First-principles study of the effects of polytype and size on energy gaps in SiC nanoclusters

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We have studied the band-gap variation and stability energy in silicon carbide (SiC) nanoclusters of different polytypes using density functional theory (DFT) based on a gradient-corrected approximation. We have obtained a series of spherical SiC nanoclusters with dimensions up to 2 nm from bulk 2H, 3C, and 4H polytype crystals. All clusters with diameters smaller than 1 nm exhibit similar energy-gap-size variations, while energy gaps for clusters larger than 1 nm show a distinct size dependence with different polytypes and approach their bulk gaps with an increase in cluster size. In contrast to their bulk behavior, the binding energy difference between polytypes of clusters within the diameter range 0.5 nm−2 nm is found to be negligible, suggesting that the problems associated with the synthesis of polytypes of SiC in bulk may disappear for small clusters. The convergence of the energy gap and binding energy with different polytypes at small size clusters and the transition between the clusters to bulk behavior in SiC systems could be exploited for making future nano-optoelectronics devices. © 2007 American Institute of Physics.

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I. INTRODUCTION

During the past several decades silicon carbide (SiC) has received significant attention because of the combination of its remarkable electronic properties and superior thermal, chemical, and mechanical stability. Electronic devices based upon these properties have been utilized at temperatures in excess of 300 °C and in harsh environments. More recently, by decreasing the size of SiC structures and devices to nanoscale, unexpected optoelectronic properties have been observed including photoluminescence from SiC nanostructures in the visible range.1–3 It is now well established that size reduction, below the exciton Bohr radius, leads to a dramatic modification in the band gap of a semiconductor due to quantum confinement.6,7 This effect has been shown both theoretically and experimentally for a number of semiconductors including silicon and cadmium selenide (CdSe)8−10. In contrast, only limited theoretical studies of the size-dependence of the band gap in SiC have been reported.11−15 In a related context, Kityk et al.11 and Kassiba et al.12 employed semiempirical molecular dynamics to study the band structure and photoluminescence of large-sized (>10 nm) SiC nanoparticles. Feng et al.13 used effective mass theory to estimate the exciton states in cubic-form 3C-SiC quantum dots. These semiempirical simulations have been used to predict the size dependence of the energy gap in SiC nanostructures qualitatively. A few ab initio studies have been reported for quantitative predictions of the energy gaps in SiC nanostructures. For example, Rurail14 reported density functional calculations on SiC nanowires grown along the ⟨100⟩ axis that exhibit broadening of the energy gap in hydrogenated nanowires resulting from the quantum confinement effect. Using ab initio simulations, Reboredo et al.15 demonstrated that surface composition and termination play a significant role in determining the optical and thermodynamic properties of cubic 3C-SiC clusters in the 1–3 nm size range. In particular, the authors show that the energy gaps of these SiC clusters can be modified to obtain absorption and emission within a broad wavelength range from green to ultraviolet (UV), with potential applications for solid-state light sources. It is important to point out here that all previous theoretical studies which have established the strong dependence of the band gap on size and surface composition, however, have mainly focused on the 3C-SiC crystal structure.

In addition to size and surface composition, the band gaps in semiconductors could also strongly depend on their crystal structures. For example, the effect of polymorphism on electronic properties, such as band gap, carrier mobility, and breakdown field, of SiC is well documented.16,17 SiC exhibits prominent polymorphism (also called polytypism), resulting in more than 200 crystalline structures with varying stacking sequences. Two of the most simplified polytypes are 3C (pure cubic stacking) and 2H (pure hexagonal stacking), which correspond to zinc-blende and wurtzite structures, respectively. The most common polytypes, on the other hand, are 4H and 6H structures, which exhibit a hexagonal symmetry with ABCB and ABCACB stack sequences, respec-
tively. Different polytypes exhibit distinct band structures and band gaps. The reported bulk values of band gaps for 3C, 4H, and 6H polytypes are 2.4 eV, 3.2 eV, and 3.0 eV, respectively.

The realization of next-generation devices, such as solid-state light sources and high-performance chemical biosensors, based on semiconductor nanostructures demands a thorough understanding of the dependence of optoelectronic properties on various parameters. These parameters include size, surface composition, polytypism, impurities, and strain and are often coupled with each other. In particular, in the case of SiC, the manifestation of polytypism at the nanoscale and its impact on the optoelectronic properties are not clearly understood. The goal of this paper is to study the effect of polytypism on the energy gaps in SiC nanoclusters.

In this paper, we report the results of density functional calculations of the energy gaps of the nanoclusters derived from three of the most commonly observed polytypes of SiC: namely, 3C, 2H, and 4H structures, as a function of size.

II. SIMULATION DETAILS

The structure, energetics, and electronic properties of various SiC clusters are carried out using density functional theory (DFT) based on the generalized gradient approximation (GGA). In particular, we have used the Perdew-Wang 91 (PW91) exchange and correlation functional based on the pseudopotential plane-wave approach with the supercell method. The core electrons are described using ultrasoft Vanderbilt pseudopotentials within the Vienna ab initio simulation package (VASP). The kinetic energy cutoff for the plane-wave basis set is 300 eV. Spherical SiC nanoclusters with dimensions up to 2 nm are derived from the bulk polytype crystals (2H, 3C, and 4H). Since our main goal is to study the effect of polytypes on the electronic properties of nanoclusters, our study has not been focused on finding the global lowest-energy configuration for these systems.

The dangling bonds of the surface atoms in the clusters are passivated using hydrogen atoms, where the initial bond lengths of Si-H and C-H are 0.147 nm and 0.107 nm, respectively. Nanoclusters are then placed in a cubic simulation cell with periodic boundary conditions. The size of the simulation cell is chosen so that the distance between the cluster and its replica (due to periodic boundary conditions) is more than 1.2 nm. Under this configuration, the interactions between the cluster and its replica are negligible. Finally, the clusters are relaxed to minimize the total energy using the conjugate gradient algorithm. The local minimum is achieved when all residual forces acting on the atoms are less than 0.02 eV/Å.

The band gap (or energy gap) in a cluster is defined as the energy difference between the highest occupied molecular orbital (HOMO, i.e., valence band) and the lowest unoccupied molecular orbital (LUMO, i.e., conduction band). It is known that the density functional methodology underestimates the band gaps of semiconductors compared to the experimental results, while the more accurate Green’s function GW method and quantum Monte Carlo calculations provide better quantitative comparison with experiments. However, previous studies of the size dependence of energy gaps in semiconductors such as Si show that the HOMO-LUMO gap predicted by DFT and the optical gap obtained by the GW and quantum Monte Carlo calculations have similar size dependences. Therefore, we anticipate that our DFT results can correctly describe the energy gap variation with both size and polytypism.

III. RESULTS AND DISCUSSION

The primitive unit cells of the three SiC polytypes in the hexagonal projection are illustrated in Fig. 1(a). The stacking sequences in the unit cell are ABC for 3C-SiC in the [111] direction and AB for 2H-SiC and ABCB for 4H-SiC in the [0001] direction, where each A, B, and C position within a sequence represents a Si-C bilayer (i.e., one layer of Si and one layer of C). As mentioned earlier, we derive the spherical SiC nanoclusters with dimensions less than 2 nm from bulk polytype crystals. The nomenclature used to refer to a given cluster reflects the polytype of the parent crystal. As shown later, very small clusters cannot be assigned with a specific polytypism due to the limited number of bilayers in their structures. For each polytype, one may generate clusters with different configurations depending upon whether the cluster is centered at a silicon atom, a carbon atom, or an interstitial site. These spherical clusters may exhibit both Si and C surface terminations. In contrast, for clusters with a different shape, one can obtain configurations where only one type of atoms (Si or C) is present at the surface. For instance, as mentioned earlier Reboredo et al. have obtained either Si- or C-terminated surfaces in cubic-shaped 3C-SiC clusters. As demonstrated by these authors, surface termination can have a significant effect on the energy gaps of small-size clusters. In particular, they observe a significant reduction in the energy gaps of nanoclusters with Si (or Si-rich) termination due to additional surface strain. SiC nanoclusters with only C or mixed Si and C terminations tend to have less surface strain compared with predominantly Si-terminated clusters. The impact of surface strain on the energy gap of a semiconductor cluster is well established.

Indeed, our results for 3C clusters are in good agreement with the data reported by Reboredo et al. for clusters with same size and surface structures. For instance, the HOMO-LUMO gap of the cluster Si$_{62}$C$_{60}$H$_{120}$ as reported by Reboredo et al. is equal to 3.0 eV, while our predicted value is 2.91 eV. The small difference between our result and theirs could be due to the different functionals used in the studies. Since our objective is to elucidate mainly the effect of polytypism on the energy gap at the nanoscale, we have opted for spherical-shaped clusters, allowing us to minimize the effects of surface composition and strain. The effect of polymorphism on the energy gap may also be investigated in varying shape nanoclusters provided that identical surface composition and strain are maintained across the different polytypes.

The size of a given cluster depends on its bulk lattice constants and the total number N of Si and C atoms. Due to the spherical shape of all clusters, the size can be determined by $a(3N/4\pi)^{1/3}$, $(3\sqrt{3}a^{2}cN/8\pi)^{1/3}$, and $(3\sqrt{3}a^{2}cN/4\pi)^{1/3}$ for 3C, 4H, and 2H, respectively, where $a$ and $c$ are the corresponding bulk lattice constants. Figure 1(b) shows atomic...
snapshots of SiC nanoclusters of varying size that were obtained from different parent polytypes. Clusters of 0.70 nm exhibit similar structures regardless of their parent polytypes. Indeed, for these clusters, the polytypism of the parent crystals is completely lost due to the limited number of bilayers. However, for 1.11-nm clusters significant structural differences among polytypes can be observed, reflecting the structure of parent crystals. Besides the structural difference, it is interesting to compare the total free energy of the different polytypic clusters at a given size. For a reasonable comparison, it is necessary to examine the clusters of different polytypes that have the same chemical composition and the same number of dangling bonds. It is known that the prominent polytypic phenomenon in SiC results from the rather small stacking-fault energy \( E_{sf} \) the difference in the total energy among SiC polytypes is a few meV/SiC. Thus, the difference in the total energies contributed from the core of different polytypic clusters is estimated to be small. Once we minimize the difference in the energies resulting from the cluster surface such as strain and passivants, we expect the energy difference between the clusters in different allotropic forms to be negligible. This assumption is supported by our results on the clusters of 2H, 3C, and 4H polytypes.

Next, we focus on the size dependence of the energy gaps in 4H-SiC nanoclusters. 4H-SiC crystals exhibit three equivalent stacking sequences: namely \( ABAB \), \( ACBC \), and \( ABAC \). However, when the crystal size is reduced, the stacking sequences can result in different (nontrivial) structures. Figure 2 shows two 4H-SiC clusters around 0.9 nm obtained from \( ABAB \) and \( ABAC \) stacking sequences, respectively. The central layer is randomly labeled as \( A \), and the top and bottom layers in the left snapshot will both be \( B \) (or \( C \)) obtained from the \( ABCB \) sequence (or \( ACBCACBC \)) stacking sequence. Similarly, three layers in the right picture can be named as \( CAB \) (or \( BAC \)) from bottom to top, which are obtained from the \( ABACABAC \) stacking sequence. In order to address whether these structural differences within 4H-nanoclusters can result in distinct energy gaps, the following calculations were performed. The HOMO-LUMO gaps of two stacking sequences \( ABAC \) (solid and open circles) and \( ABAB \) (diamonds) are plotted as a function of size in Fig. 2. The solid circles are the energy gaps of geometry-relaxed clusters. Open circles correspond to the gaps of the larger clusters on which geometry relaxations were not performed. For these larger clusters, the differences in the energy gaps between relaxed and unrelaxed ones are expected to be within 0.15 eV. Blue diamonds refer to the clusters obtained from \( ABAB \) sequence. The dashed line is a guide for the eyes. The snapshots display two SiC cluster around 0.9 nm obtained from \( ABAB \) and \( ABAC \) stacking sequences, respectively.

FIG. 1. (Color online) (a) Three-dimensional perspective views of the primitive hexagonal unit cells of 2H-, 3C-, and 4H-SiC polytypes. The stacking sequences \( AB \) (for 2H), \( ABC \) (for 3C) and \( ABAB \) (for 4H) are indicated. The Cartesian coordinate system and primitive lattice vectors are also given. (b) shows atomic snapshots of two sizes of SiC nanoclusters of 2H, 3C, and 4H polytypes. Clusters of 0.70 nm exhibit almost identical structures regardless of the polytype, while for 1.11-nm clusters, significant structural differences can be observed among the polytypes.

FIG. 2. (Color online) The variation of the DFT HOMO-LUMO gap with size for 4H-SiC nanoclusters. Red data points correspond to the clusters generated from the \( ABACABAC \) stacking sequence. The solid circles are the energy gaps of geometry-relaxed clusters. Open circles correspond to the gaps of the larger clusters on which geometry relaxations were not performed. The HOMO-LUMO gaps of two stacking sequences \( ABAC \) (solid and open circles) and \( ABAB \) (diamonds) are plotted as a function of size in Fig. 2. The solid circles are the energy gaps of the clusters whose geometries are relaxed to minimize their total energies. These calcula-
tions become computationally demanding, and relaxation of clusters larger than 1.5 nm is not performed. Hence, for clusters larger than 1.5 nm, only the energy gaps of unrelaxed structures (open circles) are displayed in Fig. 2. The difference in the energy gap between relaxed and unrelaxed clusters is less than 0.15 eV for all clusters smaller than 1.5 nm. We would expect a variation in the gaps for the larger clusters when they are optimized. As can be observed in Fig. 2, all 4H-SiC nanoclusters, regardless of their stacking sequence, exhibit identical variation of the energy gap as a function of size.

The energy gaps of 2H, 3C, and 4H SiC clusters are plotted as a function of their sizes in Fig. 3. For clusters larger than 1 nm, the variation of the energy gap with size is a strong function of the polytype. This observation is consistent with the bulk values of the band gap for the three SiC polytypes: i.e., 2.4 eV for 3C, 3.2 eV for 4H, and 3.3 eV for 2H. In contrast, for smaller clusters (<1 nm), no distinct differences in the energy gap are observed among the polytypes. This effect becomes more apparent when comparing the difference in the energy gaps of varying polytype clusters of identical size and chemical composition (Si,C,H). In Fig. 4(a), the difference between the energy gap for several pairs of 3C and 4H clusters is presented. As mentioned earlier and reiterated in Fig. 4(a), the difference in the energy gap for the small clusters (<1 nm) is negligible. However, for larger clusters (>1 nm), the energy gap ($E_g$) of the 3C cluster is apparently less than that of its 4H counterpart. We expect the difference in the energy gap of 3C and 4H clusters to gradually increase with size until a constant value of 0.8 eV, which is the expected difference in the band gap between the bulk polytypes.

Although the divergence of energy gaps for larger clusters is expected among the different polytypes, the convergence of energy gaps for smaller clusters merits further discussion. One may argue that due to the stacking sequence, the difference in the energy gap between relaxed and unrelaxed clusters is expected to be within 0.15 eV. Dashed lines are a guide for the eyes. For clusters smaller than ~1 nm, the variation of the energy gaps in three polytypes with size show indistinguishable trends. For clusters larger than 1 nm, the size dependences of the energy gaps become apparent, exhibiting the same order of their bulk band gaps.
polytypes is negligible. This suggests that the problems associated with the synthesis of bulk polytypes may not appear at the nanoscale. Such methodology, in turn, would allow for the fabrication of emitters and detectors for ultraviolet wavelengths from SiC nanoclusters with minimal or no polytype stability issues. Differences in the energy gap between polytypes are predicted to be present for cluster sizes larger than 1 nm. These differences can potentially be utilized to create heterostructures that emit or detect light at UV wavelengths. Heterojunctions may also become possible in deep UV if two small clusters of different polytypes are joined or brought in close proximity.

In summary, using density functional method we have investigated the combined effect of polytype and size on the energy gaps in SiC nanoclusters in the size range of 0.5–2.0 nm. We found that for clusters smaller than 1 nm, regardless of the parent polytype, an identical-size energy-gap dependence is achieved. For clusters larger than 1 nm, different polytypes exhibit distinct energy-gap values, systematically approaching the bulk band gaps. The critical size of 1 nm is correlated with the number of bilayers and the stacking sequences within the clusters. These studies suggest how the structure, energetics, and electronic properties evolve with size in SiC for different polytypes and could have immense impact on future optoelectronics materials and nanodevices.

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