Shell-Tunneling Spectroscopy of the Single-Particle Energy Levels of Insulating Quantum Dots

E. P. A. M. Bakkers,[†] Z. Hens,[†] A. Zunger,[‡] A. Franceschetti,[‡] L. P. Kouwenhoven,[§] L. Gurevich,[§] and D. Vanmaekelbergh[†]

Debye Institute, University of Utrecht, P.O. Box 80000, 3508 TA Utrecht, The Netherlands, National Renewable Energy Laboratory, Golden, Colorado 80401, and Department of Applied Physics and ERATO Mesoscopic Correlation Project, Delft University of Technology, P.O. Box 5046, 5600 GA Delft, The Netherlands

Received June 20, 2001; *Revised Manuscript Received July 31, 2001*

ABSTRACT

The energy levels of CdSe quantum dots are studied by scanning tunneling spectroscopy. By varying the tip–dot distance, we switch from "shell-filling" spectroscopy (where electrons accumulate in the dot and experience mutual repulsion) to "shell-tunneling" spectroscopy (where electrons tunnel, one at a time, through the dot). Shell-tunneling spectroscopy provides the single-particle energy levels of the CdSe quantum dot. The results of both types of tunneling spectroscopy are compared with pseudopotential many-body calculations.

1. Introduction. Insulating nanocrystals with diameters in the 1−10 nm range might play an important role in future optical and electrical devices. Consequently, significant research is directed toward better control of the size, shape,

Electron−electron Coulomb interactions in the quantum dot may have a profound effect on the tunneling spectra. Resonant tunneling spectra depend sensitively on whether a carrier tunnels through an otherwise empty dot where interelectronic interactions are absent or whether carriers are accumulated inside the dot where interelectronic interactions occur, resulting in additional peaks. These limiting scenarios are decided by the dynamics of electron tunneling in to and out of the quantum dot.[14,15] Consider, for instance, resonant tip-to-dot-to-substrate tunneling occurring at positive bias ($V > 0$). At the first resonance the probability to find one electron in the LUMO of the quantum dot is

in which Γ_s^{in} stands for the rate at which an electron with given spin tunnels from the tip into the empty s orbital, and Γ_s^{out} for the rate of tunneling from the occupied s orbital into the substrate electrode.

In the "shell-tunneling" case $\Gamma_s^{in} \ll \Gamma_s^{out}$; therefore, $P(s^1) \cong 0$, and a single electron tunnels through the nanodevice at the time. Tunneling leads to polarization of the dot by a single electron (i.e., dielectric solvation,[16] which depends on the dielectric discontinuity $\epsilon_{in} - \epsilon_{out}$ between the dot and its environment), but Coulomb interactions between two (or more) additional electrons do not occur (see Figure 1a). This still holds when the electrochemical potential of the tip electrode is increased further, such that tunneling from the tip to the second level (a p-type level) also occurs. In this type of *shell-tunneling* spectroscopy, the peaks in the conductance spectrum correspond to the single-particle energy levels, with their attendant degeneracies (two for s, six for p).

In the "shell-filling" case $\Gamma_s^{in} \gg \Gamma_s^{out}$; therefore, $P(s^1) \cong 1$, and the s orbital will be occupied with a single electron at the first resonance. When μ_e^{tip} is further increased, a second resonance will occur, corresponding to the filling of the s orbital with a second electron (see Figure 1b). The energy difference between the first and second resonance corresponds to the electron−electron Coulomb energy in the s orbital. The third resonance corresponds to the occupation

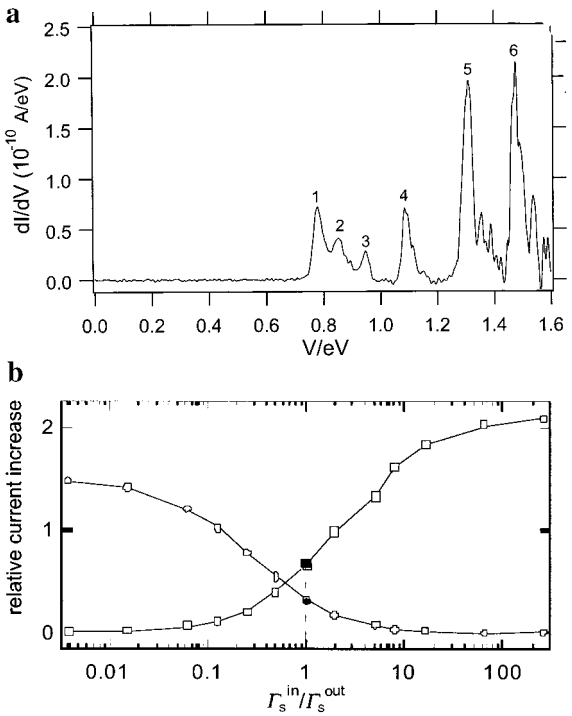

Figure 3. (a) Spectrum (at 4.2 K) of a 4.3 nm CdSe quantum dot in the positive bias range obtained with a smaller tip−dot distance than in Figure 2: set point 60 × 10

used to acquire the shell-tunneling spectrum in Figure 2. This means that the tip has been brought closer to the dot and that the ratio of the rates of tunneling into vs out of the dot is considerably increased. Under these conditions we first find three closely spaced peaks, *decreasing* in intensity. There is also some additional structure (i.e., small satellites) close to peaks 5 and 6. The occurrence of closely spaced peaks indicates the breakdown of the spin and orbital degeneracy due to electron−electron Coulomb interactions in the CdSe quantum dot. In other words, more than one electron is present in the dot at a given time. This is validated by the results acquired at even smaller tip−dot distances (larger set-point currents) showing a large number of closely spaced peaks. We infer that the results presented in Figure 3 reflect (partial) shell-filling.

3. Interpretation of "Shell-Filling" Spectra (Figure 3). We simulated the (*I*, *V*) tunneling spectra of CdSe quantum dots using a Monte Carlo algorithm. We used as input a scheme for the single-particle orbitals predicted from pseudopotential theory;[20] this means in order of increasing energy: the first orbital is s-type, the second orbital is p-type, the third orbital is d-type, the fourth orbital is s-type (denoted as s′), and the fifth orbital is f-type. We assume a substrate/dot/tip double-barrier tunnel junction with one-dimensional barriers; the width of the dot−substrate barrier is constant, the width of the tip−dot barrier can be varied. This mimics the experimental conditions. For a given value of the electrochemical potential of the tip (source) electrode with respect to the energy level system we monitor the state transitions in the quantum dot and the current using a stochastic sequence of 10^5 resonant electron tunneling steps via the electron energy levels of the dot. By repeating this procedure for a wide range of tip electrochemical potentials, the $I-V$ relationship is simulated for a given structure of the junction. (Injection of holes in the valence levels is not possible here due to the large HOMO−LUMO gap of the CdSe quantum dot, and the asymmetric distribution of the bias over both tunneling barriers.) Comparison of the simulated and experimental spectra enables us to assign the peaks in the experimental spectra unambiguously. We found that the spectrum of Figure 3 is acquired under conditions where tunneling into the dot is as fast as tunneling out of the dot,[22] thus reflecting *partial* shell-filling. Table 1 shows the assignment of the peaks in terms of specific transitions between two states of the quantum dot. The transitions change the occupation of the electron levels; the valence hole levels remain fully occupied. The third column gives the theoretical chemical potential for the transitions. In Table 2, we present the charging energies, i.e., the differences between the chemical potentials of Table 1. The pseudopotential values for the model CdSe quantum dot[20] are given in the third column. The experimental separations between the peaks, averaged over four CdSe quantum dots (4.3 ± 0.4 nm) [and corrected for $V_{\mathrm{tip-dot}}/V = 0.84$[22]] are given in the fourth column.

It follows from Table 2 that the energy difference between peak 2 and peak 1 is equal to the Coulomb energy between the two electrons in the s-orbital J_{s-s}. The calculations[20] give $J_{s-s} = 280$, 180, and 80 meV for $\epsilon_{\mathrm{out}} = 2$, 4, and 20,

from the partial shell-filling spectra (see foregoing section) are also given.

The experimental separations follow the trend predicted by pseudopotential theory. For instance, $\epsilon_d - \epsilon_p$ is larger than $\epsilon_p - \epsilon_s$, in agreement with the prediction. Quantitatively, the experimental separations between the second and first, and between the third and second, are significantly smaller than the pseudopotential values for $\epsilon_p - \epsilon_s$ and $\epsilon_d - \epsilon_p$, respectively, while the experimental separations between the fourth and third, and fifth and fourth peak, are in good agreement with the predicted values of $\epsilon_{s'} - \epsilon_d$, and $\epsilon_f - \epsilon_{s'}$. Possible reasons for the discrepancies between theory and experiment find their origin in a number of experimental uncertainties. The first uncertainty is related to the size distribution of the CdSe nanocrystals (4.3 nm $\pm$ 10%) leading to $\pm$ 20% uncertainties in the energy-differences between

(20) *Pseudopotential calculations*: We considered theoretically a faceted and surface-passivated nearly spherical CdSe quantum dot with a diameter of 4.7 nm. This model quantum dot comes closest to those investigated experimentally. The single-particle electron and hole levels are first calculated using a plane-wave-basis with a nonlocal pseudopotential, as described in refs 5, 6, and 16. In the second step, the pseudopotential wave functions are used to compute the screened ($\epsilon_{in} = 6.8$) interelectronic Coulomb (*J*) and exchange (*K*) integrals, as well as the polarization energies (Σ), as a function of the dielectric constant of the immediate environment around the dot, ϵ_{out}, as described in ref 16. Pseudopotential calculations show that the polarization and Coulomb interaction energies for a given quantum dot depend strongly on ϵ_{out}.

(21) Bakkers, E. P. A. M.; Vanmaekelbergh, D. *Phys. Rev. B: Condens. Matter Mater. Phys.* **2000**, *62*, R7743−R7746.

(22) *Estimation of the tunneling rates and the structure of the tip/dot/substrate double-barrier tunnel junction.* It follows from our 0.6oa1nctiondiele425 0 t1 Tf 3.2498 01 T9119