Journal of Alloys and Compounds 509 (2011) 10003–10006

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: www.elsevier.com/locate/jallcom

Studies of photovoltaic properties of nanocrystalline thin films of CdS–CdTe

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ARTICLE INFO

Article history:
Received 5 April 2011
Received in revised form 31 July 2011
Accepted 1 August 2011
Available online 10 August 2011

Keywords:
Photovoltaic
Nanocrystal
Photoluminescence
Raman spectroscopy

ABSTRACT

Nanocrystals of CdS and CdTe were synthesized by aqueous chemical route. From the optical absorption spectra the particle sizes (diameter) were estimated to be around 7 and 4 nm for CdS and CdTe, respectively. The photovoltaic device was fabricated using these nanocrystalline materials on an indium tin oxide (ITO) coated glass substrate using a spin coating method. From the room temperature photoluminescence study a drastic quenching of photoluminescence the CdS–CdTe thin film was observed. Light intensity dependent current–voltage measurements of CdS–CdTe thin film shows photovoltaic effect; with increase in light intensity the current density increases, however, the open circuit voltage does not show any change. The low efficiency of the device has been explained on the basis of the defects and diffusion of Te ions into CdS.

1. Introduction

Semiconductor nanocrystals are of great research interest due to quantum confinement of charge carriers within the spatial dimension of the nanocrystals [1–3]. As a consequence, the band gap of these materials can suitably be tuned by controlling the size of the nanocrystals. Due to their size tunable optical as well as physical and chemical properties, nanocrystals are the potential candidates for various applications, such as optoelectronics, photovoltaics, solid state laser, etc. [4–6]. The progress in nanotechnology in the field of photovoltaic has been intensified in the last few decades; however, there are still challenges over controlled fabrication of solar cell based on semiconductor nanomaterials and improvement of the efficiency [7–10]. Thin films of *n*-type CdS and *p*-type CdTe have been reported to show photovoltaic effect with efficiency of up to 16.5% [11]. Nanocrystals of CdS, CdSe and CdTe have been separately incorporated with other large band gap materials, such as TiO_2 and ZnO which show improved photovoltaic effect [12–14]. Moreover, quantum dots of CdS and CdTe have been used to fabricate solar cells [15,16]. However, attempts to fabricate and study of photovoltaic based on quantum dots of CdS and CdTe is still lacking. In this report, we have synthesized nanocrystals of CdS and CdTe and investigate their photovoltaic properties.

2. Experimental details

CdS nanocrystals were synthesized at room temperature by chemical precipitation route in aqueous medium. All the chemicals were purchased from Alfa Aesar with 99.99% purity and used directly without further purification. For CdS nanoparticles, aqueous solutions of $Cd(CH_3COO)_2$ (0.5 mmol) was prepared. While stirring this solution, 25 ml of Na_2S (0.5 mmol) aqueous solution was added slowly which resulted in the precipitation of CdS nanoparticles [17]. CdTe nanocrystals were synthesized via aqueous chemical route as reported elsewhere [18]. 2:1 molar ratio of $NaBH_4$:Te was taken in 2 ml aqueous solution and kept under ice for 3 h. 0.704 g of $Cd(ClO_4)_2$ with desire amount of thioglycolic acid (TGA) and thioglycerol (TGOL) were dissolved in 500 ml of water. To the above solution $NaBH_4$:Te was added drop by drop. The reaction was maintained at 100 °C and after 1 h of reaction samples were collected. The precipitates were removed after washing with water several times and dried. CdS thin films were prepared on ITO coated glass substrate (8 mm × 6 mm) by spin coater at 2000 rpm for 180 s (20 drops of CdS aqueous solution) and after each coating the film was dried at 120 °C. The thickness of CdS was around 100 nm. Similarly, CdTe nanocrystal thin films were deposited on previously deposited CdS layers by repeating the above process. The thickness of CdTe was around five times thicker than that of CdS layer. The Raman scattering measurements were carried out using 514.5 nm line of Ar ion laser as the excitation source and analyzed using a double-monochromator (Jobin-Yvon T64000), equipped with liquid nitrogen cooled charge coupled device (CCD) detector. Room temperature photoluminescence was recorded using the above Raman instrument and the same laser was used as excitation energy source. UV–visible absorption spectrum was recorded using a UV spectrometer lambda 2S in which xenon lamp was used as the excitation source. The cross-sectional image of the solar photovoltaic device was obtained using a field emission scanning electron microscope (FESEM-JEOL JSM-7500F SEM). The current–voltage measurements of the

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doi:10.1016/j.jallcom.2011.08.011

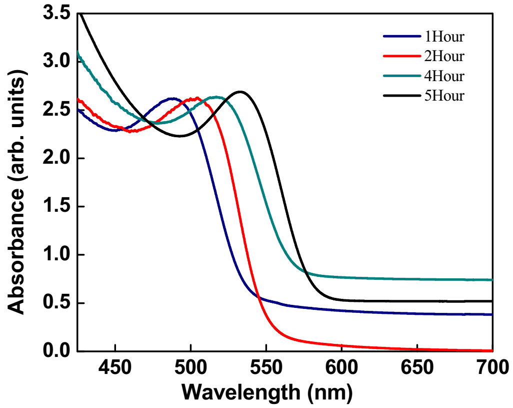

Fig. 1. Room temperature absorption spectra of CdTe nanocrystal as a function of particle size.

photovoltaic device were performed using a Keithley-6517 instrument.

3. Results and discussion

Fig. 1 shows the optical absorption spectra recorded for CdTe nanocrystal solution taken at different time (1, 2, 4 and 5 h) of its preparation. It can be seen from Fig. 1 that with the increase in reaction time the absorption peak position shows a systematic red shift. (For interpretation of the references to color in this text, the reader is referred to the web version of the article.) This essentially means that during initial stage of reaction smaller nanocrystals are formed and gradually their size increases with time. One can also see that there is a minute difference in the FWHM of the absorption peaks which could be due to small polydispersity in the particle size distribution. Here we want to point out that bulk CdTe has a band gap of 1.44 eV (861 nm) [19]. However, in our case we observed the optical absorption peak from 500 to 550 nm which correspond to the energy of 2.48–2.24 eV respectively. Such a large increase in bandgap is essentially due to quantum confinement of charge carriers in nanocrystals. We estimate the particle size (diameter) by using the Brush's equation which is given by [20],

$$E^* = E_g^{bulk} + \frac{\hbar^2\pi^2}{2er^2}\left(\frac{1}{m_e m_0}+\frac{1}{m_h m_0}\right) - \frac{1.8e}{4\pi\varepsilon\varepsilon_0 r} - \frac{0.124e^3}{\hbar^2(4\pi\varepsilon\varepsilon_0)^2}\left(\frac{1}{m_e m_0}+\frac{1}{m_h m_0}\right)^{-1} \qquad (1)$$

where E_g^{bulk} is the band gap of bulk material, m_e and m_h are the mass of electron and hole, respectively, $2r$ is the diameter of the nanoparticle. The particle size (diameter) was found to be around 4 nm for the band gap of 2.24 eV. For photovoltaic fabrication we used the solution containing 4 nm CdTe nanoparticles. Fig. 2 shows the absorption spectra of CdS nanoparticles. The absorption peak was found to be at 430 nm corresponding to the energy of 2.88 eV. The observed band gap of CdS nanoparticles is 0.68 eV larger than that of the bulk CdS which has a band gap of 2.2 eV. The blue shift of the band gap is essentially due to quantum confinement in small nanocrystals [20]. We also calculate the particle size (diameter) using Eq. (1) and which was found to be 7 nm. The band gap of both CdS and CdTe nanocrystals, those were used to fabricate the photovoltaic device in the present study, are compared in Fig. 2.

Both CdS and CdTe are direct band gap semiconductor materials. Fig. 3 shows the room temperature photoluminescence (PL) of CdTe and CdS nanocrystals recorded independently. One can see that for nanocrystals of CdTe the PL peak position is around 2.24 eV which is close to its absorption peak position. This indicates that the CdTe nanocrystals have lesser defect states. On the other hand, in case of CdS nanocrystals the PL peak position is around 2.17 eV which is much smaller than its absorption peak position. This could be due to the fact that CdS nanocrystals may have some defect states in between the conduction and valance bands and these defect states usually arise due to Cd or S vacancy [21]. These defects states account for the non-radiative transition processes and hence band to band transition is less probable than transition from defect level

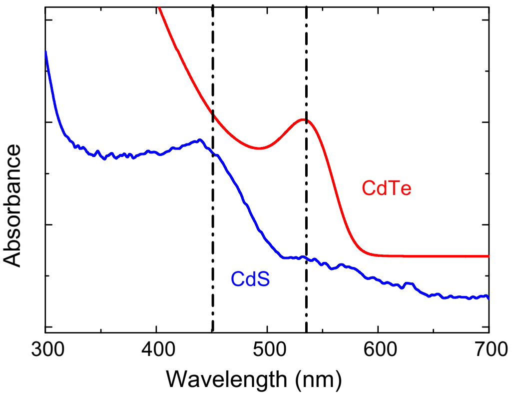

Fig. 2. Comparison of optical absorption of CdTe (4 nm) and CdS (7 nm) nanocrystals. These nanocrystals are used to fabricate photovoltaic device.

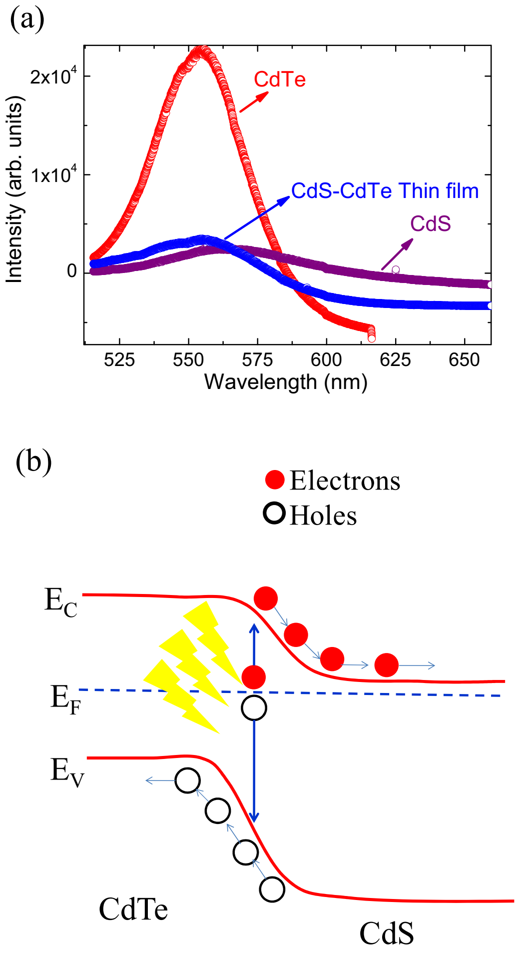

Fig. 3. (a) Comparison of room temperature photoluminescence of CdTe (4 nm), CdS (7 nm) and CdTe–CdS thin film made out of 4 nm CdTe and 7 nm CdS. (b) Schematic representation of band-alignment between CdS and CdTe and the process involving electron hole generation.

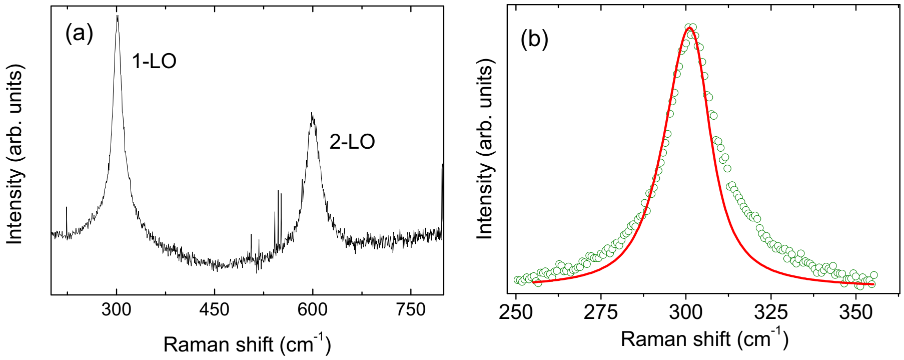

Fig. 4. (a) Raman spectra of CdS nanocrystals. (b) Comparison of Raman spectra (open circles) of 1-LO phonon of CdS with that of calculated (solid curve) Raman lineshape.

to valence band [21]. Thus the observed PL band can be attributed to defect related transitions. A room temperature PL spectrum of the thin film, consisting of CdS at the bottom and CdTe at the top, is also shown in Fig. 3(a). It is found that the PL intensity was quenched drastically compared to pure CdTe nanocrystals. Similar behavior in quenching of PL has been reported in other photovoltaic materials [22]. The proper band alignment between CdS and CdTe accounts for charge carrier separation, as sequence quenching of PL is observed. The photovoltaic effect involves three processes; optically generated electron-hole pairs, electron–hole pair separation with an internal electric field. This has been shown schematically in Fig. 3(b), the band alignment between CdS and CdTe is also shown.

In order to further confirm the presence of defects in CdS nanocrystals we perform Raman scattering measurements in CdS nanocrystals. Fig. 4(a) shows the room temperature Raman spectra of CdS nanocrystals, one can see that there are two distinct peaks around 298 and 594 cm^{-1}. These two peaks correspond to the 1-longitudinal optical (LO) and 2-LO phonon modes of CdS, the latter is a second order Raman scattering process. The first order LO phonon Raman spectra was analyzed using phonon confinement model which is given by [17]

$$I(\omega, d) = \int \frac{\left|C(q,d)\right|^2}{[\omega - \omega(q)]^2 + (\Gamma_0/2)^2} d^3q \tag{2}$$

where $C(q, d)$ is the Fourier transformation of the confinement function, $\omega(q)$ is the phonon dispersion curve and Γ_0 is the natural linewidth of zone-center optical phonons in bulk CdS. We calculate the Raman lineshape for CdS nanocrystals of size 7 nm using Eq. (2) and the calculated line shape is compared with that of the experimental data which is shown in Fig. 4(b). It can be seen that the calculated Raman lineshape does not match well with the data. Similar results have been reported in other nanocrystals and the disagreement between the calculated Raman lineshape and the data has been explained on the basis of defects [23,24]. Along with phonon confinement, defects also cause broadening in the Raman spectra. This confirms that our CdS nanocrystals have associated defects.

Fig. 5(a) shows the cross-sectional field emission scanning electron microscope image of the photovoltaic device. The bottom is the glass substrate and on top of it a clear thin film of ITO (∼100 nm thickness) can be seen. The second layer from the glass substrate is a thin film of CdS nanocrystals of about 100 nm in thickness. A distinct third layer of CdTe nanocrystals over CdS thin film can be seen and the thickness is about 500 nm. Fig. 5(b) shows the schematic representation of the present photovoltaic configuration. Here the ITO works as bottom electrode and a 20 nm thick platinum deposited on CdTe thin film is used as top electrode. The light was focused from the bottom of the glass substrate for photovoltaic measurements. Fig. 6 shows the current–voltage response for dark and illuminated conditions. The open circuit voltage V_{OC} and the short circuit current density J_{SC} were found to be 0.112 V and 10 nA cm^{-2} for light density of 2.22 mW cm^{-2}. *I–V* measurements were performed by varying the intensity of the light ranging from 2.22 to 6.66 mW cm^{-2} and are shown in Fig. 7. One can see that with increases in light intensity the current density increases, however, the open circuit voltage does not show any change. The plot of current density as a function of incident light intensity varies linearly, as shown in the inset of Fig. 7. Recently Fan et al. [25] have reported an improved efficiency of CdS–CdTe based photovoltaic consisting of CdS nanowires and CdTe quantum dots. In our case, the efficiency is much less than that reported. Now we will discuss the possible mechanism that accounts for the lesser efficiency of our device. The efficiency losses in solar photovoltaic arises due to the fact that during energy conversion process photons of specific energy ($h\nu < E_G$) cannot fully be converted into

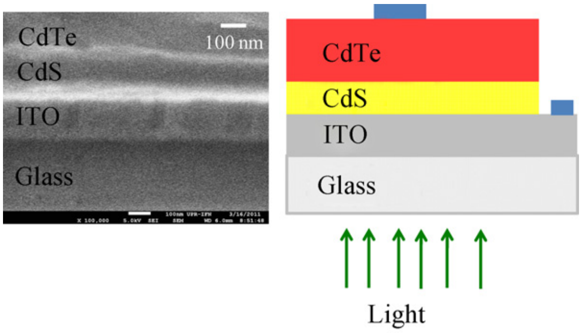

Fig. 5. (a) Cross-sectional FESEM image of CdS–CdTe photovoltaic device and (b) schematic view of different layers in the CdS–CdTe photovoltaic device.

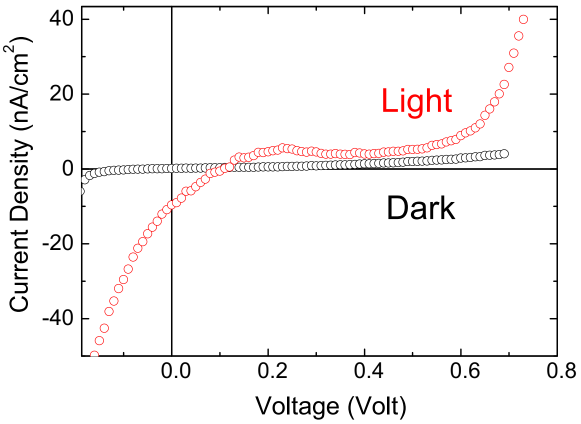

Fig. 6. Current–voltage response of CdS/CdTe thin film in dark and light conditions.

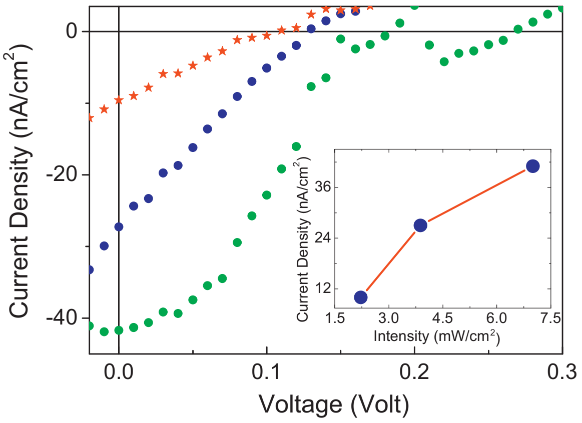

Fig. 7. Current–voltage response of CdS/CdTe thin film photovoltaic as a function of incident light intensity. Inset shows the plot of current density of the device verses incident light intensity.

electrical energy. However, the introduction of intrinsic defects that create sub-band gap, can easily convert photon energy into electrical energy. In the present case, as discussed earlier (from the PL and Raman studies on CdS nanoparticles), intrinsic defects associated with the CdS nanoparticles can possibly alter the electronic properties of CdS nanoparticles. Thus, one expects improved efficiency of the solar photovoltaic, but in contrast, we observed a low efficiency (Fig. 7). Secondly, due to large surface area of small nanoparticles it is highly possible that at the interface of CdS and CdTe, Te can diffuse into CdS. It has been reported that the diffusion of Te into CdS results in reduction in the efficiency of the photovoltaic device [26].

4. Conclusions

In conclusion, CdS and CdTe nanocrystals were synthesized by chemical route. The particle sizes were estimated to be 4 and 7 nm respectively. Solar photovoltaic device was prepared using spin coating of CdS and CdTe thin films on ITO. The current density varied linearly with increase in the light intensity. The low efficiency of the photovoltaic device is possibly due to diffusion of Te into CdS nanocrystals.

Acknowledgements

This research was made possible by funds from the Institute for Functional Nanomaterials (NSF Grant # 1002410), PR NASA EPSCoR (NASA Cooperative Agreement # NNX07AO30A and NNX08BA48A), and PR DOE EPSCoR (DOE Grant # DEFG02-08ER46526). We would like to acknowledge the help of Mr. Oscar Resto for the help with FE-SEM.

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