

Effect of oxygen on single-wall silicon carbide nanotubes studied by first-principles calculationsÁ. Szabó¹ and A. Gali^{1,2,*}¹*Department of Atomic Physics, Budapest University of Technology and Economics, Budafoki út 8, H-1111 Budapest, Hungary*²*Department of Physics and School of Engineering and Applied Sciences, Harvard University, Cambridge, Massachusetts 02138, USA*

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According to the predictions of first-principles calculations, single-wall silicon carbide nanotubes exhibit several unusual properties: they are semiconducting independently of their chirality, superior material for hydrogen storage, and have strong nonlinear optical coefficients. Nevertheless, only a single experiment indicates, in our knowledge, that a tubular form of silicon carbide (SiC) exists. It is known that the surface of bulk silicon carbide is oxidized in the presence of oxygen; therefore, oxygen may destabilize its tubular form. We applied *ab initio* density-functional theory calculations to investigate this important issue. We found that (i) the structure of silicon carbide nanotubes remain intact in ambient oxygen, (ii) but the oxygen molecule dissociates as interstitials on silicon carbide nanotubes even at room temperature, and (iii) the interstitial oxygen is a fast diffuser on SiC nanotubes.

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I. INTRODUCTION

Silicon carbide (SiC) is a bioinert wide band-gap material that can be routinely *p*-type or *n*-type doped. This makes SiC a promising candidate both for high power, high-temperature electronics and biological sensor applications.¹ In addition, it has been recently shown by first-principles calculations that its simplest tubular form, the single-wall SiC nanotubes (SWSiCNT), is superior over the single-wall carbon nanotubes (SWCNT) in several aspects.^{2–12} SiC nanotube tips were suggested for atomic force microscopy and/or scanning tunneling microscopy.¹³ SWSiCNTs exhibit, with some exceptions of ultrasmall (*n*,0) tubes with *n*=3,4,¹¹ uniform semiconductor behavior independently on their chirality.^{2–5,7} In addition, the electrical^{7,14} and magnetical¹⁵ properties can be tuned by appropriate doping. The electronic structure is sensitive to the hydrogen^{14,16–18} and nitrogen-related^{14,19,20} molecules in the environment, therefore, it may be used as gas sensors. SWSiCNT can store more hydrogen in a given volume than SWCNT⁶ that is an important property for green environment technology. Beside that, SWSiCNT exhibits strong nonlinear optical behavior¹² making them promising candidates for special (nano)optical applications. While theoretical studies showed that SWSiCNTs are metastable form of SiC (Refs. 2, 4, 7, 21, and 22) only a single experiment indicated that multiwall SiC nanotubes can be formed,²³ in our knowledge. The other SiC “nanotubes” reported were hollows of nanometer size in *crystalline* SiC where the outer surface was oxidized.²⁴ These “nanotubes” are distinct structures from the tubular forms of SiC because they consist of fourfold coordinated Si and C atoms. In this study we consider the tubular form of SiC.

It is well known that the surface of silicon carbide is oxidized in ambient oxygen. The main process of oxidation is that an incoming oxygen molecule reacts with the surface and substitutes the carbon atom by an oxygen atom while the other oxygen atom and the outgoing C atom form a CO molecule emitted from the surface.²⁵ While theory showed that SWSiCNTs would be very advantageous for several types of nanodevices, it has not yet been investigated so far

what is the effect of ambient oxygen on the stability of SWSiCNTs. If SWSiCNTs are oxidized such as the surface of SiC then SWSiCNTs would not be stable in ambient oxygen. The oxidation of SWSiCNTs may explain why tubular form of SiC has been reported only in a single experiment.²³

In this work, we performed *ab initio* density-functional theory calculations to investigate the interaction of oxygen and SWSiCNTs. We found that (i) the structure of SWSiCNT remains intact in ambient oxygen, (ii) but the oxygen molecule dissociates on SWSiCNT *even at room temperature*, (iii) the resulted interstitial oxygen defects are fast diffusers in SWSiCNTs. These results indicate that interstitial oxygen²⁶ will interact with any adsorbed molecules in SWSiCNTs that may be detrimental for sensor applications. It is also expected that these interstitial oxygen atoms can interact with the hydrogen molecule present in the environment. Our results suggest that the effect of oxygen should be investigated in detail for all the possible applications of silicon carbide nanotubes.

II. METHODOLOGY

We carried out supercell calculations with using density-functional theory (DFT) within local density approximation as parameterized by Perdew and Zunger (LDA-PZ).²⁷ We relaxed the atomic positions until all the forces were lower than 0.02 eV/Å with the SIESTA code.²⁸ We used 10 Å vacuum between the nanotubes in the nonperiodic directions and Monkhorst-Pack *K*-point sampling²⁹ along the wire axis in order to converge the charge density. We first optimized the primitive cell of the SiCNTs including the lattice constant, then we constructed the supercell structures from the optimized geometry of the primitive cells in order to study the isolated defects. During the geometry optimization of the defects all the atoms were allowed to relax but the lattice constant was kept fixed. We applied an optimized double- ζ polarized basis set and Troullier-Martins pseudopotentials.³⁰ We used 180 Ry mesh-cutoff because of the oxygen atom in the system. The other technical details and convergence tests are given in Ref. 7. For the calculation of the barrier energies

we applied the drag method: we mapped the potential energy surface along a well-chosen reaction coordinate.

III. RESULTS AND DISCUSSION

We selected two representative SWSiCNTs that were already used in our previous studies,^{7,14} namely, the (8,0) armchair and (6,6) zigzag nanotubes. The optimized geometry and electronic structure of these perfect SiC nanotubes were described previously.⁷ Here, we briefly mention that the average diameter of these nanotubes are about 8 Å and 10 Å, respectively. We investigated the isolated oxygen impurity on these nanotubes by putting one or two oxygen atoms into the SiC nanotubes. We used a 128 atom supercell for (8,0) and 144 atom supercell for (6,6) SiC nanotubes. The calculated LDA gaps are 1.21 and 2.03 eV, respectively.

First, we describe the effect of a single oxygen atom in the SiC nanotubes. We investigated the oxygen substitutional at both Si (O_{Si}) and C (O_C) sites as well as the interstitial oxygen both at the inner and outer sides of the tubes. We found that interstitial oxygen forms very similar structure at both sides of the tubes. For the smaller diameter (8,0) nanotube the outer configuration is about 0.3 eV more feasible than the inner configuration, while for the (6,6) nanotube this difference is about 0.4 eV. The reason for the preference of the outer configuration is the favorable relaxation of the neighbor Si atom. We describe the results for the outer configurations in detail. There are two inequivalent sites for the interstitial oxygen atom: (i) off-axis configuration where the plane of Si-O-C bonds is perpendicular to the axis of the tube, (ii) on-axis configuration where the plane of Si-O-C bonds is not perpendicular to the axis of the tube, though it is not exactly parallel to the axis of the tube in the case of (8,0) nanotubes. We found that the off-axis configuration is favorable in both zigzag and armchair nanotubes. The oxygen interstitial went to a strongly buckled position between the C and Si atoms. The distance between these C and Si atoms was elongated by about 12% (from 1.78 Å to 2.01 Å) while the C-O and Si-O bondlengths were about 1.45 Å and 1.69 Å, respectively. These relatively strong Si-O and C-O bonds do not produce defect levels in the fundamental band gap. The stable and metastable configurations in (8,0) tube are shown in Fig. 1.

O_C forms a peculiar configuration in both tubes (see Fig. 2). Oxygen binds to two silicon neighbor atoms with forming a typical bondlength of 1.69 Å. The dangling bond of the third neighbor Si atom will be sterically repulsed by the lone pair of the oxygen atom. As a consequence, this Si atom is pushed out from the SiCNT lattice. We found that this structure is the most stable configuration. This defect forms a deep donor level localized strongly on the defect (see Fig. 3). The projected density of states of oxygen orbitals indicates that the donor level is mostly localized on the oxygen atom as also apparent in Fig. 2.

O_{Si} is only metastable in its simplest form, where oxygen binds to three neighbor C atoms. We found a more stable configuration in both tubes than the simplest form (see Fig. 4). In both tubes a pentagon like ring is formed around the Si vacant site, where a relatively short C-C bond of 1.43 Å

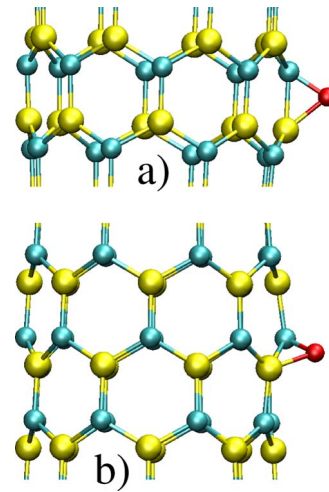


FIG. 1. (Color online) The optimized geometry of the metastable on-axis (a) and stable off-axis (b) interstitial oxygen in (8,0) nanotube. The cyan (small), yellow (big), and red (smallest) balls represent the carbon, silicon, and oxygen atoms, respectively.

appears while the wall of the tubes reconstructs strongly. However, the oxygen atom behaves differently in the tubes. In (6,6) nanotube the oxygen binds to one carbon atom and one silicon atom with bondlengths of 1.32 and 2.05 Å, respectively, while in (8,0) nanotube it binds to only one carbon atom with the bondlength of 1.25 Å. We believe that this discrepancy arises from the curvature of the (8,0) nanotube hindering the favorable bonding situation between the oxygen and neighbor silicon atoms. This is an amphoteric defect possessing deep acceptor and donor levels in the fun-

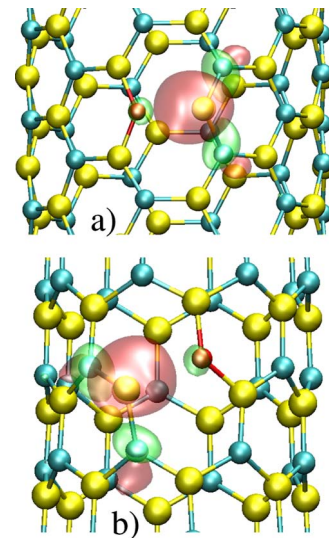


FIG. 2. (Color online) The optimized geometry of substitutional oxygen at C site in (a) (6,6) and (b) (8,0) nanotubes. The cyan (small), yellow (big), and red (smallest) balls represent the carbon, silicon, and oxygen atoms, respectively. The transparent red (dark gray) and green (light gray) surfaces represent the isosurfaces of the wave function of the donor level in the Γ point with positive and negative values, respectively. The calculated LDA donor level is at VBM+0.89 eV in (6,6) nanotube and VBM+0.69 eV in (8,0) nanotube, where VBM is the calculated valence band edge.

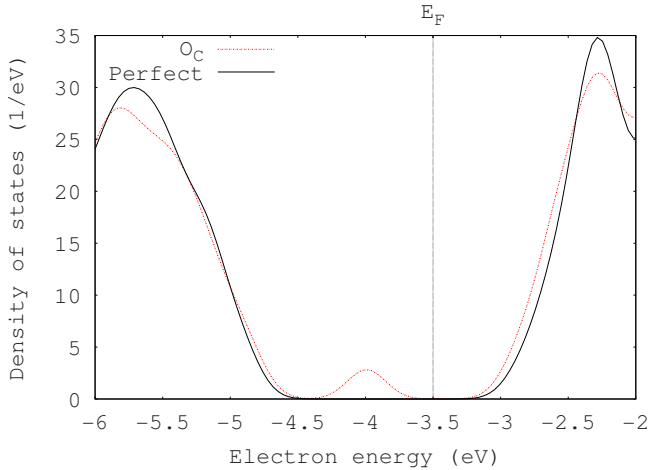


FIG. 3. (Color online) Calculated density of states (DOS) of the perfect (black line) and defective (dotted gray line) (6,6) tubes. A smooth Gaussian broadening of 0.2 eV was applied in the construction of DOS. The occupied defect band clearly shows up in the band gap below the calculated Fermi level (E_F).

damental band gap (see Fig. 5). The defect states are strongly localized on the core of the defect (see Fig. 4). In (8,0) we found an additional localized occupied state resonant with the valence band top.

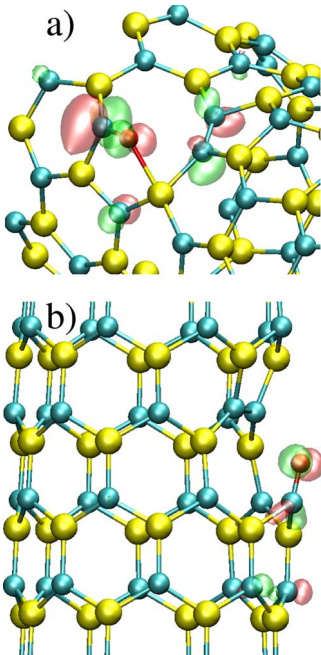


FIG. 4. (Color online) The optimized geometry of substitutional oxygen at Si site in (6,6) (a) and (8,0) (b) nanotubes. The cyan (small), yellow (big), and red (smallest) balls represent the carbon, silicon, and oxygen atoms, respectively. The transparent red (dark gray) and green (light gray) surfaces represent the isosurfaces of the wave function of the donor level in the Γ point with positive and negative values, respectively. The calculated LDA donor and acceptor levels are at VBM+0.55 eV and VBM+1.06 eV in (6,6) nanotube, while at VBM+0.88 eV and VBM+1.19 eV in (8,0) nanotube, where VBM is the calculated valence-band edge.

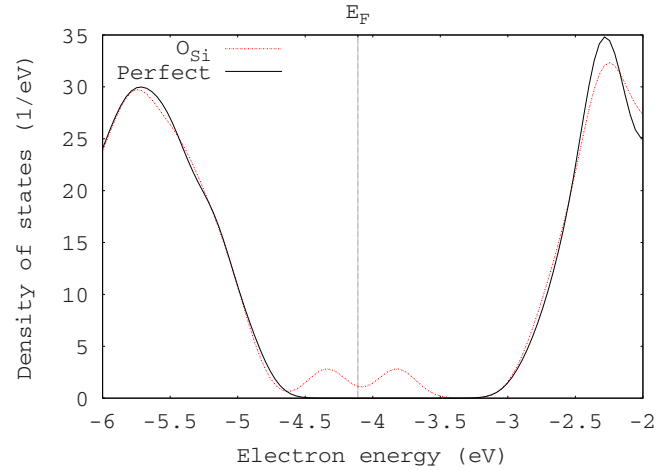


FIG. 5. (Color online) Calculated DOS of the perfect (black line) and defective (dotted gray line) (6,6) tubes. A smooth Gaussian broadening of 0.2 eV was applied in the construction of DOS. The occupied and unoccupied defect bands clearly show up in the band gap below and above the calculated Fermi level (E_F).

It is important to compare the relative stability of these defects. The results are summarized in Table I. We assumed stoichiometric nanotubes in the calculation of the formation energy of the defects (see details in Ref. 7). O_{Si} is less stable than O_C by about 4.3 eV. Similar trend was found in bulk SiC.³¹ The reason of this trend that oxygen has much higher electronegativity than Si atom while this difference is much smaller between oxygen and carbon atoms, therefore, oxygen can easily substitute carbon but hardly the silicon. The formation energy of O_{Si} is highly positive ($>+1.9$ eV), while that of O_C is *negative*. So, the formation of O_{Si} is not favorable. The calculated formation energies of O_C and interstitial oxygen are within 0.02 eV in (8,0) nanotube, while it is favorable for the latter by about 0.43 eV in (6,6) nanotube. Thus, the formation energy of interstitial oxygen is also negative. This indicates that interstitial oxygen and the O_C defects would dissolve into SiC nanotubes. We discuss the formation of these defects later.

Next, we summarize briefly the results on the defects consisting of a pair of oxygen atoms. We studied the pair of oxygen interstitials, oxygen interstitial and oxygen substitutional at both sites, as well as the pair of substitutionals in each configuration. Here, we found that the pair of interstitial oxygen defects, the pair of O_C , or the pair of interstitial oxy-

TABLE I. The calculated formation energies of the most important defects in stoichiometric SiC nanotubes. The energy unit is eV. These numbers are valid at 0 K.

	(6,6)	(8,0)
O_i	-2.41	-2.36
O_C	-1.98	-2.38
O_{Si}	+2.31	+1.85
$(O_i)_2$	-4.86	-5.39
$(O_C)_2$	-5.01	-5.22
O_i-O_C	-8.29	-8.08

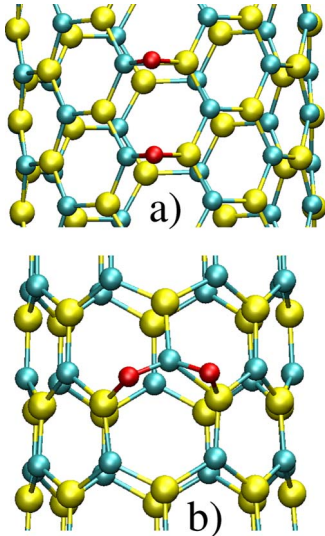


FIG. 6. (Color online) The optimized geometry of the pair of interstitial oxygen in a) (6,6) and b) (8,0) nanotubes. The cyan (small), yellow (big), and red (smallest) balls represent the carbon, silicon, and oxygen atoms, respectively.

gen defect with O_C are the most stable configurations.

For the pair of interstitial oxygen defects we investigated all the possible symmetrically inequivalent combinations. For the isolated oxygen interstitials the off-axis configuration is the most stable structure. We found the same trend for the oxygen pairs: both oxygen atoms went to the off-axis positions that are closest to each other in the SiC nanotube. In the armchair (6,6) nanotube these nearest off-axis sites are relatively far from each other while they are close in the zigzag (8,0) nanotube (see Fig. 6). In the latter case the interstitial oxygen defects can interact with each other, therefore, the neighbor C and Si atoms relaxed more than for the isolated interstitial oxygen defect. No defect levels appear in the fundamental band gap. As a consequence of the different configurations in the nanotubes, the binding energy of the pair defect is only 0.05 eV in (6,6) nanotube while it is 0.66 eV in (8,0) nanotube. This means that the formation energy of these defects is very negative (more than twice of that of the isolated ones).

The pair of O_C defect has similar formation energies as the pair of interstitial oxygen defects, and possesses localized defect levels close to the valence band edge within 0.05 eV.

In the case of the pair of O_C and interstitial oxygen defects a localized acceptor level appears at $VBM+1.96$ eV in the fundamental band gap in (6,6) nanotube, while no defect level was found in (8,0) nanotube. This has the deepest formation energy (around -8.0 eV) among the defects considered in this study.

Our calculations revealed that the formation energy of O_C defects is negative, therefore, it is highly probable that if oxygen is present *during* the growth of SiC nanotubes then oxygen can readily build into SWSiCNT in the form of isolated O_C or a pair defect with O_C or interstitial oxygen, especially, at elevated temperatures. This may be the reason why only a single experiment reported the formation of multiwall SiC nanotubes.²³ We have to note that these SiC nano-

tubes have been synthesized via the reaction of SiO with multiwall carbon nanotubes at different temperatures.²³ Our results indicate that if the obtained structure was indeed multiwall SiC nanotube in the experiment then it was presumably contaminated by oxygen.

Next, we investigated the formation of these defects with assuming that pure SWSiCNT was already formed and it is taken to the environment consisting of oxygen molecules. We basically considered two types of reaction of the oxygen molecule with the nanotubes: (i) one oxygen atom builds into the carbon site while a carbon emitted together with the other oxygen atom as a CO molecule,



a similar process takes place at the surface of bulk SiC;²⁵ (ii) the oxygen molecule dissociates at the surface of nanotubes such as a pair of oxygen interstitials,



In order to avoid the basis set superposition error we calculated the energy of the isolated oxygen molecule (or CO molecule) and the nanotube in the same box of the simulation by putting the molecules far from the nanotubes where they cannot interact with each other. The oxygen molecule has $S=1$ ground state, therefore, we performed spin-polarized calculations for those configurations, where the oxygen atoms are close to each other.

For reaction (1) we found -2.51 and -2.12 eV in (8,0) and (6,6) nanotubes, respectively. For reaction (2) we obtained -5.34 and -4.85 eV in (8,0) and (6,6) nanotubes. These numbers indicate that both processes are favorable, so *SiC nanotubes would be oxidized in ambient oxygen, if the barrier energy for dissociation was gained at the given temperature*. In addition, one can conclude that reaction (2) is much more feasible than reaction (1). Beside the calculated binding energy, the barrier energy for dissociation is very different for these processes: the relatively strong C-Si bonds should be broken in reaction (1) that needs several eV of barrier energy to dissociate. In reaction (2), the oxygen molecule approaches the SiC nanotube. In this case the formation of Si-O and C-O bonds occurs simultaneously that requires much less barrier energy than for reaction (1). So, we concluded that the most dominant process is reaction (2). This conclusion may be not expected since in bulk SiC reaction (1) occurs frequently. However, the chemical situation is different. In bulk SiC the C and Si atoms are fourfold coordinated and according to Ref. 25, the oxygen atoms can form easily Si-O-Si bridges with emitting CO molecules, where these Si atoms will have again four bonds at the end of the reaction. In the case of SiC nanotubes all the atoms are threefold coordinated in the beginning. The incoming oxygen tries to bind only to two atoms in SiC nanotubes. In reaction (1) an O_C forms where the oxygen indeed binds to two Si atoms but the third neighbor Si atom will be only twofold coordinated. This is a very unpleasant situation for that Si atom and there is no path to form the basic SiO_2 units of the oxide. Despite the strong Si-O-Si bonds in O_C making reaction (1) favorable, reaction (2) will be much more feasible because O_i s are created in which a strong Si-O bond will

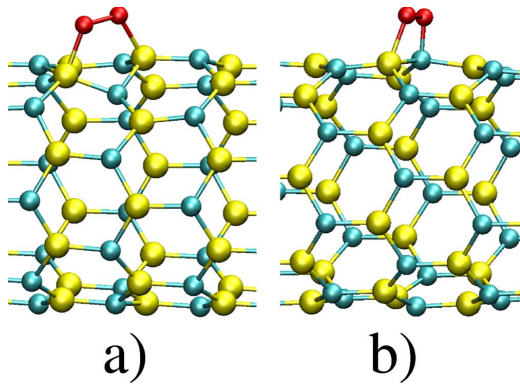


FIG. 7. (Color online) Metastable configurations of oxygen molecule approaching SiC nanotube: (a) Si-O-O-Si bridge and (b) Si-O-O-C bridge. The cyan (small), yellow (big), and red (smallest) balls represent the carbon, silicon, and oxygen atoms, respectively.

form and the common neighbor Si atom will have four nearest neighbors. We conclude that reaction (2) could be the most dominant process and must be analyzed in detail.

The above-mentioned binding energies were calculated in quasistatic approximation, that is valid at 0 K. We checked the binding energies calculated from formation enthalpies. The calculation of formation enthalpies for H-related defects in SiC nanotube was given in Ref. 14 in detail, and we do not refrain here. The same formalism should be used for the oxygen-related defects, just the chemical potential of oxygen must be set accordingly. The chemical potential of the oxygen depends on the environment of the nanotube. In the most of the applications the nanotubes are taken to the air in standard conditions, so we simulated this condition. The partial pressure of oxygen molecule is about 0.21 atm in air. At room temperature we found that the chemical potential of oxygen molecule is about 0.24 eV lower than at 0K, and due to the vibration entropy of the oxygen defect in the nanotube, the total enthalpy of the defect increases by about 0.07 eV. Finally, the formation enthalpy (so, the binding energy) under these conditions increased by only ≈ 0.31 eV. This yields still far negative binding energies [again, the values at 0 K are -5.34 and -4.85 eV in (8,0) and (6,6) nanotubes]. By raising the temperature up to 1400 K, the increase in the binding energy is about 1.66 eV, so the binding energy is still negative. Even taking into account the deficiencies of the LDA exchange-correlation functional we can certainly conclude that *SiC nanotubes would be oxidized as interstitial oxygen atoms at the surface in ambient oxygen (for instance, in air), if the barrier energy for dissociation was gained at the given temperature.*

Next, we calculated the barrier energy for dissociation of oxygen molecule close to the SiC nanotube. As the oxygen molecule was approaching the SiC nanotube we found two metastable structures. If the oxygen molecule was about 2.7 Å away from SiC nanotube then the Si atoms start to interact with oxygen atoms. Finally, a metastable Si-O-O-Si bridge structure forms [see Fig. 7(a)] where the O-O and Si-O distances are 1.42 Å and 1.79 Å, respectively. The structure conserves its triplet ground state. No barrier energy found until this point. We found another metastable structure

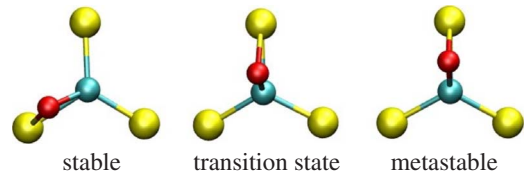


FIG. 8. (Color online) The stages of the diffusion path of interstitial oxygen. Left: the most stable off-axis configuration. Right: metastable on-axis configuration. It is less stable by around 0.3 eV than the most stable configuration. Middle: the transition state during the diffusion that is around 0.29 eV higher in energy than the metastable configuration. The cyan (small), yellow (big), and red (smallest) balls represent the carbon, silicon, and oxygen atoms, respectively.

that is more favorable than the Si-O-O-Si bridge. If the oxygen molecule was placed closer to the SiC surface then the Si-O-O-C bridge forms [see Fig. 7(b)]. In this configuration the O-O, C-O, and Si-O distances are 1.48 Å, 1.46 Å, and 1.74 Å, respectively. The C-Si bond was elongated to 1.94 Å. Here, the singlet state is the ground state, so the original double bond of oxygen molecule is transformed to a single bond. Most probably, both metastable structures can appear during the absorption of the oxygen molecule. As the Si-O-O-C configuration is more favorable by about 0.3 eV, we calculated the dissociation barrier energy of this structure in order to form two isolated interstitial oxygen defects. We found that this barrier energy is about 0.55 eV. We note that the van der Waals interaction is not correctly taken into account by LDA functional, but we believe that this error should be less than the calculated dissociation barrier energy needed to break the single bond between the oxygen atoms.³² So, we concluded that 0.5–0.6 eV is a good estimate for the dissociation energy barrier of oxygen molecule in SiC nanotubes.

We also calculated the barrier energy of diffusion of the interstitial oxygen defect. We show the basic route of diffusion in Fig. 8. During the diffusion of oxygen interstitial the oxygen from the off-axis configuration (left panel in Fig. 8) has to wander to the nearest off-axis configuration. As apparent from Fig. 8 this can be achieved via the metastable on-axis configuration that is in half way between the two most stable off-axis configurations. Due to the mirror symmetry between the off-axis—on-axis—off-axis configurations, the potential-energy surface should be calculated between the off-axis (stable) and on-axis (metastable) configurations. We chose the line connecting the oxygen atom at the stable (left panel in Fig. 8) and metastable (right panel in Fig. 8) configurations as the reaction coordinate. Then we defined a plane that was perpendicular to this reaction coordinate and included the oxygen atom. We displaced this plane together with the oxygen atom along this line and at each point we optimized the geometry. In these geometry optimizations all the atoms were allowed to relax freely except the oxygen atom which was constrained to move only in the above defined plane. In these calculations we could map the potential energy surface of the oxygen atom and we found the transition state (middle panel in Fig. 8) together with the corresponding saddle point in the potential-energy surface. We

found that the barrier energy is around 0.59 eV.

Interestingly, the barrier energy for both dissociation of the oxygen pair and the diffusion of the isolated oxygen interstitial is ~ 0.6 eV, thus the dissociation and the diffusion occurs at similar rates. The time (τ) needed for the dissociation of the oxygen pair on the SiC tube may be calculated as

$$1/\tau \approx \nu \exp(-\Delta E/kT)$$

where ν is the typical phonon frequency of the system, ΔE is the barrier energy, kT is the Boltzmann-factor multiplied by the temperature. The typical phonon frequency in bulk³³ and amorphous³⁴ SiC is around 10^{13} Hz. We adopt this assumption for the SiC nanotube, nevertheless, it will be clear shortly that even one order of magnitude change of this frequency would not alter our conclusions. By taking $\nu = 10^{13}$ Hz we estimate the *typical time needed for dissociation to be only 0.2 ms at room temperature*. This means that *SiC nanotubes in air dissociate oxygen molecules at room temperature very fast*. Since the diffusion of the isolated oxygen interstitials occur at the same rate (~ 0.2 ms) we conclude that the interstitial oxygen can readily diffuse in SiC nanotubes, and can directly react with other adsorbed molecules on the tube. It is also expected that these fast diffusing oxygen defects can interact with the hydrogen molecules in the environment that can significantly influence the hydrogen storage of SWSiCNTs. According to our calculations, the interstitial oxygen defects (isolated or pairs) do not modify the band structure, so they cannot be detected electrically. At high temperatures, the oxygen may build into the carbon site that is electrically active.

IV. SUMMARY

In summary, we showed that the formation energies of interstitial oxygen and O_C defects are negative, therefore, SiC nanotubes could be heavily contaminated by oxygen if oxygen is present during the growth of SiC nanotubes, especially, at elevated temperatures. We also showed that pure single-wall silicon carbide nanotubes are oxidized in ambient oxygen, especially, in air with standard conditions. The oxidation does not destroy the basic structure of the SiC nanotubes at low temperatures but interstitial oxygen defects are formed. At elevated temperatures the electrically active O_C defect may be formed too that changes the stoichiometry of the SiC nanotubes. The interstitial oxygen defects are electrically inactive in SiC nanotubes but they diffuse fast even at room temperature. Therefore, it is highly probable that interstitial oxygen defects will interact with other adsorbed molecules at the surface that could cause problems for sensor applications. The effect of oxygen on the applications of SWSiCNTs in hydrogen storage or tips for atomic force microscopy and/or scanning tunneling microscopy should be taken into account in the forthcoming studies.

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