PHYSICAL REVIEW B, VOLUME 63, 081303(R)

Identification of surface states on individual CdSe quantum dots by room-temperature conductance spectroscopy

Boaz Alperson, Israel Rubinstein, and Gary Hodes*
Department of Materials and Interfaces, The Weizmann Institute of Science, Rehovot 76100, Israel

(Received 2 October 2000; published 5 February 2001)

We describe the direct observation of surface states on individual CdSe quantum dots by conductive scanning force spectroscopy at room temperature and the dependence of these states on size quantization and humidity conditions. Peaks corresponding to surface states that lie within the gap appear at both voltage polarities after exposing the sample to dry nitrogen, but disappear after exposure to moist air. The effect is reversible, indicating that the surface states are passivated by adsorbed water. This directly observed passivation correlates with that inferred from previous optical measurements.

DOI: 10.1103/PhysRevB.63.081303 PACS number(s): 73.61.Ga, 81.07.−b, 82.45.−h

As the size of a semiconductor quantum dot (QD) decreases below a limiting value, associated with its exciton Bohr radius, its energy band structure changes. The band gap increases and the electronic states open up from a continuum to a ladder of discrete, quantized energy states.[1] Decreasing size also implies an increase in the surface-to-volume ratio in the quantum dot: in a 5 nm diameter dot, about every third atom will be located at the surface, hence surface defects and dangling bonds are expected to play an increasing role. Unsaturated surface atoms were found even in surface-capped CdSe quantum dots, using x-ray photoelectron spectroscopy,[2] and in CdSe (Ref. 3) and CdSe (Ref. 4) nanocrystals using nuclear magnetic resonance spectroscopy. It is not surprising, therefore, that a large number of optical processes have been assigned to surface-induced effects in QD's.[5–9]

Recently, a sub-bandgap response in CdSe QD films was detected using surface photovoltage spectroscopy and the ambient atmosphere was found to determine the photovoltage direction due to interaction of water vapor with surface traps.[10] Water vapor was also found to quench the sub-bandgap photoluminescence attributed to surface states in the same CdSe films and to enhance the (close to) band-to-band recombination.[11] Here we describe direct room-temperature observation, using scanning force spectroscopy, of surface states in CdSe QD's, electrochemically and chemically deposited on gold, and show their dependence on quantum dot size and on atmospheric humidity conditions.

Epitaxially oriented CdSe nanocrystals (typically 4–5 nm diameter) were cathodically electrodeposited at 90 °C from a dimethylsulfoxide solution containing 50 mM $\mathrm{Cd(ClO_4)_2}$ and saturated with elemental Se, onto evaporated, $\{111\}$ textured gold on mica. Exact deposition conditions, yielding isolated dots on the gold surface, are described elsewhere.[12] CdSe QD's (ca. 3–4 nm diameter) were chemically deposited onto gold from a solution containing 110 mM sodium nitrilotriacetate and 80 mM cadmium sulfate, adjusting the pH to ca. 8 using potassium hydroxide solution, then following the addition of 80 mM of sodium selenosulfate, adjusting the final pH to 10.[13] Subsequent to the appearance of color in the originally colorless solution, evaporated gold-on-mica substrates were introduced into the solution and the system was kept in a constant temperature bath at 5 °C for 20 min. Transmission electron microscopy showed that the Au was partially covered by aggregates of QD's.

Using a scanning force microscope (AFM) with a conducting tip (Au/Pd alloy coating, evaporated onto silicon or silicon nitride AFM tips), and the force between tip and surface as feedback control, conductivity and current-voltage spectroscopy characteristics were obtained at contact. Previously, we were able to measure, using this technique, the band gaps of isolated CdSe QD's and to observe single electron tunneling at room temperature into the dots[14] and subsequently extended the technique, using low-temperature scanning tunneling microscopy, to correlate directly energy structure and charging features with QD size.[15]

A current-voltage spectrum obtained at normal ambient conditions, i.e., in humid air at room temperature, is shown in Fig. 1(a). The zero-current region in the spectrum corresponds to the band gap of the dot,[16,17] plus the charging energy $E_c = e^2/C$, where C is the effective capacitance of the QD.[14] In large dots, due to their relatively large capacitance, this energy is negligible at room temperature. In the present system, since the CdSe QD's are very small, E_c must be taken into account as it is typically ca. 0.2 eV. Hence, current flows in the system only when there is resonance between the tip filled band and the quantized energy levels of the nanocrystal, and the tip has acquired enough energy to overcome this charging energy. The I/V curve is approximately symmetric with respect to zero bias, i.e., current onset begins at ca. the same magnitude of the bias in both bias directions, indicating a midgap Fermi level.[18] The structure in the region of current flow, clearly apparent in the positive sample bias polarity, has been attributed to the Coulomb blockade effect.[19] No features are seen within the gap under these conditions.

The situation is strikingly different when the spectrum is taken after exposing the sample to dry nitrogen for several hours. In most samples, peaks that lie within the zero current gap appear at both polarities, as seen in Fig. 1(b). The current in each peak flows according to voltage polarity i.e., the current has the same sign as the applied bias. In some cases, only one peak was present, with no preference for a specific polarity. It is important to note that this effect was reversible upon changing humidity conditions: when the sample was exposed again to moist air, no peaks within the zero-current gap appeared in the spectra. Not all the spectra obtained under dry conditions were symmetric with respect to zero

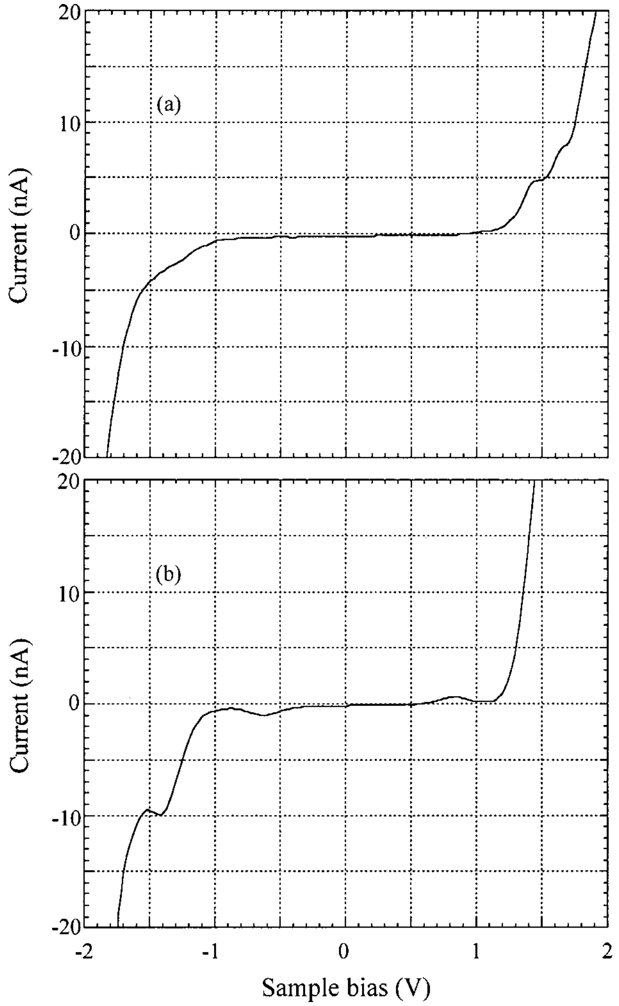

FIG. 1. Current-voltage spectra of a CdSe quantum dot at normal ambient conditions (a) and of another dot on the same sample after exposing the sample to dry nitrogen for several hours (b). Thermal drift precluded obtaining both spectra on the same QD.

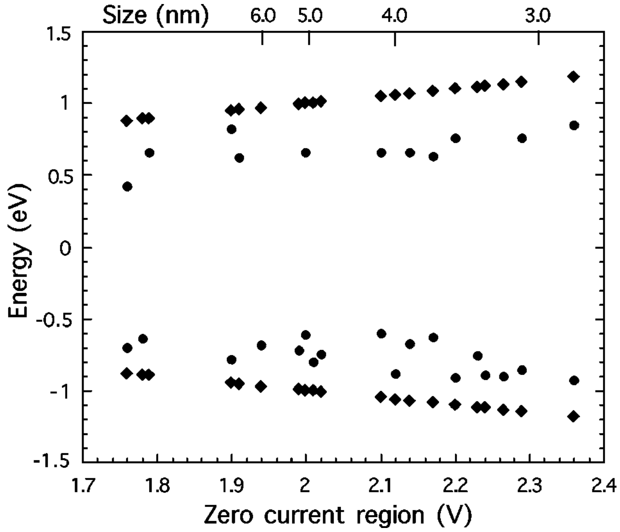

FIG. 2. Positions of the ''conduction'' (upper diamonds) and ''valence'' (lower diamonds) levels and the centers of the corresponding surface state peaks (upper and lower circles, respectively) from 20 different spectra as a function of dot diameter, the latter estimated from Ref. 22. Some of the spectra were corrected for asymmetry variations (see text). The real band gaps were probably slightly higher ($\leq$0.1 eV) than the zero-current region value (see text).

bias. While most of the symmetrical I/V curves exhibited two peaks, in most of the asymmetric spectra, only one peak was present, with no obvious correlation to the direction of the asymmetry.

The fact that surface state peaks, rather than steps, are seen in the current-voltage spectra is an example of negative differential conductivity (NDC). NDC has been observed in many systems. In the present case, it could be explained by filling of surface states: when these states are full, no more current can flow until the tip Fermi level moves above (below) the conduction (valence) level.

In order to map the position of the surface states with respect to the delocalized levels, we have taken 20 current-voltage spectra and plotted the peak positions of the surface states together with the positions of the delocalized levels (Fig. 2) and plotted them against the zero-current gap [the energy between the onsets (not the surface state peaks)] at both polarities. To do this, we have taken several points into consideration.

The positions of the surface state peaks have been adjusted for charging energy (which will cause the real position to be at a lower absolute value of voltage than that measured in the spectra). From our previous studies, the charging energy adds typically 0.2 eV to the band gap (measured from the first charging peak): the onset at each polarity therefore moves ca. 0.1 V. For larger quantum dots, this value is less and for smaller ones, greater: we have used values between 0.06 to 0.15 V depending on size (estimated from the zero-current gap).

The zero-current region is an indication of band gap, although not necessarily identical to it. In principle, band gap can be measured by subtracting the charging energy from the energy difference in current onset peaks (rather than the current onset itself) in the conductivity spectra.[20] This was not done here since both these peak positions, and also the charging energy, were often ambiguous or even not measurable. The current onset, on the other hand, was more easily measured. We have noted in general that the zero-current gap value (for spectra where there are no surface states) is close to the band gap measured by subtracting half the charging energy from the first conductivity peaks at both polarities. In the present case, where charging of surface states is taken into account, this will add a further charging energy which should be subtracted from the zero-current region to give the band gap, and this has been done in Fig. 2. Since the same charging energies are used to adjust both surface state positions and those of the delocalized levels, this adjustment does not affect the measurement of the depth of the various surface states (the parameter which interests us in particular). We should note that it is assumed that only one electron is added to (removed from) the surface states at any time: if many different states were filled, the zero-current region would be much larger than measured.

When necessary, the spectra were corrected for asymmetry variations so that the data could be presented on a uniform energy scale. This manipulation causes the band edges to move symmetrically on the energy scale with change of size. From the infinite barrier effective mass picture, the conduction edge is expected to move more (by a factor of about 3) than the valence edge due to the lower effective mass of electrons compared with holes. A more realistic finite barrier calculation will reduce this factor. From a more accurate tight-binding model,[21] the relative shift is about a factor of 1.5 for the size regime involved in this study. In addition, it should be kept in mind that the QD diameter was determined from the estimated band gap. For these reasons, no interpretations should be drawn from the band edges vs QD size. However, since our main concern is with the positions of the gap states relative to the band edges, this procedure is justified.

The zero-current region, taken for the purpose as the band gap, was correlated with the expected crystal size evaluated from the room-temperature experimental data of Murray *et al.*[22] for wurtzite CdSe. This is shown on the top scale of the *x*-axis. This correlation gives a distribution with most of the crystals between 3 and 6 nm in reasonable agreement with our previous measurements;[23] the zero-current region is probably slightly smaller (by less than 0.1 eV) than the band gap.

All of the samples in Fig. 2 are electrodeposited CdSe except for one (the one with a zero-current region ca. 2.7 V), which is chemically deposited (CD). CD samples are more difficult to measure than electrodeposited ones, since they are usually strongly aggregated and two or more crystals in series are usually measured. This results in additional grain boundary barriers and therefore large zero-current regions due to these barriers.[24] However, it was important to verify that the surface states measured here occur also on the CD samples, since previous optical spectral measurements with which the present results are correlated below were carried out on CD samples. We note that the CD samples are sphalerite structure with a slightly higher band gap (by ca. 0.07 eV) than the electrodeposited wurtzite crystals of the same nominal size. The similar results obtained from samples prepared by two different methods and with different surface chemistries means that they may be expected to be at least somewhat general rather than very specifically sample dependent.

The separation between the peaks of the gap states and the respective delocalized levels (as approximated by the current onset in the spectra) is ca. 0.4 eV for the conduction levels (we use the term conduction (or valence) ‘‘level’’ since in quantum dots, the bands have not yet developed) and ca. 0.3 eV for the valence levels. These separations show small variations with crystal size; however, in view of the large scatter in gap state positions, particularly those near the valence levels, these variations are not very meaningful, at least for the valence polarity. For the gap states near the conduction levels, line fitting gives a shift of 80 meV away from the conduction level for the small dots compared to the large ones. Localized states are expected to shift less than the band edges with decreasing dot size[25] to an extent depending on the depth of the state. In our measurements, this is seen to a moderately small extent for the conduction polarity and little, if at all, for the valence polarity.

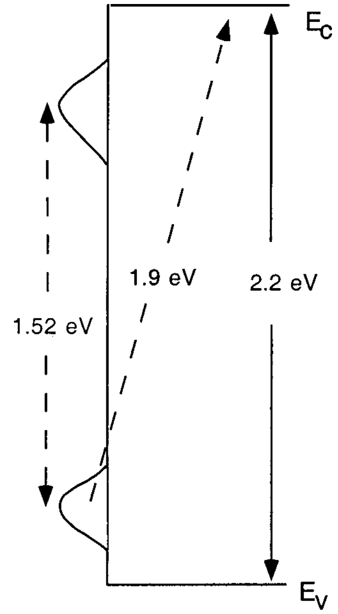

FIG. 3. Energy diagram of the surface states and delocalized levels for ca. 4 nm quantum dots. This was constructed using average values of the delocalized levels and of the surface states (onsets and center of states) from different samples (see text).

In order to correlate these results with previous optical spectral studies of surface states on 4.5 nm chemically deposited CdSe quantum dots (band gap ca. 2.2 eV), the averages of the gap-state positions relative to the conduction or valence levels (the onset of the gap states closest to the band edge, the center state position and the far edge position) were calculated for all the samples with a zero-current region between 2.1 and 2.3 eV (9 samples). This gives an average picture of the shapes of the gap states and their positions relative to the delocalized levels for a 2.2 eV band gap. A band gap of 2.2 eV was used for this construction since this is the approximate band gap of the samples to be discussed below. This energy diagram is shown in Fig. 3, together with the energies of some transitions.

Previous photoluminescence (PL) measurements of chemically deposited CdSe nanocrystallites (4–5 nm) in a water-free atmosphere showed a PL band in the red-near-infrared region with the band center located at 1.6 eV, about 0.6 eV below the corresponding absorption edge. Only a very small signal corresponding to a band-to-band emission was observed. Light intensity and temperature dependent PL studies indicated that this deep emission band was characteristic of a donor-acceptor recombination.[11] It was deduced that this band corresponds to a recombination between an electron, trapped at a shallow surface state and a hole, trapped at a deeper surface state. The fact that these states were located at the surface and were not interior states was evidenced by the asymmetric nature of optically detected magnetic resonance spectra.[26]

The effect of water adsorption was to shift the dominant PL emission to higher energies corresponding essentially to a (near) band-to-band emission with only a small contribution from trapped carrier recombination.[11]

Surface photovoltage (SPV) measurements on CdSe films similar to those used for the above PL measurements showed a similar effect of water vapor on the spectra.[10] In the presence of water vapor, only a band-to-band absorption at 2.2 eV was observed. In the absence of water (dry N_2 or vacuum), the SPV signal showed a well-defined onset at ca. 1.8 eV (a weak, very gradual onset could be discerned starting at 1.5–1.6 eV). This signal was attributed to promotion of electrons from relatively deep hole traps to the conduction band.

The emission from the (centers of) the gap state close to the conduction level to that close to the valence level in Fig. 3 is 1.5 eV compared with 1.6 eV measured from the PL spectra. The PL emission will be somewhat blue-shifted due to Coulomb interaction between the trapped electron and hole, which means that the energy separation between the two traps will be somewhat lower than the 1.6 eV measured.

The absorption transition from the (center of the) gap state above the valence level to the conduction level is 1.90 eV: this is compared with ca. 1.8 eV measured for this transition from the SPS measurements. The very weak onset in the SPV spectrum (starting at ca. 1.5–1.6 eV) might be due to transitions between the gap states (1.5 eV in Fig. 3) which would be expected to be weak.

The present results require some reassessment of our previous interpretation of the SPV and, more radically, the PL results. We had previously concluded, from the PL and SPV measurements, that the surface state energies involved a deep state ca. 0.6 eV from the valence level and a shallow one <0.1 eV from the conduction level. This was based on an assumed much larger shift ($\times 3$) of conduction level than valence level and the expectation that relatively deep levels would move much less than the delocalized ones upon quantization. As discussed above, both these effects appear to be much less than we had previously expected. The mapping of states from the present studies can be successfully correlated with the previous results of both the PL and SPV studies.

In conclusion, we have observed surface states within the band gap of CdSe nanocrystals under water-free conditions and monitored the depths of these states as a function of crystal size. The results were compared with luminescence and surface photovoltage measurements. The similar effect of water vapor on both the current-voltage and optical spectroscopies indicates that the same surface states are involved. Scanning probe spectroscopy is a unique method of observing the effect of surface states on the optoelectronic properties of QD's, as studies up to date were based mainly on optical rather than electrical techniques.

This work was supported by the Israel Ministry of Science, Contract No. 8461-1-98 and by the United States Israel Binational Science Foundation.

---

*Email: gary.hodes@weizmann.ac.il

[1] A. D. Yoffe, Adv. Phys. **42**, 173 (1993).

[2] J. E. Bowen Katari, V. L. Colvin, and A. P. Alivisatos, J. Phys. Chem. **98**, 4109 (1994).

[3] L. R. Becerra, C. B. Murray, R. G. Griffin, and M. G. Bawendi, J. Chem. Phys. **100**, 3297 (1994).

[4] J. R. Sachleben, E. W. Wooten, L. Emsley, A. Pines, V. L. Colvin, and A. P. Alivisatos, Chem. Phys. Lett. **198**, 431 (1992).

[5] L. Spanhel, H. Haase, H. Weller, and A. Henglein, J. Am. Chem. Soc. **109**, 5649 (1987).

[6] M. O'Neil, J. Marohn, and G. J. McLendon, J. Phys. Chem. **89**, 3435 (1990).

[7] M. Nirmal, C. B. Murray, D. J. Norris, and M. G. Bawendi, Z. Phys. D: At., Mol. Clusters **26**, 361 (1993).

[8] S. A. Majetich and A. C. Carter, J. Phys. Chem. **97**, 8727 (1993).

[9] S.-H. Kim, R. H. Wolters, and J. R. Heath, J. Chem. Phys. **105**, 7957 (1996).

[10] L. Kronik, N. Ashkenasy, M. Leibovitch, E. Fefer, Y. Shapira, S. Gorer, and G. Hodes, J. Electrochem. Soc. **145**, 1748 (1998).

[11] E. Lifshitz, I. Dag, I. Livtin, G. Hodes, S. Gorer, R. Reisfeld, M. Zelner, and H. Minti, Chem. Phys. Lett. **288**, 188 (1998).

[12] Y. Golan, L. Margulis, I. Rubinstein, and G. Hodes, Langmuir **8**, 749 (1992).

[13] S. Gorer and G. Hodes, J. Phys. Chem. **98**, 5338 (1994).

[14] B. Alperson, S. Cohen, I. Rubinstein, and G. Hodes, Phys. Rev. B **52**, R17 017 (1995).

[15] B. Alperson, I. Rubinstein, G. Hodes, D. Porath, and O. Millo, Appl. Phys. Lett. **75**, 1751 (1999).

[16] X. K. Zhao, L. D. McCormick, and J. H. Fendler, Langmuir **7**, 1255 (1991).

[17] S. Ogawa, F.-R. F. Fan, and A. J. Bard, J. Phys. Chem. **99**, 11 182 (1995).

[18] R. M. Feenstra and P. Mårtensson, Phys. Rev. Lett. **61**, 447 (1988).

[19] U. Meirav and E. B. Foxman, Semicond. Sci. Technol. **10**, 255 (1995).

[20] As pointed out by Franceschetti and Zunger [Appl. Phys. Lett. **76**, 1731 (2000)], the optical band gap is obtained from this electrical measurement by subtracting the electron-hole Coulomb energy, rather than the charging energy, from the zero-current gap. For the quantum dot size range involved in this study, this difference is mostly within 10 meV, and not larger than 30 meV. This is well below the experimental error of these measurements.

[21] P. E. Lippens and M. Lannoo, Phys. Rev. B **41**, 6079 (1990).

[22] C. B. Murray, D. J. Norris, and M. G. Bawendi, J. Am. Chem. Soc. **115**, 8706 (1993).

[23] Y. Golan, L. Margulis, B. Alperson, *et al.*, in NATO ASI Series 3, High Technology, Vol. 18, edited by J. H. Fendler and I. Dékány (Kluwer Academic, Dortrecht, 1996), p. 167.

[24] D. Behar, I. Rubinstein, G. Hodes, S. Cohen, and H. Cohen, Superlattices Microstruct. **25**, 601 (1999).

[25] L. Brus, J. Phys. Chem. **90**, 2555 (1986).

[26] E. Lifshitz, I. Dag, I. D. Livtin, and G. Hodes, J. Phys. Chem. B **102**, 9245 (1998).