Electronic Structure of Metal-Semiconductor Nanojunctions in Gold CdSe Nanodumbbells

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The electronic properties of metal-semiconductor nanojunctions are investigated by scanning tunneling spectroscopy of gold-tipped CdSe rods. A gap similar to that in bare CdSe nanorods is observed near the nanodumbbell center, while subgap structure emerges near the metal-semiconductor nanocontact. This behavior is attributed to the formation of subgap interface states that vanish rapidly towards the center of the rod, consistent with theoretical predictions. These states lead also to modified Coulomb staircase, and in some cases to negative differential conductance, on the gold tips.

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Significant progress has been made in recent years in fabricating and understanding the physical properties of single-phase shape-controlled semiconductor (SC) nanostructures [1–6]. However, the research of hybrid metal-SC nanostructured systems is still at its infancy. A fundamental and intriguing problem associated with such systems is the mechanical and electronic properties of metal-SC nanojunctions. In bulk systems, such an interface is characterized by the space-charge region and the corresponding Schottky barrier [7]. The spatial extent of this interface region is typically tens of nms, comparable, and in many cases larger than many SC nanostructures prepared today. Hence, the bulk concepts for the metal-SC interface should be revisited for nanoscale contacts. From the technological point of view, understanding the properties of such nanocontacts is a major step in the route towards the implementation of SC nanocrystals (as well as molecules) in nanoelectronic device architectures. The metal-SC nanojunction problem was treated theoretically by Landman *et al.* [8], who studied the nanocontacts formed between Si nanowires (a few nm long) and Al nanoelectrodes. These authors predicted the induction of subgap states near the Si-Al interface, which rapidly decay into the Si, and the development of relatively large Schottky barriers.

The difficulty of achieving reliable metal-SC nanocontacts limited thus far the experimental study of such nanojunctions primarily to carbon nanotube based systems [9,10] and heterostructured nanowires [11]. Recently, selective growth metal (Au) nanodots (tips) onto the apexes of semiconductor (CdSe) nanorods was demonstrated, forming ''nanodumbbells,'' (NDBs) [12], and representative transmission electron microscopy (TEM) images are shown in Fig. 1. Such NDBs represent a unique model system manifesting metal-SC nanocontacts. Optical absorption measurements exhibit significant broadening upon the Au growth, while the photoluminescence is significantly quenched, both indicating strong coupling between the metal and SC parts [12]. However, the electrical properties of these nanostructures were not yet investigated.

To obtain detailed understanding of the electrical properties of these hybrid nanostructures, and, in particular, to unravel the nature of the Au-CdSe nanocontacts, we use here cryogenic scanning tunneling microscopy (STM) and spectroscopy. The tunneling spectra exhibit large spatial variations along a single particle. While the spectra taken on the gold dots typically portray single electron tunneling (SET)-like features (namely, the Coulomb blockade and Coulomb staircase), albeit with unequal steps, those measured near the middle of the rod show large energy gaps, comparable to those observed previously on CdSe rods [13]. A more complex behavior is found near the Au-CdSe interface, where subgap states emerge and then vanish when moving towards the rod center. Moreover, in some cases pronounced negative differential conductance features appear in spectra measured near the interface, manifesting a unique interplay between resonant tunneling and ''conventional'' SET effects.

NDBs consisting of CdSe nanorods, about 3 nm in diameter and lengths varying between 15 to 40 nm, and Au dots (tips) having diameters in the range of 2.2–4.5 nm, were prepared as described in Ref. [12]. The STM measurements were all performed at 4.2 K in He exchange-gas

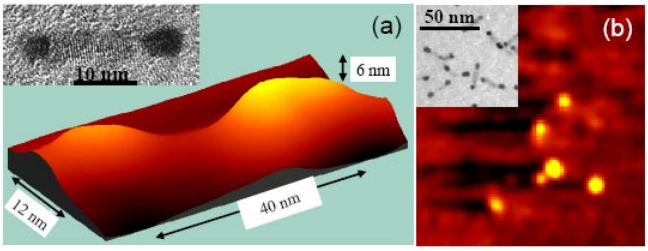

FIG. 1 (color online). (a) STM topography image of a single Au-tipped CdSe nanorod (nanodumbbell) taken with $V_B = 2$ eV. (b) STM current image (150×150 nm^2) acquired at a subband gap bias (0.5 eV) showing the gold tips of three nanodumbbells. The insets show high resolution (a) and low resolution (b) TEM images of nanodumbbells.

environment (inserted after evacuating the STM sample space), on isolated NDBs (encapsulated by organic ligands), either deposited on highly oriented pyrolitic graphite (HOPG) or on hexane-dithiol-coated Au(111) film, as described elsewhere [6,14]. We note in passing, that in contrast to our previous measurements [6,14], the data did not depend much on the deposition configuration. In the topography images, taken with various bias voltages (V_B), the gold dots are usually very clearly observed. On the other hand, the CdSe rod can be seen only in images taken with V_B larger than ~1.5 V, high enough to overcome the corresponding energy-gap. An STM topography image of a single NDB deposited on HOPG is shown in Fig. 1(a). A current image acquired on the same sample, but with a subgap sample bias, is presented in Fig. 1(b), where only the gold dots are revealed.

Spatially-resolved tunneling spectra [I-V and dI/dV vs V characteristics, the latter being proportional to the local density of states], were measured by positioning the STM tip above a single NDB, thus forming a double barrier tunnel junction (DBTJ). Tunneling spectra were then taken on different regions of the particle by moving the tip along the NDB from the gold dot, across the interface region, to the middle of the CdSe rod, as illustrated in Fig. 2.

Representative spectra acquired on a single NDB (40 nm long CdSe rod, 2.2 nm diameter Au dot), moving from the Au dot to the CdSe rod center, are presented in Fig. 2. Curve 1, measured on the dot, shows a series of peaks

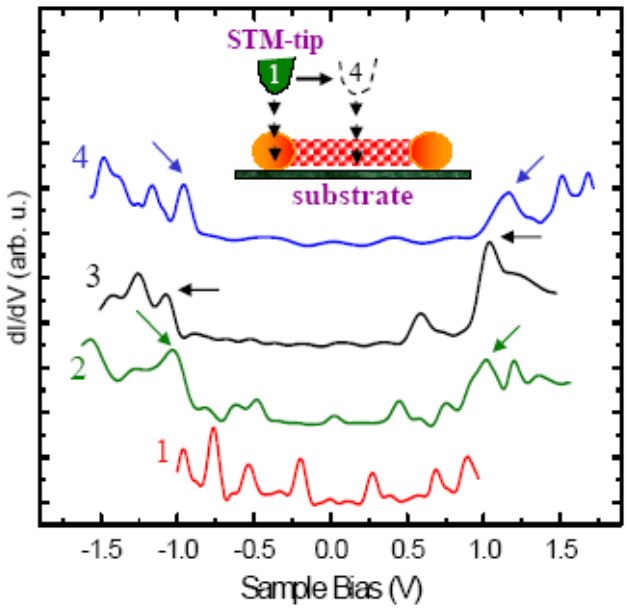

FIG. 2 (color online). Evolution of tunneling spectra (at 4.2 K) along the NDB, moving from the Au dot (curve 1) to the rod center 4. Curves 2 and 3 were taken on the CdSe rod, about 1 and 4 nm from the dot, respectively, showing subgap structure attributed to localized surface states induced by the Au-CdSe contact. The arrows mark the onsets of the CdSe conduction and valance bands. Inset: a scheme of the measurement configuration.

resembling the Coulomb staircase commonly observed on metal particles, but with some nonequidistant spacings. Curve 4, acquired near the center of the rod resembles those measured on "bare" CdSe rods (Ref. [13]), showing a similar energy gap free of subgap structure. New features emerge, however, in the data obtained on the rod, but close enough to the CdSe-Au interface (curves 2 and 3). Additional peaks are clearly observed now inside the gap region. The number of the additional peaks, and the subgap spectral weight altogether, decreases as the tip moves away from the interface, as illustrated by the spectral evolution from curve 2 (taken nominally ~1 nm from the interface) through 3 (~4 nm from the interface) to curve 4 (~15 nm, near the rod center). Interestingly, a reminiscent subgap level structure was detected in the tunneling spectra of CdSe quantum dots electrodeposited on gold [15].

The appearance of subgap structure specifically near the interface region can be attributed to localized metal-SC interface states, possible due to unpassivated atoms at the interface or to the effect of interface strain. We show below that the nonequidistant Coulomb staircase on the Au dots (curve 1) can also be explained within this framework. Another feature that is revealed in Fig. 2 is the small shift towards lower energy, by about 0.15 eV, of curves 2 and 3 with respect to 4, which may be attributed to a Schottky contact effect [7].

These results are in qualitative agreement with theoretical predictions of Landman *et al.* for the behavior of subgap states induced in metal-SC nanojunctions, as detailed in Ref. [8]. In this latter work, the subgap states decay on a very short length scale of less than 1 nm, whereas in our measurements, structure indicative of subgap states still exists even more than 5 nm from the interface (see below). However, one should consider the spatial resolution in our experiment. Technically, the exact location of the interface is not always clear in the topographic image [it is much sharper in the subgap current images, Fig. 1(b)]. More importantly, the locality of the tunneling spectra holds only up to roughly the Bohr radius (~5.7 nm in CdSe), and consequently the signature of the localized states could extend further away from the interface into the CdSe rod. Ref. [8] also predicts that a Schottky barrier is formed at the Al-Si (metal-SC) nanocontacts, but with heights much larger than that suggested by our observations. Clearly, quantitative agreement cannot be expected in light of the differences in materials and dimensions studied.

We turn now to a more detailed analysis of the tunneling spectra, considering also the effect of NDB dimensions. Tunneling spectra measured on the gold dot (~2.2 nm in diameter) and at the center of the CdSe rod (~40 nm long) of a NDB deposited on HOPG are plotted in Figs. 3(a) and 3(b), respectively. Corresponding data acquired on a NDB (placed on the gold substrate), consisting of a larger dot (~4 nm diameter) and a shorter rod (~17 nm long) are presented in Figs. 3(c) and 3(d). The spectra obtained on

these two nanorods exhibit the same qualitative behavior, but differ in the details. First, while the spectrum in Fig. 3(b) (long NDB) shows no evidence for subgap states, that measured on the shorter rod [Fig. 3(d)] depicts weak, but noticeable subgap spectral weight. This structure is attributed to the above localized states developed near the Au-CdSe interface, and could thus be detected only when the STM tip is close enough to it (a distance not much larger than the Bohr radius). In addition, the characteristics acquired on the larger Au dot [Fig. 3(c)] portray a denser peak structure as compared to that measured on the smaller dot [Fig. 3(a)], consistent with the expected size dependence of the dot charging energy, E_C.

The nonequidistant SET-like peak structure in Fig. 3(a), and the corresponding unequal stepped I-V characteristic presented in the inset, can be ascribed to a perturbation of conventional SET through the Au dot by a contribution of discrete electronic levels. More specifically, some peaks in the spectrum are arranged in a typical equidistant Coulomb blockade and Coulomb staircase pattern (with $E_C \sim 0.5$ V), and in between them additional (smaller) peaks appear, attributed to tunneling through the above localized interface states (and not to discrete Au-dot levels). This conjecture is corroborated by comparison with measurements taken on isolated colloidal gold nanodots having similar diameters to the Au tips, where only SET related peaks, nearly equidistantly spaced and with no additional structure, were observed [Fig. 3(c), upper blue curve].

The spectra acquired on the gold tips were simulated using the "orthodox model" [16] for SET in a DBTJ, modified to treat the contribution of discrete energy levels [6], namely, the interface localized states. Such a simulation is presented in Fig. 3(a) (lower, red line). Good agreement with the corresponding experimental curve was obtained with capacitance and resistance values of $C_1 = 1.9 \times 10^{-19}$ F, $C_2 = 3 \times 10^{-19}$ F and $R_1 \sim R_2 \sim 1.6 \times 10^8\ \Omega$, for the STM tip-NDB and NDB-substrate tunnel junctions, respectively, and assuming the presence of two localized subgap levels at energies 0.15 eV and -0.2 eV. Such energies are much larger than the estimated value for level spacing (intrinsic quantization) in gold dots of comparable size, $\delta = 4E_F/3N < 10$ meV (where E_F is the Fermi energy of gold and N is the number of free electrons in the dot). This intrinsic level quantization probably manifests itself in mild fluctuations of the width of the Coulomb staircase steps that are frequently observed, on both the NDB gold tips and the "free" Au nanodots, but cannot account for the additional structure discussed above. To further appreciate the role of discrete levels, we present in Fig. 3(c) (lower, red curve) a simulation performed using the *conventional* orthodox model, with the following parameters: $C_1 = 1.1 \times 10^{-19}$ F, $C_2 = 1.3 \times 10^{-18}$ F, $R_1 = 4.5 \times 10^7\ \Omega$, $R_2 = 4.5 \times 10^8$ W, and "fractional offset charge" [16] $Q_0 = 0.5e$. It is evident that while most of the peaks can be accounted for by the Coulomb staircase

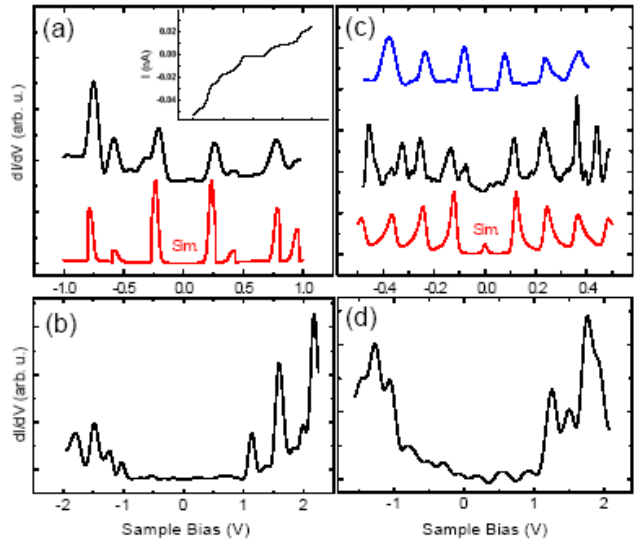

FIG. 3 (color online). Typical tunneling spectra measured at 4.2 K on the Au dots [(a, top) and (c, middle) black curves], and on the center of the CdSe nanorod [(b) and (d)], for NDBs (~2.2 nm dot diameter, ~40 nm long rod), placed on HOPG [(a) and (b)] and for NDBs (~4 nm dot, ~17 nm long rod), deposited on a dithiol-coated gold film [(c) and (d)]. The lower red curves in (a) and (c) are simulations, calculated as described in the text. Inset: I-V curve corresponding to the spectra shown in (a). A tunneling spectrum acquired on an isolated gold nanoparticle, ~4 nm in diameter is shown in (c) (upper blue curve).

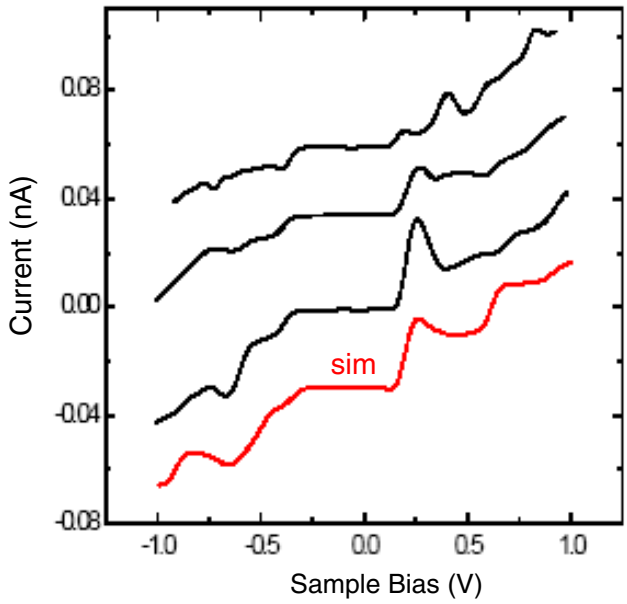

FIG. 4 (color online). Tunneling I-V curves (at 4.2 K) acquired on the Au-CdSe interface of a ND (2.5 nm Au dot, 40 nm long CdSe rod), exhibiting NDC superimposed on Coulomb staircase steps. The lower curve is a simulation based on the model described in the text.

(with $E_C \sim 0.12$ V), there are additional peaks in the measured spectrum, associated with the localized interface states.

By and large, modified SET-like patterns were always observed in measurements taken on the gold tips, with relatively large variations of E_C and discrete level values from one NDB to another, reflecting fluctuations in Au-dot size and Au-CdSe binding properties. Such ''nonuniversal'' behavior is expected to take place in hybrid nanoscale systems, a problem that could hamper the development of nanoelectronic devices and should therefore be addressed.

The localized interface states manifest themselves in some cases also via negative differential conductance (NDC) peaks in I-V characteristics measured on the Au dots, but nearly at the interface. These features were found only on about 5 of about 25 NDBs measured in detail. Then, however, their existence was robust (for both deposition configurations), although the strength of the peaks fluctuated between consecutively acquired spectra, as demonstrated in Fig. 4. These variations can be partly due to small shifts of the tip location. Note also that the NDC peaks appear to coincide with the onset of the Coulomb staircase steps.

NDC has been previously observed in STM measurements on SC or metallic nanoparticles deposited on either metal or SC substrates [15,17,18]. However, there are no reports for NDC in systems consisting of two closely contacted (e.g., metal and SC) nanoparticles. A few models were suggested to account for this phenomenon in the former and related [19] systems, none of which, however, can adequately account *by itself* for our results. We therefore suggest the following mechanism for the NDC in our case: In conditions where the energies of the localized interface state and onset of a Coulomb step coincide, transport through the Au dot and the localized state may take place in parallel, resulting in an ''overshoot'' of the current compared to the bare Au dot. The localized state may then be partially charged, thus increasing the electrochemical potential of the nearby located gold tip, and consequently decreasing the current through it. Such an effect was demonstrated by Heij *et al.* in a (lithographically fabricated) device consisting of two capacitively coupled Coulomb islands [20]. A simulation based on this model (and assuming two localized states centered at 0.25 eV and -0.6 eV) is presented by the lower (red) curve in Fig. 4.

In summary, spatially resolved tunneling spectroscopy on NDBs, consisting of gold nanodots grown onto the apexes of CdSe nanords, show that the electrical properties of this system, and, in particular, the Au-CdSe nanocontacts, are largely influenced by localized surface states residing near the Au-CdSe interface. These interface states modify the single electron tunneling characteristics measured on the gold dots by adding additional structure to the Coulomb steps and in some cases give rise to pronounced NDC peaks in the I-V characteristics. On the CdSe side of the nanojuction, subgap peaks emerge in the tunneling spectra, vanishing towards the center of the NDB, where the ''clean'' energy-gap of the CdSe rod is recovered, in qualitative agreement with theoretical predictions. We have also demonstrated that the NDBs provide a unique model system to study the physical properties of metal-semiconductor nanojunctions, a fundamental problem of significant importance in the quest for reliable nanoelectronic devices.

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