Silicon carbide nanotube tips: Promising materials for atomic force microscopy and/or scanning tunneling microscopy

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Using ab initio techniques we examine the structural properties and energetics of novel nanotip and nanocone materials based on silicon carbide nanotubes. The effect of various structural and topological defects on the highest occupied molecular orbital (HOMO)–lowest unoccupied molecular orbital (LUMO) gap and the stability of these tips are investigated. The HOMO–LUMO gaps range from zero to 2.0 eV due to the defects, providing possible applications in band gap engineering. These tips which combine the elastic and mechanical properties of nanotubes with the stiffness of silicon carbide materials can find applications as atomic force microscopy and scanning tunneling microscopy probes. © 2006 American Institute of Physics. [DOI: 10.1063/1.2221418]

Scanning probe microscopy (SPM) has been shown to be a tremendously useful technique in scientific applications. The main characteristic of SPM is that a probe tip investigates and reads the surface of an object. An ideal tip should be as precisely defined as the object which is going to be investigated and should maintain its structural integrity despite repeated use. The first material used for SPM tips was metal nanowires since they have excellent electronic properties and fairly good mechanical behavior.

Following the discovery of carbon nanotubes (CNTs) an effort was initiated to take advantage of their superior mechanical and elastic properties and use them as tips. First Dai et al. managed to attach individual nanotubes several micrometers in length to the silicon cantilevers of conventional atomic force microscopes. Because of the flexibility of the nanotube, the tips were resistant to damage from tip crashes, while their slenderness permitted imaging of sharp recesses in surface topography. In addition to this, carbon nanotube tapers are of considerable interest as candidates for scanning probe tips due to their unique morphology. A nanotube taper consists of series of straight nanotube sections with decreasing diameter via topological defects.

More recently, in 2001 a novel kind of nanotubes were fabricated, namely, the silicon carbide nanotubes. Even though their structural and electronic properties were extensively studied, their potential applications remain unexplored.

The purpose of the present study is to exploit the superior mechanical properties of SiC materials and explore the structure and stability of silicon carbide nanotube (SiCNT) tapered and conelike tips. Recently, Huczko et al. managed to synthesize various types of one-dimensional (1D) SiC structures. Among these structures tapered SiCNTs and tubes with spherical caps were observed. In this letter, we examine the energetics and electronic structures of various types of SiCNTs ending in sharp or conical tips.

In the present calculations we employ density functional theory based on the resolution of the identity approximation (RI-DFT) code of TURBOMOLE. For the geometry optimizations, the BP86 functional was applied along with the single valence polarized (SVP) basis set. The dangling bonds at the one end (opposite to the tip ends) of the nanotubes were saturated with hydrogen atoms. All the geometries presented in this work are fully optimized without any symmetry constraints.

The studied structures are divided into two main categories: (1) the taper tips and (2) the conical ones. The taper structures are constructed by shrinking the diameter of the nanotubes via the formation of octagons and squares (a) or via the introduction of pentagons and heptagons (b). In case (a), only Si–C bonds are present, whereas in case (b), C–C and Si–Si bonds are present. Similarly to case (b), the conical structures are formed via the introduction of pentagons.

The most interesting structures of the first category are presented in Fig. 1. The binding energy (BE) per atom is taken as a stability criterion for each structure and is calcu-
related with respect to dissociation to the corresponding elements given by the equation

\[
\text{BE per atom} = \frac{E(\text{tip}) - xE_C - yE_{\text{Si}} - zE_{\text{H}}}{x + y},
\]

where \(x\), \(y\), and \(z\) are the number of carbon, silicon, and hydrogen atoms, respectively, in the tip and \(E_C\), \(E_{\text{Si}}\), and \(E_{\text{H}}\) are the corresponding atomic energies of the elements.

Structural stability: Category 1. We have considered several taperlike tubes of both zigzag and armchair types. In our studies both chirality and diameter dependences were taken into account. In particular, we consider the case of an \((8,0)/(4,0)\) taper [i.e., an \((8,0)\) SiCNT narrowing to \((4,0)\) [Fig. 1(a)] and also a \((12,0)/(6,0)\) taper. Furthermore, for the armchair case, \((8,8)/(4,4)\), \((6,6)/(3,3)\), and \((4,4)/(2,2)\) tapers were studied. These tapers contain more than two pairs of octagons and squares. The fully optimized structures are shown in Fig. 1. Our results indicate that their stability increases in proportion to the diameter of the tapers. This is consistent with previous works on SiCNTs.\(^5\) The BE per atom for the \((4,4)/(2,2)\) taper is \(5.64\) eV and reaches up to \(5.78\) and \(5.81\) eV for the \((6,6)/(3,3)\) and \((8,8)/(4,4)\) tapers, respectively. The same trend is also observed for the zigzag tapers. The BE per atom for the open ended \((8,0)/(4,0)\) and \((12,0)/(6,0)\) tapers are calculated to be \(5.48\) and \(5.57\) eV, respectively. For the zigzag tapers, the closed end configurations were also investigated. In this instance, more stable structures are formed due to the saturation of the dangling bonds present in the open ended case. All zigzag tapers, either closed or open end, are less stable than their armchair counterparts.

We have also considered other possible configurations for the tapers containing only one octagon-square pair. The fully relaxed \((4,4)/(3,3)\), \((5,5)/(4,4)\), and \((6,6)/(5,5)\) SiCNT tapers in these configurations are shown in Fig. 2. Once again, the stability increase is found to be proportional to the tube diameter. The corresponding BE per atom values are \(5.69\), \(5.74\), and \(5.78\) eV, respectively. Structures 2(c) \([(6,6)/(5,5)]\) and 1(d) \([(6,6)/(3,3)]\), which originate from a \((6,6)\) SiCNT, have almost the same value of BE per atom. This result suggests that the closing is dependent on the number of square-octagon pairs and depends only on the initial tube. The \(2(a)\) \([(4,4)/(3,3)]\) and \(1(c)\) \([(4,4)/(2,2)]\) tapers do not follow the above trend, since the \((2,2)\) SiCNT has very large strain energy due to its small diameter.

Following the notation of Saito et al.,\(^3\) tapered nanotubes may also be constructed by the introduction of a single pentagon-heptagon pair. Since these defect rings are made of odd number of atoms, formation of C–C or Si–Si bonds cannot be avoided. One can think of such bonds as “defects” in these nanotubes. The effect of all possible types of defects has been considered for the \((5,5)/(4,4)\) SiCNT tapers, in particular, the presence of only C–C defects (a), the formation of only Si–Si bonds (b), the formation of C–C bonds in the pentagons and Si–Si bonds in the heptagons (c), and the introduction of Si–Si defects in the pentagons and C–C in the heptagons (d). All geometry optimizations end up in stable structures as seen in Fig. 3. Larger deformations in tapers appear when Si–Si bonds are present as we reported recently.\(^6\) Si–Si bonds are not energetically preferable and large distortions formed. The most stable situation appears when only C–C bonds are formed. In this case, the BE per atom is calculated to be \(5.79\) eV. This structure is also more stable than the previous case of the \((5,5)/(4,4)\) taper [structure 2(b)], which is formed via a square-octagon pair. This suggests that the closing is more favorable through pentagonal-heptagonal defect pairs rather than with the formation of square-octagon. The presence of SiC squares is known to induce large intrinsic strain.\(^12\)

Structural stability: Category 2. The conical structures are created via the addition of a SiC cone with 120° disinclination to an \((8,0)\) and a \((12,0)\) SiCNT. Again, the two possible cases are considered: the formation of Si–Si defects (a) and C–C defects (b). All four structures are presented in Fig. 4.

The same trend is also observed as in the first category, i.e., the stability increase is found to be proportional to the tube diameter. The formation of Si–Si bonds also causes destabilization of the conical structures. Once again, it is energetically more favorable to cap the tubes in the presence of C–C bonds rather than with Si–Si. When Si–Si defects are present in the \((12,0)\) SiC cone, the BE per atom is calculated to be \(5.61\) eV, while it is only \(5.93\) eV in the presence of only C–C defects.

Band gap engineering. In forming the carbon nanotapers, nanotips, and nanocones, structural defects are unavoidably incorporated in the undefected SiCNT structures. This has as a result defect states to be generated which are

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**FIG. 2.** (Color online) Various armchair SiCNT tapers (fully relaxed) containing only one square-octagon pair.

**FIG. 3.** (Color online) Optimized \((5,5)/(4,4)\) SiCNT tapers with one pentagon-heptagon defect pair. The pentagon-heptagon defects are presented in larger ball and stick models for clarity.

**FIG. 4.** (Color online) Conical SiCNT tips with pentagon defects. The caps of the tips are formed by squares of Si or C.
associated with the interface, the structural or topological defects, the top of the tip (top-tip states), and the terminating-edge states (in the occurrence of open ends in tips and/or tapers). These defect states produce dramatic changes in the gap between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO). The HOMO-LUMO gap (HLg) was found to be very large (of the order of 3.0 eV) in the undefected type-1 SiC nanotubes.\(^7\) It should be recalled that type-1 DOS of the SiC taper made of octagon-square pairs terminating-edge states orbital changes in the gap between the highest occupied molecular tips and/or tapers.

Another interesting feature that is found is the HLg of zigzag tapers and tips [as, for example, the (8,0)/(4,0) tapers and (8,0) tip systems shown in Figs. 1(a), 1(h), 1(g), 4(a), and 4(b), the (12,0)/(6,0) tapers and (6,0) tips of Figs. 1(b), 1(h), 1(i), 4(c), and 4(d)] have very small HLg and can be considered as semiconductors or semimetals. Their HLg appears to be independent of the diameter and the type of the defects present (i.e., presence of Si–Si and C–C bonds, presence of either heptagon-pentagon or octagon-square pairs, being closed or open ended). The gap value is found to be in the range of 0.00–0.10 eV for the tapers and attains greater values for the conical tips (0.21–0.61 eV). It is, thus, worth noting that the conical ending tips behave quite differently than those of the hemispherical ending. Finally, in the case of conical tips, the nature of atoms forming the top of the tip appears to be significant. That is, the presence of the additional Si–Si bond (along the diagonal of the square ring) at the top of the tip lowers the HLg value.

It is worth noting that, there is a very good correlation between the stability (i.e., the BE) and HLg. It is observed that the HLg can be considered as a good measure of stability and be used as a stability criterion.

Another interesting feature that is found is the HLg of the armchair open ended tapers which is very large in the presence of an octagon-squarepair (1.78–2.0 eV). If the octagon-square pairs are removed and substituted with pentagon-heptagon pairs (containing Si–Si and/or C–C bonds), the value of the HLg of the armchair tips gets smaller (~0.80 eV). This is in agreement with our previous report\(^11\) in which it was demonstrated that the presence of Si–Si and C–C bonds leads to SiC nanotubes (type 2) with smaller HLg. This is further supported in the case of the defected SiC tips where it is observed that the saturation of the Si dangling bonds with the additional Si–Si bond, associated with the diagonal of the square of the octagon-square pair, leads to the enhancement of HLg. However, the presence of this extra bond does not seem to affect the HLg of the zigzag tapers in the same way as a result of the direction of the Si–Si bond relative to the tube axis.

The effect of the various defects on the value of the HLg becomes more apparent by plotting the electron density of states (DOS) for representative cases selected from the above studied systems. In Fig. 5, the DOS for various configurations of the (5,5)/(4,4) taper are presented. As can be observed, the presence of the octagon-square defect in the Si–C tip leads to a large HLg at the Fermi energy while the heptagon-pentagon pair with C–C defects brings the HLg value close to that of a corresponding carbon-only (5,5)/(4,4) taper.

In summary, we have performed density functional theory calculations in order to investigate the most suitable SiC structures for AFM and STM tips. We find that edges made of single atom, such as structures 1(f)–1(i) are less stable than the multiatom edges. The formation of square defects in SiCNT is also not energetically favorable, since it causes large intrinsic strain. Tips with edges containing pentagon-heptagon defects are found to be energetically more favorable than edges containing four-membered rings. Structures 4(a) and 4(c) are among those tips with the largest BE per atom and, therefore, ideal one for AFM and STM applications. The negative charged on this tip (~0.6 eV) would cause it to behave differently when interacting with surfaces with positive (attractive forces) or negative charges (repulsive forces).

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