Imaging the charge transport in arrays of CdSe nanocrystals

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A novel method to image charge is used to measure the diffusion coefficient of electrons in films of CdSe nanocrystals at room temperature. This method makes possible the study of charge transport in films exhibiting extremely high resistances or very small diffusion coefficients.

Electric-force microscopy (EFM) has been used to probe the electrical properties of microscopic systems, such as DNA molecules, carbon nanotubes, SiGe dots, and single nanocrystals (NCs). However, there are few examples in which EFM data are analyzed quantitatively.

We describe a new method, based on EFM, to image the charge motion in a regime not accessible to traditional transport measurements. We use it to directly obtain the charge diffusion coefficient in films of CdSe NCs. Semiconducting NC arrays made to date are so resistive that it is difficult to study them. The current through such arrays after application of a voltage step decays with time, so that the steady-state current corresponds to a resistance that is too large to measure by conventional means. Our technique could have wide application in highly resistive thin films.

The charge transport is imaged in three-dimensional arrays of CdSe NCs using a field-effect transistor geometry. The EFM measurements are made after the voltage on the source electrode is turned on and off. The device, illustrated in Fig. 1, consists of two Au electrodes separated by ~5 µm, a 350nm thick SiO2 layer, and the degenerately doped Si substrate. Highly monodispersed NCs, capped with tri-octylphosphine oxide with a diameter of 1.1 nm between nearest neighbors, are self-assembled into ~0.2 µm thick films on top of the devices. We show data for two samples, with NC diameters 6.1 nm (Fig. 2) and 4.7 nm (Fig. 4). These NCs are synthesized using different preparations, as described in Ref. 2 and Ref. 1, respectively. Negative dc-voltage Vdc is applied to the source electrode to charge the NCs, while all other voltages are zero (Fig. 1). Our approach is different from the standard EFM technique in which an ac-voltage is applied to the tip.

We first discuss how the EFM provides a measure of the charge distribution. A small conductive tip oscillates in the z-direction and is scanned parallel to the sample surface (Fig. 1). The electrostatic force F between the sample and the tip modifies its resonant frequency and introduces a phase shift \( \Delta \phi(x, y) \propto dF/dz \). An image is produced by measuring the phase shift as a function of the tip position in the xy-plane at a constant height. The electrostatic force on the tip results from the capacitive coupling between the tip and the electrodes (or the gate) and from the Coulomb interaction between the static charges on the sample and the charges induced on the tip and the electrodes (or the gate). Krauss et al. have discussed the force from a point charge. We use a similar argument before extending it to a charge distribution in the film. The charge \( q \) induces \( q_1 \) on the gate and \( q_2 \) on the tip. Following Ref. 2, \( q_1, q_2 \propto q \), and ignoring contact potentials because we work with large voltages, one can show that \( F \propto q^2 \) for \( Vdc = 0 \). The EFM signal is then \( \Delta \phi \propto q^2 \), proportional to the square of the charge.

We argue that the EFM signal for a continuous charge distribution is similarly proportional to the square of the charge in a small area of the film below the tip. We scan the tip ~400 nm above the film-SiO2 interface where the charge density resides. Because the oxide is ~350 nm thick, the image charge density in the gate is ~350 nm below that in the film. Thus, at lateral distances larger than ~400 nm the charge density in the film will be equal and opposite to the image charge in the Si substrate, giving a very small net force on the tip. The tip is only sensitive to charge within a radius of ~400 nm. Considering only charges \( q_1, q_2 \) within this radius, the argument above applies and the force is once again proportional to \( q^2 \).

We use a Digital Instruments atomic-force microscope with conducting tips. The tip scans twice over each line along x in the xy plane above the sample. In the first pass, the tip traces the topography by scanning close to the surface. In the second pass above the same line, the tip is raised to a larger height (200 nm). Using the topographic profile, the tip is maintained at a constant height while the EFM signal is recorded. Each scan takes \( 3 \text{min} \). At the end of each scan, the tip is moved back to the top of the image before the next scan. Because of significant spatial drifts over long time periods, we scan the topography of every line before each EFM scan. Samples are measured in a nitrogen gas atmosphere to prevent degradation.

Figure 2(a) shows the time evolution of EFM images with \( Vdc = -40V \) applied to the source electrode. The topographical contour of the same region containing the electrodes is superimposed. \( Vdc \) is changed from 0V to \( -40V \) at the top of the first scan, and it is held constant during the following scans. The second image is recorded 39 minutes after the first image. As expected,
the grounded drain electrode cannot be seen in the EFM image. The EFM signal changes in time and the charged region around the source grows as the charge spreads into the film (Fig. 2(a)). Similar measurements on identical devices without depositing a film show no growth of the charged region at the electrode, guaranteeing that the charge motion is a property of the film.

Figure 2(b) shows the time evolution of the EFM images as the film discharges after the voltage on the source is set back to zero. Before the first line scan, the film has been charged for \( \approx 60 \) minutes at \( V_{dc} = -40V \). Note that the voltage has been set to zero shortly after the scan has begun. The second scan is initiated 9 minutes after the first image. We have imaged samples charged for up to \( 60 \) minutes at \( V_{dc} = -40V \). From the best fit parameters. The actual measured values \( \tau_{ch} = 60\text{min} \) and \( t_1 = 0.05\text{min} \) are much shorter than the best-fit values. Allowing \( \tau_{ch} \) and \( t_1 \) to be larger than measured has the effect of broadening the initial charge distribution. This may be compensating for our finite spatial resolution, not included in the model. For \( j \geq 2 \), the difference in \( t_1 \) is insignificant.

The same NC film was also imaged during illumination with green laser light (with energy above the CdSe NC bandgap). From the fits to the discharging data in this case \( D = (4.9 \pm 0.2) \times 10^{-3}\mu m^2/s \).

As argued above, the charging data in Fig. 2(a) are not recorded at a constant height. Specifically, the applied voltage \( V_{dc} \) causes the source to appear larger than for \( V_{dc} = 0 \); the apparent increase \( \sim 1.4 \) times of the electrode height implies that the height at which the EFM signal is recorded varies from 200nm to 245nm across the scan. From the measured \( z \)-dependence \( \Delta \phi(x, y) \propto V_{dc}^2/\epsilon_{NC} \), we infer that the EFM signal above the electrode is \( \approx 80\% \) of the value expected for a specified height of 200 nm.

Figure 4 shows the EFM images, under the same conditions as for Fig. 2, for a device with 800\( \mu m \) long parallel electrodes, separated by \( \sim 4\mu m \). The NC diameters are \( \approx 4.7nm \). Fig. 4 (a) shows the EFM image after charging of the film for 48 min, while Fig. 4 (b) shows the discharging of the film, previously charged for \( \approx 2\)hrs. The four images are slices \( (0 < y < 5\mu m) \) of EFM scans which are begun 0, 3, 6 and 9 min after \( V_{dc} \) is turned off. Fig. 4 (c) shows the measured and calculated EFM signal plotted along the \( x \)-axis for \( y = 4\mu m \) from the top of the scan, during the discharging. Line scans are shown for \( t_1 = 0.33\text{min}, t_2 = t_1 + 3(j-1)(\text{min}) \), for \( j = 1 \) to 4. The calculated curves are from a 1D diffusion and we use \( t_1 = 1.8\text{min} \), larger than the actual value as for Fig. 3. We find \( D = 3.6 \times 10^{-3}\mu m^2/s \) for the film.

The resistance per square of the film \( R = 1/\epsilon C \), where \( \epsilon \) is the capacitance per unit area. The capacitance \( C = \epsilon_0 \epsilon_r \approx 10^{-16}F/\mu m^2 \), where \( \epsilon_r \approx 4 \) for SiO\(_2\), and \( h = 350nm \) is the thickness of the SiO\(_2\) layer. For \( D = 3 \times 10^{-3}\mu m^2/s \), \( R \approx 3 \times 10^{18}\Omega \) per square. Even for the geometry in Fig. 2, this corresponds to \( R \approx 10^{16}\Omega \) and a steady-state current \( I \approx 10^{-15}A \) at \(-40V\). This could not have been detected in previous experiments. We estimate that this technique could be used to measure resistances per square as high as \( \approx 10^{20}\Omega \) using thicker oxides.

In conclusion, we have imaged the charge transport in films of CdSe NCs, and have measured the diffusion coefficient directly. This method can be applied to systems with currents so small that they cannot be measured by conventional methods. It will also allow quantitative studies of anomalous diffusion, which may result from electron interactions. Higher spatial and temporal res-
olution can be achieved using thinner oxides and small sample areas, respectively.

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FIGURE CAPTIONS

Figure 1. Schematic diagram of the device and the EFM measurement setup. CdSe NCs are deposited on top of a device described in the text. For voltage \( V_{dc} < 0 \) on the source electrode electrons are injected into the film from the source; no charge injection is observed for positive voltages on the source. \( q \) is the charge on the sample, while \( q_1 \) and \( q_2 \) are charges induced by \( q \) in the gate and in the tip, respectively.

Figure 2. (COLOR) (a) Charging and (b) discharging of a CdSe film as a function of time as described in the text. A topographic contour containing the two electrodes is shown. The circle to the right of the electrodes is a flaw in the NC film.

Figure 3. The measured and calculated EFM signal plotted along the x-axis during the discharging of the film. The calculated curves \( (Q(x, t_j))^2 \) are obtained from the best fit of a diffusion model, described in the text. The diffusion coefficient from the fit is \( D = (2.8 \pm 0.2) \times 10^{-3} \mu m^2/s \). The comparison between data and theory shown for \( t_j, j = 1, 4, \ldots, 19 \). Inset: Positions of maxima \( x_{max,j} \) vs time \( t_j, j = 1 \) to 21, and a linear fit \( x_{max}^2 = 4Dt \), giving the same value of \( D \).

Figure 4. (COLOR) EFM images for a device with long parallel electrodes. (a) Charging of the film, 48 min after \( V_{dc} = -40V \) is turned on. The topographic contours of the electrodes are shown. (b) Slices of EFM images \( (0 < y < 5 \mu m) \) showing discharging of the film 0, 3, 6 and 9 min after \( V_{dc} \) is turned off. (c) Measured and calculated EFM signal plotted along the x-axis as described in the text.

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