Charge Separation via Strain in Silicon Nanowires

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ABSTRACT

Axial charge separation in small diameter, partially strained silicon nanowires is predicted from ab initio calculations with electrons and holes located in different ends of the wires. We show that this effect can be understood from the topologies of near-gap wave functions, and that it is enhanced by quantum confinement. The possibility of utilizing partial strain for charge separation at the nanoscale opens up a new avenue for designing solar cells by morphology control, where effectively a type-II homojunction is formed and charge separation is facilitated by thermalization.

Research on new types of photovoltaics (PV) has received increased attention due to the limitations and potential environmental damage of fossil-based energy sources. The dominant material in use today for the active layer in commercial PVs is crystalline silicon (Si), which though reasonably efficient is also too costly at present (involving high-temperature high-vacuum processing) to reach the scales needed to meet global energy demands. Achieving the goal of substantially less expensive solar cells, comparable to the costs of fossil-based electricity, from abundant, environmentally benign materials will require major scientific and technological breakthroughs.

Toward this end, the use of nanoscale materials in solar cells is a promising direction because of the potential for low-cost manufacturing, and also because the electronic and optical properties of nanomaterials can be engineered via size, shape, and surface morphology. For example, nanoparticles, nanorods, and nanowires (NWs) have been used in hybrid organic polymer/inorganic nanocrystal solar cells and in dye-sensitized solar cells to improve charge collection efficiency. In these cells, type II heterojunctions are formed at the interfaces between the nanocrystal and the polymer or dye-monolayer to facilitate charge separation upon photoexcitation. Another type of nanostructure-based solar cell relies on the traditional doped p-n junction to transport charge carriers in a direction orthogonal to light collection, for example, coaxial Si NWs as solar cells for nanoelectric power sources were realized recently.

Photoexcited electrons and holes in a pure semiconductor typically occupy the same regions spatially in the absence of an external field, and the large wave function overlap between electrons and holes causes a high rate of recombination. As a result, efficient charge separation is a key to efficient PV devices, which require positive and negative charge carriers to diffuse in opposite directions. Since the electronic and optical properties of semiconductor nanocrystals can be tuned by varying their size and shape, it is possible to separate electrons and holes within a pure nanocrystal by morphology control, instead of conventional doping or blending with other materials. Recent work in this direction includes the effect of tapering to induce axially dependent electronic effects. However, genuine breakthroughs that could have broad impacts must come from changes to materials that can be realized inexpensively and robustly. It is thus of great interest to explore further routes to charge separation that arise from control over morphology and to understand the separation mechanism from a fundamental point of view.

In this letter, we present a technique for separating charge carriers in Si NW solar cells that would eliminate the need for p-n doping, possibly allowing the use of substantially lower quality silicon without degrading efficiency, while concomitantly relying on simple, scalable changes in the manufacturing process. Utilizing ab initio calculations based on density functional theory (DFT), we find that applying partial strain on a Si nanowire along the wire axis gives rise to well-separated electron and hole states. The effect is shown to result from the topologies of band-edge wave functions, which have different energy shifts under strain. These results indicate that solar cells could be designed that separate charge...
carriers via morphology control in a pure nanomaterial, wherein thermalization of the photoexcited carriers would serve the beneficial purpose of driving electrons and holes to different spatial locations, as opposed to typical carrier diffusion in the p-n junction of conventional solar cells.

In our calculations, structural and electronic properties are computed for Si nanowires passivated with H atoms. Wire axes are oriented along the [011] direction, since small-diameter (d < 10 nm) Si NWs grow primarily along this direction. Calculations are carried out with the linear combination of atomic orbital basis implemented in the SIESTA package, using the Perdew–Burke–Ernzerhof generalized gradient approximation for the exchange-correlation energy and norm-conserving pseudopotentials for the core–valence interactions. A double-ξ polarization (DZP) basis is used for all atoms, in which the cutoff radii of the basis orbitals are determined by fixing the energy shift of atomic eigenvalues to 0.02 Ry and a split norm of 0.15. It is found that this DZP basis reproduces well the DFT bulk Si lattice constant and band structure obtained from a well-converged planewave basis calculation. The size of the periodically repeating unit cell is set so that there is at least 2.0 nm of vacuum between NWs. An energy cutoff of 200 Ry is sufficient to converge the grid integration of the charge density, and all NWs are fully relaxed until the maximum atomic force is less than 0.01 eV/Å. A 1 × 1 × 16 k-point grid is used for structural optimizations, and a more dense k-point grid to obtain electronic band structures.

As a general guide for this work, we note that the use of nanostructure morphology control to separate charge carriers is possible simply by breaking the translational symmetry along certain directions such that the energy gaps in different regions are staggered. Strain is both a powerful and economical approach to modulate the electronic structure of a material to improve device performance. For example, in the case of Si NWs a significant enhancement of carrier mobility has been observed with strain, and calculations have shown that for small diameters the band structures and gaps can be significantly modified. In experiment, up to 2% uniaxial tensile or compressive strain on Si NWs can be obtained through an embedded SiGe process, or through depositing a capping layer (such as Si$_3$N$_4$) on top of a Si layer. In our calculations, uniaxial strain is applied to Si NWs by changing the unit-cell size along the wire axis accordingly.

Our computed electronic band-structures for a strained [011] 2.2 nm diameter Si NW are plotted in Figure 1a, which shows that a 2% compression shifts both the valence band maximum (VBM) and conduction band minimum (CBM) energies higher by ~0.2 eV, while a 2% tension shifts them down in energy by a similar amount. The band-structure plots also reveal that under compression the energy (E$_{C1}$) of the lowest conduction band C$_1$ shifts up, while the next lowest band energy E$_{C2}$ shifts down; in contrast, under tension the energy E$_{V1}$ of the highest valence band V$_1$ shifts down, while E$_{V2}$ shifts up. Thus, in both cases strain leads to a direct-to-indirect band gap transition in the NW. Under compression, the CBM changes from band C$_1$ at the Γ-point to band C$_2$ near (0, 0, 0.4)2π/c, where c is the unit-cell length along the wire axis; under tension, the VBM changes from band V$_1$ at the Γ-point to band V$_2$ near (0, 0, 0.1)2π/c. Note that the magnitudes of strain-driven energy-shifts (∆E) for the C$_1$ and V$_1$ bands at the Γ-point are much larger than those for the C$_2$ and V$_2$ bands at their lowest/highest-energy k-points, respectively.

Figure 1b shows the behavior of energy shifts ∆E$_{VBM}$ and ∆E$_{CBM}$ and the change in the gap (∆E$_g$) as a function of strain up to ±4%. Before the direct-to-indirect band gap transition occurs at around 2% strain, ∆E$_{VBM}$ and ∆E$_{CBM}$ correspond to energy changes of the V$_1$ and C$_1$ bands at the Γ-point, respectively, and they vary linearly with strain; therefore ∆E$_g$ decreases (increases) slowly and linearly with increasing tensile (compressive) strain. After the transition to an indirect gap, ∆E$_{VBM}$ decreases under compression (energy shift of band V$_2$) while ∆E$_{CBM}$ increases under tension (energy shift of band C$_2$) with increasing strain, leading to a dramatic decrease in $E_g$ as strain is increased.

The above results of the impact of strain on the band structure can be understood from an analysis of the NW crystal structures and topologies of the near-gap wave functions shown in Figure 2. The wave function corresponding to band V$_1$ (Figure 2a) has alternating positive (red) and negative (blue) values both along and perpendicular to the wire axis, leading to nodal surfaces both perpendicular and
parallel to the wire axis (Figure 2b). On the other hand, band \( V_2 \) (Figure 2c) has positive regions extending continuously along the wire axis and negative regions extending in the confinement plane so that its nodal surfaces are mostly in the axial direction (Figure 2d). For the \( V_1 \) band, a uniaxial compressive strain decreases the distance between nodal surfaces perpendicular to the wire axis, resulting in higher kinetic energy and hence increased energy of the band \( E_{V1} \); uniaxial tensile strain has the opposite effect. We note that in the meantime due to the Poisson effect, a uniaxial compressive (tensile) strain along the wire axis causes a smaller biaxial tensile (compressive) strain in the confinement plane with a Poisson ratio \( \nu = -(1/2)(d - d_0)/d \) with \( \nu \), the uniaxial strain and \( d_0 \) and \( d \) the wire diameters without and with strain \( \varepsilon_z \), respectively. \( \nu = 0.15 \) for the 2.2 nm wide NW, which is in good agreement with previous calculations.\(^{17} \) Although this biaxial strain counters the effect of the uniaxial strain on \( E_{V1} \), its magnitude is much smaller and thus the uniaxial strain dominates the shift in \( E_{V1} \). In the case of the \( V_2 \) band, we observe an effect opposite to that of \( V_1 \); uniaxial strain barely changes \( E_{V2} \) because the nodal surface of the \( V_2 \) band runs mainly along the wire axis, while the resulting small biaxial strain changes the distance between nodal surfaces, shifting \( E_{V2} \) in a direction opposite to \( E_{V1} \) by a smaller amount for the same applied uniaxial strain.

The two conduction bands \( C_1 \) and \( C_2 \) (Figure 3) have nodal structures qualitatively similar to \( V_1 \) and \( V_2 \), with alternating positive and negative values along or perpendicular to the wire axis for \( C_1 \) and surfaces essentially parallel to the axial direction for \( C_2 \). As a result, \( \Delta E_{C1} \) and \( \Delta E_{C2} \) behave similarly to \( \Delta E_{V1} \) and \( \Delta E_{V2} \) for the same strain, leading to a simultaneous upshift or downshift of the CBM and VBM under small strains and the direct-to-indirect band gap transition under larger strains, as indicated in Figure 1b. These effects on band-edge states of quantum-confined Si NWs suggest that by applying partial strain one might be able to tailor positive and negative charge carrier separation; we note that recent experiments have already succeeded in partially straining Si NWs.\(^{18} \) In order to illustrate this effect, we computed the electronic structure of a 10 nm long 2.2 nm wide Si nanorod with one-half under 2% tension and the other half without strain, as shown in Figure 4. Our results show that the lowest unoccupied molecular orbital (LUMO) in this partially strained nanorod is located on the strained side, while the highest occupied molecular orbital (HOMO) resides on the unstrained side. Thus, these near-gap states are spatially separated along the wire axis, similar to the effect predicted in tapered NWs.

We note that while standard DFT calculations underestimate quasiparticle gaps\(^{19} \) and neglect excitonic effects,\(^{20} \) they are expected to capture the rearrangement of electron density at interfaces that is important for predicting trends in

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**Figure 2.** Isosurfaces of wave functions of the (a) \( V_1 \) band and (c) \( V_2 \) band, as indicated in Figure 1a, at the \( \Gamma \) point. Here red and blue represent positive and negative values, respectively. Their node surfaces are shown in (b) and (d), respectively.

**Figure 3.** Isosurfaces of wave functions of the (a) \( C_1 \) band at the \( \Gamma \) point and (c) \( C_2 \) band near the \( X \) point, as indicated in Figure 1a. Their node surfaces are shown in (b) and (d), respectively.
transition happens under smaller strain (due to smaller increasing diameter, because the direct to indirect band gap (upshift of VBM) is not sensitive to diameter, while the under 2% tension (compression), the downshift of the CBM compression as a function of diameter. Figure 5 shows that computed the band-edge shifts of Si NWs under 2% tension or degree of quantum confinement in the nanowire, we com-
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to the zero strain where the LUMO and HOMO are both type-I junction) under compression or tension, in contrast will be located in the strained region (forming an effective smaller. For even larger strains, both LUMO and HOMO are still located in different regions but the energy difference of band-edge states (LUMO or HOMO depending on whether compression or tension) across different regions becomes smaller. For even larger strains, both LUMO and HOMO will be located in the strained region (forming an effective type-I junction) under compression or tension, in contrast to the zero strain where the LUMO and HOMO are both distributed in the whole wire.

In order to understand how this effect depends on the degree of quantum confinement in the nanowire, we computed the band-edge shifts of Si NWs under 2% tension or compression as a function of diameter. Figure 5 shows that under 2% tension (compression), the downshift of the CBM (upshift of VBM) is not sensitive to diameter, while the downshift of the VBM (upshift of CBM) decreases with increasing diameter, because the direct to indirect band gap transition happens under smaller strain (due to smaller $|E_{V1} - E_{C2}|$ or $|E_{C1} - E_{C2}|$) for wider NWs than narrower ones. This suggests that for large-diameter (above the quantum confinement limit) Si NWs, both compression and tension would need to be applied uniaxially on each side, respectively, in order to effectively separate the CBM and VBM states spatially. Thus the unique Si NW structure makes it possible to separate charges by applying strain differently along the wire axis, while quantum-confine ment enhances the strain effects so that only one type of uniaxial strain is required on one side of a NW.

The DFT calculations can provide a reliable estimate of the trends, even for small-diameter wires where excitonic effects have been shown to be important, provided that the predicted band offset that develops between strained and unstrained wires is significant compared with typical exciton binding energies. Moreover, the analysis presented above suggests that the symmetry of these wave functions determine the sign of the energy level change ($\Delta E_i$ with $i = CBM/VBM$), and because many-body corrections to the wave functions are not likely to alter their topologies significantly, DFT calculations are expected to predict the correct trend of $\Delta E_i$ for Si NWs under strain.

It is also worth noting that by controlling the magnitude of strain, the locations of the near-gap states of this partially strained NW can be completely changed. For relatively small strains, the LUMO and HOMO are located in different regions as shown in Figure 4 (effectively forming a type-II junction within the material), while for larger strains (beyond the direct-to-indirect transition) the HOMO and LUMO are still located in different regions but the energy difference of band-edge states (LUMO or HOMO depending on whether compression or tension) across different regions becomes smaller. For even larger strains, both LUMO and HOMO will be located in the strained region (forming an effective type-I junction) under compression or tension, in contrast to the zero strain where the LUMO and HOMO are both distributed in the whole wire.

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Electronic level alignment and band offsets. In this work, the DFT calculations can provide a reliable estimate of the trends, even for small-diameter wires where excitonic effects have been shown to be important, provided that the predicted band offset that develops between strained and unstrained wires is significant compared with typical exciton binding energies. Moreover, the analysis presented above suggests that the symmetry of these wave functions determine the sign of the energy level change ($\Delta E_i$ with $i = CBM/VBM$), and because many-body corrections to the wave functions are not likely to alter their topologies significantly, DFT calculations are expected to predict the correct trend of $\Delta E_i$ for Si NWs under strain.

The prediction of charge separation in these Si NWs points to the possibility of an approach for designing solar cells where thermalization, that is, relaxation of photoexcited electrons and holes to the energy levels near the CBM and VBM, respectively, through thermal equilibrium, could spatially separate the electrons and holes into different ends of these wires. Present nanostructured solar cells are based on either p-n (homo)junctions or type II heterojunctions for charge carrier separation. In the p-n-junction approach, charge separation is achieved as the minority charge carriers move into the other side of the junction through the bulk of the cell. The minority carrier diffusion length, the built-in electric field, and the ability to control doping play an important role in the efficiency and manufacturing expense of these cells. In the heterojunction based PV cells, including dye-sensitized and hybrid organic solar cells, strongly bound excitons (in contrast to free charge carriers in conventional Si crystalline PV cells) are generated in dye molecules or organic polymers, and they dissociate mostly at the hetero-junction interfaces. Therefore, the interfacial properties and the exciton diffusion length play an important role in the cell characteristics, and nanostructure engineering has been used to maximize the acceptor/donor interface area to balance efficient charge separation with poor exciton diffusion lengths and low mobilities. On the other hand, in the partially strained NWs discussed here, a type-II homojunction would be formed by morphology control, and charge separation facilitated by the thermalization process. Thus, the phonon bath and the morphology-induced gap-edge energy offsets govern the properties of this possible novel type of PV cells.

Compared with doping, morphology control may be easier and cheaper for nanostructures because doping small-size nanomaterials remains a major challenge due to large statistical fluctuations of dopant density, self-purification effects, and the fact that many materials can only be doped either n-type or p-type. In addition, cheap materials often have a high level of impurities or a high density of defects, resulting in small diffusion lengths (shorter lifetime) of the minority carriers and degrading the charge collection efficiency for p-n junctions. The tapered or partially strained NWs may tolerate higher defect or impurity levels because the shortened lifetime of charge carriers are still much longer than the thermalization time. Comparing with organic PV
cells, these novel structures would not rely on an interface between two materials to separate charges. However, it is also important to mention that the gap-edge energy offsets depend strongly on wire size and shape. In order to sufficiently absorb light, these wires must be long enough (∼1 µm), and in very narrow wires, the excited electrons and holes could be bound due to quantum confinement. In this work, DFT was used to calculate the electronic properties of nanorods 10 nm in length and a few nanometers in diameter; appropriate simplified models are needed to investigate the energy offsets and the transition rate of electron states mediated by phonons as a function of wire length, diameter, and shape.

In summary, we have presented a possible route toward low cost solar cells by morphology control at the nanoscale. The mechanism underlying this new approach is to separate photoexcited electrons and holes into different regions in nanostructures by breaking translational symmetry, such that the thermalization process can transport electrons and holes in opposite directions. A key implication is that within this approach charge separation can be realized in a pure material without doping (traditional p-n junction approach) or mixing with other materials (heterojunction approach). Using the example of partial axial strain, we demonstrate that charge separation can be realized in a pure Si NW. Our results also point to the prospect that other nanocrystals beyond Si NWs may be suitable or even better for this purpose; numerous other morphological modifications would also induce this property. For example, we found that if Si nanorods are functionalized with different chemical groups on their end surfaces, they attract each other and form longer chains in which the HOMO and LUMO states are located separately in the building blocks with different functional groups. Another possibility includes multispecies surface chemistries along the wire axis. In addition to the possible use in PV devices, these unique nanostructures could exhibit other interesting physical properties in their electronic and thermal transport and conductivity, optoelectricity, piezoresistance effects, and ferroelectricity. Further theoretical and experimental studies of these types of tailored nanostructures could lead to their applications in nano-optics and nanoelectronics.

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