

A Comparative Study on the Optical Properties of Multilayer CdSe / CdTe Thin Film with Single Layer CdTe and CdSe Films

M. Melvin David Kumar*, Suganthi Devadason

Thin Film Laboratory, Department of Physics Karunya University, Coimbatore – 641 114 India

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CdTe and CdSe single layer thin films and CdSe / CdTe multilayer (ML) thin film were prepared by using physical vapour deposition method. Optical properties of CdSe / CdTe multilayer thin film shows different behavior due to type II band structure alignment. Energy band gap value of CdSe / CdTe ML thin film is shifted to higher value than that of single layer CdTe film. This is due to decrease in crystallite size to dimension smaller than the Bohr exciton radius of CdTe (14 nm). Crystallite size of the multilayer sample was calculated with the predictions of the effective mass approximation model (i.e., Brus model). It is observed that the photoluminescence peak of CdSe / CdTe ML thin film is red shifted compared to the peaks corresponding to individual CdSe and CdTe thin films. This may be due to the presence of type II quantum dot formation in the CdSe / CdTe heterostructure multilayer thin film.

Keywords: CdSe, CdTe, Multilayer, Heterostructure, Quantum confinement.

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1. INTRODUCTION

Multilayer thin films of II-VI semiconductors provide opportunity to analyse quantum effects such as carrier confinement, spin-orbit coupling, splitting of valence bands [1, 2]. Quantum dot is a portion of matter whose excitons are confined in all the spatial dimensions. It leads to larger spacing between the energy levels as the size of the particle is reduced. Qualitatively this confinement effect is similar to the problem of particle in a box. Size dependant reactivity [3], optical non linearity [4], efficient photo electron emission [5] and melting point reduction [6] are some of the interesting properties exhibited by nano particles. Size controlled spectral tunability adds advantage to quantum dots in the fields of optoelectronic devices, bio-labeling and photovoltaic applications [7, 8]. The nanostructures of II-VI materials such as CdS [9], CdSe [10], CdTe [11] have attracted more attention for their great fundamental, experimental and applied interests. Combination of heterostructures for “band engineering”. Heterostructure multilayer thin films result in the formation of Type I and Type II band alignments [12] as shown in Fig. 1.

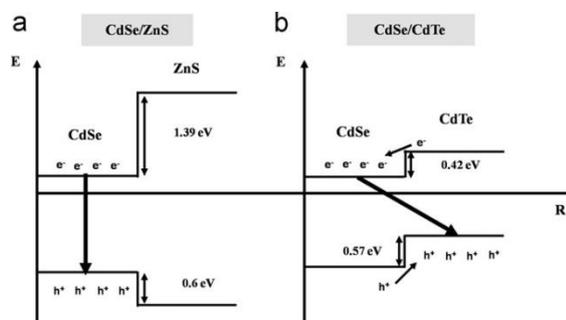


Fig. 1 – Schematic diagrams of a) Type I and b) Type II heterojunction band alignment

* mailtomelvindavid@gmail.com

In Type I heterostructure thin films, the energy levels (valance band and conduction band) of lower band gap semiconductor is placed in between the energy levels of higher band gap material. Whereas in type II heterostructure thin films, only valance band energy levels of lower band gap semiconductor is kept in between the energy levels of higher band gap semiconductor. The conduction band of lower band gap material is seen above the conduction band of higher band gap semiconductor. Type II heterostructure nanocrystals spatially separates photo generated carriers within the nanostructure such that the electron wave function mainly resides in one semiconductor and hole wave function in the other [13]. Recent investigations of type II CdSe / CdTe heterostructure nanocrystallites are ideal materials for their long range photo-induced charge separation and could be applied in photovoltaic devices [12, 14, 15]. CdSe, CdTe and CdSe / CdTe tetrapod nanocrystals perform well in nanocrystal-polymer hybrid solar cells [16-18]. Few researchers have prepared Type II CdSe / CdTe tetropod nanocrystals in chemical synthesis route [19-21]. In the present work, we reported the formation of Type II heterostructure nanocrystals in CdSe / CdTe multilayer thin films prepared by using Physical Vapour Deposition method where thickness of each layer can be controlled accurately up to few nanometers. Optical properties of CdSe / CdTe ML thin film is compared with that of single layer CdSe and CdTe thin films.

2. EXPERIMENTAL DETAILS

CdSe / CdTe nanocrystalline multilayer and single layer thin films were prepared by consecutive thermal evaporation of CdSe and CdTe (99.99 % Aldrich Chem. Co.) from two independent molybdenum crucibles at a vacuum at a pressure of 5×10^{-5} mbar. Glass substrates were not intentionally heated during the deposition process. The nominal film thickness and deposi-

tion rate of each sub-layer were controlled by calibrated quartz crystal monitor. The substrates were fixed at the greatest possible distance for which the tooling factor was calculated. A step-by-step procedure was applied in the deposition of each sub-layer in the multilayer structures. Variation in thickness of each layer and total number of layers tremendously altered the properties of materials in multilayer thin films. CdSe / CdTe ML thin films were prepared with thicknesses as shown in Table 1.

Table 1 – Details of the CdSe / CdTe multilayer thin film samples preparation

No	Material	Number of Layers in the sample	Thickness of Sub-layers (Å)		Total Thickness of the film (Å)
			CdTe	CdSe	
1	CdSe	1	–	500	500
2	CdTe	1	500	–	500
3	CdSe / CdTe	10	500	200	3500

To compare the properties of multilayer film with the single layer films, CdTe and CdSe film of 50nm thickness were prepared. The absorption and emission properties of the samples were studied by using uv-vis spectrophotometer (JASCO V - 550) and photoluminescence spectrometer (FLUOROLOG – 3 HJY) respectively.

3. RESULTS AND DISCUSSION

3.1 Optical Properties of CdSe / CdTe Heterostructure Multilayer Thin Films

CdSe / CdTe heterostructure multilayer and single layer thin film samples coated on glass substrates were subjected to optical absorption using JASCO V-550 UV-VIS spectrophotometer in the range of 300-1100 nm. As both CdSe and CdTe are the members of II-VI semiconductor compounds, conduction band is non degenerate and almost isotropic whereas the valance band (mostly constituted of the telluride (or) selenide anion p orbital) [22] is threefold orbitally degenerate. The absorption edge of this material exhibits three excitonic peaks [23] usually labeled as A (valance band of Γ_9 symmetry), B (valance band of Γ_8 symmetry) and C (valance band of Γ_7 symmetry) [24]. Based on the works done by Baldeschi & Lipari [25], the transitions close to the fundamental band gap (E_g) of II-VI semiconductors arise due to the spin-orbit split of valance band energy levels. A direct band to band transition energies of CdSe / CdTe heterostructure multilayer and single layer thin film samples were found out by plotting a typical graph between energy($h\nu$) and $(\alpha h\nu)^2$ as shown in Fig. 2 and 3, respectively.

As seen from Fig. 3, the energy band gap values of CdSe / CdTe ML film has two transitions near to the band gap value of the bulk CdTe material (1.54 eV). Thus the transitions equivalent energies (1.62 and 1.8 eV) are lying in between the energy values of the individual CdSe (1.9 eV) and CdTe (1.5 eV) thin films. The transitions in CdSe / CdTe ML film shows the presence of spin-orbit split of valance band energy level [25].

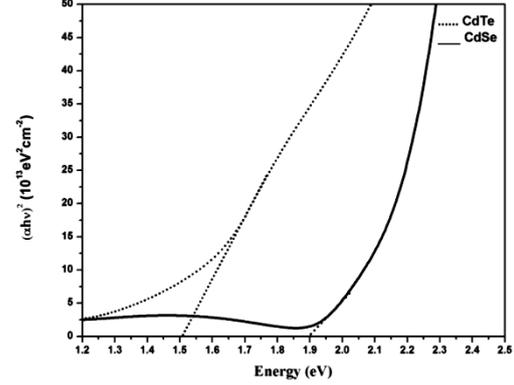


Fig. 2 – $h\nu$ vs $(\alpha h\nu)^2$ graph for the single layer CdSe and CdTe thin films

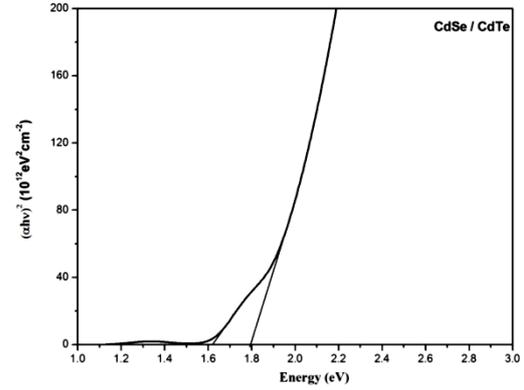


Fig. 3 – $h\nu$ vs $(\alpha h\nu)^2$ graph for the CdSe / CdTe ML sample

The same behavior is observed in the absorption spectra which are shown in Fig. 4, of CdSe / CdTe ML and single layer thin films. This result agrees well with the results produced by the researchers who have prepared type II CdSe / CdTe quantum dots in colloidal form by chemical synthesis method [19-21]. It is known that the quantum confinement effect can be observed if the radius of nanocrystallites becomes less than the Bohr excitonic radius of the corresponding material. The bulk Bohr diameter of the Wannier exciton in CdTe is 14 nm [26]. Size of the crystallite for ML sample was calculated from the shift in energy gap by using Brus equation as given,

$$E_{g(optical)} = E_{g(bulk)} + \frac{2\hbar^2\pi^2}{\mu d^2} \quad (1)$$

where, $E_{g(optical)}$ is the band gap values obtained from optical studies, $E_{g(bulk)}$ is the band gap of bulk CdTe ($E_g = 1.54$ eV), d is the diameter of the crystallites and μ is the effective mass of electron-hole pair given by,

$$\frac{1}{\mu} = \frac{1}{\mu_e^*} + \frac{1}{\mu_h^*} \quad (2)$$

where, μ_e^* and μ_h^* are effective mass of electron and hole, respectively.

It is evident that the nanocrystallite sizes of the CdSe / CdTe heterostructure multilayer thin film sample is much smaller than the Bohr exciton diameter. If the ratio of nanocrystallite size to Bohr exciton diame-

ter is lesser than 2, then the sample exhibits a single particle confinement behavior in which electrons and holes are independently confined. Hence, the prepared CdSe / CdTe heterostructure multilayer thin film may exhibit the strong quantum confinement effect.

The average size of the nanocrystallites calculated using equation (1) is 12 nm for CdSe / CdTe ML film.

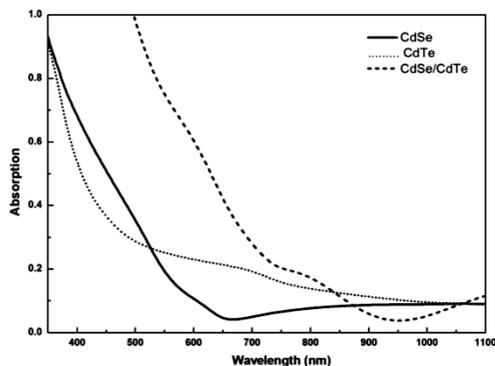


Fig. 4 – Absorption Spectra of CdSe, CdTe and the CdSe / CdTe ML samples

3.2 Photoluminescence Studies

Emission spectra of CdSe, CdTe single layer films and CdSe / CdTe heterostructure multilayer thin film are shown in Fig. 5. The peaks of CdSe / CdTe hetero

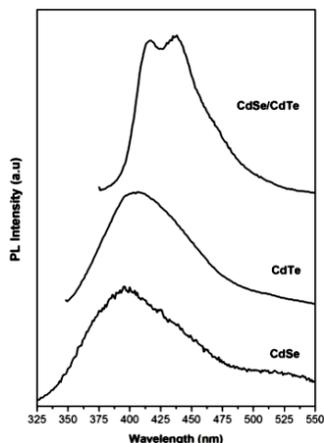


Fig. 5 – Emission Spectra of CdSe, CdTe and the CdSe / CdTe samples structure multilayer thin film have apparently shifted from the peaks of CdSe, CdTe individual layers towards red region in the emission spectra

Moreover, the emission of the CdSe / CdTe heterostructure ML sample is more structured than the individual CdSe and CdTe bands. There is a splitting of the emission maximum observed with the bands centered on 410 and 435 nm in the ML sample. This may be due to the emissions from the split up of neighboring excited energy state. In this type of heterostructure multilayer thin films, the energy of the emission thus depends on the band offsets of the two materials (lesser band gap and higher band gap) which results in emission of energies lesser than the energy band gap of both the materials.

Therefore, formation CdSe / CdTe crystallites can tune the energy band gap from visible to NIR region depending on the thickness of the individual layer of CdSe and CdTe materials.

4. CONCLUSION

A novel method of preparing CdSe / CdTe heterostructure multilayer thin film has been proposed in this study. It is found that the transition energies (1.62 and 1.8 eV) for CdSe / CdTe ML film are lying in between the band gap values of the individual CdSe (1.9 eV) and CdTe (1.5 eV) thin films. There is a red shift observed in the emission peak of CdSe / CdTe heterostructure multilayer thin film with respect to the peaks of CdSe, CdTe single layer thin films. Quantum confined effects in the optical properties of CdSe / CdTe have been observed. It is very useful to tune the band gap from visible to NIR region especially in case of semiconductors such as Se, Te etc., which form nanocrystals of very different sizes in a standard crystallization procedure. Further studies will be carried out in order to produce II-VI semiconductor nanocrystals with suitable sub-layers.

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