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5 **Growth mechanisms and selectivity for graphene or carbon**
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8 **nanotube formation on SiC (000 $\bar{1}$): A density-functional**
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10 **tight-binding molecular dynamics study**
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52 **Abstract**
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55 We have performed density-functional tight-binding simulations mimicking the
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58 thermal decomposition of the SiC (000 $\bar{1}$) surface to reproduce the experimentally
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5 observed growth of either graphene or carbon nanotubes. A graphene-like network was
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8 obtained from a layer-by-layer decomposition of the SiC surface. The interaction
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11 between graphene and SiC was found to be relatively weak. Meanwhile, carbon
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14 nanotubes grew when a five-membered ring was initially formed together with a carbon
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17 chain. The simulation results suggest that growth selectivity depends on the overall
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20 carbon network connectivity and carbon aggregation speed at the very initial stage of the
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23 decomposition process.
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31 I. Introduction

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33 Since their discovery and isolation, graphene and carbon nanotube have attracted
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36 great attention due to their superior electronic properties [1,2]. The extremely high
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39 carrier mobility of graphene is expected to play a key role for post-silicon electronic
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42 devices [3]. Among many graphene growth techniques, epitaxial graphene growth by
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45 thermal decomposition of SiC enables direct growth on a semi-insulating substrate [4].
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48 This technique is then suitable for fabricating transistor electronics using the existing
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51 silicon-based technology. In particular, for ultra high-speed and high-frequency
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54 transistor applications, a cut-off frequency of 300 GHz was reported using graphene on
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57 SiC [5].
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The SiC {0001} surfaces upon which graphene grows contain the Si-terminated (0001) and the C-terminated ($000\bar{1}$) faces. Graphene can be grown on both of them, but its features then differ significantly [6,7]. On the Si-face, homogeneous graphene with a controlled number of layers can be grown, and the presence of a buffer layer between graphene and SiC reduces the carrier mobility [8,9]. On the C-face, either carbon nanotubes or multilayer graphene tends to grow, and the carrier mobility in the case of the latter is higher than that of graphene on the Si-face due to the weak interaction with the substrate, in spite of the rotational stacking disorder [7, 10]. In fact, a record maximum oscillation frequency of 70 GHz was reported recently for a field effect transistor fabricated using graphene grown on the C-face [11].

To achieve high-quality graphene growth on the C-face, an understanding of the growth mechanism is indispensable. Experiments concerning the mechanism of graphene growth on the Si-face showed that it nucleated around the step and grew over the terrace [12]. On the C-face, our previous work revealed that the decomposition starts not only at the step-edge, but also on the terrace, and graphene grows in all directions on the surface [13]. In addition to graphene growth, an aligned carbon nanotube (CNT) film can also be grown on the C-face [14]. Characteristic features of the CNT film include a high-density vertically aligned forests, zigzag-selectivity, and

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5 strong attachment to the substrate [15-17]. The CNTs tend to grow best experimentally
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8 by introducing a small amount of oxygen in the growing atmosphere [18]. However, in
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11 both cases, the atomic scale phenomenon is Si removal and C atom rearrangement. It
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14 has not been clarified how the C atoms rearrange into graphene yet. In the present study,
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17 our motivation is to reveal the differences between graphene and CNT growth
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20 mechanisms on the C-terminated SiC by density-functional tight-binding molecular
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23 dynamics (DFTB/MD) simulations.
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28 There have been several reports about theoretical studies of graphene growth on
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31 the Si-terminated SiC [19-23]. These reports focused mostly on the thermodynamically
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34 most stable structure when positioning the carbon atoms on the SiC surface in static
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37 electronic structure calculations, or in Monte Carlo growth simulations. Although there
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40 has been a report that graphene can form on the 2×2 reconstructed C-terminated surface
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43 due to the Si-adatom [24], no theoretical discussion of the growth mechanism of
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46 graphene on the C-face was reported. We have preliminary reported the behavior of the
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49 C atoms at 2000 K after carpeting two graphene layers on the C- and Si-faces by quantum
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52 mechanical molecular dynamics calculations [25,26]. According to these previous
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55 studies, graphene readily wrapped to form a nanocap on the C-face, while the Si-face
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58 attached graphene sheet did not readily wrap, and kept a flat two-dimensional structure.
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Theoretical studies that reproduce the decomposition phenomena consisting of silicon sublimation and carbon rearrangement at high temperature on the C-face are still lacking. In this study then, our goal was to uncover the behavior of carbon atoms after the stepwise removal of silicon atoms on the C-terminated SiC (000 $\bar{1}$) surface by DFTB/MD simulations, following the spirit of our previous nonequilibrium DFTB/MD simulations [26]. In particular, in the present work, we focus on the selectivity of the growth of graphene or CNTs.

II. Computational details

II. a. Quantum mechanical molecular dynamics simulations

All simulations in this study were performed with a direct nonequilibrium MD method based on the self-consistent-charge (SCC) DFTB quantum chemical potential. In all calculations, periodic boundary conditions were employed using the Gamma-point approximation, following the spirit of our previous works [25,26]. At first, we performed structural optimization of the initial structures using the conjugate gradient method until the force component with the maximal absolute value was less than 1×10^{-4} Ha/a₀. After optimization, we performed constant temperature MD simulations using a velocity Verlet integrator with a time step of 1.0 femtoseconds (fs), starting from the

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5 initial structure and random velocities drawn from a Boltzmann distribution. The
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8 temperature in the NVT ensemble was maintained via a Nose-Hoover chain thermostat
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11 (chain-length 3) connected to the degrees of freedom of the system. The nuclear
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14 temperature (T_n) was maintained at 1500 K or 2000 K throughout the simulations. A
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17 fractional orbital occupation Fermi-Dirac distribution was employed with an electronic
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20 temperature (T_e) of 2000 K in order to improve SCC convergence, and in order to enable
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23 the description of multiradical electronic structure during the chemical transformations
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26 occurring during the reactive MD simulations.
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33 II. b. Model system and silicon removal process

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36 We prepared the C-terminated SiC surfaces with several morphologies as the
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39 initial substrate. Figure 1 shows the initial structures. First, we assumed graphene
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42 growth on a flat terrace as shown in (a), (b), and (c). For this case, we used a supercell
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45 containing $5 \times 5 \times 0.5$ unit cells of 6H-SiC. The bond length of Si-C used was optimized
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48 to be 1.89 Å, and it is consistent with crystallographic data. To achieve
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51 two-dimensional slab periodicity, periodic boundary conditions were employed in the x - y
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54 plane, and a unit cell size of 1000 Å in the direction perpendicular to the surface was used.
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58 To mimic the bulk effect in the direction away from the surface under investigation, the
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dangling bonds of the bottom SiC bilayer are passivated with hydrogen atoms, and the movements of hydrogen atoms are frozen during the simulations. Another initial model is shown in Fig. 1(d). This model consists of 19 unit cells in the hexagonal shape. In order to investigate the effect of the surface morphology, we also used the step model shown in Fig. 1(f).

To mimic the decomposition process, we removed Si atoms one by one at intervals of 1.0 pico seconds (ps). We also used atomic Si removal intervals of 0.1 ps and found the difference was small between these two interval choices. In addition, we recently succeeded to reproduce the graphene step-edge nucleation and the growth on the Si-face of SiC using the interval for removing Si atoms of 1.0 ps [27]. This was remarkably consistent with our experimental results [12]. Thus, in this work, we will only discuss the results of 1.0 ps atomic Si removal intervals. The removal order is also depicted in Fig. 1 by way of circled numbers. In the terrace-linear model (a), for example, after 25 Si atoms were removed in the illustrated order in the first bilayer, the second SiC bilayer started to be decomposed in the same removal order and at the same intervals. In each model, a new SiC bilayer was added under the bottom SiC bilayer, after one SiC bilayer was decomposed. This procedure was necessary due to limitations in the computational resources. The Si atom removal/layer addition processes were

repeated until 4 SiC bilayers were decomposed, since the carbon atom density of a graphene layer requires the decomposition of about three SiC bilayers [8].

III. Results and Discussion

We first discuss the computational results for the terrace model. Figure 2 shows snapshots of the terrace-linear model after (a) one, (b) two, and (c) three bilayer decompositions at 2000 K. Top views with four supercells are also shown in (a'), (b'), and (c'). We performed five trajectories for each model, and obtained the qualitatively same results. We also found that both the terrace-linear and terrace-random models gave the similar results, hence we here show only the results for the terrace-linear model. We provide this trajectory as a movie in the Supplementary Data (SD, GrapheneGrowth_F.mp4) [28]. Snapshots in all other trajectories are also shown in SD (Fig_S1). In Fig. 2(a), we can find short carbon chains, and some carbon atoms in them form bonds with the SiC surface. After the second layer decomposition, newly provided free carbon atoms attached to the SiC surface, and five- and six-membered rings started to self-assemble. These rings form a connected network after decomposition of three bilayers, as shown in Fig. 2(c). Although some carbon atoms in this network are detached from the SiC surface, the network retained a two-dimensional, sheet-like

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5 structure, although local areas with positive and negative curvatures are visible. The
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8 orientation relation between the network and the substrate is not uniquely determined,
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11 and this might result in the rotational stacking often observed in graphene on the C-face
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14 [10]. When we carefully examined the trajectories, we found that some of the silicon
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17 atoms actually moved under the nascent carbon network.
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21 In order to provide a more quantitative analysis, we counted the number of five-,
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24 six-, and seven-membered rings in each frame. The result of this ring count is shown in
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27 Fig. 3. During the first layer decomposition, only few rings were detected, indicating
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30 that at first carbon chain formation is occurring. The five- and six-membered ring
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33 started to form during the second layer decomposition. The number of the
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36 six-membered ring increased dramatically as the third layer decomposition. These
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39 observations correspond to the formation of the carbon network and its expansion. We
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42 notice that five-membered rings remained even at the 100 ps mark. Within our limited
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45 calculation time, the five-membered ring are not completely converted to hexagons. An
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48 important reason for the prevalence of pentagons is that when the carbon chains gather
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51 and form Y-junctions, they easily make pentagon and then ring structures, as revealed in
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54 two former DFTB/MD studies on CNT cap nucleation [29] and graphene formation on a
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57 Ni metal surface [30]. In both cases we had reported that five-membered rings are
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5 always found to form first. Further annealing turns the metastable five-membered rings
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8 into the thermodynamically more stable six-membered hexagonal ring structures,
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11 however on timescales that are only accessible to Monte Carlo-type simulations as
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14 reported in such a study of defect healing of graphene on a metal surface [31]. The
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17 longevity of the pentagons is apparent also in Figs. 3 and 6. As ref. 31 showed, by
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20 annealing the carbon network on longer timescale, a perfect hexagonal, two-dimensional
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23 graphene network will be obtained. The only requirement for this graphene formation
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26 from a defective network is that all carbon islands become connected at a relatively early
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29 stage to each other, so that no isolated CNT caps can nucleate, further growing into
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32 longer nanotubes.
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37 Figure 4 shows a schematic graphene growth mechanism. When the terrace of
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40 the C-terminated SiC surface starts to decompose locally, the free carbon atoms form
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43 dispersed chains as shown in Fig. 4(a)-(c). Here, it is important for the graphene growth
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46 that the carbon chains are dispersed and soon connected on the surface. During the
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49 second layer decomposition (d), the carbon chains start to form a two-dimensional
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52 network. After the third layer decomposition, the network is almost complete and
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55 covers the surface. This growth mechanism is qualitatively consistent with our previous
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58 experimental results [13].
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Figure 5 shows snapshots of the terrace-linear model after (a) 25, (b) 50, (c) 75, and (d) 100 ps at 1500 K. After the first layer decomposition, a five-membered ring was present in the center and, as shown in the inset, carbon chains were extended radially from the ring. In the second layer decomposition, a small network was formed and it started to curve. In (c) and (d), a carbon nanocap-like structure is apparent. This nanocap-like structure would become a nanotube after further growth. Figure 5(e)-(j) illustrates the growth mechanism of a CNT. The difference from Fig. 4 is the presence of the localized ring after the first layer decomposition (g), and curved nature of the product during the second layer decomposition (h). As noted before, longevity of carbon network islands will favor CNT nucleation, consistent with our previous DFTB/MD simulations on metal catalyst surfaces [29,30].

Figure 6 shows the evolution of the number of the rings in this trajectory. Some five-membered rings form in the second layer decomposition, but their number stays almost the same until the fourth layer starts to decompose. On the other hand, the number of six-membered rings increases continuously from the second layer decomposition onwards.

It should be noted here that a major difference between trajectories shown in Figs. 2 and 5 is the temperature: 2000 and 1500 K, respectively. Simply put, graphene and

CNT readily seemed to grow at higher and lower temperatures, respectively. This suggests that the heating temperature could be one key factor to adjust the selectivity of graphene and CNT. A lower temperature would lead to a low carbon surface diffusion probability and then to initial ring formation. However, there was also a trajectory at 1500 K in which the two-dimensional carbon network was formed instead of the nanocap. In such a trajectory, the five-membered ring and the surrounding arms as shown in the inset in Fig. 5(a) were not present.

One might suspect that an important difference between the trajectories depicted in Figs. 2 and 5 was the curvature radius of the initial caps. In order to consider the difference in the curvature radius, we should use larger supercells, which can involve both the large and small radius caps. However, because of the high calculation cost, such simulations are prohibitively expensive. When we analyze all the trajectories of the terrace-linear model (See Supplementary Data, Fig. S1), the carbon atoms made planar configurations, suggesting the basic tendency to form graphene. But the side-view like Fig. 2(c) shows some of the carbon atoms are detached from the substrate, indicating the weak interaction with the substrate, which was experimentally shown. The carbon atoms at the edge of the supercell tends to form bonds with the substrate, and their position determines the curvature. This suggests that when the five-membered ring was

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5 formed in the center, the curvature radius seemed to be small. In other words, we
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8 suppose that the non-dispersed carbon chains gathered at one point and formed a
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11 five-membered ring, serving as the apex of the nanocap. In order to validate this
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14 assumption, we introduced another, somewhat more artificial Si removal model: the
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17 spiral removal model.
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21 Figure 7 shows snapshots of the terrace-spiral model at 2000 K; the corresponding
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24 movie is shown in the Supplementary Data (CNTGrowth_F.mp4) [28]. The
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27 decomposition started at the center, and carbon atoms gathered in the crater thus formed.
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30 After the first layer decomposition (a), the carbon chains contacted around the center.
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33 This contact results in the new carbon atoms being absorbed and then became the core of
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36 the nanocap. Once the cap-structure was formed, the newly provided carbon atoms
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39 approached the edge of the cap, and helped propel the growth to form a nanotube. The
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42 other trajectories shown in Fig. S2 in the SD also revealed formation of the cap-like
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45 structure, and hence, they support the above mechanism [28].
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50 Based on the above results, we here discuss the growth selectivity of graphene or
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53 the CNT. The selectivity is determined in the very initial stage during the first and
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56 second layer decomposition. At this stage, if the carbon atoms are dispersed widely, the
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59 carbon chains and the added carbon atoms form a two-dimensional network. On the
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other hand, if the carbon atoms gather and form five-membered ring, the network starts to bend, leading to the formation of a nanocap. Therefore, we suggest that controlling the degree of carbon localization at the very initial stage, which could be controlled experimentally by the heating temperature, the heating rate, the vacuum pressure, and the atmosphere, is important to produce selective growth.

Finally, we also investigated the effect of the surface morphology on the growth of the nanocarbon structure. Figure 8 shows the side- and front- views of the final structure in the step model after 90 ps at 2000 K. The other trajectories are shown in Fig. S3 in the SD. As was shown in Figs. 2, 5, and 7, 90 carbon atoms are enough to form a network. However, in Fig. 8, a small network consisting of six-membered rings and many carbon chains are separately present. Difference between Figs. 2, 5, 7 and 8 related to the surface morphology. It is apparent that Figs. 2 and 5 (terrace-linear model) corresponds to the lateral decomposition on the surface including the planar dislocations or steps, Fig. 7 (spiral model) to the one with the spiral dislocations or the surface point defects, and Fig. 8 (step model) to the surface with high-steps. One important fact is that the spiral decomposition facilitates the CNT cap formation, and the other is that the presence of a surface step does not positively help carbon network formation, which is in marked contrast with the effect of steps on graphene growth on the

Si-face. In the experimental and theoretical results of graphene growth on the Si-face, graphene nucleated at the step on the surface and grew laterally, while it did not nucleate on the terrace [12,27]. On the C-face, large network was formed in the terrace model, while the small network was in the step model. The small network may expand to form graphene when further carbon atoms are provided, although they were not enough in the present results. We show the result of the step model at 1500 K in the Fig. S4. It shows more carbon chains and less rings. Further decomposition is at least necessary for large graphene growth in the step model. However, the formation of the small network will act as the nucleus of graphene. It indicates that on the C-face graphene can be nucleated both on the terrace and at the step, which is in agreement with the experimental results [13].

IV. Conclusions

In summary, we carried out quantum mechanical nonequilibrium molecular dynamics simulations of nanocarbon growth by thermal decomposition of the SiC (000 $\bar{1}$) surface using a variety of model systems and temperatures. If there are dispersed carbon chains present at the very initial stage of decomposition, they grow into graphene, by absorbing surrounding carbon atoms. High temperature facilitates the rapid formation

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5 of the two-dimensional carbon ring network structure, which will eventually anneal into a
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8 planar hexagonal graphene sheet as discussed in refs. 30 and 31. On the contrary, if the
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11 carbon surface diffusion is low, for instance at a lower temperature, five-membered ring
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14 forms initially, leading to growth of isolated carbon nanotube caps that will then
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17 transform to vertically aligned CNT forests by further low-temperature carbon
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20 decomposition.
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Figure Captions

Figure 1(color online) Initial structural models. The large bright (light-blue) and small dark (purple) balls correspond to the silicon and carbon atoms, respectively. The circled numbers denote the removal order.

Figure 2 (color online) Graphene growth in the terrace-linear model at 2000 K. (a), (b), and (c) are snapshots after first, second, and the third SiC bilayer is decomposed. (a'), (b'), and (c') are the corresponding top-views.

Figure 3 (color online) Time-evolution of the number of the five-, six-, and seven-membered rings in the terrace-linear model at 2000 K.

Figure 4 (color online) Graphene growth mechanism. Each SiC bilayer is illustrated as a double line.

Figure 5 (color online) CNT growth in the terrace-linear model at 1500 K, and the CNT growth mechanism.

Figure 6 (color online) Time-evolution of the number of rings in the terrace-linear model at 1500 K.

Figure 7 (color online) CNT growth in the spiral model at 2000 K. Snapshots in (a), (c), (d), and (e) are after one, two, three, and four bilayer decomposition, respectively.

Figure 8 (color online) Carbon network and chains formed in the step model at 2000 K.

Figure1

(a) Terrace-linear

(b) Terrace-random

(c) Side-view of (a) and (b)

(d) Terrace-spiral

(e) Side-view of Terrace-spiral

(f) Step

Figure2

(a) 1st layer
(25 ps)

(b) 2nd layer
(50 ps)

(c) 3rd layer
(75 ps)

(a')

(b')

(c')

Figure3

Figure4

Figure5

Figure6

Figure7

(a) 19 ps

(b)

(c) 38 ps

(d) 57 ps

(e) 76 ps

Figure8

(a) Side view

(b) Front view

Graphene

Carbon nanotube cap