Impact of dithiol treatment and air annealing on the conductivity, mobility, and hole density in PbS colloidal quantum dot solids

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Crosslinking molecules have recently been combined with colloidal quantum dots to build robust, closely packed, conductive solid-state devices. Ethanedithiol (EDT) has been used in PbS quantum dot photovoltaic devices to assist in film formation during fabrication. However, there is evidence that EDT influences the electronic properties of the colloidal quantum dot (CQD) films. We fabricate thin film field-effect transistors and find that EDT treatment increases the majority carrier mobility by a factor of 10. We attribute this increase to a reduction in interparticle spacing which we observe using transmission electron microscopy. However, this increase is accompanied by a decrease in the majority carrier concentration. Using x-ray photoelectron microscopy, we find that EDT reduces the extent of the surface oxidation which is acting as a p-type dopant in these materials. We find that by lightly reoxidizing, we can redope the CQD films and can do so without sacrificing mobility gains. © *2008 American Institute of Physics*. [DOI: 10.1063/1.2917800]

Electrical and optical devices based on nanoparticle thin film solids have lately benefited from the use of short-chain organic crosslinking molecules.[1–3] The role ascribed to the crosslinking molecules in these devices has variously included aiding the fabrication of high quality films, improving charge transport properties, and altering the charge carrier concentration of the quantum dot film. For example, in a work published by Talapin *et al.*,[1] thin film field-effect transistors (FETs) fabricated from PbSe nanocrystals (NCs) were treated with hydrazine (a bidentate ligand possessing amine end groups) in order to alter the charge carrier concentration and improve transport.

We recently reported the use of ethanedithiol (EDT) molecules in the fabrication of PbS NC-based photovoltaic (PV) devices.[2] These devices demonstrated infrared (IR) power conversion efficiencies of 1.3%, a fiftyfold improvement over earlier work which had not utilized EDT linker molecules. In these PV devices, the EDT linkers enabled the fabrication of high quality NC films on textured, high surface area electrodes. In addition to aiding in the fabrication of PV devices, we expect that EDT has an effect on the electronic properties of PbS colloidal quantum dot (CQD) films.

To further understand the interaction between PbS NCs and EDT, we set out to examine the impact of EDT treatment on interparticle spacing, conductivity, mobility, and carrier concentration. Interparticle spacing was investigated using transmission electron microscopy (TEM). Butylamine ligand-exchanged PbS NCs (synthesized through an organometallic route described previously)[4] with an excitonic transition of 1400 nm were drop-cast from solution onto copper grids. The ligand exchange procedure is carried out to replace the majority of the original oleic acid ligands with butylamine ligands. This procedure is used to improve the electrical conductivity in the CQD films and is the initial processing step employed before solid-state devices are fabricated.[2,5,6]

TEM images (taken with a Hitachi HD-2000 scanning TEM) of untreated NCs and EDT treated NCs can be seen in Fig. 1. The EDT treatment consists of soaking the CQD film in 4% by volume solution of EDT in acetonitrile for 5 min. Examining the images, one can see that the PbS NCs films treated with EDT have a higher packing fraction than those without EDT treatment. Center-to-center spacing for the untreated NCs is about 9 nm. After EDT treatment, center-to-center spacing decreases to about 6.6 nm. With an average NC diameter of 5 nm, this center-to-center spacing corresponds to a distance between individual NCs of 4 nm in the case of the untreated films and a distance of 1.6 nm in the EDT treated films.

The reduction of interparticle spacing also results in an introduction of voids in the NC film. Figure 1(b) shows a film after EDT treatment with voids ranging in sizes from a few nanometers up to about 50 nm. In device applications, voids can lead to pinholes and to islands of isolated groups of NCs. To fill these voids, three rounds of deposition were employed in earlier work fabricating PV devices from NCs.[2] The observation of distinct and of individual NCs after EDT treatment additionally indicates that the film has not been changed into a polycrystalline material.
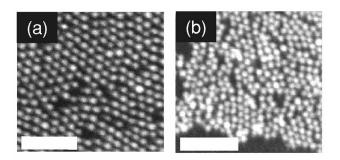

FIG. 1. (Color online) TEM images of PbS NCs (a) before and (b) after EDT treatment. Scale bar is 50 nm in both images. Interparticle spacing starts at 4 nm and reduces to 1.6 nm as a result of EDT treatment. The reduction in interparticle spacing contributes to the measured increase in mobility of thin solid films treated in this manner.

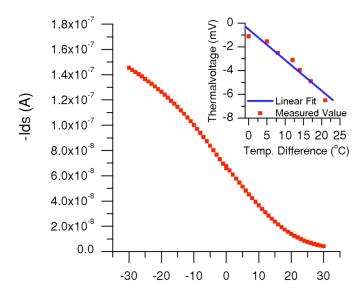[a)]Author to whom correspondence should be addressed. Electronic mail: ted.sargent@utoronto.ca.

FIG. 2. (Color online) PbS NC thin film FET characteristics for a device at the final stages of treatment. The V_{gs} vs I_{ds} transfer curve of the device indicates that it behaves as a *p*-FET with *p*-type conduction and majority hole carriers in the NC thin film. The inset of shows the measured thermal voltage confirming that the majority carriers are *p* type.

TABLE I. Summary of electronic properties of a CQD PbS thin film at progressive stages of treatment.

Stage of treatment	Conductivity $(S\ cm^{-1})$	Mobility $(cm^2/V\ s)$	Hole density (cm^{-3})
Untreated	4×10^{-7}	3×10^{-5}	8×10^{16}
Ethanedithiol treated	6×10^{-7}	1×10^{-4}	2×10^{16}
Air Heated	4×10^{-6}	2×10^{-4}	1×10^{17}

the V_{gs} versus I_{ds} transfer curve with fixed V_{ds}.

As deposited, the partially oxidized NCs have a measured conductance of 4×10^{-7} S cm^{-1}. The field-effect hole mobility calculated from the transfer characteristic of the *p*-FET is 3×10^{-5} cm^2 V^{-1} s^{-1}. The relationship $\sigma = pe\mu$, relating conductance (σ), mobility (μ), and carrier density is used to calculate the hole density (p), where e is 1.602×10^{-19} C.

The majority carrier density for the initially untreated PbS CQD film was found to be 8×10^{16} cm^{-3}. These results are summarized in Table I. It should be noted that the mobilities reported here have been extracted from the transfer curves assuming ideal FET behavior even though initially, the on/off ratio was quite low (about 2). Despite potential problems with this assumption, this model has been used elsewhere in work with semiconducting polymers and quantum dot films where other low on/off ratio devices have been reported.[8,9]

To observe the impact of EDT on the electronic properties of the CQD solid, the same FET was then treated with 4% EDT in acetonitrile for 5 min. The FET transfer characteristics and film conductivity were remeasured, and it was found that the conductivity increased to 6×10^{-7} S cm^{-1} and the mobility increased 1×10^{-4} cm^2 V^{-1} s^{-1}. On the other hand, the hole concentration was found to decrease to 2×10^{16} cm^{-3}.

These measurements indicate that while EDT has increased the mobility of a CQD film, it has simultaneously decreased the doping level in the film. This observation has important implications in the application of EDT in fabricating practical devices. Control over doping levels is a crucial determinant of device properties ranging from transistor gain and photodetector sensitivity to the built-in voltage in junction devices. An understanding of the nature of the interaction between EDT and doping is desired in order for this treatment to be used in the fabrication of NC-based devices.

Thiols are known to interact readily with metal nanoparticles and are expected to coordinate with the Pb atoms on the surface of PbS NCs. In light of this ready interaction and the large surface to volume ratio found in small nanoparticles, it is expected that EDT may be altering the doping level in a CQD film. As such, we turn to x-ray photoelectron spectroscopy (XPS) to examine the impact EDT has on the composition of PbS CQD films and, in particular, on the film's oxide content.

As-exchanged PbS CQD films were examined by taking an XPS spectrum of a drop-cast film using a using a PHI 5500 XPS spectrometer. We examine the O1*s* spectra [Fig. 3(a)] which reveals that a number of oxidation products, including PbO, are present on PbS nanoparticles. The deconvolution of the O1*s* spectra was performed by fitting a sum of Gaussian–Lorentzian functions to the experimental data. In addition to PbO, the PbSO$_3$ and PbSO$_4$ contents were also

To understand the impact of EDT treatment on the electronic properties of our CQD films, we fabricate thin film FETs. The FETs consisted of a highly doped Si substrate with 100 nm thick SiO$_2$ thermal gate oxide and Au source and drain electrodes 5 μm wide and 3 mm long, separated by a 14 μm gap. The doped Si serves as the gate contact. PbS NC films that were 20 nm thick were spincoated onto the substrates.

Application of a gate voltage modulates the current through the NC film. The majority carrier type can be determined by examining the FET gate voltage (V_{gs}) versus drain current (I_{ds}) transfer curve. Figure 2 shows that as V_{gs} becomes more negative, I_{ds} increases in magnitude. This is a characteristic of *p*-FET operation and indicates that the film is *p* type. The slope of the transfer curve in the linear regime yields a value for the field effect hole mobility.

A thermoelectric measurement was carried out to provide confirmation that the PbS films have majority *p*-type carriers. A NC film was spincoated onto a glass substrate which was then mounted on two hot plates using thermal paste. Electrical contacts were made to the film using Au electrodes that were 3.2 cm apart. Au contacts were used as Au has been seen to form an Ohmic junction with PbS NCs.[5] A thermal gradient is applied by heating one hot plate and keeping the other at room temperature. The voltage between the probes was measured using a Kiethley 6517A electrometer. Majority carriers diffuse away from the hot probe with the polarity of the measured voltage indicating the sign of the majority carriers. A graph showing measured thermal voltage for increasing temperature is shown in the inset of Fig. 2. The polarity of the voltage confirms that the film has majority *p*-type carriers. As a control, *p*-type Si was measured, which produced the same polarity thermal voltage as that observed for PbS NCs.

To calculate the majority carrier field-effect mobility (μ), the FET transfer curve is examined in the linear operating regime where I_{ds} increases linearly with V_{ds}.[7] Here, μ is calculated from the slope (i.e., the transconductance, g_m) of
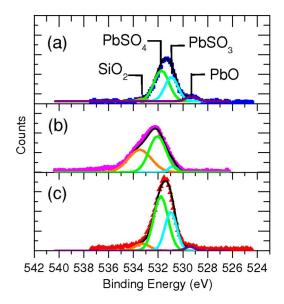
FIG. 3. (Color online) XPS O1*s* spectra of PbS NC films used to following the oxidation content at different stages of treatment. Experimental data is fit using a sum of four curves indicating the presence of PbO, PbSO$_3$, PbSO$_4$, and SiO$_2$ (from the Si substrate). In (a) untreated PbS, NCs show the presence of all three oxidation products. (b) Indicates that PbS NCs which have been treated with EDT show a reduction in the PbO and PbSO$_3$ content. (c) EDT treated PbS NCs heated in air exhibit a return of PbO and PbSO$_3$ content.

identified. PbO was identified using a peak centered at 529.3 eV.[10] PbSO$_3$ was identified using a peak centered at 530.8 eV,[11] while PbSO$_4$ was centered at 531.8 eV (Ref. 10) and SiO$_2$ (from the Si substrate) was centered at 533.3 eV.

An XPS spectrum was also taken of a PbS CQD film after treatment with EDT. The EDT treatment consisted of soaking the CQD film in a 4% by volume solution of EDT in acetonitrile for 10 min. The spectrum [Fig. 3(b)] reveals that the PbO content has been removed by the EDT and that the PbSO$_3$ content has been substantially reduced. However, the PbSO$_4$ signal remains strong.

That a reduction in the oxide content should have an impact on *p*-type doping in these films is in keep with previous work. It has been shown that oxygen is effective in the formation of D^- acceptor states in naturally occurring galena and in synthesized microcrystalline PbS films.[12] Bulk *n*-type PbS and PbTe can be doped to *p*-type behavior by annealing in air or O$_2$. This conversion is stable and effective in creating photosensitive films useful in IR photodetection.[13]

These findings raised the following question. Are high mobility and strong doping quantities that must be traded off against one another or can a material processing strategy be devised such that it simultaneously achieves mobility and doping?

We sought to bring back the doping density by lightly oxidizing our FET devices in an effort to redope the CQD film. The same FET device used in Fig. 2 was heated in air at 90 °C in order to reoxidize the CQD film and device characteristics were measured at different time intervals. The maximum conductivity was measured after 3 min of air heat-

ing and was found to be 4×10^{-6} S cm^{-1}. The mobility after this initial heating was found to be 2×10^{-4} cm^2 V^{-1} s^{-1}, a slight increase over the initial gain in mobility brought about by EDT treatment. It was also found that air annealing brought up the hole concentration to 1×10^{17} cm^{-3}.

It should also be noted that as films were heated further, mobility began to decrease. After about 90 min, the mobility had gone down by about an order of magnitude, reversing the gains achieved through EDT treatment. This reduction is attributed to an over oxidation of the NCs which eventually forms a barrier impeding dot-to-dot charge transport in the CQD film.

To confirm that heating NCs after EDT treatment corresponds to growth in oxide content, an EDT treated film was heated in air and examined with XPS. One can see in Fig. 3(c) the reintroduction of PbO as well as an increase in the PbSO$_3$ content.

Another feature of the O1*s* spectra that should be discussed is the variation in the strength of the SiO$_2$ peak arising from the surface oxide layer on the Si substrates used for the XPS samples. The drop-cast NC films used for XPS measurements were substantially thicker ($\sim$3 μm) than those used for FET and TEM measurements. It was found that in these drop-cast samples, the CQD films contained drying cracks and that EDT treatment lead to further cracking of the thick films. The distribution and extent of the cracks contributed to the variations observed in the intensity of the SiO$_2$ signal.

In this work, we have shown that EDT treatment of PbS CQD films results in nearly a tenfold increase in mobility but is accompanied by a reduction in the *p*-type doping of the film. The loss of doping is attributed to a reduction of the surface oxides in the NC film by EDT. By heating in air, one can reintroduce oxide content and increase the hole concentration without sacrificing gains in mobility. This finding represents a practical organic-inorganic route to doping control in NC films.

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