CHAPTER 9

Chalcogenides-Based Quantum Dots: Optical Investigation using First-Principles Calculations

9.1 INTRODUCTION

The IV–VI semiconductors in semiconductor periodic table are among the most interesting materials in solid-state physics. The most widely studied compounds in this group are PbS, PbSe and PbTe. These materials have narrow band gap, which are usually less than 0.5 eV and whose temperature coefficient $\alpha_T = \frac{\partial E_g}{\partial T}$ is positive, and they have high mobility [167]. These lead salts show interesting factors in optoelectronic applications [168]. It is advantageous to use the computational method based on total energy calculations to study the phase transition from the coordinated number Nc = 4 to 6 fold [158]. Third-generation approaches to photovoltaics (PVs) aim to decrease costs and significantly increase efficiency but maintain the economic and environmental cost advantages of thin-film deposition techniques [159]. There are several approaches to achieve such multiple energy threshold devices [160]; tandem or multicolor cells, concentrator systems, intermediate-level cells, multiple carrier excitations, up/down conversion and hot carrier cells [6].

Luo *et al.* [181] have successfully synthesized water soluble germanium-doped cadmium sulfide quantum dots (Ge:CdS q-dots) by a facile one-pot method, and used as fluorescent probes for labeling live MCF-7 cells. The optical properties of the q-dots and several key parameters of the synthesis conditions were studied, and the mechanism of these parameters was also discussed. Furthermore, the toxicity of CdS quantum dot decreased after doping with germanium due to its low toxicity, which greatly improved the CdS quantum dots biocompatibility. Then the doped quantum dots modified with Folic Acid (FA) to use as fluorescent probes, which expanded the application of semiconductor quantum dots in the biomedical field. While, El-Rabaie [182] have investigated the growth of PbTe quantum dots embedded in a novel fluorogermante glass matrix. Optical absorption shows a large blue shift which implies that the prepared PbTe quantum dots reflect strong quantum confinement effect.

The nanoparticle sizes calculated from optical absorption spectra are found to be 3.2, 3.6, 6.1 and 7.3 nm for the glass samples heat-treated at 500 °C for 30, 60, 120 and 180 min, respectively. The optical band gap E_g values showed a decrease from 2.52 to 1.95 eV with increasing of nanoparticle size. XRD analysis confirmed the formation of PbTe nanocrystals, which exhibit cubic structure. Moreover, Strong *et al.* [183] have researched gallium arsenide diodes with and without indium arsenide; quantum dots were electron irradiated to investigate radiation induced defects. Baseline and quantum dot gallium arsenide pn-junction diodes were characterized by capacitance–voltage measurements, and deep level transient spectroscopy.

Carrier accumulation was observed in the gallium arsenide quantum dot sample at the designed depth for the quantum dots via capacitance-voltage measurements. In the quantum dot sample after 1 MeV electron irradiation, QD–E3 (E_C - 0.28 eV), QD–E4 (E_C - 0.49 eV), and QD–EL2 (E_C - 0.72 eV) defects, similar to the baseline sample, were observed, although the trap density was dissimilar to that of the baseline sample. The quantum dot sample showed a higher density of the QD–E4 defect and a lower density of QD–E3, while the QD–EL2 defect seems to be unaffected by electron irradiation. However, Udipi *et al.* [115] have presented semi classical simulation results for the potential energy profile and electron density distribution in 200 nm silicon quantum dot. For the solution of the continuity equation, the efficient difference approximations proposed by Scharfetter and Gummel [116] have extended to three dimensions. In essence, they have followed the two-dimensional approach due to Selberherr *et al.* [117] extend two to three dimensions.

Although the dielectric constant can be increased to some extent at higher loading level, increasing the dielectric strength remains a great challenge. Instead, the addition of extra load usually results in the considerable loss of dielectric strength of the materials. The investigation of further materials research is interesting when one tries to gain some information about the diameter dependence of the compounds; especially it is proved with some of other materials [173]. It seems that, it is more fundamental to relate the diameter dependence behavior to the bonds between nearest atoms. By controlling the evolution with diameter dependence of the compound, it could attempt to link the effect of quantum dot diameter to the quantum dot potential. In this context, we have used this procedure for testing the validity of our model [121] of QDs potential. The obtained energy band gaps are used to calculate the quantum dot potential and to predict materials for QDs.

The aim of this work is to verify our model [121] for calculating the diameter dependence on QDs potential for dot diameters down to 71 nm, 69 nm and 68 nm for $PbS_{0.75}Te_{0.25}$, $PbS_{0.5}Te_{0.5}$ and $PbS_{0.25}Te_{0.75}$ alloys, respectively using the Full Potential Linearized Augmented Plane Wave (FP-LAPW), in addition to investigate the optical properties of refractive index and optical dielectric constant using specific models for the mentioned alloys.

9.2 CALCULATIONS

The effect of increasing the tellurium concentration on the optical properties of the lead sulfide telluride $PbS_{1-x}Te_x$ ternary alloys (x=0.0, 0.25, 0.5, 0.75, 1.0) is researched using the full potential linearized augmented plane wave method. The 'Special Quasirandom Structures' (SQS) Zunger's approach [165], is used to reproduce the randomness of the alloys for the first few shells around a given site. The system size is divided into nanoscale basing on optimization