On Possible Use of Capped Quantum Dots in Memory Devices

M. Dokukin[1], N. Guz[1], R. Olac-Vaw[2], V. Mitin[2], and I. Sokolov[1, *]

[1] *Department of Physics, Clarkson University, Potsdam, NY 13699-5820, USA*
[2] *Department of Electrical Engineering, University of Buffalo, The State University of New York, Buffalo, NY 14260-1920, USA*

Here we report on the analysis of a possible use of semiconductor quantum dots (QDs) in memory storage devices. We analyze the charging and discharging behavior of capped CdSe QDs deposited on graphite in ambient conditions. Individual QDs can be addressed (charged) with the synergistic action of light and mechanical interaction with a probe of an atomic force microscope (AFM). The analyzed QDs allow recording information at a density up to 1 Tb/cm². We demonstrate that it is possible to attain the charging time (writing) down to 10 ns while keeping discharging (storage) for more than 1000 years.

Keywords: Quantum Dots, Memory Devices.

RESEARCH ARTICLE

Unique properties of semiconductor nanocrystals,[1, 2] quantum dots (QDs), make them useful for a wide range of applications, from detectors,[3–5] light-emitting diodes,[6] lasers,[7–9] and solar cells[10] to biological markers[11] and nanosensors.[12] Cadmium selenide (CdSe) QDs are one of the most popular QDs,[13–15] which show nontrivial photoelectric properties such as fluorescence lifetime fluctuations,[13] spectral shifts[14] and intermittent fluorescence.[15] The appearance of dark and bright periods in the photoluminescence intensity of single CdSe nanocrystals is linked to photoionization[16] of the QD followed by its neutralization. Such blinking occurs frequently in the organically capped dots, while inorganic capping reduces the ionization frequency and leads to longer on-period.[17] It has recently been shown[18] that organically-capped CdSe QDs can be photoionized individually by squeezing the capping layer with the probe of an atomic force microscope. A lifetime for the charge state of several hours has been reported. All these nontrivial properties make organically capped QDs promising candidate not only for photonic devices but also for information storage.

In the present work, we analyze the charging and discharging of organically capped quantum dots deposited on graphite from the point of view of using them in memory devices. We show that it is possible to decrease the charging time (writing) down to tens of nanoseconds microseconds while keeping discharging (storage) for more than 1000 years.

Figure 1 shows a system of QDs deposited on graphite substrate, which is a material of choice because of the ease of preparation of atomically flat and clean surfaces. Laser light can be used to induce photoionization of illuminated QDs. A conductive AFM probe, Figure 1(a), can scan over the surface and 1. Accelerate the charging of individual QDs (or "write" information) 2. Detect single electron charges on QDs[18] (or "read" the information). As was found,[18] the AFM probe can accelerate photocharging of QDs as shown in Figure 1(b). This is due to the squeezing of a relatively soft organic tri-*n*-octylphosphineoxide (TOPO) layer capping the QDs. While a photoionized electron can also escape from the QDs to the conductive band of graphite, there is a slow charging solely due to photoionization. Figure 1(b) also shows the case of slow discharging of a positively charged QD by tunneling of an electron from graphite to the QD.

The life time of an electron inside a capped QD (QD charging time) can be estimated as follows:[19]

$$\tau_{\text{out}} = \tau_{\text{b}} \exp\left(\frac{2}{\hbar} \int_0^a \sqrt{2m(U(x) - E_{\text{electron}})} \, dx \right) \quad (1)$$

where m is the electron mass, E_{electron} is the kinetic energy of electron, a is the thickness of the potential barrier $U(x)$. $U(x)$ can be approximated by a linear potential $U(x) = (\Phi_2 - \Phi_1)x/a + \Phi_1 + U_0$, where Φ_1 and Φ_2 are the work functions of CdSe and either graphite (in the case of tunneling to the substrate) or chromium (in the case of tunneling to the AFM probe), and U_0 is an effective potential energy of the dielectric capping layer. The τ_{b} is the time
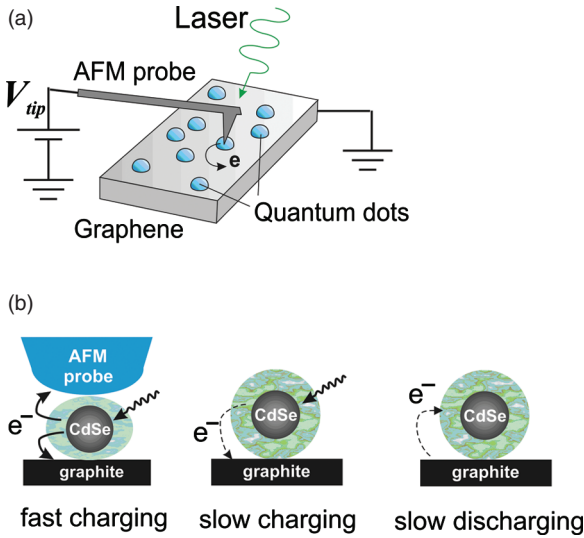
Fig. 1. (a) A system of QDs deposited on graphite substrate. A conductive AFM probe, can scan over the surface and 1. Accelerate the charging of individual QDs (or write information) 2. Detect single electron charges on QDs (or read the information); (b) (Left image) The AFM probe can accelerate photocharging by squeezing the capping layer of QDs. (Central image) Without such squeezing, the charging is rather slow. (Right image) The case of slow discharging of a positively charged QD by tunneling of an electron from graphite to the QD.

that the electron is located near the boundary of the quantum dot. It can be estimated as $\tau_b = 2R_{QD}/v_e$, where R_{QD} is the radius of the QD, v is an electron velocity in the QD.

In the case of discharging, $U(x)$ gets an additional Coulomb energy term because the QD is charged. Thus, the lifetime of a charged QD can be found as:

$$\tau_{in} = \tau_b' \exp\left(\frac{2}{\hbar} \int_0^a \sqrt{2m(U'(x))} \, dx \right) \quad (2)$$

where $U'(x) = (\Phi_1 - \Phi_2)x/a + \Phi_2 + U_0 - \frac{1}{4\pi\varepsilon_0} \frac{q^2}{R_{QD}+x}$. Here ε_0 is the permittivity of vacuum, q is the electron charge. τ_b' is the time that a free electron in the substrate material is located near the outer boundary of the quantum dot.

Thus, the charging and discharging time can be estimated for known materials and QD/dielectric layer size. The later can be estimated, for example, from transmission electron microscopy images. Both times τ_{in} and τ_{out} depend only on two unknown parameters U_0 and τ_b'. U_0 can be estimated from experimental data, in ambient condition it takes about 40–50 minutes for the photo-excited electrons to escape the QD through the dielectric layer.[18] To find U_0, we take the following values required in Eq. (1): $E_{electron} = h\nu - E_{QD}$, where $h\nu$ is the energy of exciting photon, $E_{QD} = 1.96$ eV is the QD band gap (estimated from fluorescence measurements), $d \sim 1.4$ nm (from the TEM data, assuming two TOPO monolayers of the organic capping[20]), $\Phi_{CdSe} = 5.35$ eV, $\Phi_{Cr} = 4.5$ eV, $\Phi_{graphite} = 4.65$ eV, and the $\tau_b \sim 1 \times 10^{-13}$ sec (here $R_{QD} = 2.4$ nm

and $\nu_e \sim 10^6$ cm/sec[21–23]). Taking $\tau_{out} = 45$ min, one can obtain $U_0 \sim 1.8$ eV from Eq. (1).

The second unknown parameter τ_b' can be evaluated by substituting the obtained U_0 in Eq. (2), and using the experimental value of τ_{in}. This value was measured by scanning of the same area of charged TOPO capped CdSe QDs dispersed on a highly ordered pyrolytic graphite film as described in Ref. [18]. It was found that $\tau_{in} \sim 24$ h. Thus, one can find from Eq. (2) that $\tau_b' \sim 10^{-11}$ sec.

We now have a complete set of parameters to make predictions regarding the charging and discharging (writing and storing) information by using the QD system. Let us first calculate the time required for photoionized charging (the case shown in the middle image of Fig. 1(b)) and discharging with respect to the thickness of the QD capping barrier (the case shown in the right image of Fig. 1(b)). Figure 2 shows the charging and discharging times for a 4.8 nm CdSe QD as a function of the barrier thickness. Furthermore, because one can use different materials for the capping, the potential value of the barrier was was varied from half to twice the value of the calculated value U_0, i.e., from a range of (0.9–3.6) eV.

As one can see from Figure 2, the charging (writing) or discharging (storage) times of the QDs are rather close, especially for the higher barrier thicknesses. The largest observable difference for charging–discharging times is in the range of 1 second. To have a single QD as a reasonable bit of information storage, we need to increase charging speed, and at the same time, to keep discharging time as long as possible. To achieve that we can use the squeezing action of the AFM probe to decrease the thickness of the dielectric capping layer around the QD at the moment of photoionization.
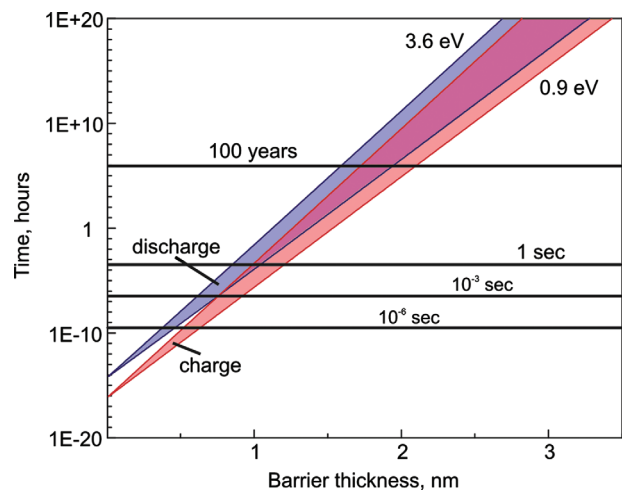

Fig. 2. The charging (writing) or discharging (storage) times of the capped QDs as a function of the thickness of surrounding dielectric capping layer (barrier). The charging time was calculated for the case of photoionization when using 523 nm illuminating (excitation) light. The barrier potential was chosen from 0.9 to 3.6 eV. Horizontal time lines are shown for convenience.

Let us now calculate the writing time for the case of the squeezed dielectric capping layer's thickness shown in Figure 1(b) (left image). The results of this calculation as well as the storage times are shown in Figure 3. One can see that the decrease of the dielectric thickness at the moment of light illumination leads to a substantial decrease of the charging (writing) time. As an example, one can use the thickness of the capping barrier of 2.1 nm (which corresponds to three TOPO monolayers of 0.7 nm each[20]) to obtain the storage time between 5000 to 280×10^6 years. Compressing the initial dielectric TOPO layer two times, one obtains the charging time below 1 second (zone 2 in Fig. 3). Additional squeezing leads to decreasing charging time up to 10^{-6}–10^{-8} seconds in the case of 25% of the initial TOPO thickness (zone 3 in Fig. 3). Obviously, there are no regular AFMs that are capable of moving probe that fast right now. However, theoretically it is still possible to do with very stiff AFM cantilevers, or just by using a different deformation method.

It is interesting to estimate the recording information density by using the described system of QDs. If we arrange QDs placed 10 nm from each other (the distance at which one can ignore electromagnetic cross-talking between QDs) then 1 cm^2 would carry 1 Tb of information. This is almost 20 times higher than the modem density of magnetic recording.

It is worth noting that the recorded charges on QDs are surprisingly stable in open air environment. We are demonstrating it with an attempt of forced discharging of the charged QDs prepared as described in Ref. [18]. The initially charged area of QDs was supplied by air flow of negative ions created by an air purifier with negative ion source. Figure 4(a) shows an area with charged QDs. The charges were clearly seen during the scanning from the top to the

bottom. When the probe was in the middle of the image, the flow of negative ions was introduced (shown with an arrow). One can see instant disappearance of the charges. This indicates that we are dealing with positive charges on QDs. After switching off the ion source (Fig. 4(b)) while scanning goes from the top to the bottom, one can clearly see the reoccurrence of the charges. The whole scan took about 90 seconds. One can see that the recovery of the charges happened within approximately 1 minute. This behavior can presumably be explained by the diffusion of the negative ions on the TOPO layer to the conductive graphite substrate, where the ions are neutralized/reduced. The same area was measured 10 hours later (Fig. 4(c)). The presence of the majority of charges was confirmed. Typically charges disappeared after 24 hours. The same mechanism of diffusion can explain this longevity of the charges in ambient conditions, where a number of negative ions are typically present. This demonstration is intended to show the robustness of the described system. In a real memory storage device, it is quite unlikely to expect that storage surface will be exposed to open air. Moreover, the
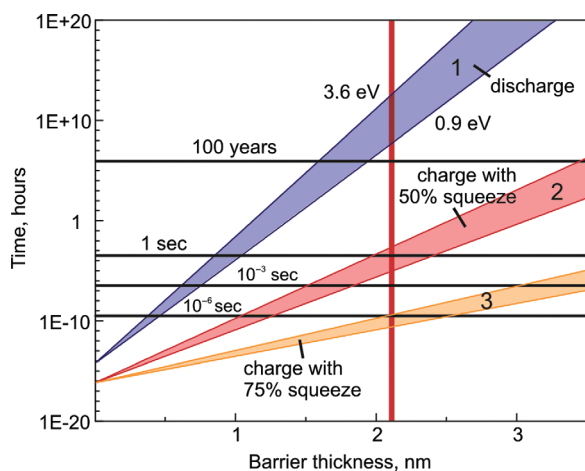

Fig. 3. The storage time needed to discharge (zone 1) and the writing time needed to charge (zones 2 and 3) QDs shown as a function of the thickness of the capping dielectric barrier. The charging time is calculated when the capping barrier around a QD can be squeezed while the QD is illuminated by 532 nm light. The barrier potential was chosen in the range of (0.9–3.6) eV. Horizontal time lines are shown for convenience.
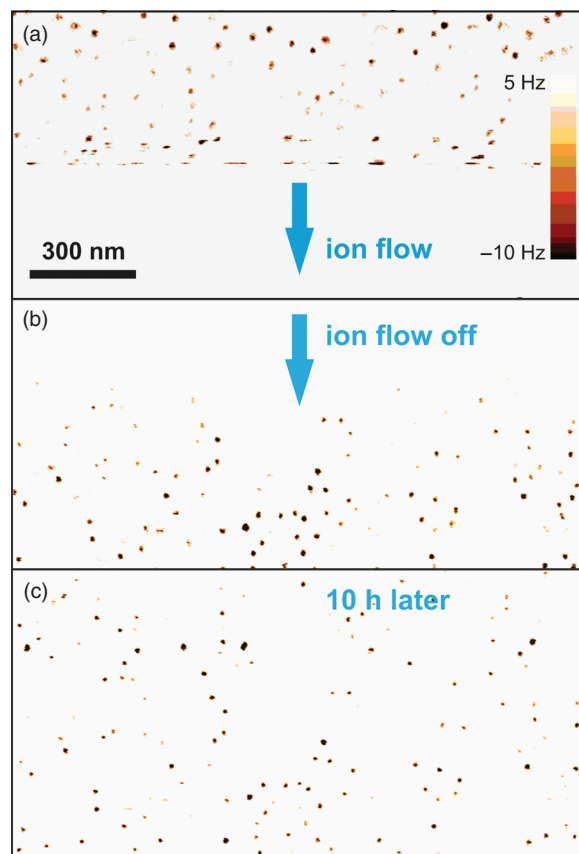

Fig. 4. Images of the resonance frequency shift/charge, which correspond to a single electron charge, as a function of time and action of a flow of negative ions. The slow scan direction is shown by the arrows. (a) The sample was subjected to a negative ion beam shot at the middle of the scan. (b) The charges are recovering after turning off the ion beam. (c) The frequency shift after 10 h of storage in ambient conditions.

RESEARCH ARTICLE

environment will have to be sealed to prevent oxidation of QDs in the open air.

In conclusion, we demonstrated that semiconductor QDs, in particular organically capped CdSe QDs could be used in memory storage devices. Using the synergetic action of photoionization and mechanical squeezing action of the AFM probe, it is possible to charge individual QDs with times which are either comparable or superior to modern recording devices. At the same time, our calculations show that the recorded information can be stored for thousands years. It was estimated that the planar arrangement of QDs could allow recording information at a density up to 1 Tb/cm^2. This is almost 20 times higher than the modem density of magnetic recording.

References

1. D. J. Norris, A. Sacra, C. B. Murray, and M. G. Bawendi, *Phys. Rev. Lett.* 72, 2612 (**1994**).
2. D. V. Talapin, A. L. Rogach, A. Kornowski, M. Haase, and H. Weller, *Nano Lett.* 1, 207 (**2001**).
3. M. Keller, B. Lange, K. Hayasaka, W. Lange, and H. Walther, *Nature* 431, 1075 (**2004**).
4. S. Komiyama, O. Astafiev, V. Antonov, T. Kutsuwa, and H. Hirai, *Nature* 403, 405 (**2000**).
5. G. Konstantatos, I. Howard, A. Fischer, S. Hoogland, J. Clifford, E. Klem, L. Levina, and E. H. Sargent, *Nature* 442, 180 (**2006**).
6. N. Tessler, V. Medvedev, M. Kazes, S. H. Kan, and U. Banin, *Science* 295, 1506 (**2002**).
7. V. I. Klimov, A. A. Mikhailovsky, D. W. McBranch, C. A. Leatherdale, and M. G. Bawendi, *Science* 287, 1011 (**2000**).
8. V. I. Klimov, A. A. Mikhailovsky, S. Xu, A. Malko, J. A. Hollingsworth, C. A. Leatherdale, H. J. Eisler, and M. G. Bawendi, *Science* 290, 314 (**2000**).
9. A. A. Mikhailovsky, A. V. Malko, J. A. Hollingsworth, M. G. Bawendi, and V. I. Klimov, *Appl. Phys. Lett.* 80, 2380 (**2002**).
10. B. J. Landi, S. L. Castro, H. J. Ruf, C. M. Evans, S. G. Bailey, and R. P. Raffaelle, *Solar Energy Materials and Solar Cells* 87, 733 (**2005**).
11. F. Patolsky, R. Gill, Y. Weizmann, T. Mokari, U. Banin, and I. Willner, *J. Am. Chem. Soc.* 125, 13918 (**2003**).
12. C.-Y. Zhang and L. W. Johnson, *Anal. Chem.* 81, 3051 (**2009**).
13. G. Schlegel, J. Bohnenberger, I. Potapova, and A. Mews, *Phys. Rev. Lett.* 88, 137401 (**2002**).
14. S. A. Empedocles, D. J. Norris, and M. G. Bawendi, *Phys. Rev. Lett.* 77, 3873 (**1996**).
15. M. Nirmal, B. O. Dabbousi, M. G. Bawendi, J. J. Macklin, J. K. Trautman, T. D. Harris, and L. E. Brus, *Nature* 383, 802 (**1996**).
16. R. G. Neuhauser, K. T. Shimizu, W. K. Woo, S. A. Empedocles, and M. G. Bawendi, *Phys. Rev. Lett.* 85, 3301 (**2000**).
17. Y. Yamasaki, H. Asami, T. Isoshima, I. Kamiya, and M. Hara, *Science and Technology of Advanced Materials* 4, 519 (**2003**).
18. M. Dokukin, R. Olac-Vaw, N. Guz, V. Mitin, and I. Sokolov, *Appl. Phys. Lett.* 95, 173105 (**2009**).
19. D. J. Griffiths, Introduction to Quantum Mechanics, Pearson Prentice Hall, Upper Saddle River, NJ (**2005**).
20. J. Jiang, T. D. Krauss, and L. E. Brus, *J. Phys. Chem. B* 104, 11936 (**2000**).
21. J. M. M. P. A. J. L. S. Franco, *IEEE Electron Device Letters* 18, 258 (**1997**).
22. W. T. Masselink, *Semicond. Sci. Technol.* 4, 503 (**1989**).
23. W. T. Masselink, *Appl. Phys. Lett.* 59, 694 (**1991**).