PbS colloidal quantum dot photoconductive photodetectors: Transport, traps, and gain

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We investigate experimentally the origins of gain in PbS colloidal quantum dot photodetectors. We employ measurements of photocurrent, its transient behavior, and dark current over a wide range of temperatures. We find the hole mobility to have an activation energy of 0.16 eV, and we identify photosensitizing centers at ~0.1, 0.2, and 0.3 eV below the conduction band edge. These centers account for the 60, 300, and 2000 ms fall times observed in the transient response of the photocurrent at room temperature. These centers enable us to account for the constancy of photoconductive gain across the wide temperature range of 250–340 K. © *2007 American Institute of Physics*. [DOI: 10.1063/1.2800805]

The sensitive detection of light is of central importance in imaging, environmental sensing, and spectroscopy. Photodiodes made using silicon provide one route to the sensitive detection of visible light. The use of complementary metal-oxide semiconductor silicon is attractive because it enables image sensor realization via monolithic integration of photodetection and analog gain and even digital processing on a single chip.[1]

An equally convenient, but more versatile, alternative to silicon-only photodetection has recently emerged. It has been shown[2] that it is possible to fabricate, by simple solution processing, a top-surface visible-wavelength photodetector monolithically integrated with an arbitrary substrate. These sensors can exhibit responsivities vastly exceeding those of silicon photodiodes, and low-noise performance that leads to noise-equivalent intensities rivaling silicon. The versatility of these recent devices arises from the ease with which the bandgap of the light-absorbing material may be tuned: colloidal quantum dots are widely known for their capacity to exhibit size-effect tuning, leading to corresponding controlled variations in the spectrum of photodetector responsivity,[3] laser emission wavelength,[4] and modulator bandwidth.[5]

In contrast with silicon photodiodes, which exploit electron-hole separation across a *p-n* junction, recent reports of sensitive colloidal quantum dot photodetection have relied instead on photoconduction. In a hole-based photoconductor, absorption of a photon results in the generation of an electron-hole pair whose electron is rapidly captured into a trap with (long—microsecond, millisecond, or even second) lifetime τ_c. Under an applied bias, the flowing holes transit the device in a time τ_t. As long as the trapped electron is substantially immobilized, $G=\tau_c/\tau_t$ holes worth of current may be collected for every electron-hole pair created. The responsivity of the device R is then given by $\eta qG/h\nu$, where η is the absorbance (also known as quantum efficiency). High gain and responsivity thus originate from efficient transport of one carrier combined with long-lived trapping of the carrier of the opposite type.[2,3]

Since extended trap state lifetime lowers the speed of response—if excessive, it can lead to unacceptably long lag in imaging applications—control over the trap states present in a quantum dot solid is of high importance. There exists a considerable body of evidence pointing to the existence of a multiplicity of trapping centers in colloidal quantum dot solids. Recent reports on PbS, for example,[2] found that the frequency-dependent response varied systematically with the level of illumination: longer-lived, deeper-lying traps were presumably filled first, providing gain but slow response at low light, and lower gain but faster response under higher levels of illumination.

For these reasons, we set out herein to elucidate in greater detail a physical picture of the trap states that exist in PbS colloidal quantum dot films. Bulk PbS has been widely studied, and below we compare our findings with past reports on these materials. However, since conventional polycrystalline PbS and colloidal quantum dot PbS differ substantially—in their characteristic dimensions (50–150 versus 1–10 nm), their surface passivation (oxides and sulfates versus organic ligands plus oxides and sulfates), and the absence or presence of quantum confinement—we begin with a detailed presentation of our experimental findings in the case of PbS nanocrystals.

We fabricated photoconductive photodetectors by spin-casting PbS nanocrystals of ~3 nm in diameter onto a gold interdigitated electrode. The nanoparticles making up these films were capped with 2-nm-long oleate ligands. We carried out a solid-state ligand exchange to the much shorter *n*-butylamine ligand to improve transport.[2] Absorption and photocurrent responsivities both exhibited onset near 800 nm. The interelectrode spacing on the substrate was 5 μm and the length was 3 mm. The thickness of the colloidal quantum dot film was measured to be ~250 nm. All optoelectronic studies were performed under vacuum inside a liquid nitrogen cryostat. For transient photocurrent measurements, samples were illuminated using a 640 nm light-emitting diode modulated using a square wave (rise and fall times less than 1 μs) at a frequency of 100 mHz. Temperature dependencies were explored in 10 K increments with an increase rate of 1 K/min; samples were left to equilibrate 10 min at each temperature level. Samples were measured at

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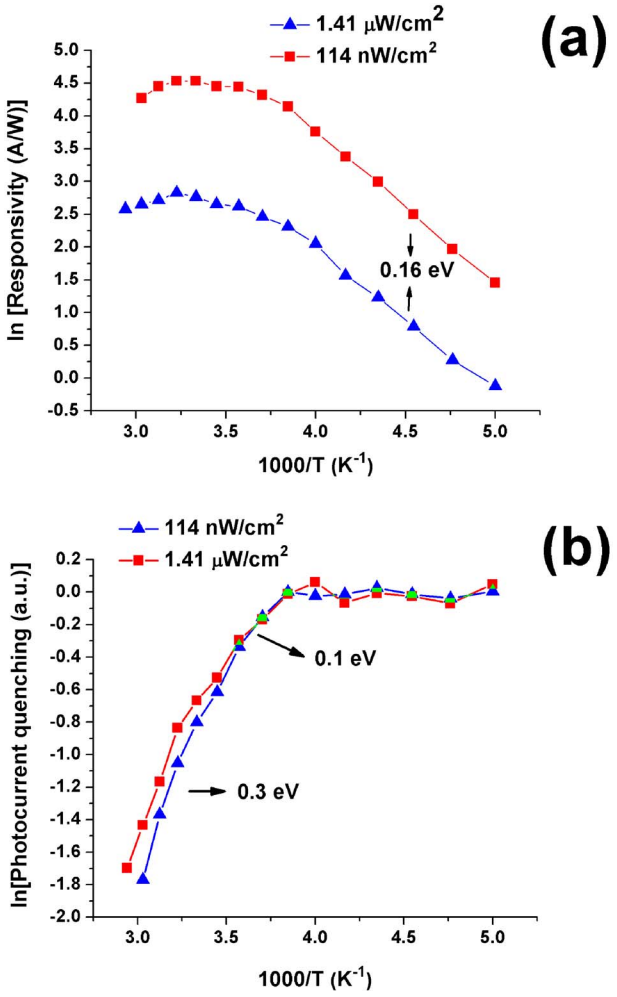

FIG. 1. (Color online) Determination of sensitizing centers via photocurrent thermal quenching. (a) Photocurrent as a function of temperature at two illumination levels. The activation energy of the photocurrent is determined by the mobility activation energy. At higher temperatures photocurrent quenching is observed. (b) Photocurrent quenching taken as the photocurrent at higher temperatures with the mobility contribution component subtracted. The slope of the quenching provides the depth of the sensitizing centers from the conduction band. Two sensitizing centers are discovered with energy depths of ~0.1 and 0.3 eV from the conduction band.

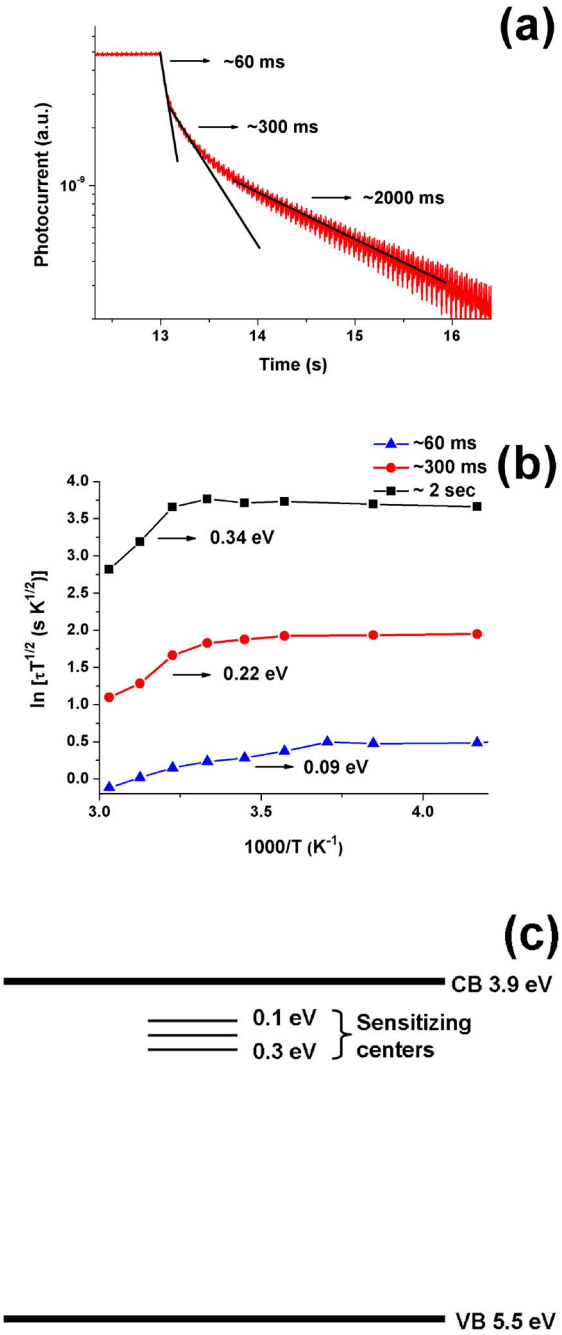

FIG. 2. (Color online) Determination of sensitizing centers via transient photocurrent measurements. (a) Transient photocurrent measurements as a function of temperature exhibit three exponential decay components with time constants at room temperature of 60 ms, 300 ms, and 2 s at 300 K. (b) The plot shows the dependence of the time constants as a function of temperature and provides additional information on the sensitizing centers' depths. This technique reveals in the addition of the 0.1 and 0.3 eV another center 0.22 eV from the conduction band. (c) Band diagram of the proposed model for photoconductivity in PbS quantum dot photodetectors.

room temperature before and after the full temperature and measurement cycles; before-and-after hystereses of less than 5% were observed.

Photocurrent levels and transient provide the most direct insight into sensitizing trap states; we begin with these results. In Fig. 1(a) we present the logarithm of responsivity as a function of temperature. At low temperatures (below 250 K), photocurrent shows a single activation energy of 0.16 eV. We separately measured dark currents and found these to exhibit the same activation within experimental uncertainty over this same temperature range. Since photocurrent and dark current are both linearly proportional with mobility, we attribute the growth in photocurrent with temperature up to 250 K to improved transport, and we associate the 0.16 eV activation energy with mobility. Thermally activated hopping transport has previously been observed in colloidal quantum dot solids.[6]

At temperatures above 250 K, photocurrent shows a dramatic saturation, whereas dark current continues to grow at or above the rate of 0.16 eV. In this higher-temperature regime, thermal energy is presumed to become sufficient to accelerate the emptying of the electron traps whose long lifetimes are responsible for photosensitivity.

To reveal this photocurrent quenching more fully, we plot in Fig. 1(b) the photocurrent quenching—defined as photocurrent divided by mobility—as a function of temperature. The quenching activation energies that are revealed as a result enable a first estimation of the energy depth of the sensitizing centers measured relative to the conduction band edge. Figure 1(b) indicates two levels, ~0.1 and ~0.3 eV. The smooth transition between the two suggests a distribu-

tion in sensitizing center energies as opposed to purely discrete levels.

The quenching rate is expected to be proportional to $N_c/N_s \exp(-\Delta E/kT)$, where N_c is the density of states in the conduction band, N_s is the sensitizing center density, and ΔE is the energy depth from the conduction band. By subtracting the mobility contribution to photocurrent, we estimate $N_{s1} \sim 10^{18}$ cm^{-3} associated with the 0.1 eV center and $N_{s2} \sim 10^{14}$ cm^{-3} associated with the 0.3 eV.

The particulars of the multicomponent transient response to changing illumination give considerably more direct information on trap state levels. The emission rate of a trap state into the conduction is given by $\tau^{-1} = \sigma_n N_c \upsilon_{\text{th}} \exp(-\Delta E/kT)$, where σ_n is the capture cross section of the trap, N_c is the density of states in conduction band, υ_{th} is the thermal velocity of the carriers, and ΔE is the energy depth of the trap measured relative to the conduction band edge. The transient decays of photocurrent revealed three main components, each having its own temperature-dependent time constant. Figure 2(b) shows the three temporal components that at room temperature exhibit characteristic time constants of ~60 ms, 300 ms, and 2 s. Figure 2(b) illustrates the natural logarithm of the product $\tau T^{1/2}$ (plotted to account for the dependence of thermal velocity on temperature and thus simplify the extraction of the exponential activation process). These components exhibit characteristic activation energies of 0.09, 0.22, and 0.34 eV, the deeper center accounting for the slower components of temporal response. These values agree well with the activation energies extracted from the photocurrent quenching analysis above, indicating that accelerated trap emptying substantially accounts for the striking temperature invariance of gain at room temperature.

We propose in Fig. 2(c) simple picture of the inferred trap levels. When the photodetector is illuminated, the quasi-Fermi levels move toward their respective band edges. When the electron quasi-Fermi level encompasses the sensitizing centers, intensity-dependent saturation results.

We now compare these findings with those observed in polycrystalline PbS photodetectors. Sensitizing centers attributable to oxidation sites on PbS (Ref. 7) have been found to lie 0.16 and 0.32 eV below the conduction band of bulk PbS (Ref. 8) and depend on the growth mechanism and deposition conditions. If the sensitizing centers in PbS nanocrystals were due purely to highly localized states at the nanoparticle surface and were uninfluenced by quantum-confined electron states within the nanoparticles, one would expect to see at least one much-deeper electron trap in the quantum dot case compared to the bulk. Since this is not observed experimentally, it appears that the combination of dot surface passivation and quantum confinement together determine the trap state energy.

In summary, this work provides physical insight into the operation of sensitive high-gain PbS colloidal quantum dot photodetectors via investigation of the dependence of photocurrent on temperature. The energy levels of the sensitizing centers responsible for high gain have been determined experimentally. The findings presented herein facilitate device optimization, pointing as they do toward trap state engineering aimed at improving further the temporal response of photoconductive devices for low-lag imaging applications.

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