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Thin film photodiodes fabricated by electrostatic self-assembly of aqueous colloidal quantum dots

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ABSTRACT

We demonstrate a thin film photodiode structure consisting of multi layers of colloidal quantum dots (QDs) which has application in photovoltaics and photodetection. The CdTe QDs with either positively or negatively charged capping ligands are self-assembled layer-by-layer on an indium tin oxide (ITO) substrate by electrostatic attraction in aqueous solution. A photolithographically patterned photoreisist window defines the device active area and an evaporated aluminum (Al) thin film serves as the top electrode. The built-in electric field due to the work function difference between Al and ITO separates photo-excited electron-hole pairs and generates photocurrent. Since the ligands used for QD synthesis are short (less than 0.5 nm), no additional steps of ligand exchange or annealing is needed for enhancing the thin film photoconductivity. Thiol passivation and self-assembly in an inert environment help reduce surface traps, leading to less fermi-level pinning which also improves the device performance.

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1. Introduction

Colloidal semiconductor nanocrystal/quantum dots (QDs) are of great interest to photovoltaic research due to their size-dependent band gap, solution-processable fabrication and the potential for efficient conversion of solar energy [1,2]. Recently, all-inorganic Schottky junction solar cells based on PbSe or PbS QDs have shown exceptionally high external quantum efficiency up to 65% in the visible wavelength range and power conversion efficiency more than 4% in the infrared region [3–5]. However, in order to achieve efficient charge transport between adjacent QDs, these devices require complicated solution-phase [4] or solid-state [3,6] post-chemical treatment that replaces or removes long alkyl chain ligands, such as oleic acid (OA) and trioctylphosphate oxide (TOPO), on the as-prepared QD surface. Some devices also require high temperature annealing to further remove these insulating organic molecules between QDs [7]. In this work, we demonstrate thin film photodiodes fabricated by electrostatic layer-by-layer self-assembly of QDs that are inherently capped with short ligands during the synthesis. Therefore, no ligand exchange, ligand removal or annealing is needed to enhance the thin film photoconductivity. This method simplifies the preparation of QD thin films, making it easier for large-area device application, and facilitates its integration with substrates which are sensitive to prolonged chemical treatment or vulnerable to high temperature annealing. It has been demonstrated previously that CdSe/Au nanoparticle photodetectors can be fabricated directly on a complementary metal-oxide-semiconductor (CMOS) silicon chip based on this method [8].

In addition to shortening of inter-dot distance, surface passivation of QDs has shown beneficial effects on their photovoltaic device performance [6,9]. It has been reported that thiol treatment can enhance external quantum efficiency by reducing mid-band gap states, which serve as recombination centers, and increase open circuit voltage by reducing metal-semiconductor junction interface states, which result in fermi-level pinning [9]. We use two kinds of thiol ligands for CdTe QDs synthesis in this work, 2-mercaptoethanol (positively charged) and thioglycolic acid (negatively charged). Both kinds of molecules have one thiol-terminated end which forms covalent bond with Cd and passivates the CdTe QD surface.

In terms of compatibility with existing fabrication processes, the electrostatic layer-by-layer self-assembly method used in this work shows higher flexibility than conventional QD deposition techniques, such as spin-coating, drop-casting and layer-by-layer dip coating [3,6]. In order to achieve uniform thickness, highly evaporative organic solvent, such as hexane or chloroform, needs to be used in these methods. However, the solvent is reactive with underlying organic layers, such as a photoreisist layer for photolithographic patterning. Therefore, by organic solution-processing, it is hard to fabricate structures that require patterning, such as side-by-side pixels or vertical heterojunctions. In contrast, since the electrostatic layer-by-layer self-assembly process is conducted in water, there is no solvent incompatibility issue when fabricating two dimensional arrays or multi-layer structures composed of colloidal QDs. In our...
previous work [10], we have demonstrated using electron beam lithography to define the pixel position and size of colloidal QD photodetectors.

In this work, we fabricate a metal-intrinsic-metal photodiode structure composed of a CdTe QD thin film sandwiched between an indium tin oxide (ITO) substrate and an aluminum (Al) thin film, both of which serve as electrodes. The built-in electric field due to the work function difference between ITO and Al separates the photo-excited electron-hole pairs, generating the photocurrent. Whereas, for the photodetectors in our previous work [10], the effect of work function difference cancels each other due to the opposite orientation of the two identical photodiodes. As a result, its photocurrent is mainly driven by external applied bias and amplified by photoconductive gain. The device thus achieved the function of photodetection only but not photovoltaic. Furthermore, here we greatly increase the efficiency by improving the dialysis method for positively charged CdTe QD capping unimpaired and reduce the QD surface states resulting from oxidation during the fabrication.

2. Experimental section

2.1. Substrate preparation

An ITO/aluminosilicate (20 nm/0.7 mm in thickness) chip (1.5 cm at each side) is taken to photolithography to open a 100 μm gap that separates two ITO substrates, as shown in Fig. 1(a). Subsequently, the chip is treated with oxygen plasma at 1.45 × 10^4 Pa and 40 W for separates two ITO substrates, as shown in Fig. 1(b). Subsequently, the chip is treated with oxygen plasma at 1.45 × 10^4 Pa and 40 W for

2.2. Positively and negatively charged CdTe QDs synthesis

The synthesis of colloidal CdTe QDs in aqueous solution is mainly based on a previous report by Gaponick et al. [11], with selection of extremely short ligands, 2-mercaptoethylamine (MA) for positively charged and thioglycolic acid (TGA) for negatively charged ligands. The process is similar to our previous work [10] but with modified conditions. The precursors are formed in the ratio of Cd^{2+} : Te^{2-} : ligand = 1 : 0.5 : 2.4 under appropriate pH conditions (11.6 for TGA and 5.8 for MA), and the concentration of Cd^{2+} is kept at 37.6 mM for all samples. The QDs are grown by refluxing the precursor mixture at 100 °C and the particle size is determined by refluxing time which is controlled to be 24 h for both MA- and TGA-CdTe QDs. We then perform post-synthesis purification which is important to effective electrostatic self-assembly. For MA-CdTe QDs, since the amine capping is relatively unstable, we use dialysis to remove non-reacted precursors from the QD solution. The dialysis is performed with membrane molecular weight cutoff=25,000, constant control of pH ~6 and degassing with nitrogen in solution for 6 h. For TGA-CdTe QDs, a common precipitation procedure is applied. It starts with adding 2-propanol drop-wise to the as-prepared TGA-CdTe QDs solution under stirring until it becomes turbid. Then the solution is taken to centrifugation at 3000 rpm for 3 min, followed by decantation of supernatant. The precipitate is redispersed in deionized water to the original volume. Finally, the pH value of all purified QD solutions is adjusted to ~7 using diluted HCl or NaOH to obtain the best assembly result.

2.3. Electrostatic Layer-by-layer self-assembly

The self-assembly of QDs is performed by pipetting the QD solution (50 μL) on one side of the ITO substrates, as shown in Fig. 1(b). After waiting an hour in dark, the chip is rinsed with copious amount of deionized water and dried in vacuum. Since the ITO is modified with positively charged amines from APTES molecules, the first deposition
is negatively charged TGA-CdTe QDs, followed by positively charged MA-CdTe QDs and then the procedure is repeated alternately. It continues until the desired thickness of QD film is achieved. For the device reported in this work, 65 layers of QDs were deposited. The whole self-assembly process was performed in a nitrogen-filled glove box to avoid oxidation. To study the effect of this process, a control sample was prepared by the same procedure except with self-assembly performed in ambient condition, and the characterization results are compared.

2.4. Photolithography and metal evaporation

After the self-assembly, a thin layer (less than 1 μm in thickness) of photoresist (AZ1512) is spin-coated on the chip and two square windows (1 mm × 1 mm) are opened by photolithography, as shown in Fig. 1(c). The window size defines the active area of the photodiode. Finally, a thin layer (~50 nm in thickness) of Al is deposited by electron beam evaporation with evaporation rate 0.5 nm/s and vacuum level around 6.67 × 10^{-4} Pa. The resulting device structure is illustrated in Fig. 1(d).

2.5. Measurement

Characterization of the device is performed in an ambient environment. We use a Newport LQA 405-40P continuous-wave 405 nm laser and a Newport LQA 405-40P continuous-wave 405 nm laser as the light source illuminating from the ITO side and a Keithley 6430 subfemtoampere meter as the source meter. A Newport LQA 405-40P continuous-wave 405 nm laser is negatively charged TGA-CdTe QDs, followed by positively charged MA-CdTe QDs and then the procedure is repeated alternately. It continues until the desired thickness of QD film is achieved. For the device reported in this work, 65 layers of QDs were deposited. The whole self-assembly process was performed in a nitrogen-filled glove box to avoid oxidation. To study the effect of this process, a control sample was prepared by the same procedure except with self-assembly performed in ambient condition, and the characterization results are compared.

![Fig. 2.](image)

**Fig. 2.** (a) The illustration showing the structure of MA- and TGA-CdTe QDs. (b) The absorbance (Abs) and photoluminescence (PL) spectra of MA- and TGA-CdTe QDs. Both QDs have PL peaks around 610 nm.
and the metal changed the energy band tilting direction and led to the opposite polarity of open circuit voltage, as depicted in Fig. 4(c). In addition, QD surface states mostly resulting from surface oxidation during the fabrication serve as recombination centers and facilitate the electron-hole recombination rate in the QD thin film. Therefore, the short circuit current density of the photodiode with self-assembly under ambient condition (5.7 μA/cm²) was much smaller than in glove box (43.2 μA/cm²). Under positive applied voltages (Fig. 6), the photodetector exhibits external quantum efficiency (EQE), which is defined as the number of charge carriers generated due to photo-excitation and collected by the electrodes per incident photon = 0.66% at 0 V (short-circuit condition) and 1.4% at 0.6 V, while the signal to dark current ratio (SDR) decreases from ~3000 to 200 as applied voltage increases from 0 V to 0.6 V. The EQE and SDR are significantly higher than those of our previously reported work [10] owing to the improved dialysis method and the inert self-assembly environment employed in this work. Both improvements contribute to the reduction of surface states by avoiding oxidation. Note that the EQE (=0.66%) at zero bias is higher than the EQE (=0.3%) at zero bias in Fig. 5. This is caused by slight oxidation of the CdTe QDs or the Al thin film during measurement in an ambient environment after sweeps in positive applied voltages. This can be improved by measuring in an inert environment or insulating the Al side with epoxy resin.

Schottky solar cells based on infrared-absorbing PbS or PbSe QDs have demonstrated high EQE in visible wavelength ranges [3–5]. Although small band gap absorbs larger portion of the solar spectrum, it comes at a price of lowering open circuit voltage. The CdTe QD thin film presented in this work with a relatively large and controllable open circuit voltage is a good candidate as a multi-junction solar cell's first layer which mainly absorbs high energy photons. Photovoltaic cells composed of CdSe QDs which have band gap close to CdTe QDs could be used for comparison. A recently reported CdSe/Si thin film solar cells fabricated by spin-coating CdSe QDs followed by magnetron deposition of amorphous-Si (a-Si) film has shown EQE ~3% at 405 nm [7]. In its multi-layer structure (ITO/CdSe/a-Si/Al), only the CdSe thin film contributes to short circuit current while the holes generated in the amorphous-Si part are accumulated and recombined at the CdSe/Si interface. The QDs and the electrostatic self-assembly process reported in this work can be incorporated into a similar device structure to achieve higher quantum efficiency without the need of ligand exchange or high-temperature annealing. Furthermore, since the deposition of QDs is performed in aqueous solution, we can use patterned photoresist to define the active device area, as shown in Fig. 1(c). The resulting CdTe QD thin film is integrable with other organic solution-processed QDs, such as PbS or PbSe QDs, to form a hetero-junction cell with broader absorption spectrum.

Some issues affecting the CdTe QD photodiode’s efficiency are to be addressed here. The CdTe QDs synthesized using cadmium perchlorate hydrate and Al₂Te₃ in aqueous solution [11] have less degree of crystallinity than organometallically prepared QDs which are synthesized in high annealing temperature (200–360 °C) as compared to 100 °C for the aqueous CdTe QDs here. As a result, the typical photoluminescence quantum efficiency of MA- and TGA-CdTe QDs is 10% [11], whereas CdSe/ZnS QDs from the organometallic method can reach 30%–50% [13]. The relatively low photoluminescence quantum yield might affect the device’s overall EQE. However, the aqueous synthesis approach shows advantages in its simplicity, high reproducibility and potential for large-scale applications [11]. In

**Fig. 3.** The top-view SEM images of the 65-layer CdTe QD thin film with (a) 50 × 10³ and (b) 150 × 10³ magnification. (c) The cross-sectional view of the QD thin film which has average thickness around 40 nm. (d) The SEM images of a CdTe QD thin film after more than 100 layers of self-assembly, wherein some ~50 nm-wide cracks are formed.
terms of surface charge stability, the one-step synthesis is also better than converting conventional TOPO-capped QDs into water-soluble ones. Another factor affecting the device performance is film thickness. In general, a thicker QD thin film is expected to increase absorption. However, due to the increasing number of deep surface traps which can serve as recombination centers, the thicker QD thin film also means lower charge carrier extraction rate. Experimentally, the optimized thickness of CdSe QD thin film for a similar MIM photovoltaic cell was found to be around 90 nm [7]. Therefore, to further increase the efficiency of the CdTe QD photodiode in this work, larger size QDs are to be synthesized, which not only increases the absorption by lowering the band gap due to quantum confinement effect, but also helps achieving thicker films with fewer self-assembly layers.

4. Conclusion

In summary, a colloidal QD thin film photodiode has been fabricated by electrostatic layer-by-layer self-assembly of positively and negatively charged CdTe QDs in aqueous solution. Since the capping ligands used for synthesis are short (less than 0.5 nm), the photodiode shows substantial photoconductivity without additional steps of ligand exchange, ligand removal or annealing which are critical for conventional colloidal QD optoelectronic devices made by organic solution-processing. The open circuit voltage of the photodiode is determined directly by the work function difference between ITO and Al, as a result of reduced surface traps through thiol-passivation and self-assembly in a nitrogen atmosphere. The CdTe thin film fabricated using this approach is a suitable layer for absorbing high energy photon and generating large open circuit voltage in multi-junction photovoltaic cells. As a photodetector, the photodiode is expected to achieve higher sensitivity with its improved signal to dark current ratio.

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