JNS 3 (2013) 17- 23

Journal of
NANOSTRUCTURES

JNS NANOSTRUCTURES
JNS.kashanu.ac.ir

Effect of PbS Film Thickness on the Performance of Colloidal Quantum Dot Solar Cells

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Article history:
Received 11/2/2013
Accepted 17/4/2013

Keywords:
Nanocrystals
Lead sulfide
Photovoltaic devices
Colloidal quantum dot
Solar cells

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Abstract

Colloidal quantum dots offer broad tuning of semiconductor band structure via the quantum size effect. In this paper, we present a detailed investigation on the influence of the thickness of colloidal lead sulfide (PbS) nanocrystals (active layer) to the photovoltaic performance of colloidal quantum dot solar cells. The PbS nanocrystals (QDs) were synthesized in a non-coordinating solvent, 1-octadecene, using oleic acid (OA) as the ligand. It was found that the device with 50 nm of thickness of active layer showed a high Efficiency (η) of 0.667 under simulated Air Mass 1.5 Global (AM 1.5G) irradiation (100 mW/cm^2) compared to the device with low thickness of active layer.

1. Introduction

Increasing worldwide demand for energy and limited fossil fuels reserves on the planet require development of reliable and renewable energy sources. Among the various technologies available nowadays, photovoltaic energy is believed to be one of the cleanest ways in achieving this goals. However, efforts are still needed to make photovoltaic cost competitive over other established technologies for energy production [1]. Integration of nanostructured materials in photovoltaic devices has been demonstrated to open the possibilities to develop low-cost solar cells [2]. Quantum dots (QDs) are tiny particles of semi-conductors that are easy and cheap to produce and can be used in solar cells to conduct the electrons [3]. Quantum dots have the potential to greatly improve solar technology and make solar energy a more viable option as an energy source. The next generation of solar cells being researched is focused on efficiency and low cost with quantum dots being the primary point of interest. Quantum dots are the main focus for next generation research because of their unique quantum properties and ability to cover both goals of the next generation of solar cells. The goals of next generation solar cells are to be cost-effective and efficient. The quantum dots are cost-effective in two respects. First, they can be produced rather inexpensively and second, they produce more energy [4]. Quantum dots are not only cost-effective, but are also versatile, highly-efficient in conducting an electrical current, and are an ethical option for the next generation of solar cells. In recent years, inorganic semiconductor nanocrystals (also known as Quantum Dots, QDs) have been found to be promising for next generation solar cell [5-6].

Colloidal semiconductor nanocrystals (NCs) have attracted tremendous attention, because of their distinct, size-dependent optical, electronic, and mechanical properties [7-8], as well as their promising technological applications in optoelectronics [9-10], and etc. Lead chalcogenides (PbS, PbSe and PbTe) and their alloys have been the subject of considerable research due to the technological importance of these materials, in crystalline and polycrystalline forms. Lead chalcogenides have much in common in their physico- chemical properties: they are isomorphous, have the same type of chemical bonding, can be prepared by similar methods, have similar phase diagrams, and can be doped in a similar manner [11]. Lead sulfide (PbS) in the bulk form is a narrow and direct band gap semiconductor (0.41 eV at room temperature) with a cubic rock-salt type structure and relatively large excitation Bohr radius (18 nm). These properties make PbS suitable for IR detection application [12]. PbS has also been used in many fields such as Pb^{2+} ion selective sensors [13], solar absorption, photoresistance, quantum dot solar cell [14-17], and solar control coatings [18], photography [19]. To date, extensive researches have been devoted to produce PbS by various deposition processes and methods. Conventionally, chemical bath deposition (CBD) [20], atomic layer epitaxy (ALE) [21], photochemical deposition (PCD) [22], successive ionic layer adsorption and reaction (SILAR) [23], electrodeposition [24-27], hot injection [28].

For non-water-soluble colloidal PbS QDs, the hot-injection approach reported by Hines and Scholes [29] seems to be the best to engineer high-quality QD ensembles. However, there is a limited body of literature documented on the syntheses, with little information on synthetic parameters affecting the optical properties of the product. This hot-injection method was conducted by heating a mixture of lead oxide (PbO) and oleic acid (OA, as capping ligands) in octadecene (ODE) at 150 °C under Ar for one hour followed by the injection of a solution of $(TMS)_2S$ (sulfur source) in ODE at 150 °C. After the hot injection, the growth was kept either at 80-140 °C or room temperature. It was declared that the growth temperature lower than 150 °C was preferred in order to separate the nucleation and growth for the absence of rapid defocusing of the size distribution. The resulting PbS QDs exhibited bandgap absorption ranging from 800 to 1800 nm.

Scholes and co-workers first reported the synthesis of size-tunable PbS nanocrystals using PbO and $(TMS)_2S]$ as the lead and sulfur precursors, respectively [8]. Several attempts have been reported to modify the recipe to enhance the passivation of the nanocrystals, such as diluting oleic acid (OA) in 1-octadecene (ODE), and introducing trioctylphosphine (TOP) as a co-ligand [30, 31]. Recently, Sargent et al. reported high-performance PbS nanocrystal-based solar cells (3.6%) by replacing the oleic acid with a shorter and tightly bound dithiocarbamate derivative as the surface ligand [8]. Nozik et al. has demonstrated long-term stable PV devices that employ PbS/ ZnO heterojunctions [32]. However, no systematic study has been reported on the correlation between the thickness of colloidal lead sulfide (PbS) nanocrystals and the performance of the resulting electronic devices. In this work, we synthesis PbS nanocrystals in a non-coordinating solvent, 1-octadecene, using oleic acid (OA) as the ligand. The nanocrystals synthesized were used to fabricate photovoltaic devices with different thickness of active layer. It was found that the device with 50 nm of thickness of active layer represented a high Efficiency (η) of 0.667.

2. Experimental section

2.1. Apparatus and chemicals

Lead(II) oxide (PbO) (99.999%), 1-octadecene (ODE) (90%), oleic acid (90%), bis(trimethylsilyl) sulfide [$(TMS)_2S$], anhydrous 2-propanol (99.5%), anhydrous hexanes (99%), anhydrous chloroform (99%), anhydrous acetonitrile (99.8%) and 1,2 ethanedithio (EDT) are all purchased from Sigma-Aldrich Co. and used as received. An indium tin oxide (ITO) coated glass substrate from Dyesol with a sheet resistance of 15Ω/sq was used.

The quantum dot solar cells performance was evaluated in AM 1.5 simulated light (Luzchem-Solar) using a potentiostat/ galvanostat (IVIUM, Compactstat).

2.2. Synthesis of PbS Nanocrystals

PbO (150 mg), oleic acid (2.5 mL), were loaded in a 100 mL three-necked flask. The mixture was degassed, after 15 minutes and 18.2 mL of ODE added in flaks and heated up to 100 °C and vacuumed for 1 h to form lead oleate and dry the solution. The solution was cooled down to 90 °C and $(TMS)_2S$ (70 μL, 1.0 mmol) was swiftly injected into the flask with vigorous stirring under dry nitrogen. The reaction mixture was kept at 85 °C for 3.0 min and quenched by pouring the mixture into anhydrous 2-propanol (50 mL) under N_2 protection. The products were centrifuged and the mixture of PbS nanocrystals and unreacted lead oleate were collected. The nanocrystals were then redissolved in 1.6 mL anhydrous hexane, and the undissolved lead oleate was removed by centrifuging at 4000 rpm for 3 min. The nanocrystals were reprecipitated by adding 1.6 mL acetone (dried over molecular sieves) into the obtained supernatant. The PbS nanocrystals were collected by flocculating the materials with a mixture of acetone and hexanes (1:1) and centrifuging twice. The nanocrystals were dried under a stream of nitrogen and then dissolved in anhydrous chloroform for Photovoltaic characterization. Fig. 1A and 1B illustrates the distribution of PbS Nanocrystals particle size observed by SEM and absorption spectra of PbS nanocrystals in tetrachloroethylene, respectively.

2.3. Photovoltaic Device Fabrication

Schottky-type PbS nanocrystal photovoltaic devices were fabricated on ITO coated glass substrate. Immediately prior to device fabrication, the ITO glass was cleaned by ultrasonic baths of organic solvents (acetone and isopropanol) for 15 min. A 5 mg/mL solution of PbS-OA in chloroform was used to prepare the active layer. The cross-linked PbS nanocrystal thin films were fabricated with a sequential layer-by-layer spin-casting method. Each NC layer was spin-cast at 2000, 5000 rpm for 30s. After casting the NC layer, the substrate was soaked into a 0.02M EDT in acetonitrile for 30s, then immediately removed from the solution and spun at 2000, 5000 rpm for 30s to dry it quickly. The desired film thickness was achieved by repeating this process. Afterward, the sample was transferred to an evaporation chamber without exposure to the air. Finally, 40 nm of Al were thermally evaporated on top of the NC layer to form the cathode. The general structure of photovoltaic cells was ITO/PbS-EDT/Al. In Fig. 2a, the device structure of the constituent materials is shown.

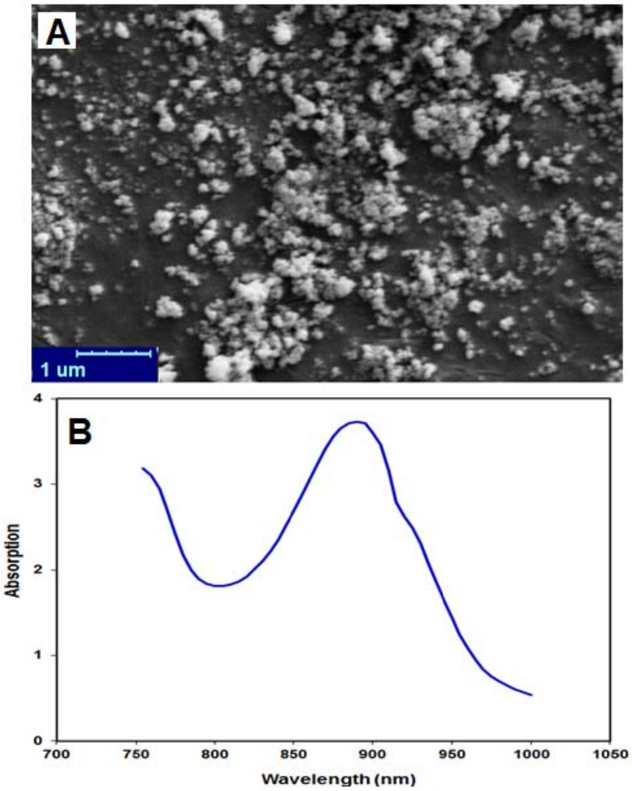

Fig. 1. SEM image of the PbS NCs (A) and Absorption spectra of PbS nanocrystals in tetrachloroethylene measured as synthesized.

3. Results and discussion

The synthesis of PbS nanocrystals was carried out by lead oleate and bis (trimethylsilyl) sulfide as precursors. The lead and sulfur precursors react and form bulk-like particles easily. Thus the key to a successful PbS QDs synthesis lies in a controlled nucleation event and subsequent particle growth. The stabilizing ligand and growth solvent are crucial in this regard because they influence ~~of~~ the reactivity monomer species and hence aid nanocrystal to growth. In this case oleice acid is a suitable material. PbO readily dissolvent in it to form lead oleate precursor, and the PbS nanocrystals are easily precipitated out of it with polar solvents. The poor conductivity of oleate-capped nanocrystal films can be overcome by exchanging the ligands with 1,2-ethanedithio. This is useful for optimizing injection of electrons and holes into the nanocrystals. Such a strategy was used to improve electroluminescence from PbS nanocrystal films [33]. 1,2-ethanedithio (EDT) as the cross-linker to replaces oleic acid and bridge the NCs. This reaction probably occurs via nucleophilic attack of oleate by EDT, followed by Pb-S bond formation and desorption of oleic acid, or by the dissociative adsorption of EDT on the NC surface to yield adsorbed $HS(CH_2)_2S$- and hydrogen, again followed by desorption of oleic acid. As a result of oleate removal, the NCs move closer together, the NC superlattice becomes disordered, and the films crack extensively [17].

Fig. 2b shows a typical energy band diagram of the Schottky cell. The cell is described with band bending at the interface of a metal and a p-type semiconductor. This band bending makes a depleted region due to a charge transfer from the electron-accepting contact to the p-type QDs film. Photovoltaic performance was investigated by changing the thickness of the active layer (CQD film) in Schottky-type PbS nanocrystal photovoltaic devices.

Photovoltaic performance was investigated by changing of the thickness of the active layer (CQD film) in Schottky-type PbS nanocrystal photovoltaic devices. So three different Photovoltaic devices were fabricated by spin-cast at 5000 rpm for 30s with a thickness 20 nm of CQD film (A) and 2000 rpm for 30s with thickness 40 nm and 50 nm of CQD film (B and C) respectively.

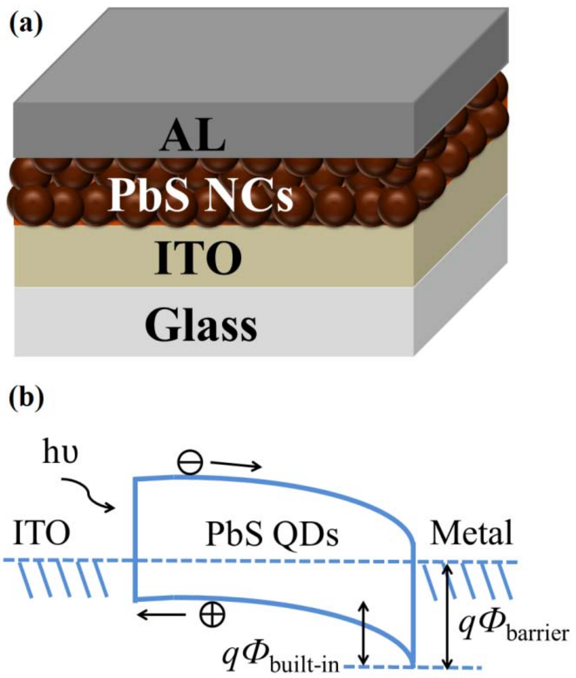

Fig. 2. (a) Scheme of a Schottky device and (b) its equilibrium band diagram. Band bending occurs at the interface between the QDs and evaporated negative electrode.

Fig.3 is obtained from the J-V characteristics of three cells which are fabricated with various thickness of active layer. Thickness values are 20, 40 and 50 nm for A, B and C respectively. As it can be seen, proportionally to the augmentation of the thickness, the performance of the devices increases (Table 1).

When the thickness of the active layer was increased, obtained efficiency of the devices were 0.667, 0.572 and 0.131 for the thickness of 20, 40 and 50 nm, respectively.

Photovoltaic performance of shows that fill factor is enhanced in the device C compared to the device A and B. Under short-circuit conditions, the device is nearly fully depleted and therefore the electric field acts upon all photogenerated carriers throughout the thickness of the device [17].

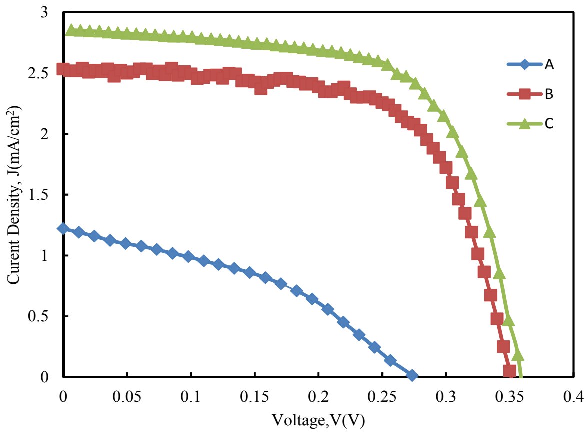

Fig. 3. Current-voltage performance under AM 1.5 conditions for various thickness of the active layer thickness values from (A) to (C) are 20, 40 and 50 nm respectively.

The resultant Schottky barrier favors the extraction of electrons from the device while presenting a barrier for hole withdrawal. From the perspective of charge-carrier transport, drift and diffusion play an important role in the operation of these devices. Achieving high efficiency in these cells requires carrier extraction before they recombine. This needs that the mobility of each carrier exceeds $\varphi_{\text{built-in}}/d^2$, where the $\varphi_{\text{built-in}}$ is the built-in potential, τ is the carrier lifetime and d is the device thickness [28]. The measured mobility in best situation is 2×10^{-3} cm^2/Vs which makes QDs so attractive for Schottky devices. The barrier height of the built-in potential can be estimated from the relation: $q\varphi_{\text{built-in}} = E_g - q(\varphi_m - \chi)$,

Where E_g is the bandgap of the semiconductor QDs, q is the charge of an electron, φ_m is the work function of the metal and χ the electron affinity of the semiconductor [34].

Table 1. Summary of photovoltaic performanc parameters for the three fabricated devices

Device	Thickness of CQD film (nm)	V_{oc} (V)	Jsc (mA/cm^2)	FF	η (%)
A	20	0.27	1.21	0.40	0.131
B	40	0.35	2.53	0.40	0.572
C	50	0.36	2.85	0.64	0.667

4. Conclusion

We showed that in PbS colloidal quantum do devices, thickness of colloidal lead sulfide (PbS nanocrystals (active layer) is the main factor i Schottky-CQDs solar cell. Increasing the thicknes of active layer up to 50 nm leads to highe photovoltaic conversion efficiencies. The devic with 50 nm of thickness of active layer represente a high Efficiency (η) of 0.667 under simulated Ai Mass 1.5 Global (AM 1.5G) irradiation (10 mW/cm^2) compared to device with low thicknes of active layer. It should be noted that, the cell i not fully optimized and better results can b anticipated.

Acknowledgment

The authors wish to thankful the Yazd Universit Research Council, IUT Research Council an Excellence in Sensors for financial support of thi research.

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