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## Abstract

Photoconductivity in nanocrystal films has been previously characterized, but memory effects have received little attention despite their importance for device applications. We show that the magnitude and temperature dependence of the photocurrent in CdSe/ZnS core-shell nanocrystal arrays depends on the illumination and electric field history. Changes in photoconductivity occur on a few-hour timescale, and subband gap illumination of nanocrystals prior to measurements modifies the photocurrent more than band gap illumination. The observed effects can be explained by charge traps within the band gap that are filled or emptied, which may alter nonradiative recombination processes and affect photocurrent.

## Disciplines

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## Comments

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# Characterization of memory and measurement history in photoconductivity of nanocrystal arrays

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Photoconductivity in nanocrystal films has been previously characterized, but memory effects have received little attention despite their importance for device applications. We show that the magnitude and temperature dependence of the photocurrent in CdSe/ZnS core-shell nanocrystal arrays depends on the illumination and electric field history. Changes in photoconductivity occur on a few-hour timescale, and subband gap illumination of nanocrystals prior to measurements modifies the photocurrent more than band gap illumination. The observed effects can be explained by charge traps within the band gap that are filled or emptied, which may alter nonradiative recombination processes and affect photocurrent. © 2010 American Institute of Physics. [doi:10.1063/1.3496036]

Semiconductor nanocrystal (NC) arrays are artificial solids with many potential optoelectronic applications.<sup>1-3</sup> NC photoproperties have been studied, including quantum yield in suspension,<sup>4,5</sup> photoconductivity in films,<sup>6-8</sup> and carrier recombination rates.<sup>9-11</sup> Photoconductivity in CdSe/ZnS NC arrays follows a simple two-site resonant-tunneling model which describes the probability of electron-hole pair separation as a function of applied electric field.<sup>6</sup> The resonant-tunneling model can qualitatively reproduce the field dependence of the photocurrent, which also depends on interparticle spacing, NC size, and surface passivation.<sup>6</sup> NC-based photodetectors have been realized,<sup>2,6-8,12</sup> but their stability over time may be compromised by charge traps that can cause variations in conductivity. In particular, the dark current, photocurrent, and photoconductivity temperature dependence of NC arrays all exhibit memory effects.<sup>12-14</sup>

In this paper, we report the effect of illumination wavelength and electric field history prior to measurement on the photoconductivity in two-terminal electrode devices containing CdSe/ZnS NC arrays. Photocurrent can be altered by cycling voltage either under illumination or in the dark prior to measurement, and the change in photocurrent saturates after a few hours. We also discover that sample exposure to subband gap illumination prior to photocurrent measurements is more effective at modifying the photoconductivity than the band gap illumination, even though subband gap illumination does not induce a measurable photocurrent. These effects can be explained by the emptying and filling of charge trap levels located within the band gap. Subband gap excitation may be closer in energy to the trap levels and is more effective at depopulating traps than light whose energy is larger than the NC band gap. These results advance the understanding of charge-transport-based semiconductor NC devices, such as photodetectors and solar cells, and suggest methods to adjust performance *in situ* by emptying or filling charge traps using light and electric fields.

Figure 1(a) shows a schematic of the SiN/Si chip with a pair of Au electrodes on the SiN window<sup>15</sup> and CdSe/ZnS NCs dispersed on the surface. Figure 1(b) shows the energy level diagram for a NC under illumination at different wave-

lengths. All photocurrent measurements were performed using 532 nm few milliwatt green laser excitation. To investigate the effects of sample history on photoconductivity we have additionally exposed samples to three different excitations (532, 650, and 980 nm) *prior* to photocurrent measurements [Fig. 1(b)]. Transmission electron micrographs (TEMs) of multilayer NC films in two electrode devices with gap widths of  $\sim 27$  nm [Fig. 1(c)] and  $\sim 230$  nm [Fig. 1(d)] reveal the overall NC coverage, and show that NCs self-assemble into disordered close-packed arrays. In addition, inspection with high-resolution TEM ensures that NCs are distinct and that no visible metal debris is present in the gap vicinity that could short the electrodes. Electrodes consisting of 30 nm of Au on top of 3 nm of Ni were fabricated using e-beam lithography. Large Au contact pads were fabricated using optical lithography. Devices were tested in a cryostat under vacuum at a temperature range of 78–295 K. We performed background measurements to ensure negligible leakage currents before dropcasting NCs. TEM imaging was performed after the dc current-voltage (I-V) transport mea-

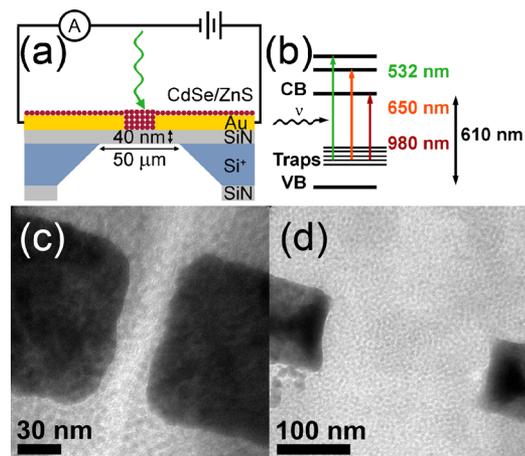


FIG. 1. (Color online) (a) Schematic of a SiN/Si chip with electrodes and NC film on the SiN window. (b) Energy level diagram showing photoexcitation of charge carriers from trap levels at various wavelengths of light. The CB, valence band, and trap levels are marked. Photocurrent is measured *only* with 532 nm and the other wavelengths are used to illuminate samples *before* the I-V measurement with 532 nm. (c) and (d) show TEM of electrode pairs containing multilayer NC films, with interelectrode distance of (c) 27 nm and (d) 230 nm.

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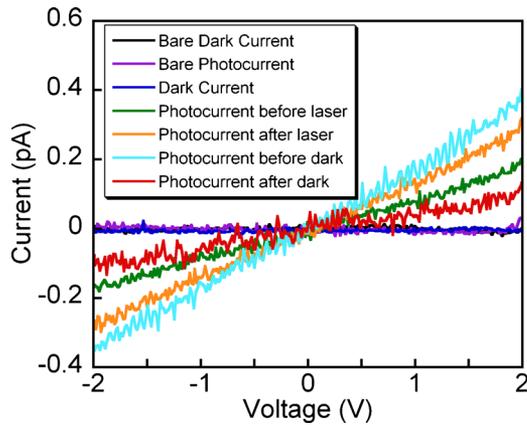


FIG. 2. (Color online) I-V curves in the dark and under 532 nm illumination. Bare device I-V curves and I-V curves after NC deposition in the dark at 295 K. NC photocurrent I-V curves at 78 K show that photocurrent is higher after voltage cycling and laser illumination than before, and lower after voltage cycling in the dark than before.

measurements, and was used to check that gaps had not visibly degraded or blown up during the electrical measurements.

We used CdSe/ZnS core-shell NCs with a mean diameter of 5.2 nm and mean ZnS shell thickness of 0.2 nm. The primary absorption peak in solution was at 610 nm and the emission peak was at 640 nm. Five microliters of NC solution were dropcast onto the  $5 \times 5$  mm<sup>2</sup> SiN/Si chip, forming a  $\sim 20$ -nm-thick multilayer NC film on the surface. The NC film was thermally annealed in vacuum by heating to 573 K for 2 h, which improved film conductivity by decreasing the inter-NC separation and increasing the coupling.<sup>8,14,16,17</sup> Annealing at this temperature improves the conductivity by about two orders of magnitude.<sup>16</sup>

Background I-V measurements, between  $-2$  and  $+2$  V at 0.04 V/s, ensured that the bare device had no dark or photocurrent. The maximum electric field magnitude in the active gap area was between  $\sim 9 \times 10^6$  and  $\sim 7 \times 10^7$  V/m, depending on gap size. The dark current after NCs were annealed was negligible, indicating that measured photocurrent was due to carrier photogeneration in the NCs and not injected carriers from the electrodes. These I-V curves are shown in Fig. 2. For photocurrent measurements, the laser beam was centered on the SiN/Si chip, and all gaps were illuminated equally. Because of the small gap size, photocurrents were on the order of picoampere which is lower than in larger devices,<sup>8,16,17</sup> but well above the dark current and the RMS noise floor of  $\sim 5$  fA.

We then investigated the stability of the photocurrent. In between photocurrent measurements, the voltage was swept continuously, and the device was either left in the dark or illuminated. Figure 2 shows I-V curves in the dark and under 532 nm illumination. The flat lines are I-V curves of the bare device at 295 K prior to NC deposition, and the other I-V curves in this figure show photocurrent at 78 K after NC deposition. The difference in these curves is a result of the different sample histories prior to the I-V measurements. In particular, after cycling the voltage while illuminating the sample with a laser overnight, the photocurrent at 78 K increases, shown in Fig. 2. Conversely, after cycling the voltage in the dark overnight, the photocurrent at 78 K decreases, shown in Fig. 2. We found this process to be reversible and reproducible for all devices.

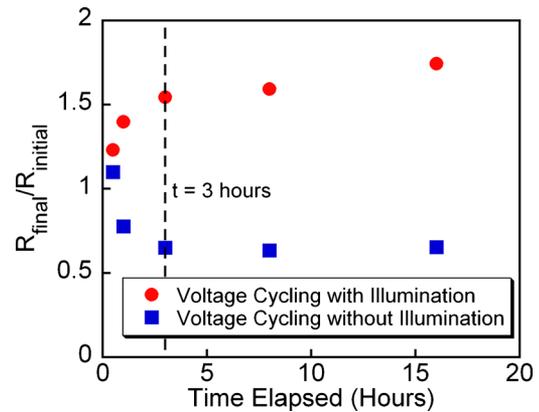


FIG. 3. (Color online) Average  $R_{\text{final}}/R_{\text{initial}}$  for devices after voltage cycling with and without 532 nm illumination vs time elapsed, where  $R = I_{78 \text{ K}}/I_{295 \text{ K}}$ . The majority of the effect on photoconductivity takes place in the first three hours (dashed line). The data in Fig. 3 are for one 230 nm gap. Other gaps measured behaved similarly. Each point is averaged over 5–15 measurement cycles and has an error of  $\pm 0.3$ . The  $R$  values for these data were in the range 0.25–15, with  $\sim 60\%$  lying between 1 and 3.

The photoconductivity of NC arrays and its temperature dependence are affected by the measurement history. To compare how sensitive the low and room temperature photoconductivity are to sample histories, it is convenient to define the ratio of photocurrents at a fixed voltage,  $R = I_{78 \text{ K}}/I_{295 \text{ K}}$  where  $I_{78 \text{ K}}$  and  $I_{295 \text{ K}}$  are photocurrents at 78 K and 295 K, respectively.<sup>12</sup> We define  $R_{\text{initial}}$  and  $R_{\text{final}}$  as the ratios of photocurrents measured during two consecutive thermal cycles. In between the two cycles, samples are exposed to a variety of conditions. We find that on average  $R_{\text{final}}/R_{\text{initial}} > 1$  after devices have been exposed to light and electric fields and  $R_{\text{final}}/R_{\text{initial}} < 1$  after devices have been kept in the dark and exposed to electric fields.

To characterize the effect of sample history on the photocurrent further, we studied how the photocurrent temperature dependence is affected by two factors: (i) the time elapsed between two consecutive measurements of  $R$  during which the sample was exposed to electric fields and light and (ii) the illumination wavelength which can be below or above the NC band gap. These measurements probe the levels of charge traps inside the band gap [as illustrated in Fig. 1(b)], the timescales over which traps can be populated and depopulated, and their overall effect on photoconductivity. The different measurement histories can modify photocurrent by changing the population of charge traps in the NCs, which may affect the rate of nonradiative recombination.<sup>12</sup> Illumination during voltage cycling reduces the trap population, temporarily lowering nonradiative recombination, which raises low-temperature photocurrent. Voltage cycling in the dark increases the trap population, temporarily raising nonradiative recombination, which lowers low-temperature photocurrent. Thus, when trap population is affected by the illumination and electric field history, the value of  $R_{\text{final}}/R_{\text{initial}}$  indicates how photocurrent temperature dependence has changed. For further details on this model, see Ref. 12.

Figure 3 shows  $R_{\text{final}}/R_{\text{initial}}$  versus time elapsed when voltage was cycled between the I-V measurements of  $R_{\text{initial}}$  and  $R_{\text{final}}$ . When the device was in the dark (squares),  $R_{\text{final}}/R_{\text{initial}}$  decreased with time, and when it was under illumination (circles),  $R_{\text{final}}/R_{\text{initial}}$  increased with time; for both cases,  $R_{\text{final}}/R_{\text{initial}}$  changes rapidly in the first few minutes and hours after exposing devices to electric fields and

light, or electric fields alone. But over time the rate of change decreases, and after three hours the subsequent change is less than 5%. These results indicate that the change in trap population slows asymptotically, initially proceeding quickly but slowing with time as the most energetically accessible trapped carriers are excited and transported out of the NC. Voltage cycling beyond the initial few hours does not appear to change  $R_{\text{final}}/R_{\text{initial}}$  significantly, meaning that it does not change the photocurrent or the trap state population significantly.

This result implies that traps can be populated and depopulated over approximately three hours and that more time does not seem to significantly affect the number of trapped carriers. Previously, carrier processes in NCs that happen over long-time scales have been observed. For example, hour-scale changes in photoluminescence lifetime of NCs in solution have been reported,<sup>18</sup> and defect emission from NCs for over an hour after initial illumination.<sup>19</sup> Slow trapping and detrapping have also been reported in CdS/CdSe/PbSe polycrystals, in the photocurrent noise power spectra.<sup>20</sup> These examples of slow recombination processes support our observation that emptying or filling traps in an insulating sample can take up to three hours for devices at this scale.

The data in Fig. 2 were obtained using the same excitation wavelength prior to the measurement and for the actual I-V measurement, a 532 nm laser whose energy (2.33 eV) is higher than the band gap energy of the NCs (2.03 eV). In addition, we used light with energy smaller than the band gap, 650 nm (1.91 eV) and 980 nm (1.27 eV), to illuminate devices prior to I-V measurements with 532 nm light. Devices were illuminated for 16 h while cycling the voltage, and this measurement was repeated three to five times for each wavelength. From the data taken on three devices, we observed larger average  $R_{\text{final}}/R_{\text{initial}}$  when we used subband gap illumination:  $4.9 \pm 1.0$  and  $3.0 \pm 1.0$  for 980 nm and 650 nm excitations respectively, compared to  $1.6 \pm 1.0$  for 532 nm excitation.

The effect of different excitation energies used prior to measuring photocurrents with 532 nm excitation can be understood from the diagram in Fig. 1(b). The energy required to excite carriers from trap states into the conduction band (CB) is less than the band gap energy, implying that subband gap illumination of NCs can affect the overall charge state of the sample by exciting carriers out of the traps. This in turn, changes the photocurrent measured *later* with 532 nm excitation. Therefore, subband gap illumination of devices affects the photoconductivity, even though subband gap excitation is not energetic enough to result in measurable photocurrent. Photocurrent lifetime wavelength dependence has also been studied using current noise spectroscopy, for energies below and above the band gap.<sup>21–23</sup> Varying the illumination wavelength alters the level of noise from generation-recombination and trapping-detrapping.<sup>23</sup> Wavelength dependence was found to be strong in the low frequency range of the photocurrent noise power spectra.<sup>22,23</sup> This was attributed to long trapping-detrapping times similar to those observed here.

These results also indicate that subband gap excitation is more efficient for charge detrapping than excitations above the band gap. Different wavelengths of light excite trapped carriers into different band gap edge states, as depicted in

Fig. 1(b). Charge carriers in higher states have a larger number of relaxation pathways available than those in the lowest conduction state. For example, they can relax into lower states, into trap states, or travel out of the NC via field-driven transport. It is possible that access to higher states could reduce the trap emptying efficiency, decreasing the memory effect. This conceptually supports our result that subband gap energy photons are preferable for trap manipulation in NC semiconducting films.

Photoconductivity of CdSe/ZnS NC arrays depends on device exposure to light and electric fields. Photocurrent can be modified by cycling voltage under illumination or in the dark, and the effect exhibits saturation after a few hours. Interestingly, while subband gap illumination does not yield measurable photocurrents, it affects the photoconductivity upon subsequent band gap illumination. This is due to the presence of charge traps that are emptied or filled by applying electric fields and light, where traps are most easily emptied with subband gap illumination. These factors are essential for the optimal and robust operation of optoelectronic devices based on semiconductor nanocrystals.

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