Cole-Cole type which gradually transforms to Debye-like behavior as the temperature is increased. A short description of the determination of the nature of internal structure of samples by determining the dielectric relaxation is given. An unusual enhancement (10^3 at RT) in dielectric constant observed in some samples has been explained in the framework of surface-space charge polarization model. Chapter 5 also discusses how impedance spectroscopic and electric modulus studies reveal the grain and grain boundary structures, defect levels, and polaron based transport in CdS and ZnS nanostructures.

Chapter 6 reports the ac and dc electrical transport properties of CdS and ZnS nanostructures. This chapter explains the reasons for assuming ac transport in defect-rich nanoparticles to be similar to that in disordered materials. It also gives a description of the analysis of ac electrical transport in the samples carried out in the light of correlated barrier hopping model. This analysis has predicted the possibility of polaron based electrical transport in the samples. Furthermore, this chapter points out that dc transport in the samples arises due to thermal activation of charge carriers and follows the Arrhenius law. A comparison of the ac and dc conductivity values in order to confirm the roles of surface defects in deciding the nature of electrical transport has also been included in chapter 6.

The main conclusions drawn from the studies performed have been brought together in to a single whole in chapter 7. The chapter highlights significant findings and novel

concepts presented in this work. The scope of further research in this field is also discussed.

List of publications

International Journals

1. **Anoop Chandran**, Soosen Samuel M, Jiji Koshy and K C George ‘Correlated barrier hopping in CdS nanoparticles and nanowires’ Journal of Applied Physics 109 (2011) 084314.
2. **Anoop Chandran**, Soosen Samuel M, Jiji Koshy and K C George ‘Dielectric relaxation behavior of CdS nanoparticles and nanowires’ Journal of Materials Science. 46 (2011) 4646.
3. Soosen Samuel M, Jiji Koshy, **Anoop Chandran** and K C George, Electric charge transport and dielectric spectroscopy of ZnO nanotubes. Current Applied Physics, 11(2011)1094.
4. Soosen Samuel M, Jiji Koshy, **Anoop Chandran** and K C George, “Dielectric behavior and electric charge transport in ZnO nanorods”, Physica B, 406 (2011) 3023
5. Soosen Samuel M, **Anoop Chandran**, Jiji Koshy, and K C George, “Correlated barrier hopping in ZnO nanorods”, Journal of Applied Physics 109 (2011) 113702.

6. **Anoop Chandran**, K. C. George, Defect induced modifications in the optical, dielectric, and transport properties of hydrothermally prepared ZnS nanoparticles and nanorods, Journal of Nanoparticle Research 16 (2014) 2238
7. **Anoop Chandran**, K. C. George, Phase instability and defect induced evolution of optical properties in Cd rich-CdS nanoparticles, J. Appl. Phys. 115 (2014) 164309
8. **Anoop Chandran**, Reenu Elizabeth John and K C George “Fluctuations in the dielectric properties of thermally unstable CdS nanoparticles: Role of lattice strain “ Journal of Physics and Chemistry of solids (Communicated)

National Journals & Conference proceedings with ISBN number

1. **Anoop Chandran**, N Francis, T Jose, KC George, “Synthesis, structural characterization and optical bandgap determination of ZnS nanoparticles”, SB Academic Review 17, 17-21
2. **Anoop Chandran**, Soosen Samuel M, Jiji Koshy and K C George “High temperature hopping conduction in ZnS nanoparticles” Macmillan advanced Research series. (2010) 147.
3. Soosen Samuel M, Jiji Koshy, **Anoop Chandran** and K C George, Optical phonon confinement in ZnO nanorods and nanotubes, Indian journal of pure and applied physics 48 (2010) 703.

4. **Anoop Chandran**, Soosen Samuel M, Jiji Koshy and K C George, “Gaussian confinement of phonons in CdS nanoparticles” AIP Conference Proceedings 1349 (2010) 329
5. Soosen Samuel M, Jiji Koshy, **Anoop Chandran** and K C George, “Correlated barrier hopping in ZnO nanotubes” AIP Conference Proceedings 1349 (2010) 325
6. Soosen Samuel M, **Anoop Chandran**, Jiji Koshy and K. C. George, Optical properties of Al-doped ZnO nanorods, AIP conference Proceedings, 1391 (2011) 555
7. Jiji Koshy, M. Soosen Samuel, **Anoop Chandran** and K. C. George, Optical Properties of CuO Nanoparticles, AIP Conf. Proc. 1391, 576 (2011)
8. **Anoop Chandran**, Reenu Elizabeth John and K C George “Optical phonon confinement in Cadmium sulfide nanoparticles and nanorods” 27th Kerala Science Congress, Alapuzha (communicated)

Papers presented in national and international conferences

1. “Dependence of electrical conductivity of nanocrystalline ZnS on annealing temperature” National workshop on ‘quantum confinement systems and nanoscale devices’ held at St. Thomas College, Pala from December 3-5.
2. “High temperature hopping conduction in ZnS nanoparticles” International conference on nanomaterials and nanotechnology (Nano-2010), KSR College of Technology, Tamilnadu, December 13-16 (2010)

3. “Gaussian confinement of phonons in CdS nanoparticles, 55th DAE solid state symposium, Manipal university, Karnataka, December 26-30, 2010, Manipal
4. “Dielectric and electrical transport properties of ZnS nanoparticles and nanorods”, Indo-US Workshop on Nano-Structured Electronic Materials: Challenges & Relevance to Electronics & Energy Research (IUSWNM 2013) CMET, Thrissur, 15th February 2013.

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