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Surface patterning by atomically-controlled chemical forces: molecular dynamics simulations

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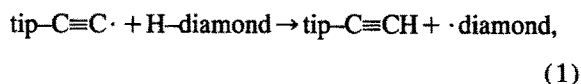
Abstract

The use of atomically-controlled reactive chemical forces via modified scanning-probe microscope tips provides a potentially powerful way of building nanodevices. In this work, we use atomistic simulations to explore the feasibility of one such system, namely the selective abstraction of hydrogen from a diamond surface using a tip with a chemisorbed ethynyl radical. We characterize reaction rates and energy flow at the tip, and conclude that they are sufficiently fast to make this approach feasible. We propose a novel tip design to perform the abstraction without inadvertently damaging the surface or probe tip.

Scanning-tunneling microscopy (STM) and atomic-force microscopy (AFM) are powerful techniques not just for imaging, but also for the engineering of matter at the atomic scale. To date, the manipulation of atomic structures with these techniques has included the controlled movement of atoms on surfaces by "sliding" the tip across the sample [1], the pick-up and movement of chemisorbed species by careful control of both the position and the potential difference between the tip and the surface [2], and the transfer of species from the tip to the surface by field emission [3]. Some of these atomic-scale manipulations are a result of the application of chemical forces in combination with field-induced forces. One approach that has yet to be realized, however, is the exploitation of specific chemical reactions with the atomic-scale precision offered by the AFM. If mastered, this approach would provide another important method for engineering new materials and devices at the atomic scale.

An ingenious use of reactive chemical forces has recently been proposed by Drexler [4], where he sug-

gested an ethynyl radical attached to the end of an STM or AFM tip could abstract hydrogen from a diamond surface with atomic-scale precision through the reaction:



Repeated application of reaction (1) would lead to an atomically precise pattern of reactive radical sites on a diamond surface, opening up the possibility of producing a myriad of new surface structures and nanometer-scale devices.

Reaction (1) would be possible, Drexler argued, because the C-H bond in ethynyl is much stronger than the tertiary C-H bond in molecules similar to diamond (experimental bond dissociation energies are 5.70 and 4.04 eV for ethyne [5] and isobutane [6], respectively). To be practical, however, a number of other crucial criteria must be fulfilled. For example, the barrier for abstraction has to be small, the rate of kinetic energy release from abstraction into bulk modes has to be fast compared to the reverse rate for reaction (1),

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rates for any competing reactions have to be small, some method is needed to signal that the reaction has taken place, and the radical on the end of the tip must be generated. Musgrave et al. [7] addressed the first issue using *ab initio* calculations, where they established that the barrier would be negligible and therefore the reaction would be very fast. The feasibility of this potentially important method, however, has yet to be firmly established given the other stringent considerations.

To further explore and quantify Drexler's idea for atomic-scale patterning of diamond surfaces, we have modeled reaction (1) with a diamond tip and diamond substrate using molecular dynamics simulations. These were carried out by integrating Newton's equations of motions with a third-order Nordsieck predictor corrector, using a constant time step of 0.25 fs. The forces were obtained from a reactive empirical bond-order (REBO) potential that accurately describes both small organic molecules and diamond and graphite surfaces [8]. The potential can be expressed as:

$$E_b = \sum_{i,j} \sum_{k < i} [V_R(r_{ij}) - B_{ij} V_A(r_{ij})], \quad (2)$$

where E_b is the binding energy, r_{ij} is the distance between atoms i and j , V_R is a pair-additive term that takes into account the interatomic core–core repulsive interactions, V_A is a pair-additive term that models the attractive interaction due to the valence electrons, and B_{ij} is a many-body empirical bond-order that modulates valence electron densities. This potential allows bonds to form and break and the hybridization of the carbon atoms to change, and has previously been used to simulate the nanomechanical and frictional properties of diamond surfaces [9].

The REBO potential used in this study includes improved analytic functions for the intramolecular interactions and an expanded fitting data base compared to previous versions of the method [8]. This data base includes molecular bond energies, barriers for abstracting a tertiary hydrogen from isobutane by hydrogen and various radicals (including $\cdot C_2H$), and vibrational frequencies and bending modes of many organic molecules, including ethyne. This extensive fitting data base combined with the reactive properties of the potential make this method very appropriate for the current study. Complete details of this new potential are provided elsewhere [10].

The system is represented as follows. A diamond (111) surface made up of thirty atoms per layer and twelve carbon layers is used; the top and bottom carbon layers are hydrogen terminated. The bottom three layers (two carbon, one hydrogen) are not allowed to evolve in time. The middle six carbon layers are allowed to evolve in time according to the atomic forces from the potential. A Langevin thermostat is also applied to these atoms, which provides random frictional forces to maintain the temperature at a constant value. The motion of the remaining atoms are governed by Newton's equations of motion with no additional constraints. Periodic boundary conditions are applied in the directions parallel to the plane of the surface to simulate an infinite slab.

The tip consists of another diamond slab with thirty atoms per layer and ten carbon layers. The top carbon layer is hydrogen-terminated, while some of the dangling bonds on the bottom carbon layer are hydrogen-terminated, and some are attached to a sharp, three-layer diamond asperity that is connected to the ethynyl radical (see Fig. 1). The top three layers (two carbon, one hydrogen) are not allowed to evolve in time, but are moved manually in the direction perpendicular to the surface. Again, the middle six carbon layers have a Langevin thermostat applied to them, and the remaining atoms have no constraints. These simulations are carried out at 300 K.

A total of six simulations were carried out where the tip is brought into the vicinity of the surface. In each case, the diamond tip and surface are equilibrated for about 1.0 ps, and then the tip is moved toward the surface at a constant velocity of 2.0 Å/ps until the average distance between the ethynyl radical and the surface is 1.6 Å. The tip remains within 0.1 Å of that position for between 0.5 and 1.0 ps, and is then withdrawn at the same rate. In each case, we observe spontaneous and irreversible abstraction of the surface hydrogen atom.

Snapshots from a representative simulation are shown in Fig. 1, and some atoms in Fig. 1a are marked for convenience. Fig. 1a is a closeup of the tip and surface at time = 1.30 ps just prior to abstraction. Fig. 1b occurs 0.01 ps later, at which point the hydrogen atom has been abstracted by the tip. The hydrogen atom is abstracted as soon as the ethynyl radical comes within about 1.5 Å of the surface. The barrier for abstraction is found to be very small for diamond (111), on the

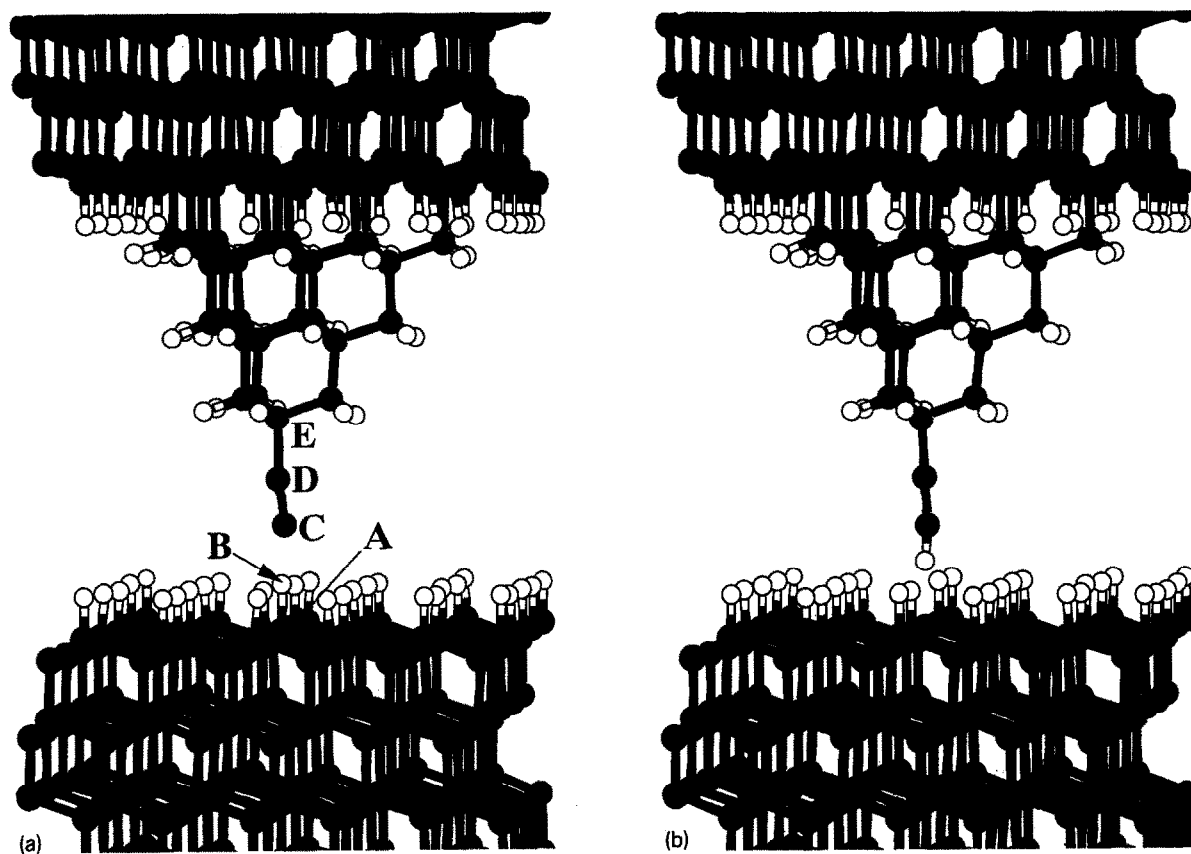


Fig. 1. From a simulation of hydrogen abstraction from hydrogen-terminated diamond (111) with a chemically modified tip. The grey spheres represent carbon atoms and the white spheres represent hydrogen atoms. (a) Time = 1.30 ps. The ethynyl radical on the end of the tip is descending towards the surface; (b) Time = 1.31 ps. The ethynyl radical has abstracted the hydrogen atom from the surface leaving behind a reactive site.

order of 10^{-4} eV, which agrees with Musgrave et al.'s estimation of a zero barrier [7]. The bond length between the two ethynyl carbon atoms (C and D) decreases from about 1.27 Å initially to 1.21 Å following the hydrogen abstraction, which is consistent with the strengthening of the triple bond as the ethynyl changes from a radical to a neutral molecule. This same change is also observed for the addition of a hydrogen atom to a gas-phase ethynyl radical.

Fig. 2 shows the distance between atoms labeled A and B, and B and C as a function of time. The tip descends until time = 1.48 ps, and then is withdrawn. Note that the curves cross at the time of abstraction (time = 1.31 ps) and that the oscillation of the B–C bond length is enhanced for approximately 0.3 ps following abstraction.

After abstraction, the atoms at the end of the tip have both excited stretching and bending modes. Characterization of the rate and mechanism of the flow of energy out of these modes is important to establish the irreversibility of reaction (1). Fig. 3 shows the kinetic energy of atoms A, B, C, D and E as a function of time. Atom A experiences an increase in kinetic energy of 0.3 eV at the time of abstraction that quickly dissipates into the lattice. In contrast, atom B has a 0.7 eV increase in kinetic energy at the time of abstraction, which dissipates more slowly in 0.8 ps.

Some of the hydrogen atom's excess kinetic energy is dissipated through the tip. Atom C experiences an increase in kinetic energy of 0.4 eV a few tenths of a ps following the abstraction. This energy is, in turn, passed further up the tip, and the kinetic energy of atom

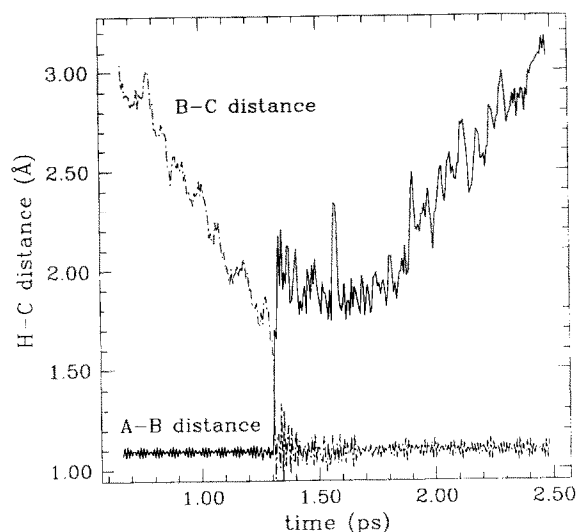


Fig. 2. The distance in (\AA) between atoms A and B (—), and B and C (---) as a function of time. The curves cross at time = 1.31 ps when the hydrogen atom is abstracted from the surface.

D increases by 0.4 eV some tenths of a ps later. However, atom E experiences no increase in kinetic energy that is above the noise. (In some simulations, an increase in energy is distinguishable from the thermal noise, but it is never greater than one third of atom D's excess energy.) This is because atom E is efficiently coupled to the bulk vibrational modes, and is therefore better able to quickly dissipate the excess kinetic energy.

Only about half of the hydrogen atom's extra energy dissipates through the tip and, therefore, another energy dissipation mechanism must exist. We find that surface collisions contribute to the energy dissipation. Following abstraction in the sample simulation, the hydrogen atom (atom B) collides ten times with four of the nearest six hydrogen atoms on the diamond surface. One particularly hard collision transfers 0.2 eV of energy, while the other collisions transfer much smaller amounts of energy, on the order of a hundredth of an eV. Both modes of energy transfer (vibrational through the tip and collisions between hydrogen atoms) are observed in each simulation, with the percentage of energy transfer via the latter mechanism varying between 35% and about 60%.

The above simulation represents an idealized situation, which is the norm in theory and the exception in

real experiments. For example, tip crashes are common occurrences in AFM and STM. To check what effect they would have on an experiment such as that outlined above, the simulation was repeated except that the tip was moved 1.4 \AA closer to the surface before it was withdrawn. When the ethynyl radical and the hydrogen atom are roughly 1.5 \AA apart the hydrogen atom is abstracted as before. However, as the tip continues downward, the ethynyl carbon atom on the end of the tip binds to the newly created radical site on the surface (atom A binds to atom C). Thus, when the tip withdraws, the ethynyl molecule and part of the tip remain behind on the surface. This neutralizes the tip and contaminates the surface.

Even if the tip does not crash into the surface, it might encounter surface defects, which are to be expected in a real system. During patterning, a common defect would be a radical site caused by a previous abstraction. Five simulations were performed in which the tip encountered a radical site. In four of these cases part of the tip becomes bound to the surface and stays behind when the tip is withdrawn.

To avoid these potential problems, we propose a new design for a tip, shown in Fig. 4. The ethynyl radical is surrounded by diamond asperities that act as sensors at the end of the tip. These sensors have several purposes: (1) they prevent the ethynyl radical from crashing into

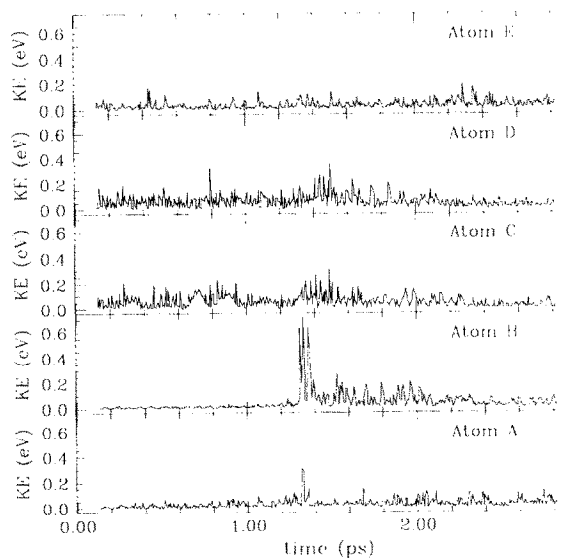


Fig. 3. The kinetic energy of the atoms marked A, B, C, D and E in Fig. 1a as a function of time.

the surface, (2) they provide precise control of the distance between the ethynyl radical and the surface through the measured load on the tip, and (3) they can detect gross features on the surface prior to abstraction.

Fig. 5 shows the load on the tip in nN/atom as a function of time as the abstraction simulation proceeds with the new tip. As the tip approaches the surface, the asperities surrounding the ethynyl radical are pressed into the surface, and, as a consequence, the load on the tip increases. When the tip is withdrawn, neither the tip nor the surface is damaged and the hydrogen atom is abstracted as desired.

Simulations of the atomic-scale manipulation of matter via reactive chemical forces have been performed to create specific reactive sites on a hydrogen-terminated diamond (111) surface and quantitative data are provided for the barrier, time scales and energetics involved. We also model non-ideal occurrences such as tip crashes or tips interacting with surface defects, and present a new design for a tip that should help prevent major tip and surface damage when tip crashes occur. This work did not address generation of the tip; however, others [4,7] have proposed methods for removing the hydrogen atom from the end of the tip to create the ethynyl radical.

Molecular dynamics simulations such as we have presented here provide encouraging results for a new

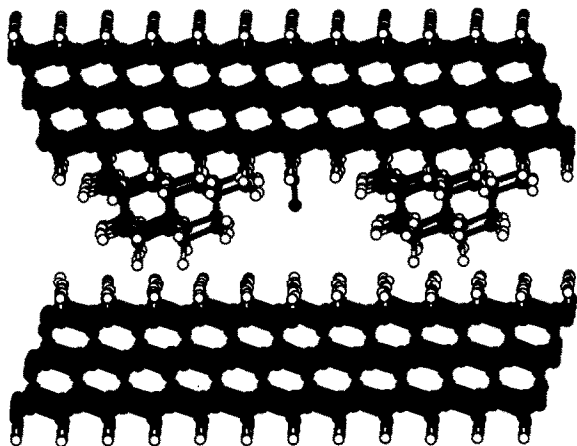


Fig. 4. Proposed design for a tip where the ethynyl radical is surrounded by asperities that act as sensors. The top two layers of the tip support and the bottom two layers of the surface are held rigid, the middle four layers of the tip support and surface have a Langevin thermostat applied to them, and the remaining atoms have no constraints placed upon them.

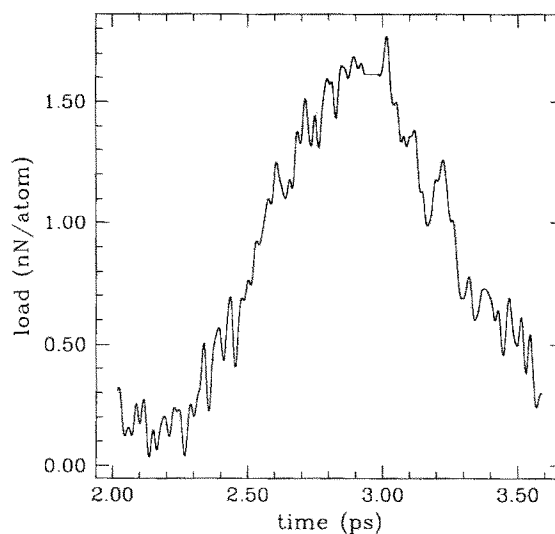


Fig. 5. Load on the tip in nN/atom as a function of time. The load increases as the tip moves downward and the sensors are pressed against the surface. As the tip is withdrawn, the load decreases. Abstraction occurs at time = 2.71 ps.

method of atomic-scale manipulation that should be applicable for a variety of surfaces in addition to diamond (e.g., silicon surfaces), and could ultimately lead to the manufacture of nanodevices and the construction of novel materials.

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