Quantum size effect in core-shell structured silicon-germanium nanowires

Ryza N. Musin and Xiao-Qian Wang

Department of Physics and Center for Theoretical Studies of Physical Systems, Clark Atlanta University, Atlanta, Georgia 30314, USA

First-principles density functional theory has been employed to study the composition dependent quantum size effect in a series of silicon-germanium core-shell structured nanowires with the diameters ranging from 0.5 to 3.2 nm. Analysis of the calculated band gap energies in Si-core/Ge-shell and Ge-core/Si-shell structured nanowires shows a nonlinear composition dependence for nanowires with fixed diameter (fixed total number $N=N_{Core}+N_{Shell}$ of Si and Ge atoms in the unit cell). In contrast, for nanowires with fixed core size and varying shell thickness, our calculation results reveal a striking linear blueshift of the direct band gap with composition. The obtained linear composition effect implies an inverse square relation between the energy of the fundamental band gap and the size of nanowire, in agreement with experimental observations. Our results provide useful guidelines for experimental gap engineering in the core-shell structured nanowire heterostructures.

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There has been fast-growing interest in nanometer-scale semiconductor materials such as quantum dots (0-D), quantum wires (1-D), and quantum wells (2-D).[1–3] These nanostructures constitute an intriguing class of semiconductor materials due to unique size dependent electronic and optical properties that are intrinsically associated with their low dimensionality and quantum confinement effect.[3,4] It has been established that the optical properties of nanocrystals strongly depend on the ratio of the nanocrystal radius, R, to the Bohr radius of the bulk exciton, R_B.[5] Three different regions, $R \gg R_B$, $R \sim R_B$, and $R \ll R_B$, corresponding to weak, medium, and strong confinement regimes, respectively, have been proposed. The confinement of electrons and holes in nanoscale crystallites leads to an increase in the electronic band gap with decreasing crystallite size and, consequently, a blueshift of the absorption and emission spectra. A qualitative quantum mechanical approach based on the effective mass approximation and particle-in-a-box models[1–5] predicts that the dependence of the band gap on the radius R of crystallites is of the form $E_g \sim 1/R^2$. More detailed analysis of the quantum confinement effect in the framework of first-principles and semiempirical methods shows that size dependence of band gaps can be described by an inverse power law $E_g \sim 1/R^n$ with a smaller parameter n being between 1 and 2.[6–8] The ability to control the physical and chemical properties of low dimensional nanomaterials by variation of their size is of crucial importance for nanotechnology applications.[2,9]

With the progress in synthesis and fabrication of low dimensional nanomaterials, semiconductor nanowires have attracted much attention because of their exceptional electronic, optical, and transport properties.[10] In these quasi-one-dimensional materials, the motions of electrons and holes are confined in the radial plane, while the charge carriers are free to move along the nanowire's axis. Semiconductor nanowires can be used as building blocks in the engineering of sophisticated nanoscale electronic and photonic devices, because of their capability to function as both devices and current carrying electrical contacts.[11] It is now well recognized that nanometer-scale silicon and germanium wires have immense potential for the fabrication of a new generation of optoelectronic devices within well-established silicon based

microelectronic technology.[12–15] More recently, due to the technological importance, much effort has been focused on the core-shell structured semiconductor quantum wires.[16–18] These composite nanowire heterostructures are far more promising than those of single-component semiconductors. One of the distinctive features of the core-shell structured nanomaterials is the composition dependence of their electronic, structural, and optical properties.[19–21]

Our previous theoretical analysis of the silicon-germanium core-shell structures[18] shows that fundamental band gaps of the nanowires can be readily estimated from the bulk band folding on to the nanowire orientations. Analysis of compositional variation of the band gap energies of Si-core/Ge-shell and Ge-core/Si-shell nanowires shows a nonlinear relationship between band gap and composition for nanowires with total number of atoms in unit cell $N=74$, 82, and 110. Direct-to-indirect transition for the fundamental band gap was found in Ge-core/Si-shell nanowires. The energy gap is direct over the compositional range $0 \leq x \leq 0.4$, and indirect over the range $0.4 < x \leq 1$. On the other hand, Si-core/Ge-shell nanowires preserve a direct energy gap almost over the whole compositional range with the exception of the $x=0$ point associated with a pure Ge structure. For both types of core-shell structured nanowires, a comparison of the band gap energies of different nanowires with $N=74$, 82, and 110 (nanowires with different diameters) has revealed a strong radial size dependence of the calculated band gap energies associated with the quantum confinement effect and the spreading of the core electronic wave function into the shell region.

In this paper we extend the first-principles density functional study by focusing on the composition and size dependence of the fundamental band gap in a series of [111]- and [110]-oriented silicon-germanium core-shell structured nanowires. The calculations have been performed within the framework of the density functional theory (DFT) and local density approximation (LDA) with the exchange-correlation potential of Ceperley-Alder.[22] We have employed the ultrasoft gradient corrected pseudopotential.[23] For a given core-shell structures and chemical compositions, the geometry optimization was carried out using the conjugate-gradient
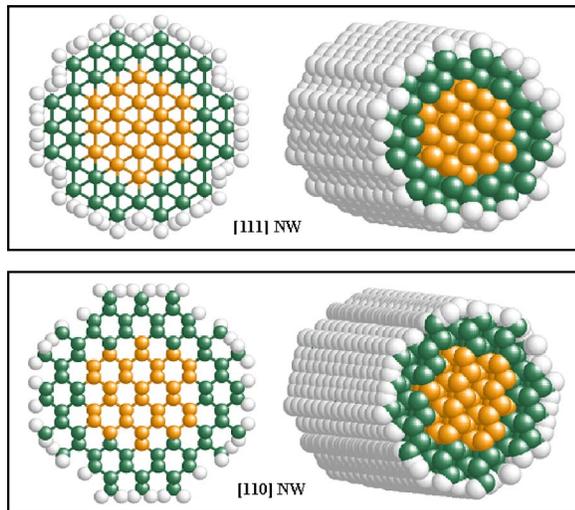
FIG. 1. (Color online) Ball-and-stick representation (cross sectional and side view) of the core-shell structured nanowire heterostructures oriented along [111] and [110] directions. Green or black and gold or gray balls correspond to silicon (germanium) and germanium (silicon) atoms of the Ge-core/Si-shell (Si-core/Ge-shell) nanowires, respectively. White balls represent hydrogen atoms.

FIG. 2. Variations of the direct band-gap energies E_g as a function of composition x (dashed lines) for Si-core/Ge-shell nanowire heterostructures with different number of atoms $N=N_{Core}+N_{Shell}$ in the unit cell: 62 (diamonds), 74 (stars), 86 (triangles), 110 (circles), and 146 (squares). Solid lines represent results of linear fitting of the calculated E_g values using expression (1) for individual nanowires with fixed number of core atoms N_{Core} =14,26,38,62,74,86 and different numbers of shell atoms N_{Shell} =$N-N_{Core}$. Numbers of core and shell atoms for nanowire with N_{Core}=26 are shown in parentheses (N_{Core}, N_{Shell}). Dotted lines denote the end points for Si-core/Ge-shell nanowires corresponding to the pure Ge (N_{Core}=0) and Si (N_{Shell}=0) structures.

algorithm of the total energy minimization. The calculations details were described in Ref. 18.

The core-shell nanowires have been created on the basis of diamond-structured nanocrystals with cylindrical shape and H-terminated surface atoms, which are known from various experimental and theoretical studies.[13,14] To create core-shell type structures the N atoms in the unit cell of the nanowire with radius R are divided on two subsets $N=N_{Core}$ $+N_{Shell}$ using certain cutoff radius $R_{Core}<R$. These two subsets of N_{Core} and N_{Shell} atoms located inside and outside of the circle with radius R_{Core}, respectively, are assigned to form cylindrical core and shell of the nanowire. The numbers of core (N_{Core}) and shell (N_{Shell}) atoms determine the chemical composition $x=N_{Core}/(N_{Core}+N_{Shell})$. The constructed Si-core/Ge-shell and Ge-core/Si-shell nanowires (see Fig. 1) with different number of atoms in the unit cell, N=26, 38, 62, 74, 86, 110, 146 for [111]-oriented and N=26, 42, 72, 94, 148 for [110]-oriented nanowires, have been used in the analysis of composition and size dependent electronic properties.

It is well known that structural and electronic properties of composite semiconductor materials depend strongly on the chemical composition, as illustrated by numerous experimental and theoretical studies.[15–21] It should be emphasized that in contrast to the binary alloys A_xB_{1-x}, where atoms of the A and B components are randomly distributed in the alloy formation process, the core-shell structured materials with ultimate segregation of the component atoms have a unique size and composition relationship. In the case of core-shell nanowires the numbers of atoms in the core (N_{Core}) and shell (N_{Shell}) determine the corresponding core and shell sizes. Consequently, the analysis of the compositional variation of electronic and structural properties for such nanowires should provide important information about the dependence of these properties on the geometrical characteristics of the

systems, such as the core size and shell thickness. There are two distinct ways to explore the composition dependent properties of the core-shell nanowires. One amounts to the variation of the composition $x=N_{Core}/(N_{Core}+N_{Shell})$ by changing numbers of core and shell atoms in the unit cell keeping the total number of atoms $N=N_{Core}+N_{Shell}$ fixed. This is the conventional approach (as in the case of binary alloys A_xB_{1-x}) that allows one to cover the whole compositional range between end points x=0 and x=1 corresponding to the single component nanowires constructed either from shell (N_{Core}=0) or core (N_{Shell}=0) atoms, respectively. Because the total number of atoms N is fixed, the diameter of the wire remains approximately the same at different compositions. Another approach to study composition effect in the core-shell systems is to fix the number of core atoms N_{Core} =const while increasing the number of shell atoms from N_{Shell}=0 (x=1) to N_{Shell}=∞ (x=0). Clearly, this corresponds to the variation of the composition x by changing shell thickness of the nanowire with fixed core size.

Figures 2 and 3 summarize the results of our calculations for the composition dependence of the band gap energies $E_g(x)$ of Si-core/Ge-shell and Ge-core/Si-shell [111]-oriented nanowires, respectively. We restricted ourselves by considering only the nanowires with direct band gaps. Therefore, all points corresponding to the indirect gaps (pure Ge [111] nanowires and Ge-core/Si-shell nanowires within the region of the direct-to-indirect band gap transition) are not included. Dotted lines on Figs. 2 and 3 show the compositional variation of the energy gaps $E_g(x)$ for individual core-shell structured nanowires with a fixed total number of Si and Ge at-
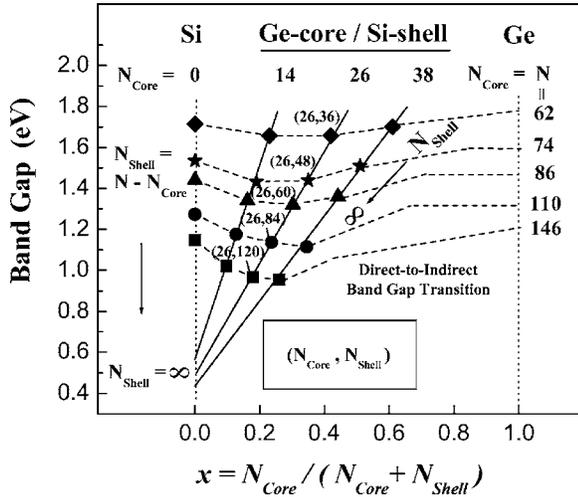
FIG. 3. Variations of the direct band-gap energies E_g as a function of composition x (dashed lines) for Ge-core/Si-shell nanowire heterostructures with different number of atoms $N=N_{Core}+N_{Shell}$ in the unit cell: 62 (diamonds), 74 (stars), 86 (triangles), 110 (circles), and 146 (squares). Solid lines represent results of linear fitting of the calculated E_g values using expression (1) for individual nanowires with fixed number of core atoms $N_{Core}=14,26,38$ and different numbers of shell atoms $N_{Shell}=N-N_{Core}$. Numbers of core and shell atoms for nanowire with $N_{Core}=26$ are shown in parentheses (N_{Core}, N_{Shell}). Dotted lines denote the end points for Ge-core/Si-shell nanowires corresponding to the pure Si ($N_{Core}=0$) and Ge ($N_{Shell}=0$) structures.

oms in the unit cell $N=N_{Core}+N_{Shell}$. The analysis of the relaxed geometry of the silicon-germanium core-shell nanowires shows that variations of structural characteristics (lattice parameters and diameter) with composition are very small <0.1 nm. For instance, the diameter d of the nanowires with $N=86$ atoms in unit cell varies between 1.43 nm and 1.48 nm, corresponding to pure Si and Ge nanowires, respectively. Thus, each dotted curve in Figs. 2 and 3 indicates composition dependence of energy gaps for individual [111]-oriented nanowires with approximately fixed diameters, namely $d\approx1.19$ ($N=62$), 1.34 ($N=74$), 1.46 ($N=86$), 1.67 ($N=110$), and 2.21 ($N=146$) nm. It can be seen that the compositional variation of energy gaps $E_g(x)$ is nonlinear for all nanowires, and the shape of calculated curves (with observable minima at $x\sim0.2$–0.5) is qualitatively similar to each other. The fairly weak nonlinear dependence can be attributed to the simultaneous opposite variation of core and shell sizes with composition x for a given nanowire with fixed diameter. These results are in qualitative agreement with experimental studies of the alloyed semiconductor quantum dots showing the possibility of the compositional tuning of the optical and electronic properties (energy gaps) without changing the crystallite size.[21]

Let us consider now the compositional variation of the energy gaps $E_g(x)$ for nanowires with fixed number of core atoms (N_{Core}) and varying number of the shell atoms (N_{Shell}). The analysis shows that an increase of shell thickness for nanowires with the same core size leads to a substantial decrease of the energy gap, indicated by solid lines in Figs. 2 and 3. Remarkably, the calculated direct band-gap energies

$E_g(x)$ exhibit a strong linear composition dependence for all direct band-gap nanowires with fixed core size $N_{Core}=14,26,38,62,74,86$. The calculated absolute values of the deviations from linearity are negligibly small <0.03 eV. The obtained linear blueshift of the energy gaps with composition for nanowires with fixed core size can be written as

$$E_g(N_{Core},x) = E_g(N_{Core},0) + k(N_{Core})x, \qquad (1)$$

where $E_g(N_{Core},0)$ is the extrapolated "bulk limit" (infinite-shell thickness, $N_{Shell}\to\infty$) value of the energy gap at $x=0$. The slope of the linear function is found to follow the rule $k(N_{Core})=A/N_{Core}$. In practice, A and $E_g(N_{Core},0)$ can be obtained from fitting of the calculated $E_g(N_{Core},x)$ values. As such, the linear compositional behavior of the energy gap observed for the core-shell structured nanowires imply an inversed dependence $E_g\sim1/(N_{Core}+N_{Shell})$ on the total number of atoms N. Because the number of layers in unit cell stacked along the axial direction is the same for all nanowires under consideration, the total number of atoms N in the unit cell determines the radial size of nanowires. Due to the approximate cylindrical shape of the nanowires, this leads to an inverse square relation $E_g\sim1/R^2$ with respect to nanowires' radius R, in accordance with experimental observations of the quantum size effect in 1-D structures. For example, an analysis of radial size dependence of the band gaps by using a cylindrical confinement potential and effective mass approximation for the energy levels $E=\hbar^2 u_{ni}^2/2m^*R^2$ has demonstrated good agreements with experimental data for pure Si nanowires[24,25] and Ge/Si core/shell nanowire heterostructures.[26] Here u_{ni} is the ith root of the Bessel function $J_n(x)$, and m^* is the effective mass. The obtained linear composition dependence (1) of the band gaps are of practical importance as it allows one to avoid the ambiguity in the definition of the nanostructure radius[25] and readily estimate band gap for core-shell structured nanowire heterostructures with different composition (with fixed radial core size and varying shell thickness).

Figures 2 and 3 show also the results of linear fitting of the calculated direct band gap energies $E_g(x)$. It can be seen that the differences between limiting (infinite-shell thickness, $N_{Shell}\to\infty$) values of $E_g(N_{Core},x)=E_g(N_{Core},0)$ at $x=0$ for the core-shell structured nanowires with different N_{Core} are very small. The extrapolated gaps $E_g(N_{Core},0)$ have reasonable values (between 0 and 1 eV). However, these results should be viewed with caution, as it is the implied limit for direct band gaps. The deviations from the experimentally observed bulk values E_g for Si (~1.12 eV) and Ge (~0.67 eV) nanowires can be attributed to LDA's systematic underestimate of the energy gaps.

The fact that the extrapolated values of $E_g(N_{Core},0)$ are very close to each other suggests that a $1/N$ dependence of the energy gaps is a very good estimate for all direct-gap nanowires. To further pursue this, we show in Fig. 4 the variation of the direct band-gap energies E_g as a function of $1/N$ (where $N=N_{Core}+N_{Shell}$ is the total number of atoms in the unit cell) for pure Si nanowires $N=N_{Core}$ ($N_{Shell}=0$) and Si-core/Ge-shell nanowires with fixed core size ($N_{Core}=26$) oriented along [111] and [110] directions (for [110]-oriented
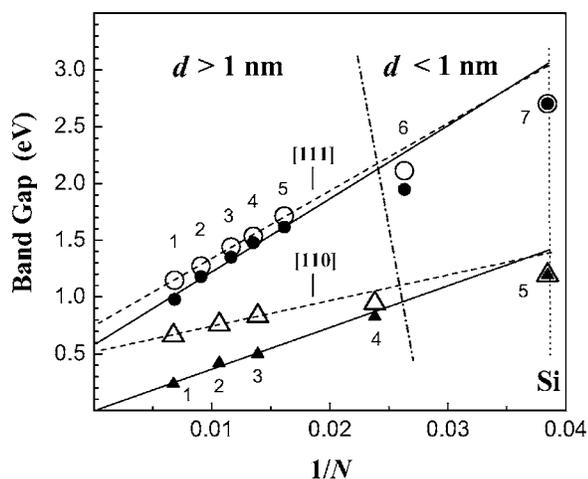
FIG. 4. Variations of the calculated band-gap energies E_g as a function of the inversed number of atoms $N = N_{Core} + N_{Shell}$ in the unit cell for the Si-core/Ge-shell nanowires with fixed core size ($N_{Core} = 26$) and pure Si nanowires ($N_{Shell} = 0$) oriented along [111] (circles) and [110] (triangles) directions. Open and filled circles correspond to pure Si: 1—(146,0), 2—(110,0), 3—(86,0), 4—(74,0), 5—(62,0), 6—(38,0), 7—(26,0), and Si-core/Ge-shell: 1—(26,120), 2—(26,84), 3—(26,60), 4—(26,48), 5—(26,36), 6—(26,12), 7—(26,0) nanowires, respectively. Open and filled triangles corresponds to pure Si: 1—(148,0), 2—(94,0), 3 —(72,0), 4—(42,0), 5—(26,0), and Si-core/Ge-shell: 1—(26,122), 2—(26,68), 3—(26,46), 4—(26,16), 5—(26,0) nanowires, respectively. Solid and dashed lines show fitting of the gaps values using expression (2).

nanowires, the surface reconstruction may lead to structures favoring indirect gaps,[27] which is beyond the scope of the present study). It is clear from Fig. 4 that for both [111]- and

[110]-oriented nanowires the dependence of the energy gap on the total number of Si and Ge atoms in the unit cell is expressed in the form

$$E_g(N) = E_g(\infty) + A/N, \qquad (2)$$

where A is an adjustable parameter and $E_g(\infty)$ is the "bulk limit" value of the energy gap corresponding to the nanowires with infinite diameter ($N \rightarrow \infty$). The obtained linear blueshift is consistent with composition dependence (1) of the energy gaps $E_g(x)$. Figure 4 shows also that this model $E_g \sim 1/N$ (as well as $E_g \sim 1/R^2$) is valid up to ultrathin nanowires with diameters as small as 1 nm. The observed deviation from linearity (flattening of the size dependence) of the energy gap for the nanowires with diameters smaller than 1 nm is similar to those reported in the literature.[28]

In summary, we have carried out the first-principles density functional study of the composition and size dependence of the fundamental band gap in a series of [111]- and [110]-oriented silicon-germanium core-shell structured nanowires. A linear blueshift of the direct energy gap with composition (up to diameters as small as 1 nm) is observed for nanowires with fixed core size and varying shell thickness. The linear composition effect leads to an inverse square relation between the energy of the fundamental band gap and the size of nanowire, in conformity with experimental observations and qualitative theoretical predictions.[24–26] The results obtained provide useful guidelines for the experimental gap engineering of the core-shell structured nanowire heterostructures.

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