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Kyoto University
Structural stability and electronic properties of SiC nanocones: First-principles calculations and symmetry considerations

G. Alfieri and T. Kimoto

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Structural stability and electronic properties of SiC nanocones: First-principles calculations and symmetry considerations

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The structural and electronic properties of SiC nanocones (SiCNCs), as a function of the disclination angle and electric field intensity and orientation, are investigated by means of \textit{ab initio} calculations. Phonon analysis revealed that SiCNCs with only three disclination angles are allowed and, among these, the band gap of only one SiCNC is affected by a transverse electric field. An interpretation of these findings, from a group theoretical point of view, is also given. © 2011 American Institute of Physics. [doi:10.1063/1.3567535]

Nanomaterials can find a great number of applications in modern-day technology, ranging from household to on-board satellite electronics, and because of the increasing need for speed and miniaturization of electronic devices, nanotechnology has become a very active field of study. At the same time, due to the rapid development silicon carbide (SiC) technology, the existence of SiC nanostructures that can exploit the superior physical-chemical properties of SiC (Ref. 1) has been investigated and, in the last few years, many studies on SiC nanotubes have been reported in the literature.²–⁴ On the contrary, little information on SiC nanocones (SiCNCs) is available.⁵ This is unfortunate, because it was proven that nanocones arrays for solar panels applications can be beneficial in terms of increased optical absorption coefficient⁶ and since space probes rely on photovoltaic power generation, solar panels based on SiCNCs arrays can be a valid alternative in terms of high-temperature, high-light intensity and high radiation conditions.

In this study, we investigated the structural and electronic properties of SiCNCs, obtained by rolling a single SiC layer with Si–C bond length of 1.78 Å, as a function of the disclination angle \( d \) (defined as the angle of the sector removed from a flat SiC sheet to form a cone), ranging from 60° to 300°, and of an electric field \( F \) (parallel or perpendicular to the cone axis), of intensities ranging from 0.05 to 0.20 V/Å. For this purpose, we employed the \textit{ab initio} calculation code SIESTA (Ref. 7) using a double-\( \zeta \) plus polarization atomic orbitals basis set (a 0.02 Ry energy shift to compress the basis set was used to speed up calculations) and by taking the effect of core electrons into account by Troullier–Martins norm-conserving pseudopotentials.⁸ The Perdew–Burke–Ernzerhof (PBE) (Ref. 10) form of the generalized gradient approximation (GGA) for the exchange-correlation potential and the calculated band gap width, \( E_{\text{gap}} \), and spontaneous dipole moment, \( D \), are also shown in parenthesis in Table I, for comparison.

The stoichiometry of the investigated SiCNCs is reported in Table I and, it can be seen that, except for \( d = 120° \) and 240°, they can be classified into C-rich or Si-rich. It can be noted that C-rich SiCNCs possess a wider \( E_{\text{gap}} \) than Si-rich SiCNCs and also wider \( d \) corresponds to more narrow \( E_{\text{gap}} \), because of increased curvature effect.⁹ The symmetry of all the investigated SiCNCs (third column of Table I) is \( C_1 \) with the exception of \( d = 120°, C_{2v} \), which, interestingly, corresponds to the highest \( E_{\text{gap}} \) value. Knowing the symmetry of the investigated SiCNCs is particularly useful because, being \( C_1 \) or \( C_{2v} \), this implies the presence of a spontaneous \( \mathbf{D} \) which, as it can be seen in the sixth column of Table I, is indeed the case (D is parallel to the cone axis or slightly deviating from it). In the last column of Table I, the binding energy per atom, \( E_B \), as defined in Ref. 4 shows no correlation to either \( d \) or point group symmetry, and the values are 1–2 eV larger than those reported by Mavrandonakis et al.⁵ in nanotube-based conical nanostructures, possibly due to the different calculation method employed.

In order to check the structural stability of the SiCNCs of the present study (or, equivalently, that the relaxed geometry is preserved), we analyzed the phonon modes (at the

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**Table I. Stoichiometry, disclination angle, point group symmetry, band gap energy, dipole, and binding energy for the eight investigated SiCNCs.** In parenthesis the value of the band gap and dipole calculated by GGA-PBE.

<table>
<thead>
<tr>
<th>Stoichiometry</th>
<th>( d ) (deg)</th>
<th>Point group</th>
<th>Tip point group</th>
<th>( E_{\text{gap}} ) (eV)</th>
<th>( D ) (D)</th>
<th>( E_B ) (eV/atom)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C_{36}Si_{33}H_{15}</td>
<td>60</td>
<td>( C_1 )</td>
<td>( C_1 )</td>
<td>0.86 (0.87)</td>
<td>2.17 (2.6)</td>
<td>6.83</td>
</tr>
<tr>
<td>C_{36}Si_{33}H_{18}</td>
<td>60</td>
<td>( C_1 )</td>
<td>( C_{2v} )</td>
<td>0.59 (0.58)</td>
<td>2.35 (2.5)</td>
<td>6.73</td>
</tr>
<tr>
<td>C_{34}Si_{36}H_{20}</td>
<td>120</td>
<td>( C_{2v} )</td>
<td>( C_{2v} )</td>
<td>1.42 (1.38)</td>
<td>3.29 (2.98)</td>
<td>6.85</td>
</tr>
<tr>
<td>C_{36}Si_{34}H_{20}</td>
<td>180</td>
<td>( C_1 )</td>
<td>( C_{2v} )</td>
<td>0.58 (0.58)</td>
<td>7.7 (7.4)</td>
<td>6.95</td>
</tr>
<tr>
<td>C_{36}Si_{33}H_{18}</td>
<td>180</td>
<td>( C_1 )</td>
<td>( C_{2v} )</td>
<td>0.50 (0.51)</td>
<td>14.4 (14.0)</td>
<td>6.81</td>
</tr>
<tr>
<td>C_{36}Si_{34}H_{18}</td>
<td>240</td>
<td>( C_1 )</td>
<td>( C_{2v} )</td>
<td>0.31 (0.30)</td>
<td>16.3 (16.1)</td>
<td>7.09</td>
</tr>
<tr>
<td>C_{36}Si_{34}H_{18}</td>
<td>300</td>
<td>( C_1 )</td>
<td>( D_{3h} )</td>
<td>0.29 (0.29)</td>
<td>14.1 (14.5)</td>
<td>7.28</td>
</tr>
<tr>
<td>C_{36}Si_{34}H_{18}</td>
<td>300</td>
<td>( C_1 )</td>
<td>( D_{3h} )</td>
<td>0.08 (0.08)</td>
<td>6.2 (6.4)</td>
<td>6.72</td>
</tr>
</tbody>
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¹Electronic mail: giovanni@semicon.kue.kyoto-u.ac.jp.
Γ-point) calculated with force constant method. This analysis provides a reliable stability test, as the presence of imaginary phonon frequencies suggests that the system is structurally unstable and a structural transformation can occur. Our results indicate the presence of imaginary frequencies in all the investigated SiCNCs, with the exception of the C_{36}Si_{34}H_{20} \[\text{d}=60^\circ, C_1, \text{Fig. 1(a)}\], C_{32}Si_{32}H_{16} \[\text{d}=120^\circ, C_{2v}, \text{Fig. 1(c)}\], and C_{40}Si_{34}H_{10} \[\text{d}=300^\circ, C_1, \text{Fig. 1(g)}\]. We point out that the three stable SiCNCs are either C-rich or possess a ratio of C/Si=1, in agreement with the literature. Yet, this is not sufficient to justify their stability, as the other C-rich or C/Si=1 SiCNCs display imaginary phonon frequencies.

Charlier and Rignane12 suggested that the presence of particular topological defects at the tip can contribute to the stability of nanocores. We take advantage of this finding to analyze the tip of our SiCNCs and propose a criterion for stability of nanocones. We take advantage of this finding to analyze the tip of our SiCNCs and propose a criterion for stability of nanocones.

In Fig. 2, the behavior of the lowest unoccupied and highest occupied molecular orbitals, LUMO (red) and HOMO (yellow), respectively, is shown for the C_{36}Si_{34}H_{20} and C_{32}Si_{32}H_{16} SiCNCs. It can be seen that application of either F_{\perp} [Fig. 2(b)] or F_{\parallel} [Fig. 2(c)], with intensities of 0.20 V/Å, on the C_{36}Si_{34}H_{20} cone yields no effect on the molecular orbitals and, in fact, no change is observed on the E_{GAP} values. For the case of C_{32}Si_{32}H_{16}, F_{\parallel}=0.20 \text{ V/Å results in the rearrangement of the HOMO (negative charges) and LUMO (positive charges) along the direction of field, at two opposite sides of the SiCNC.}

This means that two regions are formed, one of low (HOMO) and one of high (LUMO) electrostatic potential that, in terms of energy, contribute to the lowering of the LUMO and the rising of the HOMO, thus shrinking the E_{GAP}. When F_{\parallel} is applied, no rearrangement of either HOMO or LUMO can be noted and E_{GAP} does not change. As the SiCNC with C_{2v} symmetry is more responsive to F_{\parallel} than those with C_{1} symmetry it is straightforward asking whether or not this can be interpreted by using group theory. To do this, for simplicity, we consider only the HOMO, namely the C-atoms of the C_{36}Si_{34}H_{20} (C_{1}) and C_{32}Si_{32}H_{16}(C_{2v}) SiCNCs.

By employing the directed valence (DV) bonding13 on C-atoms, we obtain the following irreducible representations (irrep) \( \Gamma_{C_{1}}^{\text{irrep}}=19A'+17A'' \) (C_{36}Si_{34}H_{20}) and \( \Gamma_{C_{2v}}^{\text{irrep}}=10A_{1}+6A_{2}+8B_{1}+8B_{2} \) (C_{32}Si_{32}H_{16}). By direct product multiplication, with the representations of the s, p_x, and p_y atomic orbitals of the respective point-symmetry groups (A', A'' and A_1, B_1, B_2 for C_1 and C_{2v}, respectively) we obtain

\[ E_{\text{GAP}} = 1.35, 1.20, 1.05, \text{ and } 0.89 \text{ eV, respectively.} \]
meaning that the orbitals involved are $s$, $p_x$, and $p_y$, corresponding to the $sp^2$ hybridization of the single SiC sheet. In order to evaluate the effects of $F_\perp$ on the SiCNCs, the $\Gamma^{DV}$s are multiplied, by direct product multiplication, with the representations of $F_\perp$ and $F_\parallel$ of the respective point-symmetry groups that are $A'$, $A''$ ($C_x$) and $B_1$, $A_1$ ($C_{2v}$), for $F_\perp$ and $F_\parallel$, respectively. For $C_x$, $\Gamma^{DV}_{C_x} \otimes A'$ and $\Gamma^{DV}_{C_x} \otimes A''$ still result in $\Gamma^{DV}$, $\Gamma^{DV}_{C_{2v}} \otimes B_1 = (10A_1 + 6A_2 + 8B_1 + 8B_2)$

\[
\begin{align*}
\Gamma^{DV}_{C_{2v}} &= \left(\frac{10A_1 + 6A_2 + 8B_1 + 8B_2}{s}\right) \\
&\quad + \left(\frac{10B_1 + 6B_2 + 8A_1 + 8A_2}{p}\right) \\
&\quad + \left(\frac{10B_2 + 6A_1 + 8B_2 + 8B_1}{p}\right).
\end{align*}
\]

This suggests that the application of a $F_\perp$ to a SiCNC with $C_{2v}$ symmetry results in the coupling of $\Gamma^{DV}_{C_{2v}}$ with a final state containing the term $(10A_2 + 6A_1 + 8B_2 + 8B_1)$ not present in the initial. On the contrary, no change in the initial and final states is observed when either $F_\perp$ or $F_\parallel$ is applied to a SiCNC of $C_x$ symmetry, suggesting that the response to an electric field is different from that of SiCNs with $C_{2v}$ symmetry (nil or slower response).

In conclusion, phonon analysis revealed that SiCNs with $d=60^\circ$, $120^\circ$, and $300^\circ$ and C/Si $\approx 1$ are stable and only the $E_{\text{GAP}}$ of the SiCNC with $d=120^\circ$, is affected by a transverse $F$. These findings were interpreted by means of group theory, by considering the correspondence between the point group symmetry of the cone with that of the shape of the tip and in terms of symmetry change in the irrep of the HOMO, when an electric field is applied.

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