

STM Spectroscopy of Alloyed Nanocrystal Composite $\text{CdS}_x\text{Se}_{1-x}$

T. Abdallah, K. Easawi, A. Khalid, S. Negm, and H. Talaat

Abstract—Nanocrystals (NC) alloyed composite $\text{CdS}_x\text{Se}_{1-x}$ ($x=0$ to 1) have been prepared using the chemical solution deposition technique. The energy band gap of these alloyed nanocrystals of approximately the same size, have been determined by scanning tunneling spectroscopy (STS) technique at room temperature. The values of the energy band gap obtained directly using STS are compared to those measured by optical spectroscopy. Increasing the molar fraction ratio x from 0 to 1 causes clearly observed increase in the band gap of the alloyed composite nanocrystal. Vegard's law was applied to calculate the parameters of the effective mass approximation (EMA) model and the dimension obtained were compared to the values measured by STM. The good agreement of the calculated and measured values is a direct result of applying Vegard's law in the nanocomposites.

Keywords—Alloy semiconductor nanocrystals, STM.

I. INTRODUCTION

IN the last few decades there has been great interest in II–VI colloidal semiconductor nanoparticles (NPs) [1–9], due to the size dependent properties of these NPs [10]. However, tuning their properties by changing the particle size may cause problems in some applications [11]. To overcome these problems, a new class of alloyed semiconductor NPs have been studied [11–18], to provide a way for continuous tuning of their energy band gap without changing the particle size. The band gap of $\text{CdS}_x\text{Se}_{1-x}$ alloyed NC can be adjusted by varying the sulfur concentration [15], spanning the compositional range from pure CdSe ($x=0$) to pure CdS ($x=1$), where the band gap energies ranges from the UV to the visible. This makes $\text{CdS}_x\text{Se}_{1-x}$ a potentially favorable material for photovoltaic solar cell applications. In this work, scanning tunneling spectroscopy (STS) has been used to determine directly the energy band gap of the alloyed nanocrystals $\text{CdS}_x\text{Se}_{1-x}$ at room temperature. In STS a change of the voltage bias results in an equal change of the tip Fermi level with respect to energy levels of the nanoparticles, while the Fermi level of the substrate remains unchanged [19].

In this asymmetrical configuration, there are no linker molecules and the tip Fermi level scans over the energy levels of the nanocrystal. At positive bias, the onset of the differential of the current with respect to the voltage biasing $dI/dV > 0$ corresponds to resonant tunneling from the tip to the

substrate via a discrete unoccupied level in the conduction band (CB). At negative bias, the onset of $dI/dV < 0$ indicates resonant tunneling from the substrate to the tip via a discrete occupied level in the valency band (VB). With such asymmetrical configurations, it is possible to derive from the spectra, the band gap from the region around zero bias, in which dI/dV is close to zero. The fine structures of the electron and hole levels at room temperature are hard to detect. In the effective mass approximation (EMA) model, the energy band gap of the nanocrystals (NC) corrected for the electron hole coulomb potential, is given by [20–22]:

$$E(\text{NC}) = E_g(\text{bulk}) + \frac{\hbar^2 \pi^2}{2ma^2} \quad (1)$$

Where E_g is the bulk $\text{CdS}_x\text{Se}_{1-x}$ band gap energy, a is the radius, and m is the reduced mass of the electron and the hole. In order to calculate the band gap for the alloyed nanocrystals semiconductor, we first employed Vegard's law [23] to calculate the band gap of bulk semiconductor alloy, effective mass, and the dielectric constant ϵ , then, we use the EMA model to get the band gap of the alloyed NC. For bulk alloyed material, Vegard's law gives the following relation for the parameters of the composition [23].

$$\phi(\text{CdS}_x\text{Se}_{1-x}) = x \phi(\text{CdS}) + (1-x) \phi(\text{CdSe}) - x(1-x)b \quad (2)$$

Where ϕ stands for E_g (bulk band gap for CdSe ($=1.74$ eV) and for CdS ($=2.42$ eV), m (bulk effective mass), ϵ (bulk dielectric), and b is the bowing parameter $= 0.3$ [24]. In STS applied as single particle spectroscopy, the band gap is obtained directly from the change of dI/dV via voltage biasing. In the regular STM, the dimension of the alloyed NC is measured directly and through application of the modified EMA through Vegard's law, the energy band gap can then be obtained. On the other hand, using optical spectroscopy, a measurement of the exciton peak absorption indicates the energy lowest energy band gap in the alloyed nanocomposites. The employment of the Vegard's law is of fundamental importance to correctly obtain the parameters of alloyed nanocomposites.

II. EXPERIMENT

Alloy nanocrystals $\text{CdS}_x\text{Se}_{1-x}$ were prepared by the method of Talapin et al. [25]. A series of $\text{CdS}_x\text{Se}_{1-x}$ samples ($x = 0, 0.5, 0.67, 0.75, 1$) were prepared under the same experimental conditions by varying the amount of the second precursor (S). For example in the preparation of $\text{CdS}_{0.67}\text{Se}_{0.33}$ sample, cadmium solution was prepared by 0.3g of CdO added to 3.0 g of stearic acid, and heated up to 170°C till the red color of CdO disappears to ensure that the reaction between CdO and stearic acid is complete, and CdO is completely transformed to

T. Abdallah and H. Talaat is with Ain Shams University, Faculty of Science, Physics Department, Cairo, Egypt (e-mail: tamer_sharaf@sci.asu.edu.eg).

K. Easawi, A. Khalid and S. Negm are with Department of Mathematical and Physical Engineering, Faculty of Engineering (Shoubra), Banha University, Cairo, Egypt (e-mail: dr_easawi@yahoo.com).

Cd stearate. 2.0g of Trioctylphosphine Oxide (TOPO) and 1.0g of hexadecylamine (HDA) are added to the reaction mixture and heated at 200 °C. Sulfur solution was prepared by mixing 0.15 g of sulfur in 1.5 mL Trioctylphosphine (TOP). Selenium solution was also prepared by dissolving 0.15g of selenium in 1.5 mL TOP. Appropriate amounts of sulfur and selenium solutions were mixed together to give the above ratios. The mixture was then injected into the cadmium solution at a temperature 200°C. Small volumes of samples were taken at different time intervals after the point of injection and quenched in 5 ml of cold anhydrous toluene 25 °C to terminate the growth of the particles immediately. The resulting alloyed nanocrystals in toluene solution were precipitated out by using ethanol and isolated by centrifugation and decantation.

III. RESULTS AND DISCUSSIONS

The optical absorption spectra of the alloyed NC $\text{CdS}_x\text{Se}_{1-x}$ samples were measured to determine the electronic transition of these NPs. Fig. 1 shows the optical absorption spectra for the different ratios ($x = 0, 0.5, 0.67, 0.75, 1$) which show peaks at 565 nm, 553 nm, 532 nm, 529 nm and 473 nm respectively, corresponding to the exciton band for these nanostructures. The second derivative was employed to determine the absorption peak with more precision. Table I gives the corresponding energy band gap of $\text{CdS}_x\text{Se}_{1-x}$ as calculated from the second derivative of optical spectra.

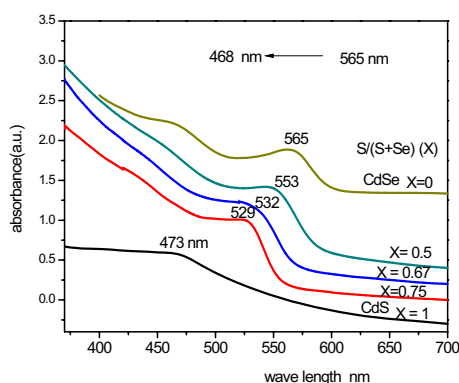


Fig. 1 Optical absorption spectra for $\text{CdS}_x\text{Se}_{1-x}$ of different molar fraction ratios as indicated

In order to obtain the EMA parameters for the alloyed NC, Vegard's law was applied to each parameter; the band gap $E_g(\text{bulk})$, effective mass, and the dielectric as discussed before. The STM images of the alloyed NC $\text{CdS}_x\text{Se}_{1-x}$ of the different ratios ($x = 0.5, 0.67, 0.75$) are shown in Fig. 2(a-c) as indicated. The corresponding measured sizes are 4.8 nm, 5.0 nm, 4.6 nm respectively. The modified EMA model and the measured sizes of the alloyed NC were used to calculate the band gap and are shown in Table I. The STS data for the band gap of the alloyed NC $\text{CdS}_x\text{Se}_{1-x}$ of the different ratios x are shown in Fig. 3. The graph shows the differential of the current with respect to the biasing voltage (dI/dV) versus the variation of the biasing voltage V on the samples. From Fig. 3,

the band gap is observed to increase from 2.20 eV to 2.68 eV as x increase from 0 to 1.

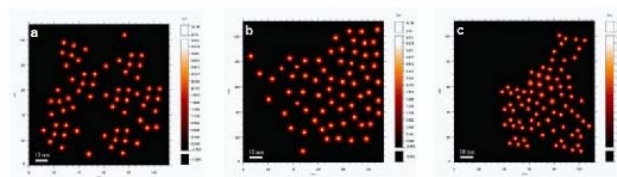


Fig. 2 STM images for alloyed $\text{CdS}_x\text{Se}_{1-x}$ where (a) $x = 0.5$ and NP size 4.8nm, (b) $x = 0.67$ and NP size 5.0nm, (c) $x = 0.75$ and NP size 4.6nm

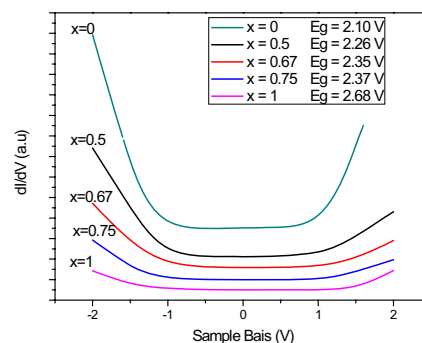


Fig. 3 The energy gap tunneling spectra for alloyed $\text{CdS}_x\text{Se}_{1-x}$

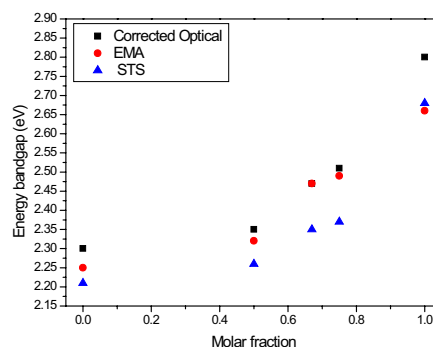


Fig. 4 The energy band gap versus different molar fraction of alloyed $\text{CdS}_x\text{Se}_{1-x}$

Furthermore, there is asymmetry in the edges of the CB and VB in all cases due to the presence of more dense holes states in VB than those of electrons in CB. Also, the holes effective mass are heavier than the electrons effective mass.

These STS results show directly the increase of the energy band gap with the increase in the molar fraction ratios x . The measured STS values lie close to the computed optical values corrected for the Coulomb potential. In this case one measures the exciton band gap, which is smaller than the single particle band gap by the electron-hole coulomb interaction. From Table I, we can observe that the difference in the values of the band gaps obtained by the above discussed three methods, STS as a direct measurement, the Vegard modified EMA model, and the corrected optical, are in good agreement within the experimental error.

TABLE I
ENERGY BAND GAP OF ALLOYED $\text{CdS}_x\text{Se}_{1-x}$ WITH DIFFERENT WIDTHS AND DIFFERENT RATIOS x AT ROOM TEMPERATURE

Molar Ratio	Size (nm)	Absorption (nm)	Energy band gap (eV)		
X	STM	λ	Corrected Optical	EMA	STS
0	4.8	565	2.30	2.28	2.21
0.5	4.8	553	2.38	2.32	2.26
0.67	5.0	532	2.47	2.47	2.35
0.75	4.6	529	2.51	2.49	2.37
1	4.8	473	2.81	2.66	2.68

IV. CONCLUSION

The energy band gap of carefully synthesized alloyed NC $\text{CdS}_x\text{Se}_{1-x}$ ($x = 0$ to 1) of almost the same size were measured directly through STS and a combined dimension measurements using STM and Vegard modified EMA applied to the optical spectra. The agreement of the results is within the experimental error and stems from the application of Vegard's law to the alloyed composite NC. The increase of the molar fraction ratio x in alloyed NC $\text{CdS}_x\text{Se}_{1-x}$ leads to corresponding increase in the energy band gap due to the increase in sulfur concentration. These variations of the energy band gap are of importance to the photovoltaic solar cell efficiency.

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