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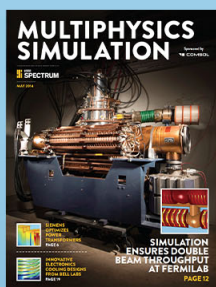Appl. Phys. Lett. **91**, 233111 (2007); 10.1063/1.2822441

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Reducing charge trapping in PbS colloidal quantum dot solids

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Understanding and improving charge transport in colloidal quantum dot solids is crucial for the development of efficient solar cells based on these materials. In this paper, we report high performance field-effect transistors based on lead-sulfide colloidal quantum dots (PbS CQDs) crosslinked with 3-mercaptopropionic acid (MPA). Electron mobility up to 0.03 cm^2/Vs and on/off ratio above 10^5 was measured; the later value is the highest in the literature for CQD Field effect transistors with silicon-oxide gating. This was achieved by using high quality material and preventing trap generation during fabrication and measurement. We show that air exposure has a reversible p-type doping effect on the devices, and that intrinsically MPA is an n-type dopant for PbS CQDs. © *2014 AIP Publishing LLC*. [http://dx.doi.org/10.1063/1.4869216]

The understanding of charge transport in colloidal quantum dot (CQD) solids has been targeted by many research groups worldwide due to their importance in the field of emerging photovoltaics.[1,2] The interest stems from the possibility to control the band gap by fine-tuning the CQD size, which allows matching the absorption of the active layer of the solar cell to the solar spectrum. When cross-linked and forced to proximity, nanocrystal arrays are able to transport electrons and holes with an increased efficiency, forming a solution-processed semiconducting thin film. This ability, in combination with the size-dependent band gap, makes of these systems excellent candidates for next generation solar cells,[3,4] infrared sensitive photodetectors, and other optoelectronic devices.[5] A broad variety of materials have been investigated in the last few years, but lead-sulfide (PbS) turned out to be the most interesting due to the easy and controllable synthesis, optimal band gap range, and high absorption.

Field effect transistors (FETs) are very useful device structures for the study of charge transport in new materials.[6] Lead-selenide (PbSe) CQD FETs treated with hydrazine were reported to show n-type transport with electron mobility of 0.4 cm^2/Vs,[1] while p-type transport was achieved with hole mobility up to 0.3 cm^2/Vs using PbSe with organic acid treatments.[7] Sintering of metal-chalcogenide-capped nanocrystals has led to n-type unipolar FETs showing band-like transport and electron mobility above 15 cm^2/Vs.[8,9] However, these devices show little or no quantum confinement, losing partially the advantages of CQDs.

The quantum confinement can be maintained, when the CQDs are cross-linked by bifunctional organic ligands. FETs based on lead-sulfide CQDs and thiol-based linkers have been fabricated in the last few years,[7,10,11] showing a variety of properties and performances. Cross-linking with ethanedithiol resulted in 10^{-3} cm^2/Vs mobility for both electrons and holes in PMMA-gated FETs,[12] while electron mobilities up to 0.1 cm^2/Vs and current modulation of 10^4 has been achieved with halide treatment and aluminum-oxide gating.[13] Charge carrier mobility around 10^{-4} cm^2/Vs for holes and

10^{-2} cm^2/Vs for electrons, and current modulation (on/off ratio) around 10^3 has been reported in lead-sulfide FETs using 3-mercaptopropionic acid (MPA) as cross-linker and silicon-oxide gating,[10] and mobility up to 1.9 cm^2/Vs and 10^5 on/off ratio were measured in the same PbS-MPA CQDs arrays when gated with highly efficient ionic-liquid-based ion gel.[10] While these results are very promising, they are insufficient for applications. Moreover, further understanding of the transport mechanism, its limiting factors, the role of the material quality are necessary for the improvement of all colloidal QD based devices.

The presence of trap states, to which can be ascribed part of the responsibility for the limited charge transport, has been shown in cross-linked PbS films.[14,15] Charge carriers trapping decreases the carrier concentration, thus the mobility; therefore, to improve mobility, the trap concentration has to be reduced. Traps can have very different origin: (i) introduced during synthesis; (ii) generated during device fabrication; and (iii) in the case of field effect transistors, traps can also be located at the interface between the active layer and the dielectric. The H$_2$O/O$_2$ redox couple has been reported to efficiently trap electrons giving rise to p-type electrical characteristics especially in semiconductors deposited on SiO$_2$ surfaces.[16] Desorption of oxygen is also suspected to cause hole de-doping in organic semiconductors.[17] While the effect of oxygen and water has not been investigated in CQDs solids, we recently increased efficiency in Schottky-type solar cells by using high quality PbS CQDs obtained with an extended washing procedure.[4]

In this work, we fabricated high performance SiO$_2$-gated ambipolar FETs using PbS CQDs and MPA as cross-linker (Fig. 1). By using high quality CQDs[4] and preventing traps to be generated during fabrication and characterization by working in ultra-clean environment, we obtain ambipolar transistor with on/off ratio up to 4×10^5 and hole and electron mobilities of 0.03 cm^2/Vs and 5×10^{-5} cm^2/Vs, respectively. The effect of oxygen and water on the transport properties is investigated by exposing the field effect transistors for 30 min to ambient conditions, which gave rise to p-type doped-like characteristics. Almost full recovery is
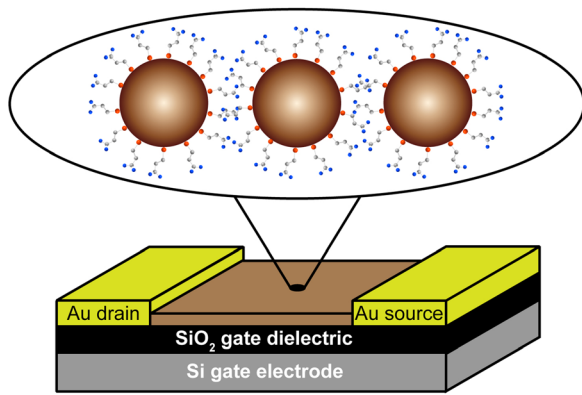
FIG. 1. Schematics of a PbS CQD field-effect transistor. The Si/SiO$_2$ substrate acts as gate electrode, the quantum dots cross-linked with MPA form the active layer of the device.

achieved after annealing the devices in dry nitrogen. This finding has strong relevance for the understanding of the trap formation mechanism in CQDs solids.

For the device fabrication, PbS quantum dots are synthetized and cleaned according to a previously described procedure, which gave highly efficient Schottky solar cells.[4] The layers are fabricated by spin-coating from a 5 mg/ml chloroform solution; the original oleic acid ligands are replaced by MPA cross-linkers upon 30 s immersion and a subsequent spin-drying step. After repeating these steps five times, the samples are annealed at 140 °C for 20 min. The films are deposited onto silicon substrates covered by a thermally grown oxide layer of 230 nm and photolithography-patterned gold electrodes with 20 µm channel length and 10 mm width. The output (I_D-V_D) and transfer (I_D-V_G) characteristics of these field-effect transistors are investigated by using an Agilent E5270B Semiconductor Parameter Analyzer. The transfer curves in the linear regime are used to extract mobilities, current modulation, and threshold values. Electron and hole mobility values are calculated from the linear current regime according to the gradual channel approximation and using parallel plane capacitor estimation for the gate electrode charge accumulation. The device fabrication and characterization was performed in highly clean (Tr.O$_2$ < 0.1 ppm; Tr.H$_2$O < 0.1 ppm), dry nitrogen atmosphere (glovebox).

Output and transfer characteristics of the best performing devices are reported in Figure 2. The transistors show strong ambipolar characteristics, with electrons being the dominating charge carriers (Figure 2(a)). This is the first report of n-channel current saturation in PbS CQD FETs. The corresponding asymmetric V-shaped transfer curves confirming the electron-dominated ambipolarity are shown in Figure 2(b). Mobility values up to 0.03 cm^2/Vs for electrons and up to 2×10^{-4} cm^2/Vs for holes are obtained. The measured electron mobility value is the highest ever reported for organic-crosslinked, SiO$_2$-gated PbS FETs. The very sharp subthreshold behavior (subthreshold swing about 2.7 V/dec) in both channels indicates outstanding material quality. Current modulation (ratio of the "on" and "off" currents) of 4×10^5 is measured in the n-channel, which is the highest ever reported for transistors using nanocrystals, including those fabricated with more efficient gating

techniques.[10,12,13] Such excellent properties in a simple co-planar SiO$_2$ bottom-gate bottom-contact device confirms the outstanding material quality.

We believe that the high electron mobility and on/off ratio are consequences of the high quality of the colloidal QDs and of the controlled fabrication conditions. We have recently demonstrated that an optimal control of the amount of ligands decorating the surface of the QDs can substantially influence the charge transport in diode structures, resulting in an increase in the short circuit current in solar cells.[4] Limited oxygen and water concentration during device fabrication may also influence the crosslinking process because of the air-sensitivity of the MPA linker.

To prove the eventual disadvantageous effect of ambient conditions on the transport properties, some devices were exposed to air for 30 min after their first characterization in glove box. The samples were then transferred back to the N$_2$ glove box and directly re-measured. Both output and transfer characteristics significantly changed upon exposure (Figures 3(a) and 3(b)). The exposed devices show quenched electron transport, with a simultaneous increase of about one order of magnitude of the hole current. No current saturation and very weak gate effect is observed in the exposed samples. The vanished ambipolarity, the strong threshold shift and the low gate modulation indicates high p-type doping, which is
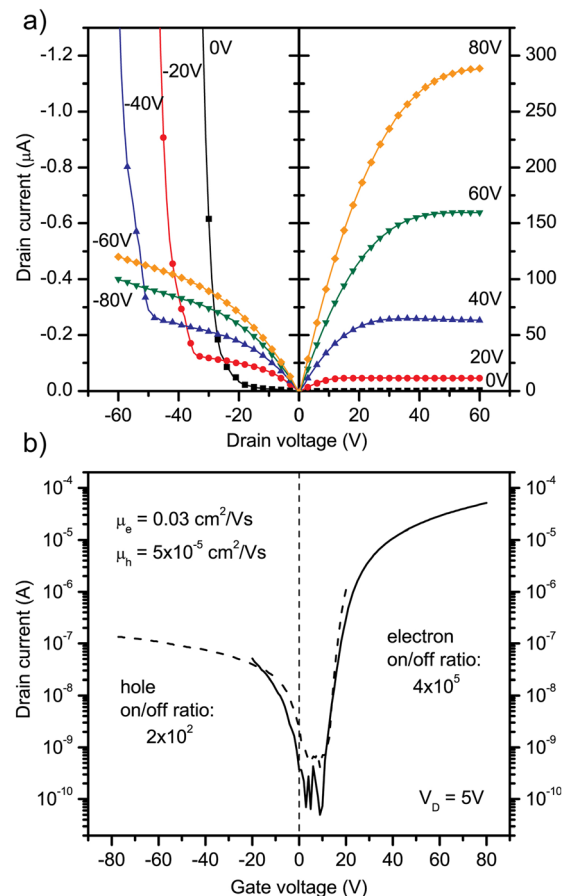

FIG. 2. (a) n- and p-channel I_D-V_D (output) characteristics of a PbS CQD field effect transistor measured at different gate voltages; (b) n-channel (solid line) and p-channel (dashed line) I_D-V_G (transfer) characteristics of the same device obtained in the linear regime.
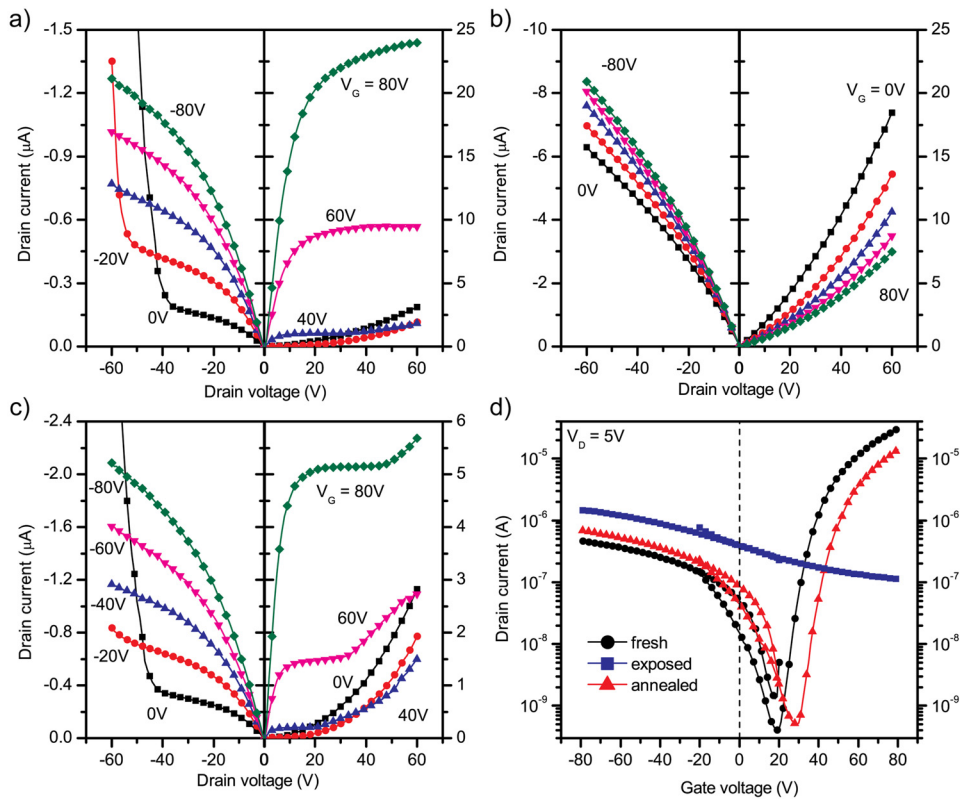
FIG. 3. I_D-V_D (output) characteristics of a transistor at different gate voltages measured (a) directly after fabrication; (b) after 30 min exposure to air and (c) after re-annealing in dry N_2 atmosphere; (d) Comparison of I_D-V_G (transfer) characteristics of a device measured before (black dots) and after (blue squares) being exposed to ambient conditions and after re-annealing (red triangles).

most probably magnified by the electron trapping induced by the oxygen-water redox couple.[16]

Enhanced p-type doping has been shown in the past for PbS bulk samples,[18] and more recently in PbS CQD thin films upon annealing in presence of oxygen,[11] assigned in both cases to oxidation of the sample surface. In our case, to understand if the doping of the active layer is determined by chemical reactions happening at the QDs surface or it is a reversible phenomenon, the samples were annealed for 1 h at 120 °C in a dry N_2 glovebox (Figure 3(c)). After re-annealing, the samples at room temperature display ambipolar behavior and almost full recovery of their pristine characteristics (Fig. 3(a)) indicating removal of the electron traps. The transfer curves of a typical device before and after exposure, and after annealing are compared on Figure 3(d). The recovery is almost complete, with the measured electron "on" current reaching the same order of magnitude as in the fresh device, while the hole "on" current drops back to the value measured in pristine devices. Additionally, the "off" current after annealing is also fairly similar to that of the fresh samples.

These observations are confirmed by the comparison of the mobility, on/off ratio and subthreshold swing values for a set of samples before exposure, after exposure and after annealing, which are summarized in Figure 4. In case of the exposed samples, the lack of electron current did not allow to extract any of these parameters for electrons. The average hole mobility slightly increased upon exposure from 8.6×10^{-5} cm^2/Vs to 1.9×10^{-4} cm^2/Vs; the current modulation plummeted from around 200 to below 10, while the subthreshold swing showed a 10-fold increase. The re-annealing process slightly decreases the hole mobility compared to the exposed sample, but the values are still
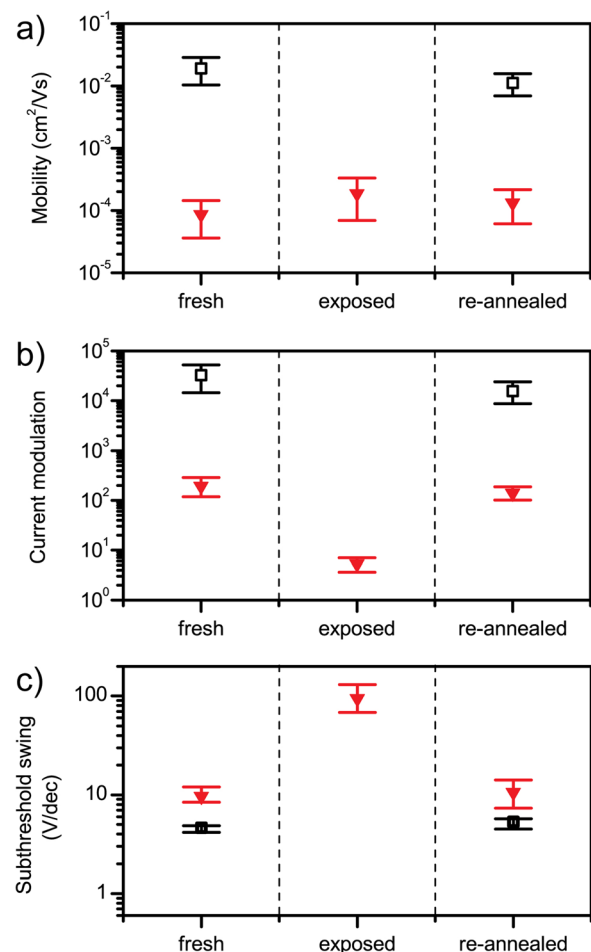

FIG. 4. Comparison of electron (black squares) and hole (red triangles) transport parameters—(a). mobility, (b) on/off current ratio, and (c) subthreshold swing—for pristine samples, exposed to ambient conditions and re-annealed.

higher than in the fresh films. Also the electron mobility reached 0.015 cm^2/Vs, which is slightly lower than what was measured in the unexposed devices.

Charge carrier trapping in localized mid-gap states easily results in lower mobility, as it decreases the effective carrier concentration in the channel. The presence of trapping states thus can explain the lower electron "on" currents in the exposed and recovered devices. If the concentration of localized states in the band gap is high, mid-gap hopping transport can occur, which may cause a "current leakage" throughout the device explaining the increased "off" current measured in the annealed samples. However, doping can eventually increase the current for similar reasons; the higher hole mobility in the recovered samples is possibly a result of permanent p-type doping upon exposure. Nevertheless, we have to mention that the huge decrease in electron concentration itself can be the cause of the enhanced hole current.

According to Martel *et al.*, the O_2/H_2O redox couple acts as an electron trap in the channel,[16] showing enhanced activity on polar surfaces due to more efficient absorption. Moreover, it has been reported that the electrical characteristics of graphene layers show significant changes upon adsorbing of small molecules,[19] which is shown to stem from net charge transfer from graphene to the adsorbates.[20] In case of PbS nanoparticles, the situation is complicated by their composite nature. Bulk PbS is an intrinsic semiconductor,[21] however, the ligand chemistry strongly influences the doping level through changing of the density of states.[22,23] This effect is irreversible in practice, as the preferred ligands for film formation bind strongly to the PbS surface changing eventually its chemical composition. In our samples, the effective doping upon exposure result to be reversible, indicating the adsorption of H_2O and oxygen molecules. However, the small irreversible part of the changes observed after annealing is probably due to oxidation of the surface of the PbS or to chemical reaction involving the ligands.

To conclude, in this work, we investigated the possibility of suppressing charge trapping in PbS CQD solids. Improved ambipolar charge transport is achieved by using high quality nanocrystals and by thoroughly controlling the fabrication and measurement environment. Record electron mobility of 0.03 cm^2/Vs and n-channel current modulation of 4×10^5 are achieved in non-sintered, SiO$_2$-gated PbS FETs, when both strategies are implemented. These results show that 3-mercaptopropionic acid is a strong n-type dopant for PbS CQDs. The device performances result to be highly sensitive on exposure to ambient condition, the original n-type material turned to p-type after exposure and restored upon mild annealing. This finding is of fundamental importance for the correct fabrication and handling of colloidal semiconductor based electronics and optoelectronics, and consequently, for their future development.

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