

Rapid Communication

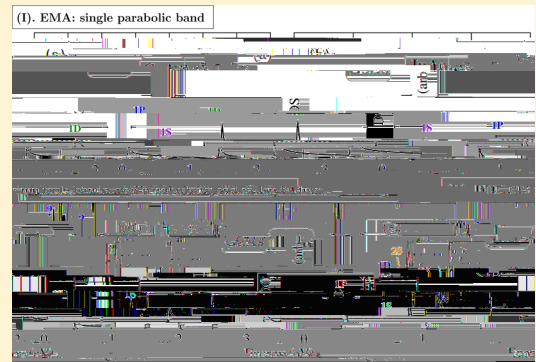
Jianing Wang,^{†,§} Jun-Wei Luo,^{†,||} Lijun Zhang,^{*,†,⊥} and Alex Zunger^{*,†}

[†]University of Colorado, Boulder, Colorado 80309, United States

[‡]National Renewable Energy Laboratory, Golden, Colorado 80401, United States

ABSTRACT: One-dimensional semiconductor nanowires hold the promise for various optoelectronic applications since they combine the advantages of quantized in-plane energy levels (as in zero-dimensional quantum dots) with a continuous energy spectrum along the growth direction (as in three-dimensional bulk materials). This dual characteristic is reflected in the density of states (DOS), which is thus the key quantity describing the electronic structures of nanowires, central to the analysis of electronic transport and spectroscopy. By comparing the DOS derived from the widely used “standard model”, the effective mass approximation (EMA) in single parabolic band mode, with that from direct atomistic pseudopotential theory calculations for GaAs and InAs nanowires, we uncover significant qualitative and quantitative shortcomings of the standard description. In the EMA description the nanowire DOS is rendered as a series of sharply rising peaks having slowly decaying tails,

with characteristic peak height and spacing, all being classifiable in the language of atomic orbital momenta 1S, 1P, 1D, etc. Herein we find in the thinner nanowires that the picture changes significantly in that not only does the profile of each DOS peak lose its pronounced asymmetry, with significant changes in peak width, height, and spacing, but also the origin of the high-energy peaks changes fundamentally: below some critical diameter, the region of atomic orbital momentum classified states is occupied by a new set of DOS peaks folded-in from other non- Γ



shows a sharp energy rise at E_{sub} and long tail of slow energy decay (in the form of $1/\sqrt{E - E_{\text{sub}}}$, where E is energy). (iii) The peak heights of doubly degenerate 1P and 1D states are higher than that of the 1S state with single degeneracy. (iv) Complying with quantum confinement effect, E_{sub} scales as $1/m^*d^2$, where m^* is electron effective mass and d is nanowire diameter. So at the same d , for InAs (Figure 1a) with the smaller effective mass ($0.024m_0$ compared with $0.068m_0$ of GaAs), the energy distances among different DOS peaks are larger. The features (i)–(iv) are standard expectations for the shape and form of the nanowire DOS in typical semiconductors.

Since in the EMA a nanostructure is described straightforwardly by the band parameters of 3D bulk material, it is perhaps not surprising that the EMA rendering of electronic states may be rather approximate, given the disparity between the 3D bulk reference and the lower-dimensional confined system being described. Differences between the EMA and direct atomistic pseudopotential theory (PPT) calculations^{26–28} for 0D quantum dots were described previously and include the fact that both valence and conduction bands derived from the EMA miss many states present in the direct calculations^{29–31} and even the orbital symmetries of some states are often misrepresented.^{32,33} Since the disparity between the 3D bulk reference and the 1D nanowire is smaller than that in the case of 0D quantum dots, it would be interesting to examine the validity of the EMA description of the nanowire electronic structure relative to the descriptions free from the approximations underlying it. With this motivation, we have recently extended our PPT calculations of the electronic structure of nanostructures from 0D quantum dots to 1D nanowires.^{34–36} The ensuing nanowire DOS of conduction bands calculated by the PPT (part II of Figure 1) for InAs and GaAs are shown in Figure 1c,d respectively, where they are compared with the EMA DOS (part I of Figure 1) of the same material, same diameter, and same passivation. Significant differences are apparent between the EMA and the atomistic

PPT calculations, includ

Secondly, we address different aspects of physical effects controlling the nanowire DOS. Briefly the following four levels of methodology from simple to complex are employed:

A. First, we start with the EMA, the model of single parabolic band (without nonparabolicity and interband coupling), assuming finite potential barrier, but the same effective mass in nanowire and its environment. Here, the electronic structure of nanowires is calculated by solving the Schrödinger eqs 1 and 2 for an infinite cylinder along the z (nanowire growth) direction with the diameter R , surrounded by the barrier with the potential height V_0 ²⁵

$$\left[-\frac{\hbar^2}{2m^*} \left(\frac{\partial^2}{\partial r^2} + \frac{1}{r} \frac{\partial}{\partial r} + \frac{\partial^2}{\partial z^2} \right) \right] \psi = E \psi \quad (1)$$

$$\left[-\frac{\hbar^2}{2m_b^*} \left(\frac{\partial^2}{\partial r^2} + \frac{1}{r} \frac{\partial}{\partial r} + \frac{\partial^2}{\partial z^2} \right) \right] \psi_b = E \psi_b \quad (2)$$

where m^* is the electron effective mass. The wave function of nanowire $\psi_w(\vec{r})$ and barrier $\psi_b(\vec{r})$ comply with the boundary condition of $\psi_w(\vec{r})_{r=R} = \psi_b(\vec{r})_{r=R}$, by which the in-plane quantum confinement effect is enforced. In this model the only material dependent parameter is m^* , which is taken from the assumed parabolic band of bulk material. The bulk effective mass m^* ($0.024m_0$ for InAs and $0.068m_0$ for GaAs) is used, and the same potential height V_0 as that of the atomistic PPT calculation (4.6 eV for InAs and 3.5 eV for GaAs) is chosen for direct comparison (as in Figure 1).

B. Second, we allow different effective masses of the nanowire and its environment. In step A, the effective mass m^* is taken as a constant across the nanowire and surrounding materials outside. This is, however, not reflecting the actual fact that semiconductor nanowires are passivated by either organic ligands or embedded in some shell materials during their growth.³⁷ To reasonably acknowledge this fact, in this step we allow an effective mass discontinuity, i.e., by making the effective masses of nanowire (in eq 1) and surrounding barrier (in eq 2) different. This is done by adding into the EMA of step A the BenDaniel–Duke boundary condition $1/m_w^* \nabla \psi_w(\vec{r})_{r=R} = 1/m_b^* \nabla \psi_b(\vec{r})_{r=R}$,³⁸

band with less dispersion. This gives rise to two aspects of effects on the nanowire DOS, as shown in Figure 4b (the nonparabolicity of SBTC in blue and EMA in green): (i) it leads to the narrower DOS peak (i.e., the first peak in blue below 0.5 eV) and the long tail from EMA has been eliminated. (ii) Resulting from the very dispersiveless feature of band at the nanowire zone boundary (see the blue band in Figure 4a), a

same nanowire by using different approaches. As expected, the ensuing DOS peak from the SBTC (the first peak in blue below 0.5 eV) exhibits a red-shift by comparison with that from the EMA (the peak in green).

Turning to the out-of-plane nonparabolicity, its effect on the nanowire DOS is reflected directly by the nanowire band dispersion (of the 1S state) along the growth direction as shown in Figure 4a. We can see that compared with the band dispersion from the EMA (the green band), the nonparabolicity (represented by the blue band of SBTC) causes a rather heavier

the 1S, 1P, and 1D states originating from Γ -valley for clear comparison with the SBTC results. Actually there are more states appearing in the PPT calculations. Figure 5 shows the complete quantized sub-band energy levels E_{sub} for InAs and GaAs nanowire with $d = 5$ nm. In terms of the band-folding picture for finite-size nanostructures, all the states can in principle be attributed to the lower-energy valley states at different k -points of the Brillouin zone in bulk band structure. We identified the valley origin of these states by using the majority representation approach,⁴⁹ i.e., by projecting their wave functions onto the complete bulk Bloch states at various k -points. In Figure 5 the valley origin of each state is labeled and its degeneracy is represented by the multiple lines at the same energy level. One immediately observes that in addition to the Γ -valley derived states (in red), there appear more states originating from the X-valley (in green) and L-valley (in blue). Particularly, in InAs nanowires (Figure 5a), two non- Γ -valley states appear in the energy window shown, and the first L-valley state is located at ~ 1.7 eV (above the Γ -valley 2P state). As to GaAs nanowire, a large number of X-valley states emerge and the first one starts from ~ 0.6 eV; the only state below it is the Γ -valley 1S state. The remarkable distinction between InAs and GaAs nanowires is attributed to the energetically close competing conduction valleys of bulk GaAs as mentioned. Note that for the non- Γ -valley states, the degeneracy is always higher than one (e.g., 3 for the X-valley state), as there are multiple valleys folded to the zone center of nanowires simultaneously.

Figures 6 and 7 show the PPT rendered band structure (left panel) and DOS (right panel) for InAs and GaAs nanowires at $d = 5$ nm. The electronic states have been classified in terms of the origin from Γ -valley (red), L-valley (blue), or X-valley (green), respectively. Consistent with Figure 5, we can clearly see substantial contributions from the L-valley and X-valley derived states for both materials. Specifically, for InAs nanowire (Figure 6), in spite of the only one L-valley state existing at the zone center (at ~ 1.7 eV), there appear a bunch of L-valley derived bands in proximity to the zone boundary, and thus, quite a number of associated DOS peaks with high intensity emerge above 1.3 eV. As to GaAs nanowire (Figure 7), the whole DOS has been predominantly occupied by the L-valley

and X-valley derived states, and there exists only a very small portion of Γ -valley derived peaks.

DOS of GaAs nanowire. We should point out that the roles of the above factors in affecting the nanowire DOS depend on the diameter of the nanowire. For example, in the case of a 5 nm diameter GaAs nanowire, the DOS is dominated by the L-valley states, while in the case of a 10 nm diameter GaAs nanowire, the DOS is dominated by the X-valley states.

