



Electrical properties of grain size tuned CdSe nanocrystal films for practical applications

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ARTICLE INFO

Keywords:

Quantum dot
CdSe nanocrystal films
Electrical properties
Activation energy
Hetero-junction

ABSTRACT

CdSe nanocrystal (NC) thin films of different NC sizes were synthesized using vacuum deposition technique. The films showed blue shift of band gap and the NC sizes calculated size using Brus equation were 9.40, 9.68 and 9.82 nm. DC conductivity and photoconductivity of as-deposited and annealed films increased and activation energy for conduction decreased with increase in the NC size. Also, both carrier concentration and mobility of the films increased with increase in the size of the NCs which was attributed to the increased electronic coupling between the NCs. The slow response part of photocurrent response pulse analyzed using power law: $I_{ph} \propto t^\alpha$ gave larger values for α for larger NC size indicating stronger electronic coupling between grains in films of larger grain sizes. Charge transport in the CdSe NC films was akin to that of solid films of CdSe quantum dots, of sizes given by Brus equation, connected together by an outer shell of CdSe material where charge carriers had free movement. Additionally, measurement of the characteristics of the hetero-junction formed by the CdSe NC film with a similarly deposited Cu_2Se film demonstrated usefulness of the CdSe NC films synthesized using the present technique for practical applications.

1. Introduction

Nanostructured films of semiconductors assembled from nanocrystal building blocks can exhibit properties that can be tuned by varying the nanocrystal size and are key materials for a variety of applications. In recent years, there have been rapid developments in the synthesis and characterization of II–VI group semiconductor thin films owing to their wide range of applications such as photoconductive devices and solar cells [1,2]. Cadmium selenide (CdSe) is a promising material for applications such as photovoltaics [3], photoconductors [4], light emitting diodes [5], nanosensors [6], biomedical imaging devices [7] and gas sensors [8]. Techniques such as thermal evaporation [9], sputtering [10], spray pyrolysis [11], self-assembly of nanocrystals [12–14], and electrodeposition [15] have been employed to synthesize CdSe nanostructured thin films.

The optical and electrical properties of colloidal semiconductor nanocrystals, QD solids, are determined by the electronic structure of the nanocrystal building blocks [16]. Charge transport properties in nanocrystal films which form the basis for the design and optimization of functions of devices based on quantum dot solids is presently being researched with great scientific and technological interest [17–23]. Electronic properties of quantum dot solids formed by close-packed arrays of semiconductor nanocrystals were reported in the case of PbS

[20,21,23], CdSe [22] and ZnO [24]. Studies on arrays of colloidal quantum dots separated by organic capping molecules showed these artificial solids to be highly insulating [25]. For easy transport of charge carrier through the quantum dot solid film, strong electronic coupling between the adjacent quantum dots should be ensured by the use of suitable surface ligands [26,27]. To increase the electrical current through solids of CdSe quantum dots stabilized by adsorbed organic capping molecules, the inter-dot separation determined by the length of the organic capping molecule was reduced by Drndić et al. [28] by annealing the solid and observed great enhancements in the dark current and photocurrent in the solids. It was proposed that mobility of the charge carriers can be further improved by replacing the organic ligand with an inorganic material that will build only a smaller barrier for electron transport [27]. Ocier et al. [21] investigated electronic transport in PbSe NC solids functionalized with chalcogenidometallate clusters and observed high electron mobility [21]. Dolzhenkov et al. [29] have recently shown that while the highest reported mobilities of CdSe NC films measured using FET structure were only about 5% of the mobility of CdSe single crystals, carrier transport increased to almost half of the single-crystal value by employing $[Cd_2Se_3]^{2-}$ ions to connect the CdSe nanocrystals which were of grain sizes 15 and 22 nm. Kagan and Murray have reviewed the reported research work in the area of charge transport in strongly coupled quantum dot solids and have

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highlighted the future prospects of these solids [22]. In a very recent article, Whitham et al. have reported the results of charge transport measurement in superlattices fabricated with PbSe quantum dots [23].

The gas-phase techniques for thin film fabrication, such as vacuum evaporation, sputtering and chemical vapor deposition which are based on heterogeneous nucleation on the substrates are capable of producing films of nanometer thickness but cannot be used for fabrication of nanostructured films using nanoparticles as the building blocks, since these techniques do not have a supersaturation stage which is essential for creation of the nanoparticles that can serve as the building blocks. The synthesis of nanostructured copper oxide and zinc oxide thin films by oxidizing respectively nanostructured Cu or Zn films deposited by creating the condition for supersaturation of the metal vapors in the deposition chamber of a vacuum coating unit was reported recently [30–32]. We present here the synthesis of CdSe nanocrystal (CdSe NC) thin films from nanoparticle building blocks generated through the condensation of CdSe vapors in an inert gas (nitrogen) at a pressure comparatively larger than the vacuum required for thin film deposition. Films with three different particle sizes were fabricated by varying the gas pressure. These films were characterized using X-ray diffraction (GIXRD), high resolution electron microscopy (HRTEM), atomic force microscopy (AFM), and micro-Raman and UV–Vis spectroscopy. Electrical conductivity of as-deposited and annealed samples of CdSe NC films was measured at different temperatures to study the charge transfer mechanism through the films. Charge transport through the CdSe film samples was further investigated through photocurrent measurements using planar electrode configuration. Also, dark current and photocurrent flow normal to the sample surface was measured. The charge transport in the present samples was interpreted based on a model in which, even though the sizes of the CdSe nanocrystals of the film samples were larger than the Bohr exciton diameter of the material, the film samples were considered equivalent to solid films of CdSe quantum dots, of sizes given by Brus equation, connected together by an outer shell of CdSe material where charge carriers had free movement. This model is capable of explaining the reported observation of improved carrier transport up to almost half of the single-crystal value in CdSe NC films of grain sizes 15 and 22 nm, which are larger than the Bohr exciton diameter, deposited using $[\text{Cd}_2\text{Se}_3]^{2-}$ as a compositionally matched solder to solder the NCs into films [29]. Additionally, measurement of the characteristics of the hetero-junction formed by a CdSe NC film with a similarly deposited Cu_2Se film demonstrated usefulness of the films of the present study for practical applications.

2. Experimental

Nanostructured CdSe thin films were deposited on glass substrates by thermal evaporation of CdSe powder (CdSe 99.995%, Alfa Aesar). Glass substrates were cleaned with detergent, etched for 5 min in dilute nitric acid, degreased with methanol and ultrasonically cleaned with acetone before deposition of CdSe films. Depositions of the films were carried out at appreciably high pressures of 6×10^{-5} , 1×10^{-4} and 2×10^{-4} mbar of an inert gas (nitrogen) and the film samples deposited at these pressures were given the sample codes CS1, CS2 and CS3 respectively. Evaporation of CdSe released the vapors into the inert gas producing supersaturation and causing nucleation of nanocrystals of CdSe in the inert gas. The nanocrystals continued to move towards the substrate due to thermal energy and finally deposited on the substrate as nanostructured CdSe films. The samples deposited at the above mentioned pressures were then heat-treated at a temperature of 200 °C for one hour (sample codes CSA1, CSA2 and CSA3 respectively).

The crystal structure of the film samples was investigated by glancing angle X-ray diffraction (GIXRD) using Bruker AXS D8 advance X-ray diffractometer equipped with Kristalloflex 780, KF.4KE ($\lambda \sim 1.5406 \text{ \AA}$) X-ray source. High resolution transmission electron microscope (HRTEM) images were obtained using a JEOL make JEM – 2100 model instrument operated at an acceleration voltage of

200 kV. The average thickness of the film samples was measured using a Veeco Dektak-6M Stylus Profilometer. AFM measurements were carried out on the film samples using Digital Instruments Nanoscope-E and using Si_3N_4 100 μm cantilever, having a force constant of 0.58 Nm^{-1} in contact mode. Optical transmission spectra of the film samples were recorded using JASCO V-650 double beam spectrophotometer. Raman measurements on the sample were performed using Labram-HR 800 micro-Raman spectrometer with 784-nm diode laser. Magnetic field dependent resistivity measurements (0–9 T), and Hall Effect measurements were carried out in a physical property measurement system (PPMS, Quantum Design DynaCool) using four-probe method.

To study the in-plane charge transport in the CdSe film samples, d.c conductivity measurements were carried out by painting silver coplanar electrodes at a separation of 2 mm on the surface of the CdSe NC films deposited on glass substrates. The separation of 2 mm between the electrodes was measured using a travelling microscope. A Tektronix Dual power supply was used as the voltage source and a Keithley model 2000 multimeter was used for current measurements. I-V measurements showed that the electrical contacts with the film samples were Ohmic. Resistance measurements were carried out by keeping the samples in a cell at a vacuum of ~ 0.001 mbar over the temperature range from 300 to 423 K for an applied voltage of 3 V. Photocurrent measurements were carried out using a Photoemission Tech Inc. make solar simulator at one sun as the source of light. The illuminated area of the sample was $\sim 20 \text{ mm}^2$. To study the charge transport properties normal to the plane of the films, dark current as well as photocurrent measurements were carried. For these measurements, nanostructured CdSe films deposited on ITO glass of sheet resistance 8–12 Ω /square were used. An ITO glass pressed against the CdSe films served as the second electrode. The illuminated area of the sample was $\sim 20 \text{ mm}^2$. To study the usefulness of the CdSe nanocrystal films for fabrication of diodes, the characteristics of the hetero-junction formed by the CdSe film with a similarly deposited Cu_2Se film was investigated.

3. Results and discussion

GIXRD patterns of the CdSe nanocrystal thin films with grain sizes of (a) 31 nm (CS1) (b) 33 nm (CS2) and (c) 43 nm (CS3) are shown in Fig. S1 (See Supplementary material). The patterns show a strong peak at 2θ value of 25.4° and a weak peak at 2θ values of 46° corresponding respectively to the (002) and (103) reflections of hexagonal CdSe (JCPDS file no. 01-071-4772) [33]. The d-values corresponding to the (002) and (103) reflections in Fig. S1 are 3.50 and 1.98 \AA respectively in close agreement the standard d-values of 3.51 and 1.9813 \AA for the hexagonal CdSe structure. The GIXRD patterns of the nanostructured CdSe film samples heat-treated at 200 °C (Fig. S2, See Supplementary material) show the same peaks as in Fig. S1 with slightly improved intensity indicating that the crystal structure of the samples remained the same as that of the as-deposited sample and that the material of the films was stable in air at elevated temperatures. While the (100) peak is the most intense peak in the standard pattern of CdSe, this peak is absent in the GIXRD patterns in Figs. S1 and S2 (See Supplementary material), and the (002) peak appears as the strongest peak indicating an oriented growth of the films along the [002] direction normal to the surface of the deposited films. The (002) peaks of all the samples are enlarged and shown together in Fig. S3 (see Supplementary material). The FWHM of the (002) peak was used to determine the grain sizes (D) of the films using the Debye-Scherrer formula [34]: $D = \frac{k\lambda}{\beta \cos \theta}$ where D is the mean grain size, k is a geometric factor ($= 0.89$), λ is the X-ray wavelength (1.5408 \AA for Cu- $K\alpha$), β is the FWHM of diffraction peak and θ is the Bragg diffraction angle. The grain sizes of the samples deposited at pressures of 6×10^{-5} , 1×10^{-4} and 2×10^{-4} mbar were respectively 31, 33 and 43 nm, and 37, 38 and 45 nm for the as-prepared and heat-treated (200 °C) samples. The variation of the size of the primary CdSe nanoparticles with m/p where m is the mass of CdSe evaporated and p

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