Band offsets: Nano is not bulk.

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Epitaxially-grown semiconductor heterostructures give the possibility to tailor the potential landscape for the carriers in a very controlled way. In planar lattice-matched heterostructures, the potential has indeed a very simple and easily predictable behavior: it is constant everywhere except at the interfaces where there is a step (discontinuity) which only depends on the composition of the semiconductors in contact. In this talk, we show that this universally accepted picture can be invalid in nanoscale heterostructures (e.g., rods, nanowires) which can be presently fabricated in a large variety of forms. Self-consistent tight-binding calculations applied to systems containing up to 75 000 atoms indeed demonstrate that the potential may have a more complex behavior in axial hetero-nanostructures: The band edges can show significant variations far from the interfaces if the nanostructures are not capped with a homogeneous shell. These results suggest new strategies to engineer the electronic properties of nanoscale objects, e.g. for sensors and photovoltaics.

METHOD

The band edge profiles in various semiconductor nanostructures have been calculated with a self-consistent tight-binding approach able to account for the charge transfers between the different materials. The charge on each atom has been computed with a fast and versatile Green's function technique allowing calculations on large systems in a few hours [1].

RESULTS

The valence band (VB) edge profile (the confinement potential for the holes) in a GaAs/AlAs core-shell nanocrystal with diameter $d = 7$ nm is plotted in Fig. 1. It shows the expected, sharp $\simeq 0.45$ eV discontinuity at the interface between the GaAs core and the AlAs shell. The potential is almost constant in each material, with fast variations only near the surface of the nanocrystal, due to the charge transfers with ligand-like atoms. The traditional model of "square wells and barriers" is therefore valid in these nanocrystals.

The case of axial nanowire heterostructures is more interesting. The band edges in a GaAs/AlAs nanowire superlattice with diameter $d = 5$ nm and half-period $l = 22.5$ nm are plotted in Fig. 2. The potential is no more constant in each material and shows significant variations along the nanowire axis. This results from the competition between the charge transfers at the GaAs/AlAs interface and the charge transfers with the surface ligands or capping material (Fig. 3). Indeed, the dipole layer at the GaAs/AlAs interface can not sustain the band offset discontinuity far away due to its finite cross section, so that the potential in each layer tends to the value it would have in pristine GaAs and AlAs segments. The latter is actually controlled by the passivation of each segment. In the present exemple, the work functions of the GaAs and AlAs segments differ by only $\simeq 0.1$ eV, which is lower than the 0.45 eV band offset.

The model of "square wells and barriers" can actually break down once an interface does not have a *closed* shape (like in Fig. 2, but not in Fig. 1) and competes with nearby surfaces. This happens in axial nanowire heterostructures when the thickness of the layers is larger than the radius of the nanowire. It has already been shown that the work functions of nanostructures can be tuned by more than 1 eV using appropriate surface chemistry. This open new routes for the design of functional nanostructures able, for example, to separate carriers for photovoltaics applications. As an illustration, the potential in a homogeneous GaAs nanowire alternating segments with and without an AlAs shell is plotted in Fig. 4. The shell controls and modulate the potential in the GaAs core, so that the holes are localized in the segments with a shell, and the electrons in the segments without a shell.

REFERENCES

[1] Y. M. Niquet and C. Delerue, Phys. Rev. B **84**, 075478 (2011).

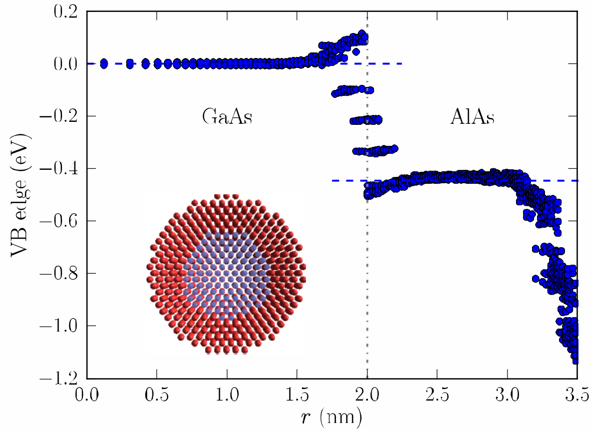

Fig. 1. VB edge in a spherical GaAs/AlAs core/shell quantum dot as a function of the radial position of the atoms (core diameter $d_c = 4$ nm; shell diameter $d_s = 7$ nm). The horizontal dashed lines indicate the VB offset in a 2D GaAs/AlAs super-lattice.

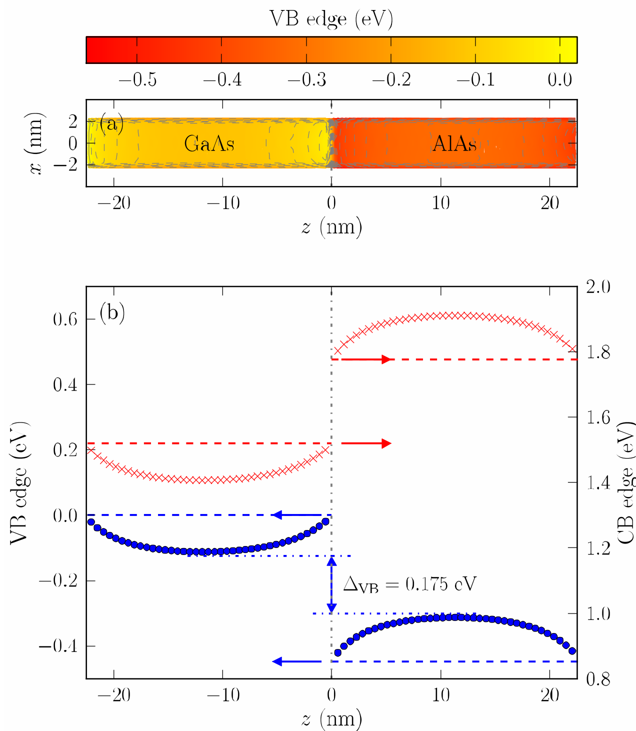

Fig. 2. (a) 2D plot of the VB edge in a section of a GaAs/AlAs nanowire super-lattice with cylindrical shape (diameter $d = 5$ nm, length of the GaAs and AlAs segments $l = 22.5$ nm). (b) VB edge (blue dots) and conduction (CB) edge (red crosses) along the axis of the nanowire super-lattice. The horizontal dashed lines indicate the VB and CB offsets in a 2D GaAs/AlAs super-lattice. The difference $\Delta_{\rm VB}$ between the VB edges in GaAs and AlAs is as low as 0.175 eV in between the interfaces, and would tend to 0.1 eV when $l \to \infty$, the difference between the VB edges of the pristine GaAs and AlAs nanowires.

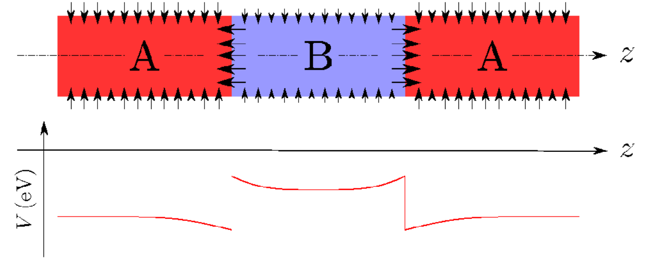

Fig. 3. Schematic representation of the dipole layers at the surfaces and interfaces of an A/B nanowire super-lattice. The contribution of these dipoles to the band offset is also plotted. The surface dipoles drive the potential to different limits in each segment far away from the GaAs/AlAs interface.

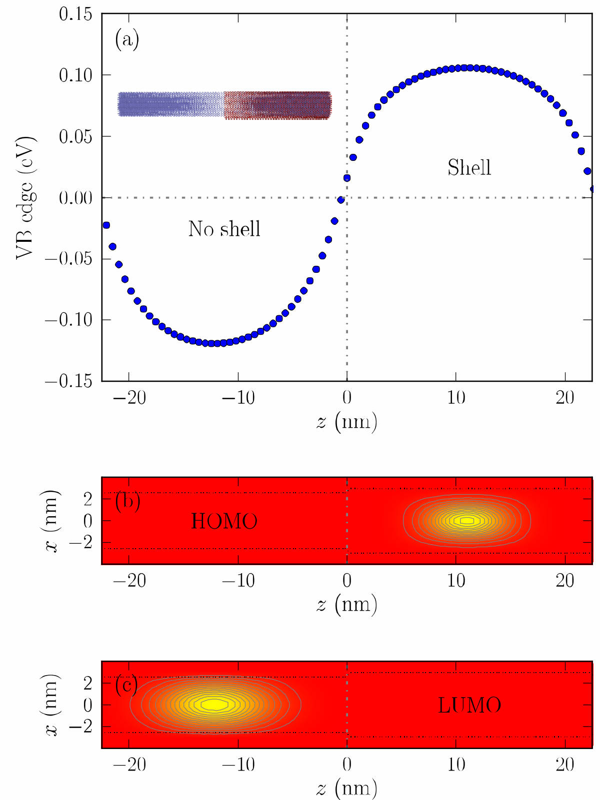

Fig. 4. (a) VB edge along the axis of a GaAs nanowire which alternates segments with an AlAs shell and segments without a shell (core diameter $d_c = 5$ nm, shell diameter $d_s = 6$ nm; length of each segment $l = 22.5$ nm). The potential would look like a smoothed $\simeq$ 0.35 eV step function around each interface when $l \to \infty$ (same surface termination as in Fig. 2). (b) and (c) 2D plots of the envelopes of the highest occupied and of the lowest unoccupied states, respectively. Note that this situation is actually ubiquitous in nanowire devices, which can feature different materials or stacks of materials around on diffent parts of the nanowire.