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# Theoretical Analysis of Diamond Mechanosynthesis. Part II. C<sub>2</sub> Mediated Growth of Diamond C(110) Surface via Si/Ge-Triadamantane Dimer Placement Tools

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This paper presents a computational and theoretical investigation of the vacuum mechanosynthesis of diamond on the clean C(110) surface from carbon dimer ( $C_2$ ) precursors positionally constrained throughout the reaction pathway by silicon- or germanium-doped triadamantane derivatives mounted on a scanning probe tip. Interactions between the dimer placement tools and the bare diamond C(110) surface are investigated using Density Functional Theory (DFT) with generalized gradient approximation (GGA) by constructing the reaction path potential energy profiles and analyzing *ab initio* molecular dynamics simulations. Similar methods are applied to study the energetics and kinetics of recharging the tool with acetylene. Molecular mechanics simulations on extended tool tips are carried out to elucidate the positional uncertainty of the carbon dimer due to thermal fluctuations, and the possibility of intermolecular dimerization and dehydrogenation of the dimer placement tools is explored.

**Keywords**: Adamantane, Carbon, Density Functional Theory, Diamond, Dicarbon, Dimer Placement, Mechanosynthesis, Nanotechnology, Positional Control, VASP.

## 1. INTRODUCTION

This paper presents a computational and theoretical investigation of the vacuum mechanosynthesis of diamond on the clean C(110) surface from carbon dimer (C<sub>2</sub>) precursors. Part I<sup>1</sup> provided a detailed atomic picture of the dimer-mediated surface chemistry during the gas-phase growth of dehydrogenated diamond C(110) from C<sub>2</sub> plasmas, deducing some of the many possible stabilized defects that can be formed early in the dimer-mediated diamond growth process. These results provided information regarding the outcomes of the misplacement of a carbon dimer and established constraints upon the required positional precision that would be needed to avoid the formation of stable defects during positional dimer placement to achieve diamond growth, or diamond mechanosynthesis, the subject of Part II of this paper.

Merkle and Freitas<sup>2</sup> have proposed the use of silicon and germanium functionalized derivatives of the hydrocarbon

cage molecule triadamantane for the fabrication of diamond nanostructures via the pick-and-place mechanochemistry of carbon dimers onto an existing diamond seed, cleaved along the C(110) surface plane. Figure 1 illustrates one scheme for a cycle of dimer-mediated diamond mechanosynthesis. The first step (left) involves the approach of the dimerized tool tip to the diamond surface, leading to a tool+substrate complex (bottom). The next step involves the retraction of the tool tip, leaving behind a deposited carbon dimer (right). The tool is then "recharged" with acetylene (top), followed by a dehydrogenation step that ultimately leads to a re-dimerized tool (left), allowing the cycle to be repeated.

Interactions between the dimer placement tools and the bare diamond C(110) surface are investigated by constructing the reaction path potential energy profiles and analyzing *ab initio* molecular dynamics simulations. Similar methods are applied to study the energetics and kinetics of a simplistic scheme for recharging the tool with acetylene. Since no specific route to the removal of molecular hydrogen from the terminal carbon dimer was presented, and because hy-

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drogen abstraction has already received substantial theoretical attention,<sup>3–8</sup> this path was left unstudied. Long-time molecular mechanics simulations on extended tool tips were carried out to elucidate the positional uncertainty of the carbon dimer due to thermal fluctuations. The structural and chemical stability of the dimerized triadamantane tools, including high temperature thermal stability and the possibility of intermolecular dimerization and dehydrogenation, were also explored.

## 2. COMPUTATIONAL METHODS

The model for the diamond surface required to study the tool-substrate chemistry must be slightly larger than the model previously employed in Part I<sup>1</sup> to study the dimermediated surface growth chemistry. Figure 2 shows a periodic clean diamond C(110) surface slab terminated with hydrogen atoms below the bottommost carbon plane. Attempted dimer depositions occur on the topmost carbon plane. The model consists of 160 carbon atoms and 40 hydrogen atoms, for a total of 200 atoms, and is confined to a periodic box with supercell dimensions of 14.245 Å and 12.604 Å along the edges surrounding the surface plane. Table 1 lists the values of the relevant internal coordinates of the DFT/GGA optimized surface slab. Subsurface carbon atoms are simply identified with the label C, while the exposed surface carbon atoms are labeled as  $C_s$ .

Merkle and Freitas<sup>2</sup> proposed that silane and germanium derivatives of the diamondoid molecule triadamantane might be useful end effectors (placement tools) for diamond mechanosynthesis. With a carbon dimer covalently attached to two terminal Si or Ge atoms, and the triadamantane either attached to a scanning probe or integrated into an extended diamond lattice, the carbon dimer can be posi-



Table 1. Internal coordinates for the relaxed clean (dehydrogenated) diamond C(110) surface.

Clean diamond C(110) surface		
Coordinate	Value	
$C_s - C_s$	1.436 Å	
$C_s - C$	1.487 Å	
C - C	1.536 Å	
$C_s - C_s - C_s$	122.7°	
$C_s - C_s - C$	109.3°	
$C_s - C - C$	100.8°/112.2°	

tioned and deposited onto a growing diamond substrate. The success of this process is based on the premise that a typical C-Si or C-Ge bond is weaker than a typical C-C bond and will dissociate first, leaving the carbon dimer covalently attached to the diamond surface.

Figure 3 shows DFT/GGA-optimized structures of the Si-triadamantane and Ge-triadamantane molecules, each containing a carbon dimer attached at the terminal end. The 1.276 Å bond length of the attached carbon dimers and the approximate bond order of three are characteristic of a  $C \equiv C$  triple bond found in alkynes and terminal acetylenes. For clarity, the carbon atoms of the terminal carbon dimer are labeled as Cad, those in the remaining portion of the triadamantane tool as Ct, and those on the diamond surface as C<sub>s</sub>. The relevant internal coordinates for the Si- and Ge-triadamantane tools are summarized in Table 2. Consistent with a bond-energy bond-order (BEBO) model, the shorter Si-Cad bond, compared with the two bonds to the adamantane carbons, is indicative of a stronger bond. That is, the carbon atoms in the C2 dimer are covalently bound more strongly to the Si atoms than with the adamantane carbon atoms. The same applies to the Ge-triadamantane molecule.

A set of additional simulations was carried out to predict the positional uncertainty of the carbon atoms in the  $C_2$ dimer. There are two ways in which the triadamantane tool could be attached at the end of a probe: either noncovalently affixed to the scanning probe tip, or covalently integrated into the scanning probe tip. In the former case, the tool piece would be prone to diffusion and rotation along the surface of the probe tip. These undesirable effects are eliminated in the latter case. The most ideal probe—one that is least subject to distortion due to lateral vibrations—would be a rigid rod, such as one fabricated from diamond. Figure 4 shows a simplified model of an extended diamondoid scanning probe composed of two Ge atoms protruding from the tip.

Application of the most sophisticated atomistic modeling methods available are required to achieve the highest accuracy in predictions of the chemical stability of the proposed dimer placement tools, tool-substrate chemical affinity and reactivity, and the acetylene recharging of the end effectors. Traditional local-orbital-based electronic structure theories-such as Hartree-Fock, perturbation theory, configuration interaction, coupled cluster theory, etc.-are only applicable for systems ranging in size from a few atoms to a little more than 100 atoms. Density Functional Theory (DFT), coupled with non-local plane-wave basis functions, has allowed the study of systems exceeding a few hundred atoms with unprecedented accuracy. Given the large size of the model required to study the tool-substrate chemistry  $(\sim 250 \text{ atoms})$ , the vast majority of the calculations performed during this study made use of plane-wave-based DFT.

All of the electronic structure calculations reported in this section were carried out using the Vienna *Ab initio* Simulation Package (VASP).<sup>9</sup> The wavefunctions are expanded in a basis consisting of plane waves with norm-conserving Vanderbilt ultra-soft pseudopotentials for the inner core electrons. The generalized gradient approximation (GGA) is used throughout. Stationary point calculations and *ab initio* molecular dynamics (AIMD) simulations were run in parallel on an in-house built PC cluster using MPI (message passing interface) for inter-node communication. Typical structural optimizations took approximately one day



Si-triadamantane dimer placement tool



Ge-triadamantane dimer placement tool

Figure 3. DFT/GGA optimized structures of the Si-triadamantane and Ge-triadamantane molecules, each containing a carbon dimer attached at the terminal end.

 Table 2.
 Internal coordinates for optimized Si/Ge-triadamantane dimer placement tools.

Si placement tool		Ge placement tool	
Coordinate	Value	Coordinate	Value
$C_{ad} - C_{ad}$	1.276 Å	$C_{ad} - C_{ad}$	1.275 Å
C <sub>ad</sub> – Si	1.828 Å	C <sub>ad</sub> – Ge	1.904 Å
$C_t - Si(4)$	1.907 Å	$C_t - Ge(4)$	2.002 Å
$C_t - Si(2)$	1.860 Å	$C_t - Ge(2)$	1.941 Å
$C_{ad} - C_{ad} - Si$	119.2°	$C_{ad} - C_{ad} - Ge$	119.4°
$C_{ad} - Si - C_t(4)$	106.0°	$C_{ad} - Ge - C_t(4)$	106.4°
$C_{ad}-Si-C_t(2) \\$	127.2°	$C_{ad} - Ge - C_t(2)$	128.2°

to run on eight nodes, with transition state calculations involving between 10 and 20 constrained structural optimizations each. AIMD simulations were performed for a total time of 1 ps using an integration time-step of 1 fs. The hundreds of *ab initio* calculations and simulations presented in this study accounted for more than 50,000 CPU hours, or 5.7 CPU years (computer time) on the in-house PC cluster. In addition to the electronic structure calculations described above, a few long-time molecular dynamics (MD) simulations were performed on extended diamond tool tips to deduce the thermal fluctuations in the normal modes of the attached carbon dimer, and their resulting positional uncertainties as projected onto the plane of the diamond surface. These simulations were carried out at room temperature (298 K) for 1 ns using the MM3 empirical force field.

## 3. RESULTS AND DISCUSSION

#### 3.1. Chemical Stability and Recharging of Dimer Placement Tools

Diamondoid molecules, including adamantane, diamantane, triamantane, pentamantane, heptamantane and up to at least undecamantane (11 face-fused adamantane cages) can be isolated from natural petroleum;<sup>10–12</sup> the direct chemical



Figure 4. Extended Ge-triadamantane dimer placement tool for diamond mechanosynthesis.

synthesis of adamantane,<sup>13</sup> diadamantanes,<sup>14, 15</sup> including [4]-diadamantane (diamantane),<sup>16</sup> triamantane<sup>17</sup> and tetramantane<sup>18</sup> has been reported; and, the molecular geometries of diamantane, triamantane and isotetramantane have been investigated theoretically using molecular mechanics, semiempirical and *ab initio* approaches.<sup>19</sup> Since the field of organosilane chemistry<sup>20</sup> is fairly well developed, constructing a synthetic route to the silo-triadamantane tool should be feasible. Although less is known of organic germanium chemistry, reports indicate the successful synthesis of a wide variety of organogermanium compounds as well.<sup>21</sup>

Assuming the proposed Si- and Ge-triadamantane dimer placement tools are synthesizable, it must then be determined whether they are structurally and chemically stable. Previous semiempirical and *ab initio* calculations<sup>2</sup> predict that the proposed Si- and Ge-triadamantane molecules are structurally stable (i.e., they are not susceptible to room temperature intramolecular isomerization or decomposition). What remains is to determine whether these molecules are susceptible to self-reaction, including intermolecular dimerization and dehydrogenation. Since the  $\sigma$  bond environment surrounding the terminal  $C \equiv C$  triple bond is distorted from the preferred planar arrangement, one may suspect an increased reactivity due to weaker  $\alpha$ - $\pi$  hyperconjugation. One possible reaction is a  $2\pi + 2\pi$  cycloaddition leading to dimerization. A wellknown representative example is the rapid dimerization of cyclobutadiene. Another possible intermolecular self-reaction is dehydrogenation. This section reports results from studies of intermolecular tool dimerization and dehydrogenation, along with an analysis of a simplistic scheme for recharging spent tool tips with acetylene.

#### 3.1.1. Dimerization of Siand Ge-Triadamantane Tools

Figure 5 shows the fully relaxed structures of the dimerized Si- and Ge-triadamantane molecules; Table 3 lists the relevant internal coordinates for both of the dimerized molecules. In order to determine the likelihood that the two molecules will dimerize via a  $2\pi + 2\pi$  cycloaddition, the dimerization reaction pathway must be known. We calculated a symmetric reaction path potential energy surface by retracting the two tools through a series of constrained geometry optimizations. Each constrained optimization was carried out using a spin-unrestricted Kohn-Sham wavefunction to ensure an accurate population of the electronic orbitals and to attempt to avoid problems of spin contamination near the transition state. However, it has already been shown that cycloaddition reactions require the use of multi-determinant wavefunctions and that single-determinant methods, such as those used here, overestimate transition state energy barriers considerably. Figure 6 shows the potential energy curves representing the dimerization pathways along a symmetric reaction coordinate. The endpoint at far left for each curve corresponds to a dimerized tool,



Figure 5. DFT/GGA optimized structures of the dimerized Si-triadamantane and Ge-triadamantane molecules.

while the endpoint at far right corresponds to a separated tool, and the energy peak corresponds to the dimerization transition state (reaction path barrier).

The potential energy curves in Figure 6 are very similar and show an exothermic reaction for tool dimerization via a  $2\pi + 2\pi$  cycloaddition between the terminal acetylenic carbon dimers. The dimerization reaction enthalpies  $\Delta H_{rxn}$ are -1.64 eV and -1.84 eV for the Si- and Ge-triadamantane molecules, and the dimerization barriers H<sup>‡</sup> are 1.93 eV and 1.86 eV for the Si- and Ge-triadamantane molecules, respectively. It is clear that the dimerization of both tools is thermodynamically favored but not kinetically favored. Due to the fact that the electron correlation errors in DFT these barrier heights may be considerably overestimated, both reactions may be kinetically accessible at room temperature. (A comparison between DFT and Coupled Cluster Theory on small molecule fragments may shed more light on these results.) Thus, if allowed to interact without individual positional restraint, free triadamantane tools would be prone to dimerization-establishing an important constraint on the manner in which these tools may initially be synthesized and later recharged.

#### 3.1.2. Intermolecular Dehydrogenation

The removal of molecular hydrogen  $(H_2)$  from one triadamantane tool by another is an example of an intermole-

**Table 3.** Internal coordinates for optimized dimerized Si/Ge-triadamantane molecules.

Dimerized Si-triadamantane		Dimerized Ge-triadamantane		
Coordinate	Value	Coordinate	Value	
$C_{ad} - C_{ad}$ (joining tools)	1.580 Å	$C_{ad} - C_{ad}$ (joining tools)	1.584 Å	
$C_{ad} - C_{ad}$ (same tool)	1.400 Å	$C_{ad} - C_{ad}$ (same tool)	1.392 Å	
C <sub>ad</sub> – Si	1.828 Å	C <sub>ad</sub> – Ge	1.910 Å	
Si – Ct	1.907 Å	$Ge - C_t$	2.004 Å	
$C_{ad} - Si - C_t$	107.7°	$C_{ad} - Ge - C_t$	$108.0^{\circ}$	

cular dehydrogenation reaction. For the dimer placement tools considered here, this reaction can be represented schematically as

$$\begin{array}{c} C_xH_yGe_2C_2+C_xH_yGe_2C_2\rightarrow C_xH_yGe_2C_2H_2+\\ C_xH_{y\text{-}2}Ge_2C_2\end{array}$$

where  $C_xH_y$  corresponds to the hydrocarbon backbone of the dimer placement tool and  $C_2$  to the terminal carbon dimer attached to the two Si/Ge atoms. The active site would presumably involve the terminal carbon dimer of one triadamantane molecule and any of two vicinal hydrogen atoms on another triadamantane molecule. Only one dehydrogenation pathway was investigated in this study, using the Ge-triadamantane molecule as a model system.

Representative structures of the reactants, transition state and products for the intermolecular dehydrogenation of Getriadamantane molecules are shown in Figure 7, and a plot of the reaction path potential energy for this reaction is shown in Figure 8. The overall reaction is exothermic with a reaction enthalpy of  $\Delta H_{rxn}$  = -0.76~eV and a reaction barrier of  $H^{\ddagger} = 0.48$  eV. Exothermic reactions with an activation energy of 0.48 eV are accessible at room temperature. Therefore, if the Si/Ge-doped triadamantane molecules were synthesized as shown in Figure 3, and allowed to freely interact without individual positional restraint, they would be prone to intermolecular dehydrogenationillustrating their relatively low conventional chemical stability in the recharged state and establishing an important constraint on the manner in which they may initially be synthesized and later recharged.

#### 3.1.3. Acetylene Addition (Energetics and Kinetics)

A similar set of constrained optimizations was carried out to determine the minimum energy pathways for the addition of an acetylene molecule to Si/Ge-triadamantane molecules lacking a terminal carbon dimer. Since covalent  $\pi$ - $\pi$ 



Figure 6. Reaction path potential energy for dimerization of the Si-triadamantane and Ge-triadamantane molecules.

interactions are non-existent for these systems, errors due to single-determinant electron-correlation are non-existent, and the calculated results should be quantitative. Fully optimized structures of the Si- and Ge-triadamantane molecules with and without a covalently attached terminal acetylene (occupying the  $C_2$  dimer position) were created, and relevant internal coordinates were established for the Si- and Ge-triadamantane molecules lacking or possessing a terminal acetylene molecule. Minimum energy reaction path potentials versus reaction coordinate for addition of acetylene to the Si/Ge substituted triadamantane molecules were also calculated. The potential energy curves shown in Figure 9 possess similar shapes, with reaction enthalpies of -4.15eV and -3.10 eV, and barrier heights of 1.37 eV and 1.49 eV for acetylene addition to the Si- and Ge-triadamantane molecules, respectively.





Figure 8. Potential energy along the reaction coordinate for the intermolecular dehydrogenation of Ge-triadamantane.

Rate constants for acetylene addition were estimated from transition state theory using the aforementioned activation energies and the general relation  $k_{rxn} = (k_BT/h)$  $(Q^{\ddagger}/Q_AQ_B)exp(-E_a/k_BT)$ . The molar rate constant expressions are  $k_{rxn}$  (Si)  $\approx 10^{11} \text{ M}^{-1} \text{ sec}^{-1} exp(-15900/T)$  and  $k_{rxn}$  (Ge)  $\approx 10^{11} \text{ M}^{-1} \text{ sec}^{-1} exp(-17300/T)$ , therefore the room temperature (T = 298 K) rate constants become  $k_{rxn}$ (Si)  $\approx 6.7 \times 10^{-13} \text{ M}^{-1} \text{ sec}^{-1}$  and  $k_{rxn}$  (Ge)  $\approx 6.1 \times 10^{-15} \text{ M}^{-1} \text{ sec}^{-1}$ . The overall reaction exhibits second order kinetics with the rate law expression  $R = k_{rxn}$  [triadamantane][acetylene]. At room temperature, pure acetylene gas decomposes by deflagration (a slow-moving decomposition to the elements) above 2 atm and can detonate above 3.2 atm;<sup>22</sup> assuming a 1 liter container occupied by 0.08 M concentration of acetylene (corresponding to a pressure of 1.96 atm), the rate expressions reduce to  $R(Si) \approx 5.4$  $\times 10^{-14}$  N<sub>triadamantane</sub> (sec<sup>-1</sup>) and  $R(Ge) \approx 4.9 \times 10^{-16}$ N<sub>triadamantane</sub> (sec<sup>-1</sup>), where N<sub>triadamantane</sub> is the number density of the dimer placement tools (triadamantane tools/liter) in the recharging container. At room temperature,



a population of  $1.9 \times 10^{13}$  Si tools or  $2.0 \times 10^{15}$  Ge tools in a 1-liter container yields one recharged tool per sec, in principle, allowing 1 Hz operation of the mechanosynthetic cycle. A more practical approach may be to recharge tools at elevated temperatures. For example, at 600 K and 0.08 M concentration of acetylene, the rate expressions reduce to  $R(Si) \approx 2.5 \times 10^{-2}$  N<sub>triadamantane</sub> (sec<sup>-1</sup>) and  $R(Ge) \approx 2.4$  $\times 10^{-3}$  N<sub>triadamantane</sub> (sec<sup>-1</sup>), requiring only a population of 40 Si tools or 420 Ge tools in a 1-liter container to obtain one recharged tool per sec, again allowing 1 Hz operation of the mechanosynthetic cycle.

After acetylene addition, two hydrogens must be removed to complete the tool recharge cycle (Figure 1), possibly using abstraction tools that have been studied theoretically elsewhere.<sup>3-8</sup>

#### 3.2. Thermal Fluctuations and Dimer Placement Accuracy

In order to explore the room temperature limits in the positional uncertainty and control of the terminal carbon dimer, a series of MD simulations of the Si/Ge-doped extended diamondoid probe structure (Fig. 4) were carried out for a total time of 10 ns each. This is an adequate amount of time to compute the phase space distribution of the positions and momenta of the terminal carbon atoms in the extended Si/Ge diamondoid tools. Figure 10 shows plots of sampled xy coordinates of the two dimer carbon atoms attached to the Si- and Ge-doped diamondoid probes, taking T = 298 K. This corresponds to the dimer coordinate plane parallel to the plane of the diamond surface. The simulation for the Si and Ge diamondoid probes are very similar, both predicting a vibrationally active  $C_2$  dimer.

The uncertainties in the positions of the terminal carbon atoms attached to the Si probe, relative to their equilibrium positions, are approximately  $\Delta x = \pm 0.25$  Å and  $\Delta y =$  $\pm 0.19$  Å, for a total positional uncertainty of  $\Delta q = \pm 0.31$  Å (0.62 Å full range). Likewise, for the Ge probe, the positional uncertainties are  $\Delta x = \pm 0.34$  Å and  $\Delta y = \pm 0.31$  Å, for a total positional uncertainty of  $\Delta q = \pm 0.46$  Å (0.92 Å full range). The larger deviations in the atomic positions of the terminal carbon atoms in the Ge diamondoid probe are due to the differences between the Ge-C and Si-C vibrational frequencies. The symmetric and asymmetric Si-C stretching frequencies are 809 and 824  $\text{cm}^{-1}$ , respectively. The symmetric and asymmetric Ge-C stretching frequencies are 558 and 629 cm<sup>-1</sup>, respectively. A larger vibrational stretching frequency is characteristic of a stiffer bond that is less subject to large amplitude thermal fluctuations (and vice versa for lower frequency molecular vibrations).

#### 3.3. Dimer Placement on Bare Diamond C(110) Surface

This section reports results from both stationary point calculations and *ab initio* molecular dynamics simulations of the Si/Ge-triadamantane placement of carbon dimers onto the bare (dehydrogenated) diamond C(110) surface.



Figure 11 shows the minimum energy reaction path potential energy surfaces for tool adsorption and retraction, for the silicon tool (above) and the germanium tool (below). There are three stationary points of primary importance for the analysis of tool adsorption and retraction. These are the separated dimerized tool+substrate (inset images at left), the tool/substrate complex (inset images at center), and the separated tool+dimerized surface (inset images at right). Table 4 lists the relevant internal coordinates of the tool/substrate complexes for the Si- and Ge-triadamantane tools.

As may be deduced from Figure 11, the anticipated sequence of events is as follows: (1) approach of the dimerized tool tip toward a predefined location on the C(110) surface of the diamond substrate  $\rightarrow$  (2) adsorption of the dimerized tool tip onto the substrate surface (deposition of the C<sub>2</sub> dimer)  $\rightarrow$  (3) retraction of the tool tip leaving behind the deposited C<sub>2</sub> dimer. In order for these events to occur as



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Figure 11. Reaction path potential energy plots for adsorption and retraction of the Si-triadamantane tool (top) and the Ge-triadamantane tool (bottom).

 Table 4.
 Internal coordinates for optimized Si/Ge-triadamantane/diamond substrate complex.

Si Tool/Diamond substrate		Ge Tool/Diamond substrate	
Coordinate	Value	Coordinate	Value
$\overline{\begin{array}{c}C_{ad}-C_{ad}\\C_{ad}-C_{s}\\C_{ad}-C_{s}\\Si-C_{ad}\end{array}}$	1.607 Å 1.529 Å 1.913 Å 1.893 Å	$\begin{array}{c} C_{ad}-C_{ad}\\ C_{ad}-C_s\\ C_{ad}-C_s\\ Ge-C_{ad} \end{array}$	1.604 Å 1.527 Å 1.913 Å 1.977 Å

predicted, the energy of the products (tool+ dimerized surface) should be lower than the energy of the reactants (dimerized tool+surface)—that is, ideally, the reaction should be exothermic. However, this is not a strict requirement because the dimer deposition may still be favored kinetically. Identifying the potential energy surface connecting reactants from products allows the prediction of events during and after the approach and retraction of the dimer placement tool.

A potential energy curve along the minimum energy pathway separating reactants from products can be constructed by computing the energies of the optimized reactants (Fig. 11, at left) and products (Fig. 11, at right). This was accomplished using an approach similar to previous reaction path curves via a series of constrained optimizations, with the results for both the Si- and Ge-triadamantane tools shown in Figure 11. As expected, the adsorption of both dimerized tools is exothermic, with surface adsorption energies of -3.53 eV and -3.69 eV for the Si- and Ge-triadamantane tools, respectively. However, an unexpected result is that the overall reaction (as illustrated from the two endpoints in Fig. 11) is endothermic, with reaction enthalpies of 1.85 eV and 0.66 eV for C<sub>2</sub> placement from the Si- and Ge-triadamantane molecules, respectively, making the tools more efficient at removing dimers than depositing them.

Following adsorption of the dimer placement tool onto the bare C(110) surface of the diamond substrate, a force is applied to retract the triadamantane tool from the surface, and during retraction, there are two pathways that can be taken. The system will always attempt to follow the lowest energy reaction path. In the two cases outlined in Figure 11, the lowest energy pathway is to retain the carbon dimer to the triadamantane tool as opposed to leaving the terminal carbon dimer bound to the diamond substrate surface. Thus, one simple interpretation of these results is that the proposed dimer placement tools fail to accomplish their designated task.

However, since every reaction channel of a branched chemical reaction has a finite probability of being sampled, depositing a  $C_2$  dimer onto the diamond surface may occur a finite percentage of the time. A small number of AIMD simulations (five for each tool) were performed to investigate the effects of internal energy on the tool retraction event. Each simulation was performed for a total time of

1 ps, and the tool was retracted by pulling the six outermost carbon atoms away from the diamond surface. All five of the simulations for retraction of Si-triadamantane failed to deposit the carbon dimer to the diamond surface. But for the Ge-triadamantane retraction simulations, one of the five simulations left the carbon dimer deposited onto the substrate surface as desired. Since the additional energy penalty of  $\sim 1 \text{ eV}$  for depositing the carbon dimer from the Ge-triadamantane is small compared to the  $\sim 17 \text{ eV}$  of internal energy, C<sub>2</sub> deposition will occur using the Ge tool a small percentage of the time ( $\sim 20\%$ ). (The Si-triadamantane has a larger additional energy penalty of  $\sim 3 \text{ eV}$  for dimer deposition, so the desired placement of the C<sub>2</sub> dimer using the Si tool will occur a correspondingly smaller percentage of the time.)

Achieving the desired dimer placement in one of every five attempts (with no deleterious changes in either tool or diamond surface during the other four of five attempts) may be an acceptable level of success for early experimental proof-of-concept demonstrations, but is inefficient from the standpoint of future high-speed, high-reliability molecularly precise materials fabrication. Further work should examine the impact of lower operating temperatures, the possible utility of Sn- and Pb-triadamantane molecules and other adamantane-based tool configurations proposed by Merkle and Freitas,<sup>2</sup> and other dimer placement tool variants that might provide a purely exothermic dimer deposition reaction.

#### 4. CONCLUSIONS

Dicarbon  $(C_2)$  terminated Si/Ge-triadamantane molecules are not predicted to be susceptible to intermolecular dimerization. If allowed to interact without individual positional restraint, free dimer-loaded triadamantane molecules would be prone to intermolecular dehydrogenation that can proceed with barriers that are thermally accessible at room temperature. Similarly, the removal of molecular hydrogen  $(H_2)$  from one triadamantane tool by another is an example of an intermolecular dehydrogenation reaction. If Si/Gedoped triadamantane molecules were bulk synthesized and allowed to freely interact without individual positional restraint, they would be prone to intermolecular dehydrogenation. These factors establish an important constraint on the manner in which C2-loaded triadamantane molecules and tools may initially be synthesized and later recharged-that is, activated tools must be positionally restrained during and prior to use.

Recharging of the dimer placement tools with acetylene requires large activation energies. Kinetics studies indicate that the rate of recharging is slow but can, in principle, be compensated by simultaneously recharging large numbers of tools or by recharging tools at elevated temperatures, plausibly allowing 1 Hz operation of the mechanosynthetic cycle. Recharging the probe with feedstock molecules constitutes a critical rate-limiting step and requires further study.

Molecular dynamics simulations of extended diamond probes predict a minimal room temperature positional uncertainty of  $\pm 0.31$  Å and  $\pm 0.46$  Å for Si and Ge dimer placement tools, respectively. From Part I,1 the minimum required positional placement accuracy for inserting a dimer onto the clean diamond C(110) surface at the desired global minimum (GM2) instead of the nearest transition state (TS') to an undesired defect (LM2-2) is  $\pm 0.6587$  Å and  $\pm 0.5377$  Å measured from the first or second carbon atom, respectively, in the second added dimer. However, purposeful construction of "defect" structures (e.g., LM2-2) could demand placement accuracies as small as  $\pm 0.2024$  Å.<sup>1</sup> Thus, when compared with distances of a carbon atom in a local minima to that of the same atom at the transition state leading to another stable minima, dimer placement accuracy appears only marginally adequate at room temperature and dimer misplacement remains a significant concern. The effects of lower operating temperatures on misplacement errors should be further investigated.

The overall deposition reactions are endothermic and, therefore, thermodynamically unfavorable for both Si and Ge tools. Retraction of the tool from the diamond substrate will retain the carbon dimer to the placement tool the vast majority of the time, so the proposed tools are inefficient at their designated task. However, depositing a C<sub>2</sub> dimer onto the diamond surface may occur a finite percentage of the time, which might be an adequate performance for early experimental proof-of-concept demonstrations. The ability of the Ge tool to deposit the dimer in ~20% of all attempts, despite its thermodynamic unfavorability, suggests that alternative dimer-loaded molecules, other tool variants or colder operating temperatures might provide improved deposition efficiency.

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