Fractal Structures in Fullerene Layers: Simulation of the Growth Process

Hui Liu, Zhibin Lin, Leonid V. Zhigilei, and Petra Reinke*

Department of Materials Science and Engineering, University of Virginia, 395 McCormack Road, Charlottesville, Virginia 22904

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The molecular-level processes responsible for fractal-dendritic growth of second-layer C\textsubscript{60} islands on large and compact first-layer C\textsubscript{60} islands deposited on graphite substrate are investigated by a combination of scanning tunneling microscopy (STM) and kinetic Monte Carlo (kMC) simulations. Molecular dynamics (MD) simulations are performed to determine the activation barriers and jump rates for diffusion of C\textsubscript{60} molecules on a C\textsubscript{60} layer. The rates of the thermally activated processes, determined in MD simulations, are used in kMC simulations performed to explore the connections between the elementary growth mechanisms and the shapes of the growing islands. The geometry of the underlying substrate is found to result in the formation of two characteristic molecular arrangements along the edges of the growing islands (A-step and B-step on a close-packed surface). The difference in molecular mobility along the A-step and B-step configurations, along with the difference in the probability of a C\textsubscript{60} molecule to diffuse from a corner of an island to A-step or B-step edges of the island, are identified as key factors responsible for the formation of characteristic triangular shapes of the fractal islands and their orientation with respect to the underlying surface structure. The fractal shapes of the second-layer C\textsubscript{60} islands predicted in kMC simulations are in a good agreement with STM images taken under comparable deposition conditions.

1. Introduction

Since the discovery of C\textsubscript{60} in 1985, many studies have been devoted to the exploration of the unique properties of fullerenes and their derivatives\textsuperscript{1-11} in a wide range of nanotechnology applications. The ability to control and optimize the performance of fullerene containing nanostructures relies critically on our understanding of the fullerene-substrate interactions and the mechanisms of thin film growth. The deposition of C\textsubscript{60} on metal and semiconductor substrates, including Au, Ag, Ni, Cu, Si, and graphite, has been extensively studied.\textsuperscript{6,12-18} For different substrate types and surface structures, the growing C\textsubscript{60} films exhibit a wide range of interfacial bonding and electronic coupling, as well as a variety of growth modes.

The C\textsubscript{60}--graphite system appears to be deceptively simple in this context, since both C\textsubscript{60}--C\textsubscript{60} and C\textsubscript{60}--substrate interactions are of the van-der-Waals type and do not involve charge transfer across the interface. A recent scanning tunneling microscopy (STM) imaging of the growth of C\textsubscript{60} layers on the graphite surface,\textsuperscript{19} however, revealed an intriguing combination of structures where the formation of fractal-dendritic islands of C\textsubscript{60} is observed on top of elliptical C\textsubscript{60} islands growing directly on the graphite substrate. The formation of islands with fractal shapes has been observed in kinetically controlled growth in some metal-on-metal systems\textsuperscript{20} and other systems\textsuperscript{21-25} and has been described within the framework of diffusion limited aggregation (DLA) model.\textsuperscript{26} On a qualitative level, the formation of the fractal C\textsubscript{60} islands can also be described within the standard hit-and-stick DLA model with a variable atom-island sticking coefficient.\textsuperscript{27}

In this paper, we report the results of a computational study aimed at providing a deeper quantitative understanding of the molecular-level processes responsible for the formation of fractal-dendritic C\textsubscript{60} islands and elucidating the critical factors that determine the observed island shapes. The growth mechanisms of the second-layer C\textsubscript{60} islands are investigated in computer simulations performed with a combination of molecular dynamic and kinetic Monte Carlo computational methods. Simulation results are compared with STM images reported in a previous publication,\textsuperscript{19} and the relation between experimental and simulated results is discussed.

2. Experimental Setup

The experiments are performed in an Omicron Variable Temperature ultrahigh vacuum scanning probe microscope (Omicron VT UHV--SPM) system that consists of a preparation chamber and an analysis chamber containing the microscope. Atomically flat highly oriented pyrolytic graphite (HOPG) surfaces are obtained by removing top layers of a graphite sample with a scotch-tape in air, and subsequent annealing at 300 °C for at least 10 h in the UHV chamber prior to deposition. The substrate cleanliness is a prerequisite for the reproducible growth of fractal structures. The C\textsubscript{60} beam is created by thermal evaporation of commercially available high-purity C\textsubscript{60} powder (MerCorp) from a BN-crucible with a graphite liner. A detailed description of the experimental procedure is provided in ref 19. STM images are recorded with a sample bias voltage of 1.2 V and a tunneling current of 0.1 nA and acquired in the constant current mode at room temperature. The STM images are displayed such that the scan lines are horizontal and scanning proceeds from the bottom to the top.

3. STM Images of C\textsubscript{60} Films

Figure 1 shows two representative STM images of C\textsubscript{60} films deposited on HOPG at different coverages. The deposition duration is 10 s in (a), which corresponds to a coverage (total
amount of fullerenes from all layers) of 0.39 monolayers (ML), as determined from the STM images. In (b) the deposition time is 35 s and the coverage amounts to 1.4 ML. The first layer of C\textsubscript{60}, which is in contact with the graphite surface, grows in the form of elliptically shaped, relatively large islands. In the second layer small fractal-dendritic islands nucleate in the central parts of the underlying C\textsubscript{60} islands. The straight lines intersecting the layer small fractal-dendritic islands nucleate in the central parts of the first-layer islands. A detailed discussion of experimental results obtained in STM imaging of C\textsubscript{60} films growing on a graphite substrate is given in ref 19.

4 Computational Method

The growth mechanisms and evolution of the shapes of the growing islands of C\textsubscript{60} molecules are investigated using the kinetic Monte Carlo (kMC) computational method. This method is ideally suited for simulation of the early stages of film deposition, when the growth process is defined by a relatively small number of elementary thermally activated events defining the mobility of a C\textsubscript{60} molecule. To perform a kMC simulation, we consider all possible thermally activated events that can be realized during the movement of fullerene molecules on the corrugated C\textsubscript{60} surface and calculate rates for all the events. In this work, the rates of all elementary processes relevant to the growth of two-dimensional islands of C\textsubscript{60} molecules on the surface of an existing close-packed fullerene island are calculated in molecular dynamics (MD) simulations. A description of the computational setups used in the MD and kMC simulations is given below.

4.1. MD Simulations of C\textsubscript{60} Diffusion. The MD method is used to determine the jump rates of C\textsubscript{60} molecules on a close packed fullerene surface in the presence of other C\textsubscript{60} molecules, which determine the local environment of each molecule. The interaction among C\textsubscript{60} molecules is described with a Girifalco potential,\textsuperscript{29} and a potential proposed by Ruoff and Hickman\textsuperscript{30} is used for C\textsubscript{60}-graphite interactions. Both potentials adopt a simplified description of the interactions, when contributions of individual nonbonding carbon–carbon interactions are averaged to provide effective C\textsubscript{60}–C\textsubscript{60} and C\textsubscript{60}–graphite potentials. The effective potentials are defined as functions of the distance between the centers of mass of C\textsubscript{60} molecules and center of mass of a molecule and the graphite plane, respectively. The cutoff distance in the interaction between C\textsubscript{60} molecules is chosen to be 3.55 nm, i.e., 10 times the radius of a C\textsubscript{60} molecule.\textsuperscript{31}

The MD computational cell consists of a monolayer of C\textsubscript{60} molecules arranged in a close-packed structure (10 \times 10 unit cells) and placed on a graphite plane as the first layer island. The close-packed structure of the first and second C\textsubscript{60} layers has been identified in high-resolution STM images presented in ref 19. A few C\textsubscript{60} molecules are placed on top of the first fullerene layer in different configurations covering the range of possible local environments realized for a C\textsubscript{60} molecule under the film deposition conditions. The temperature dependences of the molecular jump rates are determined by performing simulations at a range of temperatures, from 316 to 747 K. A velocity scaling is performed at the beginning of the simulation to define the desired temperature, which is then maintained in the bottom layer of C\textsubscript{60} molecules during the simulation.

The rates of molecular jumps from/to all possible local configurations and diffusion events are determined by counting the number of corresponding jumps observed during an MD simulation. The jump rates are then calculated by dividing the number of jumps by the time of the simulation. The temperature dependence of a jump rate can be described by the Arrhenius-type expression

\[ \nu_i = \nu_0 \exp\left(-\frac{E_i}{k_BT}\right) \]

where \( \nu_i \) is the jump rate for the diffusion event \( i \), \( E_i \) is the corresponding activation energy, \( \nu_0 \) is the prefactor (attempt
frequency) related to the frequency of molecular vibrations and the number of possible jump directions, $k_B$ is the Boltzmann constant, and $T$ is the temperature. After performing simulations at different temperatures, the curve-fitting of the jump rates to eq 1 is used to determine activation energy barriers and prefactors.

The results of the MD simulations are summarized in Table 1. The schematic representation of molecular configurations used in the first column of the table is illustrated in Figure 2 for a configuration denoted as (1b). This configuration can occur in the vicinity of an existing island, as shown in Figure 2a. The hopping events occurring on the central part of the underlying fullerene island, away from the boundary of the island include the hopping of an individual C$_{60}$ (configuration 0), as well as hopping of a C$_{60}$ adjacent to one (configurations 1c and 1b) or two (configurations 2c–h) other second-layer molecules. The mobility of a C$_{60}$ surrounded by 3 or more other molecules is found to be too low to contribute significantly to the development of morphology of the growing islands. These fullerene molecules are considered to be immobile. The rates of additional hopping events associated with the boundary of the first-layer island are listed in Table 1b. The values of the activation barriers and prefactors listed in Table 1 are based on simulations performed at several temperatures. For example, the results from 18 different MD simulations are used to make the Arrhenius plot for configuration (1b)$_2$, shown in Figure 3, and obtain the values of the activation barrier and the attempt frequency listed for this configuration in Table 1a.

### 4.2. Kinetic Monte Carlo Simulation for C$_{60}$ Film Growth
The kMC simulations are performed on a two-dimensional (2D) lattice of binding sites that correspond to all the interstitial positions on the hexagonal close-packed structure of the first fullerene island formed on graphite. The lattice of the binding sites is created by superimposing two close-packed hexagonal 2D sub-lattices built with a lattice constant corresponding to the one of the C$_{60}$ monolayer, 10.056 Å, and having 800 × 800 lattice sites each. The two hexagonal 2D sub-lattices are shifted with respect to each other by $\sqrt{3}/3 \times 10.056$ Å, so that the combined structure has all the interstitial sites of a real hexagonal close-packed surface. A round area with a radius of 250 nm, chosen to match a typical size of first-layer islands observed in STM images, is then cut from the square 2D system to generate the first-layer island used in the simulations. During the cutoff, the lattice sites connected to only one closest neighboring site are removed. The remaining lattice of 445 776 binding sites corresponds to all interstitial sites on a round 2D island composed of 222 888 C$_{60}$ molecules.

Atomic deposition is simulated by randomly placing one C$_{60}$ molecule on the surface. The number of simulation steps, which elapse until the next molecule is placed, are chosen to reproduce a deposition rate similar to the one used in our experiments. All of the C$_{60}$ molecules deposited on the spherical first-layer island are allowed to jump to one of the three nearest neighboring sites, and the probabilities of the jumps are defined by the local surface configuration (see Table 1). To introduce time into kMC simulation, we use an approach based on a fixed constant time-step that keeps track of time for the entire system, e.g., refs 32 and 33. The time-step in the kMC simulations, 1.75 ns, is chosen as the reciprocal of the total hopping rate of the C$_{60}$ molecule that has no other molecules in the three closest neighbor shells (12 nearest binding sites), configuration (0) in Table 1. The hopping rate of an individual molecule is significantly higher than any other thermally activated event on the surface, and the probability of an individual molecule to make a jump is unity at each step. One of the three jump directions is chosen at random with equal probabilities. The probabilities of other events are determined at each time-step as the product of the time-step and the rate of the event calculated based on the values of the activation barriers and the prefactors listed in Table 1. All kMC simulations reported in this paper are performed for experimental conditions of room temperature and deposition rate of about 0.04 ML/s (one C$_{60}$ molecule for every 68 392 simulation steps).

A jump upward from graphite to a C$_{60}$ layer has never been observed in any of the MD simulations and was therefore not included in the kMC simulations. Moreover, MD simulations indicate that there is a considerable Ehrlich-Schwoebel barrier for downward jumps of second layer molecules from the first layer downward to the graphite surface (see Table 1b). A similar barrier exists for the downward jumps of third layer C$_{60}$ deposited on top of the second layer. Consequently, the exchange of molecules between different fullerene layers is relatively rare and is, therefore, not included in the kMC simulation. The C$_{60}$ molecules deposited on an existing fullerene island are likely to form new islands, as confirmed by STM images shown in Figure 1, where the nucleation of the third layer islands on top of the second layer islands can be seen. The third layer islands exhibit the same growth behavior as the second layer islands and, at coverages considered in this work, contain small fractions of the deposited fullerene molecules. The growth of the second fullerene layer is, therefore, treated here as a process independent of the nucleation and growth of islands in the third layer, and the molecules deposited on top of the second layer are not included in the kMC simulations.

### 5. Simulation Results and Discussion
The growth of the second-layer C$_{60}$ islands in a kMC simulation of room-temperature deposition with the rate of 0.04 ML/s is illustrated in Figure 4. The round boundaries of the first-layer islands are depicted by circles. At the early stage of the deposition, after several molecules are deposited, two molecules can occasionally meet and form a dimer, the lifetime of which is approximately 2.75 ns, as can be estimated from the values of the activation energies and the prefactors listed for the configuration (1b) in Table 1. During the lifetime of a dimer, if another molecule attaches to it, a cluster of three molecules forms and becomes a nucleation center. The lifetime of a cluster of three C$_{60}$ molecules arranged in the configuration (2c) is approximately 2824 ns at room temperature, while the lifetime is much longer if the molecules are arranged in configuration (2d).

The stable initial clusters grow in the course of the deposition and develop into relatively compact islands of a characteristic triangular star shape with three major branches, e.g., Figure 4 at 0.02 and 0.05 ML. As the coverage increases, the island shape gradually becomes more dendritic and finally becomes ramified. Six preferred growth orientation directions can be identified at low coverages, which agree with the shapes observed in STM images shown in Figure 1. Because of the growth competition among different islands, the growth of some of the branches becomes obstructed and the islands start to merge at coverages exceeding ~0.3 ML.

There is a clear tendency of the second-layer islands to avoid nucleation close to the edge of the first-layer island, which also agrees with experimental observations, Figure 1a. The coverage of the first layer by the second layer in the STM image shown in Figure 1a is 0.09, the same as in the snapshot from kMC simulation in Figure 4c. A visual analysis of Figure 1a and 4c.
TABLE 1: (a) Energy Barriers, Attempt Frequencies, and Probabilities of Diffusion Jump Events on a Fullerene Island*

<table>
<thead>
<tr>
<th>Terrace</th>
<th>Jump to I Energy barrier (meV)</th>
<th>Attempt frequency ((\times 10^{12} \text{s}^{-1}))</th>
<th>Jump to II Energy barrier (meV)</th>
<th>Attempt frequency ((\times 10^{12} \text{s}^{-1}))</th>
<th>Jump to III Energy barrier (meV)</th>
<th>Attempt frequency ((\times 10^{12} \text{s}^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 (without neighbors - basic movement)</td>
<td>(E_{0} = 178 \pm 4) (v_{0} = 0.2 \pm 0.03)</td>
<td>(E_{0} = 178 \pm 4) (v_{0} = 0.2 \pm 0.03)</td>
<td>(E_{0} = 178 \pm 4) (v_{0} = 0.2 \pm 0.03)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1b</td>
<td>(E_{1b} = 429 \pm 57) (v_{1b} = 0.65 \pm 0.09)</td>
<td>(E_{1b} = \infty^{\dagger})</td>
<td>(E_{1b} = \infty^{\dagger})</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1c</td>
<td>(P_{1c} = 50%^{*})</td>
<td>(P_{1c} = 50%^{*})</td>
<td>(P_{1c} = 0 %^{*})</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2c (A-step)</td>
<td>(E_{2c} = 354 \pm 63) (v_{2c} = 0.06 \pm 0.01)</td>
<td>(E_{2c} = 354 \pm 63) (v_{2c} = 0.06 \pm 0.01)</td>
<td>(E_{2c} = \infty^{\dagger})</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2d (B-step)</td>
<td>(E_{2d} = \infty^{\dagger})</td>
<td>(E_{2d} = \infty^{\dagger})</td>
<td>(E_{2d} = \infty^{\dagger})</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2e</td>
<td>(P_{2e} = 98.24 \pm 0.3 %^{*})</td>
<td>(P_{2e} = 0.88 \pm 0.15 %^{*})</td>
<td>(P_{2e} = 0.88 \pm 0.15 %^{*})</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2f</td>
<td>(E_{2f} = \infty^{\dagger})</td>
<td>(E_{2f} = \infty^{\dagger})</td>
<td>(E_{2f} = \infty^{\dagger})</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2g</td>
<td>(P_{2g} = 99.86 \pm 0.1 %^{*})</td>
<td>(P_{2g} = 0.14 \pm 0.1 %^{*})</td>
<td>(P_{2g} = 0 %)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2h</td>
<td>(E_{2h} = \infty^{\dagger})</td>
<td>(E_{2h} = \infty^{\dagger})</td>
<td>(E_{2h} = \infty^{\dagger})</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3 (three or more neighbors)</td>
<td>(E_{3} = \infty^{\dagger})</td>
<td>(E_{3} = \infty^{\dagger})</td>
<td>(E_{3} = \infty^{\dagger})</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
indicates that the shapes of the islands observed in the simulation and experiment are similar. In order to perform a quantitative comparison between the experimental results and the predictions of the kMC simulation, the fractal dimension of the second-layer islands is calculated for different times during the simulation, Figure 5. To ensure the direct connection with experimental results, the same box-counting method is used to characterize the shapes of the simulated islands. In this method, the simulated images are transformed to a black-and-white mode, and the occupation number $N$ scales as $\ln N \propto D \ln A$, where $D$ is the fractal dimension. The configurations on a surface may have a fractal dimension between 1 and 2, where a fractal dimension of 1 corresponds to a linear arrangement of molecules and a fractal dimension of 2 corresponds to a round island. In the simulation, the fractal dimension of the islands increases from 1.5 to 1.9 during the deposition, with changes in the rate of increase reflecting the changes in the growth mechanisms. At the onset of the growth (coverage less than 15%), the fractal dimension increases rapidly as the individual small islands transition from their initial triangular star shapes to characteristic dendritic shapes with multiple branches, Figure 4. At these coverages, the islands are separated from each other and the growth process of individual islands is largely unaffected by the presence of other islands. At higher coverages, the growth competition among islands, coalescence of islands, and the limitation of the size of the first-layer island lead to

<table>
<thead>
<tr>
<th>Boundary</th>
<th>Jump to I</th>
<th>Jump to II</th>
<th>Jump to III</th>
</tr>
</thead>
<tbody>
<tr>
<td>j</td>
<td>$P_j^I = 45.0 \pm 1%^*$</td>
<td>$P_j^II = 10.0 \pm 0.5%^*$</td>
<td>$P_j^III = 45.0 \pm 1%^*$</td>
</tr>
<tr>
<td>ja</td>
<td>$P_{ja}^I = 99.97 \pm 0.03%^*$</td>
<td>$P_{ja}^II = 0.03 \pm 0.03%^*$</td>
<td>$P_{ja}^III = 0%$</td>
</tr>
<tr>
<td>jb</td>
<td>$P_{jb}^I = 50%^*$</td>
<td>$P_{jb}^II = 0%$</td>
<td>$P_{jb}^III = 50%$</td>
</tr>
<tr>
<td>jec</td>
<td>$E_{jec}^I = 207 \pm 4$</td>
<td>$E_{jec}^II = 354 \pm 53$</td>
<td>$E_{jec}^III = \infty^†$</td>
</tr>
<tr>
<td>$v_{jec}^I = 0.29 \pm 0.01$</td>
<td>$v_{jec}^II = 0.3 \pm 0.05$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>j2 (two or more neighbors)</td>
<td>$E_{j2} = \infty^†$</td>
<td>$E_{j2} = \infty^†$</td>
<td>$E_{j2} = \infty^†$</td>
</tr>
</tbody>
</table>

The values for the energy barriers and attempt frequencies are obtained from MD simulations as described in the text. The starting configurations are schematically shown in the first column: the hollow circles represent C$_{60}$ molecules that form a close-packed structure of the first-layer island, gray and black circles represent C$_{60}$ molecules deposited on the first-layer island. The molecules shown by black circles are immobilized by the presence of other molecules (as an example, immobile molecules in configuration 1b are shown in Figure 2a), whereas the jumps of the molecules shown by gray circles are recorded in the MD simulations. The three possible hopping destinations are marked for each mobile C$_{60}$ molecule as I, II, and III, with corresponding energy barriers, attempt frequencies, and relative jump probabilities shown in columns 2, 3, and 4, respectively. In the nomenclature used to label the jumps, the superscript denotes the hopping destination and the subscript denotes the initial configuration as illustrated in the first column. Table 1a lists information for all movements occurring on the fullerene island, except for the ones near the edge of the island. Table 1b characterizes the possible jumps of a fullerene molecule positioned close to the boundary of a first-layer island (the bottom row of 5 fullerene molecules in the schematic drawings are at the edge of the island in this case). The * denotes that the initial configuration is a metastable state. The jump rate is higher than that of the basic movement. Only the relative probabilities (P) of jumping to the three directions are recorded. The † denotes that the initial configuration is a stable state. The number of jumps at 700 K (<10 jumps per 20 ns) is insufficient to determine the activation energy and the jump frequency at room temperature.
been used extensively to explain the formation of fractal surface of a growing aggregate whenever they encounter it, has assumes that particles undergo random walk and stick to the layer island during the growth process, begin to break down.

The fractal dimensions of the second-layer islands predicted in the kMC simulation can be related to the ones calculated for STM images and shown in Figure 5 for comparison. The coverage indicated in the graph is the coverage of the first layer island with second layer islands. For the simulation this value is precisely known, but for the experimental data an error of about 10% in determination of the coverage values from the STM images is included in the graphs shown in Figure 5. The error bars for the values of the fractal dimension result from the application of the box-counting method. The agreement of the fractal dimensions is more pronounced at larger coverages, where some of the assumptions made in the computational model, such as the constant size of the first-layer island with second layer islands. For the simulation this value is precisely known, but for the experimental data an error of about 10% in determination of the coverage values from the STM images is included in the graphs shown in Figure 5. The error bars for the values of the fractal dimension result from the application of the box-counting method. The agreement of the fractal dimensions is more pronounced at larger coverages, where some of the assumptions made in the computational model, such as the constant size of the first-layer island with second layer islands.

The diffusion limited aggregation (DLA) model, which is related to the jump events close to the boundary of the first layer, affect only the island density if the deposition rate is constant. In particular, the number of the second-layer islands obtained in kMC simulations performed with various values of \( P_{1b}^{II} \), keeping all other rates unchanged, is shown in Figure 8 for the area of the simulated first-layer island of 1.96 \( \times 10^5 \) nm\(^2\). The simulations are performed for 3 \( \times 10^9 \) simulation steps with the same deposition rate of 0.04 ML/s. The value of \( P_{1b}^{I} \) reflects the magnitude of the Ehrlich-Schwoebel barrier at step edges. The number of islands is at its maximum value when \( P_{1b}^{II} = 0\% \), which means that no molecules at the step edge can jump downward. As \( P_{1b}^{II} \) increases, the number of islands decreases first and then saturates at a constant value of about 6 at \( P_{1b}^{II} > 5\% \). It is apparent from the insets in Figure 8 that the simulated second-layer islands preserve the triangular star shape independent of the value of \( P_{1b}^{II} \). The value of \( P_{1b}^{II} = 10\% \) was obtained from MD simulations and used in the kMC simulation. The average number of islands on a 1.96 \( \times 10^5 \) nm\(^2\) first-layer island in the experiment is 4.1. The discrepancy between the simulations and experiments can be related to the assumption of the fixed boundary of the first layer island in the kMC simulation.
The triangular star shape of the second-layer islands is the prominent feature of the growth of C\textsubscript{60} on graphite, Figure 1. However, both the conventional DLA model and Wynblatt’s model\textsuperscript{30} fail to predict the triangular shape of the second-layer C\textsubscript{60} islands. These models do not distinguish the A-step and B-step geometries, which are inherent to the islands growing on hexagonal close packed surfaces. For metal-on-metal systems,\textsuperscript{20,37,38} it is well-known that activation energy barriers for atomic diffusion along a A-step are different from those along a B-step, which strongly affects the shapes of the growing islands. For example, Pt growth on Pt(111) exhibits ramified islands at 300 K and compact islands of triangular shape at 400 K\textsuperscript{20}. The kinetic Monte Carlo simulations distinguish between the atomic mobility along A- and B-steps and, as a result, successfully reproduce the fractal-dendritic shapes of the second-layer C\textsubscript{60} islands.

The orientation of the dendritic islands with respect to the underlying close-packed first-layer fullerene lattice stems from anisotropy of the C\textsubscript{60} diffusion along the edges of the growing islands. It is found in the kMC simulations discussed above.

Figure 3. Example of Arrhenius plots used to determine the activation barriers and prefactors in eq 1. The results are shown for configuration (1b) in Table 1a. The calculation of the jump rate is based on 262 jump events recorded at the highest temperature and 43 jumps recorded at the lowest temperature used in this series of MD simulations.

(a) 0.02 ML  
(b) 0.05 ML  
(c) 0.09 ML  
(d) 0.12 ML  
(e) 0.16 ML  
(f) 0.20 ML  
(g) 0.25 ML  
(h) 0.29 ML  
(i) 0.34 ML  
(j) 0.38 ML

Figure 4. Sequential growth progression of the second-layer C\textsubscript{60} islands predicted in a kMC simulation. The coverages are 0.02, 0.05, 0.09, 0.12, 0.16, 0.25, 0.29, 0.34, and 0.38 ML, respectively. The round boundary of the first-layer C\textsubscript{60} island is shown by circles.

Figure 5. Fractal dimension of the second-layer islands as a function of coverage predicted in the kMC simulation and calculated from STM images (Figure 1, panels a and b, in ref 19). The fractal dimension of islands predicted by DLA model is 1.67 and is shown by the horizontal dashed line.

Figure 2. Fractal Structures in Fullerene Layers / J. Phys. Chem. C, Vol. 112, No. 12, 2008 4693
that the ratio of $E_{1b}^{III}/E_{1b}^{I}$, characterizing the relative probabilities of a corner atom to hop to either an A-step or a B-step, and the value of $E_{2c}^{I}$ ($E_{2c}^{II}$), which characterizes the diffusion along an A-step, are the most important parameters determining the shapes of the second-layer islands. From the configuration shown in Figure 2, a molecule located at a corner of an island can hop to one of the two neighboring sites adjacent to the island, I and III. If followed by a hop to a neighboring site IV, the hop to the neighbor site III can move a mobile C$_{60}$ to the A-step. Direct diffusion to the B-step is less likely since a hop to site II has an extremely high local activation barrier and an alternative pass involves a sequence of several hops. Therefore, diffusion to A-steps is much more preferable for a corner molecule than diffusion to B-steps. The results of MD simulations suggest that the edge diffusion along a B-step ($E_{2d}^{I}$, $E_{2d}^{II}$) is a very slow process, which makes the diffusion barrier along an A-step ($E_{2c}^{I}$, $E_{2c}^{II}$) a critical factor in defining the shapes of the growing islands. The mobility of a molecule along an A-step can be characterized by a diffusion coefficient defined as $D = \nu a^2/z$, where $\nu$ is the frequency of hops along the A-step, $a$ is the jump distance, and $z$ is 2 for the one-dimensional diffusion. Using the values of the energy barrier and attempt frequency listed in Table 1, the room-temperature diffusion coefficients along A-steps can be calculated to be $3 \times 10^{-14}$ m$^2$/s. A smaller value of $E_{2c}^{I}$ ($E_{2c}^{II}$) can destroy the 3-fold symmetry in the islands since the fast diffusion along A-step would counteract the anisotropy that originate in the large ratio of $P_{1b}^{III}/P_{1b}^{I}$. If $E_{2c}^{I}$ ($E_{2c}^{II}$) is too large, however, the mobility along the edges would be small and random attachments to island edges would result in islands with fragmented edges instead of the triangular star shapes observed in STM images.

Figure 6. Second-layer islands obtained in simulations performed with various values of $E_{2c}^{III}$ ($E_{2c}^{I}$) and other parameters unchanged. The simulation is performed for $3 \times 10^9$ steps with a deposition rate of 0.04 ML/s.

Figure 7. Second-layer islands obtained in simulations performed with different ratios of the jump rates to the neighbor site III and the neighbor site I, while keep the overall probability of all jump events in configuration (1b) unchanged. The simulation is performed for $3 \times 10^9$ steps with a deposition rate of 0.04 ML/s.

Figure 8. Number of the second-layer islands predicted in kMC simulations with various values of $P_{1b}^{III}$. The area of the first-layer islands is $1.96 \times 10^5$ nm$^2$. The simulations are performed for $3 \times 10^9$ steps with a deposition rate of 0.04 ML/s. Each point in the plot is calculated based on the results of 3 simulations. Insets show examples of molecular configurations for three values of $P_{1b}^{III}$.

6. Conclusion

The results of kMC simulations provide a detailed molecular-level picture of fractal-dendritic growth of second-layer C$_{60}$ islands on compact first-layer C$_{60}$ islands deposited on graphite substrate. The simulations are parametrized based on MD
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...simulations performed at different temperatures and used to determine the rates of all relevant thermally activated processes responsible for the island nucleation and growth during the deposition. The geometry of the underlying substrate is found to result in the formation of two characteristic molecular arrangements along the edges of the growing islands (A-step and B-step on a close-packed surface). The difference in the molecular ability along the A-step and B-step configurations, along with the difference in the probability of a C₆₀ molecule to diffuse from a corner of an island to A-step or B-step edges of the island, are identified as key factors responsible for the formation of characteristic triangular shapes of the fractal islands and their orientation with respect to the underlying surface structure. The fractal shapes of the second-layer C₆₀ islands predicted in kMC simulations are in a good agreement with STM images taken under comparable deposition conditions. A further refinement of the model aimed at improvement of the quantitative agreement between simulation and experiment would incorporate a description of the molecular exchange between layers and the growth of the first layer island during the deposition.

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References and Notes