SIMULATED ENGINEERING OF NANOSTRUCTURES

D.W. Brenner[a], S.B. Sinnott[b], J.A. Harrison[c], and O.A. Shenderova[a]

[a] Department of Materials Science and Engineering, North Carolina State University, Raleigh, NC 27695-7907

[b] Department of Chemical and Materials Engineering, University of Kentucky, Lexington, KY 40506-0046

[c] Chemistry Department, United States Naval Academy, Annapolis, MD 21402

ABSTRACT

Results are reported from two molecular-dynamics simulations designed to yield insight into the engineering of nanometer-scale structures. The first is the initial stages of the indentation of a silicon substrate by an atomically-sharp diamond tip. Up to an indentation depth of approximately 0.6nm the substrate responds elastically and the profile of the disturbed region of the substrate normal to the surface reflects the shape of the tip apex. The disturbed region in the plane of the surface, however, reflects the symmetry of the substrate rather than that of the tip. As indentation progresses the damage to the substrate becomes irreversible, and the profile of the damage normal to the substrate surface approximately matches that of the tip, while the in-plane profile appears roughly circular rather than displaying the symmetry of either the tip or substrate. The tip maintains its integrity throughout the simulation, which had a maximum indentation depth of 1.2nm. The second study demonstrates patterning of a diamond substrate using a group of ethynyl radicals attached to a diamond tip. The tip is designed so that the terrace containing the radicals has an atomically-sharp protrusion that can protect the radicals during a tip crash. At contact between the tip and substrate the protrusion is elastically deformed, and five of six chemisorbed radicals abstract hydrogen atoms during the 1.25 picoseconds the tip is in contact with the surface. Displacement of the tip an additional 2.5Å, however, results in permanent damage to the protrusion with little deformation of the substrate.

I. Introduction

New techniques for patterning and engineering materials at the nanometer-scale using scanning-probe microscopes (SPM) are beginning to make possible the long-standing goal of nanometer-scale mechanical and electronic devices. Examples like the direct writing of nanometer-scale metallic lines by field-evaporation from a SPM tip, lithographic processes that take advantage of the nanometer-scale resolution of electrons emitted from SPM tips, and nanomachining of surfaces via mechanical forces have all been demonstrated.[1] Despite these advances, however, formidable challenges remain to the development and especially manufacturing of nanometer-scale structures. Among these is overcoming the inherently slow through-put for single tips, routine reproducible production of high-quality nanometer-scale structures, and the positioning of nanometer-to-macroscopic-scale interfaces.

To meet these challenges in nanometer-scale device development and manufacturing not only new innovations in engineering are needed, but also a thorough understanding of the atomic-scale processes responsible for the production of nanometer-scale structures. One powerful approach that is bringing new and unique insights into materials properties at nanometer scales is atomistic molecular-dynamics simulation. In this technique, trajectories of a collection of atoms subject to given interatomic forces are obtained by numerically integrating classical equations of motion. From careful analysis of the trajectories and their relation to properties such as stress and potential energy distributions, one can understand complicated atomic-scale dynamics in terms of nanometer-scale bonding and materials properties. A number of researchers have used atomistic simulations to model tip-surface interactions.[2] These have included the indentation of various metals,[3] ionic solids[4], and covalent materials such as silicon[5] and diamond.[6] Simulations have also been used to

explore the possible patterning of a diamond surface via chemical forces using modified SPM tips.[7]

Results are reported from two representative molecular-dynamics simulations designed to yield insight into the engineering of nanometer-scale structures. The first is a simulation of the initial stages of indentation of a silicon substrate by an atomically-sharp diamond tip, where the damage profile in the substrate as well as damage to the tip is characterized. The second study demonstrates patterning of a diamond substrate using a group of ethynyl radicals attached to a diamond tip. The tip is designed so that the terrace containing the radicals has an atomically-sharp protrusion that protects the chemisorbed radicals during a tip crash.

II. Nanometer-Scale Indentation of Silicon

The focus of the simulation is the initial stages of indentation where the substrate response changes from an elastic deformation to irreversible plastic damage. Of particular interest is whether the network structure of an atomically-sharp diamond tip is sufficiently well-developed to cleanly indent a silicon substrate, and whether the shape of an atomically-shallow indent is governed by the tip shape or is determined by the substrate. Both of these are important issues in nanometer-scale materials engineering because they test the limitations of feature size and shape that can be produced on a silicon substrate via nanometer-scale machining.

For the initial silicon substrate, atoms are placed in a diamond lattice at the experimental lattice constant with the (111) surface exposed. A total of 18 layers are used, each with 256 silicon atoms, for a total of 4608 atoms. A semi-infinite slab is modeled by applying periodic boundary

conditions in the two directions in the surface plane. No initial reconstruction of the surface or termination of surface radicals is attempted. The interatomic forces used to determine the atomic trajectories are obtained from the third version of Tersoff's bond-order potential for silicon.[8] This analytic function is composed of a sum of two exponential pair-additive terms, one representing core-core repulsion and a second representing bonding from valence electrons. The many-body aspect of the potential energy function enters through empirical bond-order functions that modulate the bonding pair terms according to local atomic bonding environments. The pair terms and bond-order functions are fit to an extensive data base that includes bulk elastic properties, energies and bond lengths for a variety of low and high-coordination solid structures, and the energy of vacancies and various interstitial point defects.

The end of the tip is illustrated at the top of Figure 1a. It is pyramidal in shape with exposed (111) facets. Surface radicals on each of the facets are eliminated by chemisorbed hydrogen. The tip symmetry in the surface plane of the substrate is an equilateral triangle, and the apex is a hydrogen-terminated six-membered carbon ring. The interatomic forces for the tip atoms are derived from a bond-order function similar to that used for the silicon substrate.[9] It has also been fit to solid-state elastic properties as well as energy and bond lengths of various low and high-coordination structures. In addition, the bond-order function describes bond lengths, energies, and vibrational frequencies for a wide range of hydrocarbon molecules. Because both solid-state and molecular structures are described, the interatomic forces are appropriate for the tip where the bonding network is intermediate between these two regimes.

The interactions between the tip and substrate atoms are modeled by pair-additive Lennard-Jones 12-6 potentials with parameters taken

from reference 10. Although convenient, this choice eliminates chemical interactions between the tip and substrate because the formation of chemical bonds is not possible. Nonetheless, this choice is sufficient for modeling physical interactions and resulting dynamics in the tip and substrate.

The motion of the atoms are determined by numerically integrating classical equations of motion using a Nordsieck integrator[11] with a constant timestep of 0.5 femtoseconds. The tip and substrate are first relaxed to their minimum energy configurations. The relative positions of the atoms in the bottom two layers of the substrate and the top two layers of the tip are then held rigid by not integrating equations of motion for these atoms. To simulate indentation, tip atoms are given an initial velocity of 100 m/sec toward the substrate. This rate of indentation is then maintained by moving the atoms in the top two layers of the tip 5×10^{-5}nm at each timestep up to a total indentation depth of 1.2nm. No thermostats or other temperature regulation of the system is performed during the simulated indentation.

Figure 1b illustrates the system after the tip has penetrated the surface 1.2nm. None of the silicon atoms appear above the surface of the substrate, but instead form a highly-localized, dense region surrounding the tip. This is in contrast to metals, where indentation results in a build-up of material above the substrate surface.[12] To more clearly illustrate the indentation profile in the substrate, Figure 2 shows side and top views of only those substrate atoms whose binding energies are disturbed by more than 0.1eV ($\approx$2% of the bulk atomic binding energy of silicon). Figures 2a and d are for an indentation depth of 0.2nm. The damage profile of the disturbed region normal to the surface (the side view) approximately matches that of the tip apex. The profile in the plane of the surface, however, has three-fold symmetry indicative of the

top layer of the substrate. After the tip is removed the substrate regains its initial structure indicating an elastic deformation.

Figures 2b and e are for an indentation depth of 0.5nm, or approximately two atomic layers into the silicon substrate. The profile of the disturbed region normal to the surface again approximates the shape of the tip apex. The profile in the surface plane, however, appears as a slightly distorted hexagon. This is indicative of the hexagonal symmetry of the substrate (if more than one layer is taken into account) rather than the triangular symmetry of the indentor. After the tip is removed the substrate regains its initial structure with no permanent deformation of the lattice.

Illustrated in Figures 2c and f are profiles for an indent depth of 1.2nm. The bonding topology in the disturbed region has been altered from that of the initial substrate and forms a highly-localized disordered region surrounding the tip. The in-plane profile of the disordered region of the substrate no longer matches that of the tip or substrate. Instead, it appears approximately circular, with a few perturbed atoms visible several lattice spacings away from the disordered region.

Figure 3 illustrates the tip atoms at the maximum indentation depth. The relative displacements of the atoms are small compared to those of the silicon substrate, and the tip maintains its bonding connectivity throughout the simulation. This is despite the bonding network of a diamond lattice not being fully developed in the tip apex.

Several conclusions can be drawn from this simulation. First, the damage to the substrate is highly-localized and consists of a high-density region surrounding the tip. No atoms appear above the surface plane, and no additional long-range atomic displacements are observed. Second, the profile of the perturbed surface atoms normal to the surface is

dictated by tip shape for both elastic and plastic deformations. Third, as long as the damage is reversible when the tip is removed, the in-plane profile of the indent is governed by the substrate symmetry rather than that of the tip. However, as the damage becomes permanent due to the rebonding of substrate atoms, the in-plane profile of the indent has neither the tip nor substrate symmetry, but rather appears circular. We are currently studying stress distributions in the substrate during indentation to try to better understand the origin of this result. It appears, however, that the in-plane shape of the indent at these scales is not controlled by the symmetry of the tip. Finally, we find that the tip maintains its integrity during the indent. As discussed below, this is not true for a diamond substrate. We are currently using simulations to characterize tip stability during scraping as a function of tip shape and indent depth.

III. Surface Patterning via Chemical Forces

Exploring a suggestion first made by Drexler,[13] Sinnott *et al.* used MD simulations to model the abstraction of a single chemisorbed hydrogen atom from a diamond surface via an ethynyl radical chemisorbed to an atomically-sharp diamond tip.[7] This proposed process is another way in which the SPM can be used to nanoengineer surfaces by spatially directing chemical forces. Rates and mechanisms of energy flow after abstraction were monitored and it was concluded that energy dissipation is sufficiently fast to make this reaction instantaneous and irreversible. However, it was also found that events such as tip crashes and the radical defects can destroy the tip. To eliminate these possibilities, a novel tip design was proposed where asperities are placed around the reactive site. These asperities keep the reactive site from coming too close to the surface and the tip from being destroyed during a crash. Furthermore, it was found that the load on the tip due to the interaction of the asperities with the surface can be used as a signal that abstraction has occurred.

Building on this concept of protecting the reactive region with asperities, we have simulated hydrogen abstraction from a hydrogen-terminated diamond (111) surface using the tip design illustrated in Figure 4a. The end of the tip has a terrace on which six ethynyl radicals have been chemisorbed that surround an atomically-sharp protrusion. One of the radicals is visible in the center-foreground of the image, while two other pairs of radicals are visible on either side of the protrusion about halfway back and in the far background, respectively. The sixth radical is behind the protrusion. With this arrangement the protrusion acts as the load sensor while six abstractions can in principle be carried out simultaneously. The diamond substrate used has a hydrogen-terminated (111) surface exposed. The substrate and tip are first allowed to relax to a minimum energy configuration using the hydrocarbon/diamond interatomic forces described above. The relative positions of the top two layers of the tip and the bottom two layers of the substrate are then maintained while the tip and substrate atoms are equilibrated to 300K. The tip is lowered toward the substrate following the procedure outlined above.

Figure 4b illustrates the simulation after the protrusion contacts the substrate but before any of the abstraction reactions have taken place. The protrusion has deformed slightly, with no visible deformation of the lattice. Figure 4c illustrates the system approximately 0.5ps after the protrusion first contacts the surface. The radicals chemisorbed to the tip in the foreground and far background on the left have both abstracted a hydrogen atom from the diamond substrate. The tip is left in contact with the substrate for 1.25ps before being retracted with the same approach used to lower the tip. As illustrated in Figure 4d, five of the six radicals abstract hydrogen, with the remaining ethynyl radical visible to the right of the protrusion halfway back. Note that the initial form of the protrusion is retained after the tip is removed.

The five abstraction sites on the substrate match the pattern of the radicals on the tip. Because these are highly-reactive sites, this pattern can be used as a template in a subsequent nanometer-scale engineering step such as the chemisorption of molecular species to the surface. By continuing this process of radical formation/chemisorption, it could in principle be possible to systematically engineer complex nanostructures.

Figure 5 illustrates the system after the tip is displaced an additional 2.5 Å toward the substrate after the protrusion first contacts the surface. The protrusion has been crushed and the ethynyl radicals effectively destroyed. It is apparent from this figure that the majority of deformation occurs in the protrusion with little deformation of the substrate. This is different from the silicon substrate simulated above, and is a result of the higher hardness of the diamond substrate relative to silicon. Because the protrusion, which is identical to the first few layers of the tip used above, is destroyed before the substrate is deformed, mechanical indentation cannot be used to modify the diamond lattice. While an atomically-sharp diamond can indent a silicon substrate, apparently the network structure of diamond is not sufficiently well developed in the tip to give it a mechanical strength comparable to a bulk diamond surface.

References

[1] For a collection of papers on this subject, see *J. Vac. Sci. Technol. B*, **13**, (1995).

[2] J.A. Harrison and D.W. Brenner, in *CRC Handbook of Micro/Nanotribology* Bushan. Ed. (CRC Publishers, 1995), chapter 10.

[3] U. Landman, W.D. Luedtke, N.A. Burnham, and R.J. Colton, *Science*, **248**, 454 (1990); H. Raffi-Tabor, J.B. Pethica, and A.P. Sutton, *Mat. Res. Soc. Symp. Proc.*, **239**, 313 (1992); O. Tomagnini, F. Ercolessi, and E. Tosatti, *Surf. Sci*, **287/288**, 1041 (1993).

[4] U. Landman, W.D. Luedtke, and E.M. Ringer, *Wear*, **153**, 3 (1992).

[5] J.S. Kallman, W.G. Hoover, C.G. Hoover, A.J. DeGroot, S.M. Lee, and F. Wooten, *Phys. Rev. B*, **47**, 3318 (1993).

[6] J.A. Harrison, C.T. White, R.J. Colton, and D.W. Brenner *Surf. Sci*, **271**, 57 (1992)

[7] S.B. Sinnott, R.J. Colton, C.T. White, and D.W. Brenner, *Surf. Sci.*, **316**, L1055 (1994).

[8] J. Tersoff, *Phys. Rev. B*, **39**, 5566 (1989).

[9] D.W. Brenner, *Phys. Rev. B*, **42** 9458 (1990). The version used here includes a slightly different form that improves the elastic properties for diamond (D.W. Brenner, S.B. Sinnott and J.A. Harrison, unpublished).

[10] M.P. Allen and D.J. Tildesley, *Computer Simulation of Liquids* (Clarendon Press, Oxford, 1987), pg. 21; parameters for carbon are used for silicon.

[11] C.W. Gear, *Numerical Initial Value Problems in Ordinary Differential Equations* (Prentice-Hall, Englewood Cliffs, NJ, 1971), pg. 148.

[12] J. Belak and I.F. Stowers in *Fundamentals of Friction: Macroscopic and Microscopic-Scale Processes*, (Kluwer, Dordrecht, 1995), pp.511-520.

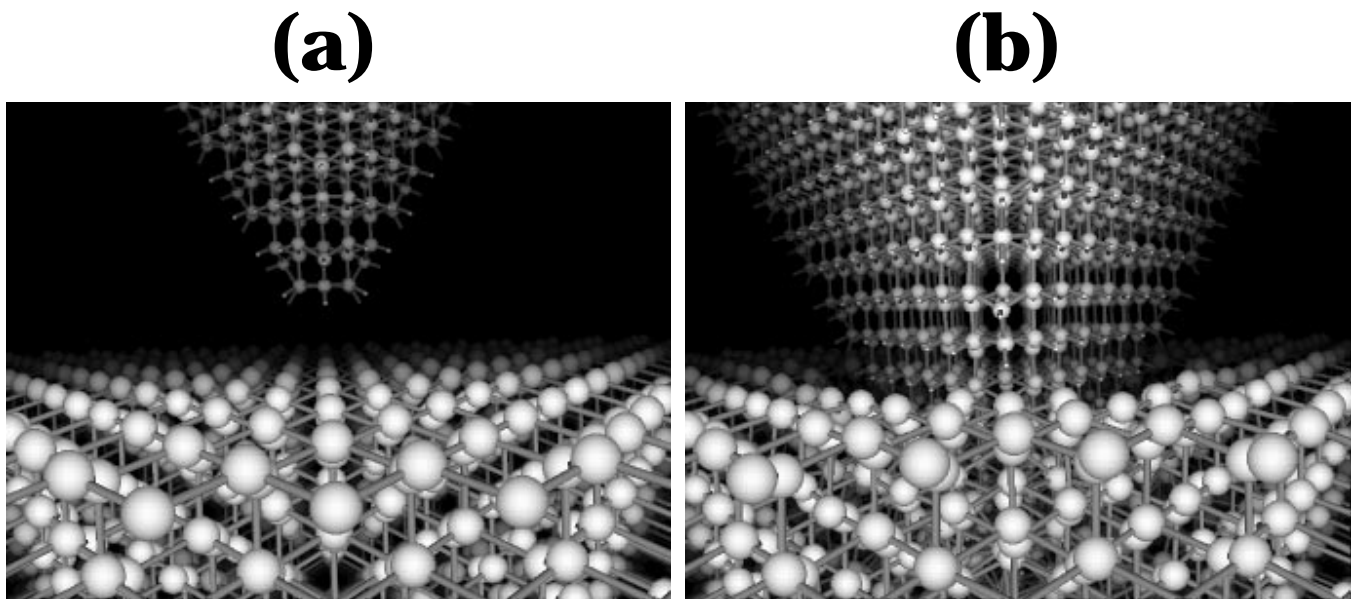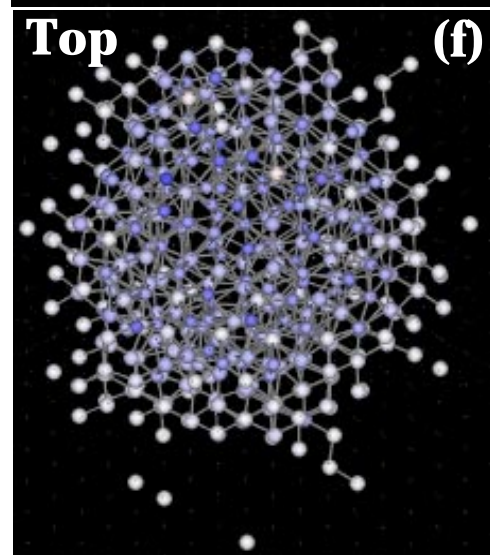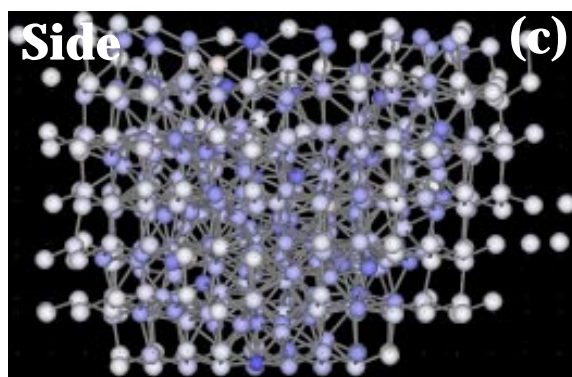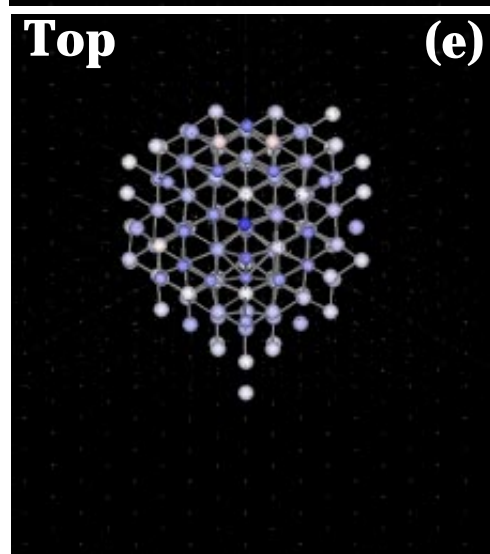[13] K.E. Drexler, *Nanosystems: Molecular Machinery, Manufacturing and Computation*, (Wiley, New York, 1992).
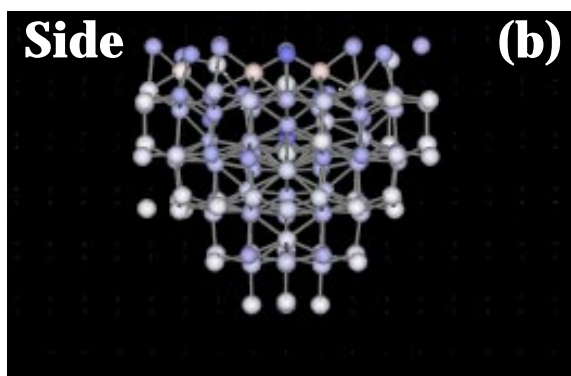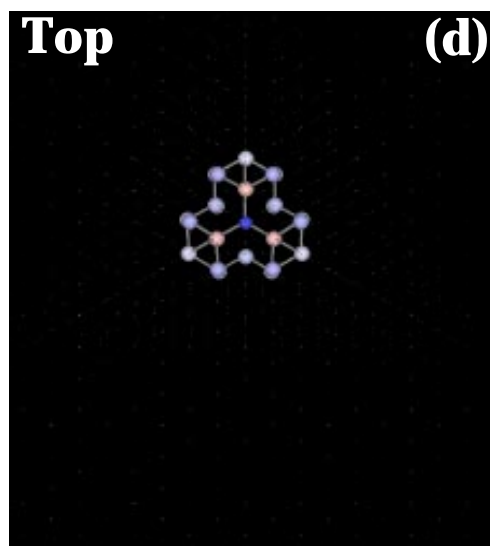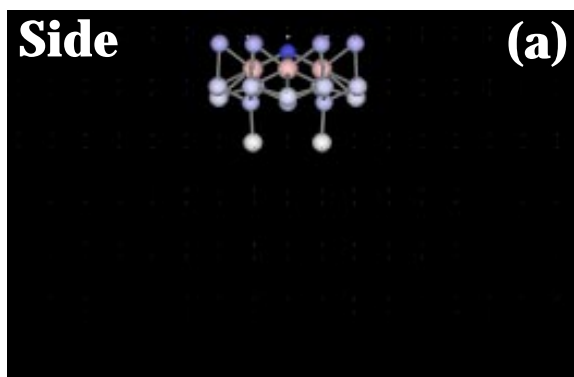
Figure 1: Snapshots illustrating the surface region during indentation. The small spheres on the diamond tip are hydrogen atoms. a) Initial configuration. (b) Indentation of 1.2 nm.

Figure 2: Illustration of silicon atoms whose binding energies are disturbed by more than 0.1eV. (a), (d) Indentation depth of 0.2nm. (b), (e) Indentation depth of 0.5nm. (c), (f) Indentation depth of 1.2nm.
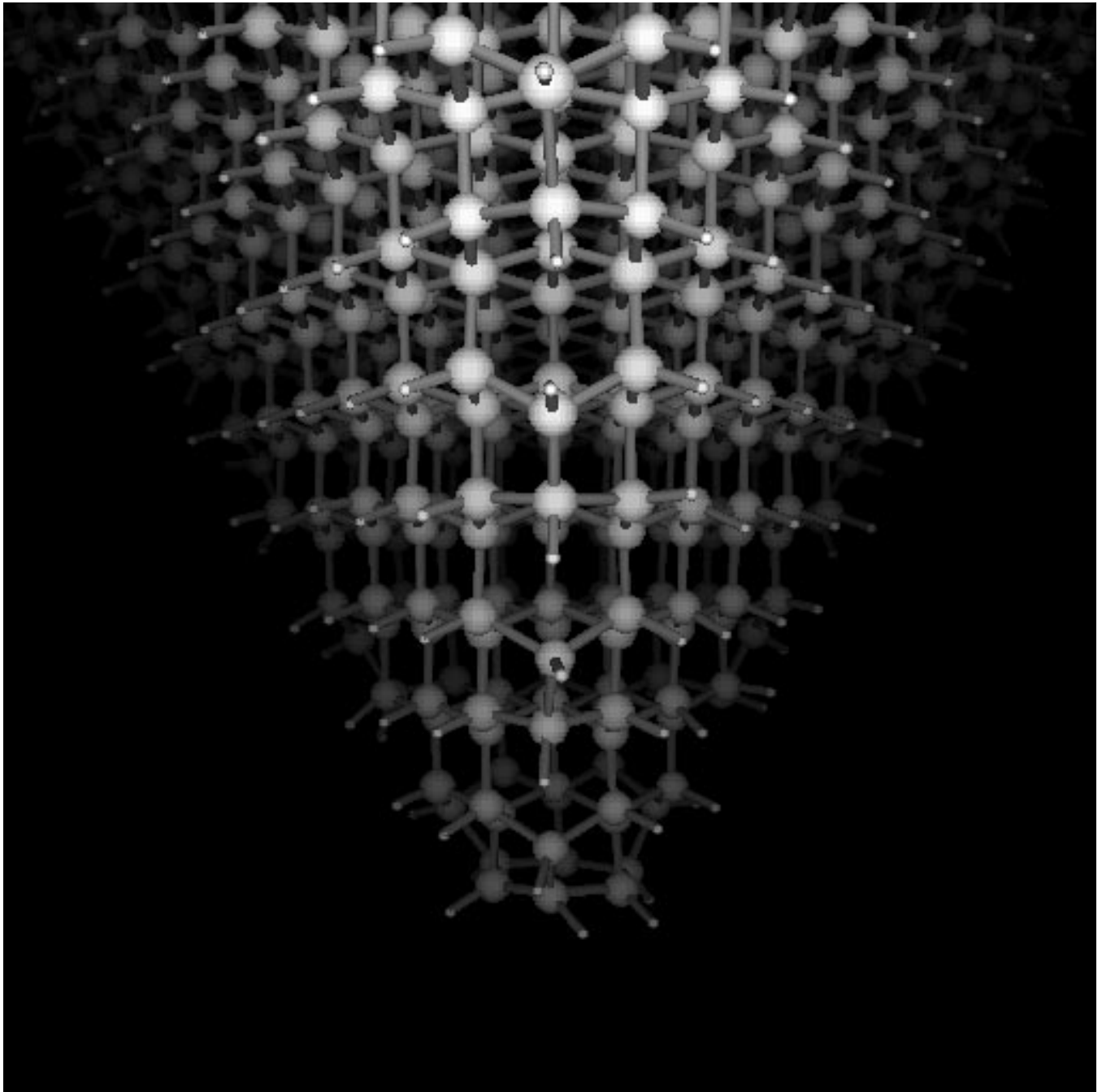
Figure 3: Illustration of the tip atoms at the maximum simulated indentation depth of 1.2nm.
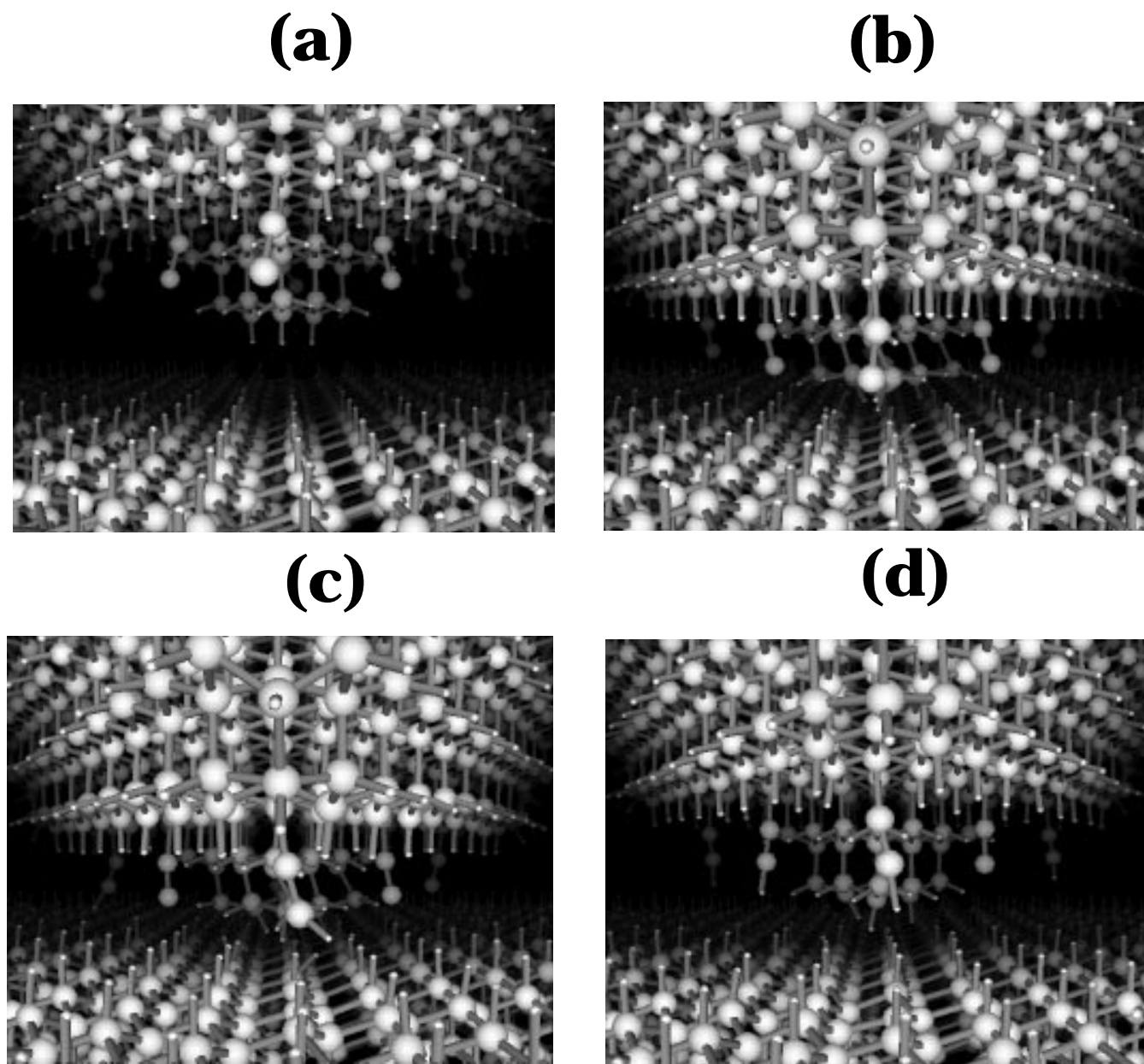
(a)

(b)

(c)

(d)

Figure 4: Snapshots illustrating the tip used to model chemical abstraction. The top of the figure shows the tip and chemisorbed ethynyl radicals, while the bottom is a hydrogen-terminated diamond (111) surface. (a) Initial configuration. (b) Just after the protrusion on the tip contacts the surface. (c) System 0.5ps after protrusion contacts surface. (d) After the tip is lifted from the substrate.
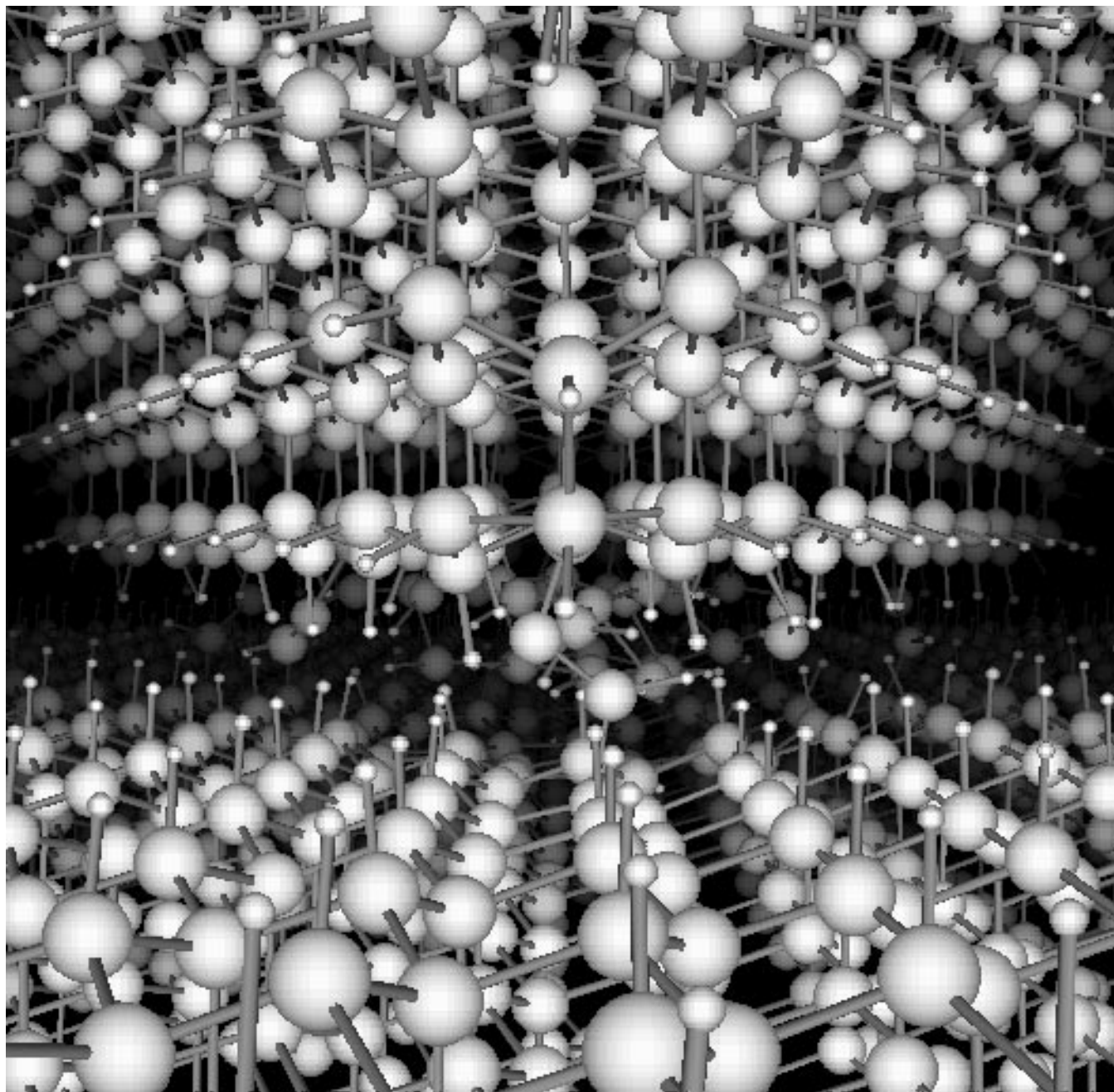
Figure 5: Illustration of the system after the tip is lowered an additional 2.5Å. The protrusion is irreversibly damaged.