Influence of Different Surface Passivation on Photoelectric Properties PbS QDs

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Abstract. The photoelectric characteristic of ITO/PbS quantum dots (QDs)/Al structure based single and hybrid iodine ions(I-) passivated PbS QDs have been investigated. The ITO/PbS QDs/Al structure with hybrid I- passivation have demonstrated a high light dark ratio of 565.5 at -2V. It is the result of removing more organic ligands on the surface of PbS QDs and introducing larger amount of I-. This work demonstrates that the hybrid I- passivated process has great potential in the performance improvement of PbS QDs based photovoltaic device.

1. Introduction

PbS QDs have attracted increasing interest due to their tunable narrow band-gap (0.4-2.0eV), a large Bohr radius (18nm), a high light absorption coefficient (≈10^4 M^(-1)cm^(-1)) as well as facile solution-processed. Nowadays, Some of the characteristics have become a new generation of low-cost photoelectric materials[2], such as solar cells[3], photodetectors[4] and light-emitting diodes[5] had been widely studied in the past few years.

The structure of the PbS QDs ([Pb(OA)2]) is composed of a PbS core with a stoichiometric ratio and a Pb shell wrapped around it. The mechanism of passivation is to replace the long chain of organic ligands bound to the Pb shell on the basis of protecting it from oxidation, in order to reduce the interparticle spacing to improve carrier mobility in the PbS QDs film. One method is called atomic ligand passivation[6,7], which the use of halide passivation (such as Br-, Cl-, and I-) to exchange oleic acid (OA) ligands on the surface of PbS QDs, and passivate trap states that lower the minority-carrier lifetime[8], and their thin film carrier mobility reaches 10^2 cm^2V^(-1)S^(-1)[9]. The other method is the organic ligands (such as EDT, EDT, MPA, etc.) replaces the long chain of the PbS QDs film, combines with Pb2+[10-12]. Successfully, Ryan W. Crisp[11]prepared PbS QDs solar cells using metal halide (PbI2, PbCl2, CdI2 or CdCl2) salt replaced the oleic acid surface ligand. In recent years report have shown that the surface electronic properties of PbS QDs can be modified by surface ligand chemistry[13]. By replacing the long chains of insulated hydrocarbon ligands to enhance the electronic coupling and carrier transport capacity of the PbS QDs[14].
Due to PbS QDs have strong quantum confinement effects and potential multi-exciton generation effects, which provide the possibility to improve the efficiency of photoelectric devices, and as active layer of PbS QDs materials have a great impact on device performance. Therefore, the paper is devoted to studying the influence of the different passivation methods on the surface composition and optical properties of PbS QDs films, and prepared PbS QDs photovoltaic devices.

2. Experiment

2.1 MAI-treated PbS QDs (PbS\textsubscript{MAI})

The synthesis of PbS QDs is referred to the previous work from Hines\cite{15,16} with certain modifications. For a MAI treatment process, 1.0 mL toluene, 0.5 mL DMF dispersed 4 mg MAI, the mixture solution was added to 2 mL PbS QDs in a vial tardily (1 drop per 10 s). Gentle shaking was applied to facilitate the formation of homogeneous solution. Note that quickly injection of MAI solution resulted in non-reversible precipitation of QDs. The QDs solution was kept in the glove box for 36 h. Toluene and acetone was employed to precipitate the QDs. Following fully drying, the PbS QDs were dispersed in octane with a concentration of 50 mg/mL.

2.2 Hybrid Passivation (PbS\textsubscript{MAI}-MAI)

As shown in Fig.1, the oleic acid-capped PbS QDs solution was treated with an MAI (PbS\textsubscript{MAI}) aqueous solution to prepare a 50 mg/ml solution of a PbS\textsubscript{MAI} QDs in octane at a low speed of 300 rpm/s 5 s, high speed 3000 rpm/s and spin for 30 s on a clean Si wafer or glass substrate, spin with 10 mg/ml and MAI methanol solution coated on PbS QDs film, and finally washed with acetonitrile.

![Figure 1. Schematic diagram of hybrid processing of PbS QDs films](image)

2.3 Device Fabrication

The ITO substrates were pre-cleaned in an ultrasonic bath with detergent, pure water, and 2-propanol, acetone, and alcohol for 15 min to remove organic residuals. A thin layer of PbS QDs was formed by spin coating at 300rpm for 5s, 3000rpm for 30s. The PbS QDs film was further annealed at 100 °C for 10min to dry organic residuals and promote crystallization of the PbS QDs film. Finally, samples were transferred to the evaporation chamber for metal contact deposition. 120nm Al was thermally evaporated at a pressure <5×10\textsuperscript{-3} Pa.

2.4 Experimental Equipment

The X-ray diffraction (XRD-7000) from Shimadzu Corporation was used to test the phase and crystal structure of PbS QDs in the experiment. Ultraviolet and Visible Spectrophotometer (UV-VIS, PE Lambda950) can be used to estimate the size and band gap of PbS QDs. The Fourier transform infrared spectroscopy (FTIR, HIMADZU FTIR-8400S) measurements were carried out. The surface elements and chemical states of PbS QDs film were examined using X-ray photoelectron spectroscopy (XPS, Thermo Fisher K-Alpha) and all binding energies were calibrated by setting the C1s signal to 285 eV. The current
density-voltage characteristics (J-V) curve were measured with the KEITHLEY-2600B equipment manufactured by Tektronix under ambient conditions. The photoelectric devices of PbS QDs were fabricated by thermal evaporating Al electrodes (120 nm, base pressure $< 5.0 \times 10^{-3}$ Pa) onto ITO substrates with spin-coated PbS QDs films. All optical measurements were performed at room temperature.

3. Result and Discussion

Fig.2(a) shows that the XRD spectra of the PbS QDs film passivated with MAI solution-phase and hybrid passivation method. The diffraction peaks observed at $2\theta$ of 25.96°, 29.50°, 43.05°, 50.95°, 62.49°, 70.28°, 78.92°, 84.79° correspond to (111), (200), (220), (311), (400), (420), (422), (511) planes respectively which are good agreement with the JCPDFNo.5-0592. It has been concluded that the deposited PbS QDs films are polycrystalline in nature with cubic structure. In Fig.2(b) shown that the first exciton absorption peaks of PbSMAI are located at 1033 nm. Compared to the untreated PbS QDs, the absorption spectra are red shifted by 8nm. The red shifts of approximately 9.3 mev and of the PbSMAI films in optical transitions due to electronic coupling reduced interparticle distance, which results in the delocalization of the electrons and holes wavefunctions, combined with the effect of the increased dielectric constant[6]. The red shift of exciton peaks in the PbS QDs film also indirectly indicates the reduction of the distance between QDs particles[17].

![Figure 2](image-url)

(a), (b) XRD and UV-VIS spectra of PbS QDs films in PbSOA and PbSMAI Solution processing

![Figure 2](image-url)

(a)
In order to further study the effect of passivation of different materials on PbS QDs photoelectric devices, a device of ITO/PbS/Al structure was prepared. As shown in Fig.3(a), (b), (c), it is the current density-voltage characteristics (J-V) curve of the untreated PbS_OA, PbS_MAI, and PbS_MAI-MAI QDs devices, respectively. It can be observed that the untreated PbS_OA QDs device has almost no photoelectric effect, and the low of the light and dark current. Under the bias voltage of -4V, the light and dark current density of the PbS_MAI QDs device is relatively small and no significant change. The photocurrent has a slight change, which may be due to a large amount of organic solvents remain on the surface of the PbS QDs affects the carrier transport. For hybrid passivation of PbS_MAI-MAI QDs devices, the devices have a large light-dark current ratio of 565.5 at -2V, and the photocurrent density has increased by four orders of magnitude.

In order to investigate the reasons for the improved performance of PbS QDs optoelectronic devices, and to further study the effect of iodine introduction on the optical properties of PbS QDs. The FTIR spectrum in the Fig.4 shown that the vibration intensity of COO-asymmetric and symmetric stretching peaks at 1398cm\(^{-1}\) and 1528cm\(^{-1}\) decreased, and the vibration peak intensity of CH(-CH\(_2\)) at 2852cm\(^{-1}\) and 2922cm\(^{-1}\) decreased. It can be seen that PbS_MAI-MAI QDs can remove of the oleic acid ligands, and it is better at removing oleic acid ligands.
As shown in Fig. 5(a), for the PbSOA, PbSMAI and PbSMAI-MAI films the I3d signal with the binding energy at 619.5 eV (I3d5/2) and 632.3 eV (I3d3/2), combined with Pb2+ to form PbI2 and further wrapped on PbS QDs, clearly demonstrate the presence of iodine on the PbSMAI, PbSMAI-MAI films. Similarly, Fig. 5(b) it observed that the C1s signal intensity was lower in the original OA ligand. The study found that the PbS QDs by hybrid passivation method is more effective than single solution-phase in removing oleic acid, and capped the surface of PbS QDs by iodine. The strategies has therefore been devoted to minimize the interparticle spacing to promote carrier transport and lower the defect density to reduce recombination loss in the PbS QDs photovoltaic device.
To determine the surface states and chemical compositions of the treatment PbS QDs films, XPS were performed and the results are shown in Fig.6. For the PbSOA, PbSMAI, and PbSMAI-MAI QDs films, the O1s signal with binding energy peaks at 529.3eV (Pb-O), 531.5eV (SO\textsubscript{4}\textsuperscript{2-}), and 532.2eV (COO\textsuperscript{-}), respectively. The signal of O element was significantly reduced and increased PbO signal intensity in PbS QDs treated by MAI solution-phase method due to PbS QDs exposure under air environment. For the PbSOA, PbSMAI, and PbSMAI-MAI QDs films the S2p signal (Fig.6(b), (d), (f)) with binding energy peaks at 160.9 eV (Pb-S), 165.1eV (S\textsuperscript{2-}), 168.5eV (SO\textsubscript{3}\textsuperscript{2-}(SO\textsubscript{4}\textsuperscript{2-})), 172.2eV ((CH\textsubscript{3})\textsubscript{2}SO), respectively. It can be seen that the S element signal is slightly reduced, due to the effective reduction of (CH\textsubscript{3})\textsubscript{2}SO, SO\textsubscript{3}\textsuperscript{2-}(SO\textsubscript{4}\textsuperscript{2-}) and the partial replacement of the S element by iodine ions, which forms PbI\textsubscript{2}. Byproducts such as PbSO\textsubscript{3} or PbSO\textsubscript{4} are formed in the air environment, which will also reduce the performance of PbS QDs photovoltaic devices[3,4]. For PbS quantum dots with a band gap of about 1.3 eV, the trap state introduced by PbSO\textsubscript{3} with an energy level of 0.1 eV is relatively shallow, which mainly plays the role of extending the effective carrier lifetime. And band gap of about 0.8 eV, the trap state introduced by PbSO\textsubscript{4} at an energy level of 0.3 eV is very deep, which acts as a recombination center. It can be known from XPS that MAI solution-phase passivation and hybrid I\textsuperscript{-} passivated of PbS QDs can effectively replace oleic acid ligand and form...
PbS(PbI₂) QDs wrapped with iodine ions, which effectively shortens the PbS QDs spacing. Comparing to the O1s and S2p spectrum, it is found that the best way to passivate PbS QDs is hybrid passivation method. Improving the carrier transport capacity will lay a certain foundation for improving the performance of PbS QDs photoelectric devices.

4. Conclusion
The paper focuses on the different passivation methods to treatment PbS QDs, including the solution-phase method and hybrid passivation method. The surface chemical composition, PbS QDs film quality, and optical properties of PbS QDs were studied. The study found that the two processes can remove organic ligands on the surface of PbS QDs, and the most obvious effect is the hybrid passivation method. The ITO/PbS QDs/Al structure with hybrid I- passivation have demonstrated a high light dark ratio of 565.5 at -2V. The organic ligands on the surface of PbS QDs are almost completely removed, and introduced a large amount of I ions, at the same time the surface forms PbS(PbI₂) QDs, which reduces the dangling bonds or unsaturated bonds on the surface of the PbS QDs. It is further reducing the interparticle distance and increased the coupling energy between the quantum dots, which speeds up hopping and tunneling mechanism. The transport ability has laid a certain foundation for the improvement of the performance of PbS QDs photoelectric devices.

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