1 of 1

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Fabrication Technology

Kenneth L. Blaedel

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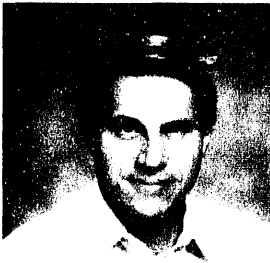Lawrence Livermore National Laboratory

Fabrication Technology

Kenneth L. Blaedel

Fabrication Technology

The mission of the Fabrication Technology thrust area is to have an adequate base of manufacturing technology, not necessarily resident at Lawrence Livermore National Laboratory (LLNL), to conduct the future business of LLNL. Our specific goals continue to be to (1) develop an understanding of fundamental fabrication processes; (2) construct general purpose process models that will have wide applicability; (3) document findings and models in journals; (4) transfer technology to LLNL programs, industry, and colleagues; and (5) develop continuing relationships with the industrial and academic communities to advance our collective understanding of fabrication processes.

The strategy to ensure our success is changing. For technologies in which we are expert and which will continue to be of future importance to LLNL, we can often attract outside resources both to maintain our expertise by applying it to a specific problem and to help fund further development. A popular vehicle to fund such work is the Cooperative Research and Development Agreement with industry.

For technologies needing development because of their future critical importance and in which we are not expert, we use internal funding sources. These latter are the topics of the thrust area.

Three FY-92 funded projects are discussed in this section. Each project clearly moves the Fabrication Technology thrust area towards the goals outlined above. We have also continued our membership in the North Carolina State University Precision Engineering Center, a multidisciplinary research and graduate program established to provide the new technologies needed by high-technology institutions in the U.S. As members, we have access to and use of the results of their research projects, many of which parallel our own precision engineering efforts at LLNL.

Kenneth L. Blaedel
Thrust Area Leader

Section 5
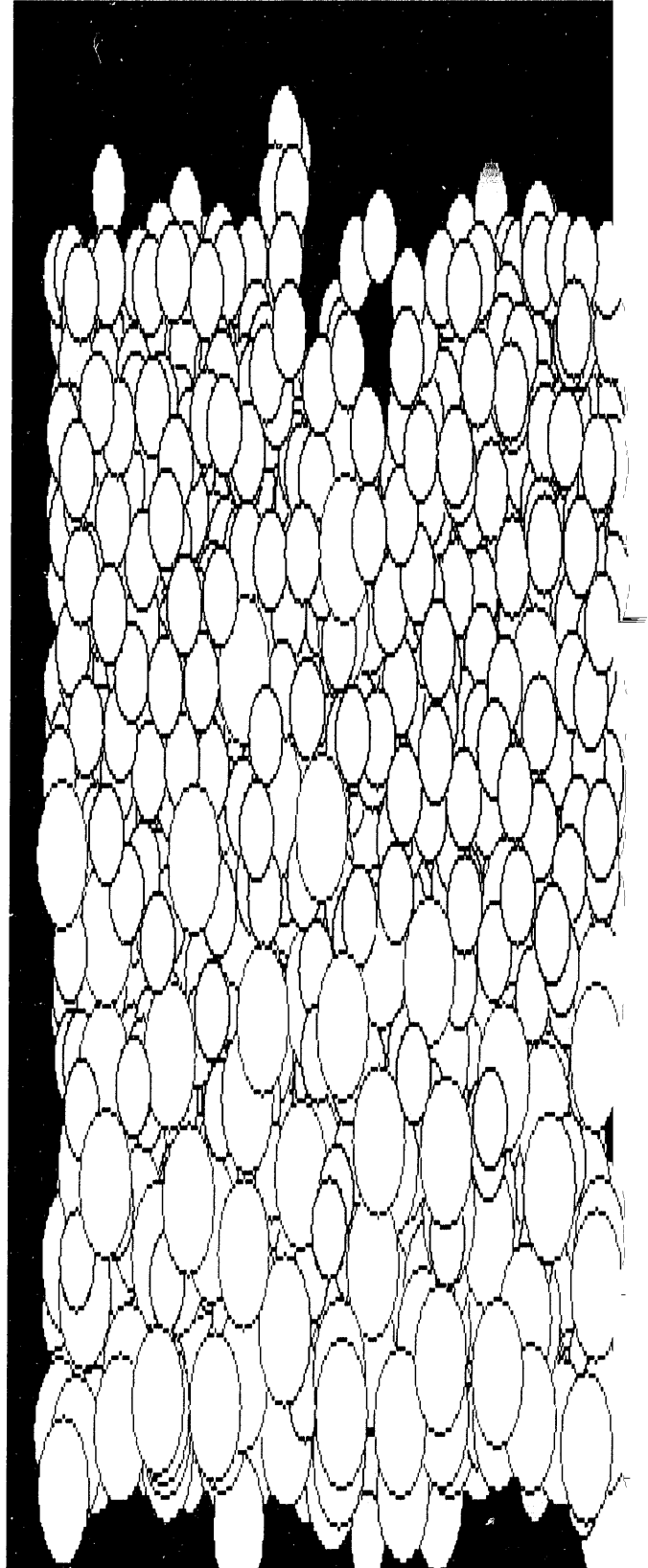
5. Fabrication Technology

Overview
Kenneth L. Blaedel, Thrust Area Leader

Fabrication of Amorphous Diamond Coatings

Laser-Assisted Self-Sputtering

Simulation of Diamond Turning of Copper and Silicon Surfaces

Fabrication of Amorphous Diamond Coatings

**Steven Falabella and
David M. Sanders**
*Materials Fabrication Division
Mechanical Engineering*

David B. Boercker
*Condensed Matter Physics Division
Physics Department*

Amorphous diamond is a hard, electrically insulating, inert and transparent form of carbon that has the sp^3 bond character of crystalline diamond, but lacks a long-range ordered structure. The potential applications of amorphous diamond (a:D) are many. This material has several important advantages over conventional chemical-vapor-deposition diamond coatings, making it a more attractive coating for applications such as cutting tools, tribological surfaces, spacecraft components, and medical implants. In FY-92, we produced carbon coatings with hardness rivaling that of natural diamond, and began to evaluate the use of this material in practical applications. We have produced amorphous diamond films on a routine basis, and have produced coatings up to 8 μm thick on carbide tool bits. The combination of extreme hardness, low atomic number, smoothness, low friction, and low deposition temperature make a:D unique in the world.

Introduction

The physical properties of diamond make it an ideal material for many critical applications. However, natural diamonds are rare, expensive, and too small for many applications. A substantial amount of work is being done to produce diamond coatings on less expensive substrates, to take advantage of the properties of diamond without the need for large diamond monoliths. There are four critical problems that need to be solved before diamond coatings will be practical:

(1)   Temperature of deposition. High process temperatures eliminate aluminum, tool steels, glasses, and polymers as possible substrate materials, limiting the usefulness of the coating. Also, heating and cooling of substrates adds time, complexity, and expense to the coating process.

(2)   Adhesion to substrate. Thin films rely on the substrate for much of their mechanical integrity, depending on adhesion to the substrate for support. Failure of adhesion usually means unpredictable and rapid failure of the coated part.

(3)   Stress. Internal stress limits the permissible thickness of a coating when the stress in the coating causes delamination or deforms the substrate.

(4)   Smoothness of coating. In tribological applications, smoothness is essential for low friction and long life. Also, for optical coatings, any coating roughness will degrade the performance of the optic.

Diamond films produced by chemical vapor deposition have difficulty in all four areas. The adhesion is poor; deposition temperature is generally above 800°C; thermally induced stress is often excessive; and the polycrystalline films produced have high surface roughness, requiring expensive polishing.

The situation is very different for a:D. Amorphous diamond coatings are produced by the condensation of carbon ions on cooled substrates (at room temperature or below). They also replicate the substrate surface finish, and can be very adherent. We feel that only adhesion and stress are still problems, and may exclude the use of some substrate materials. However, an adherent interface can be created in several ways: a thin layer of a binder material can be deposited before coating with a:D; or, since the process is ion-based, substrate biasing can form a diffuse, adherent interface. Stress can be lowered by several means:

increasing the incident ion energy by rf-biasing the substrate during deposition; increasing the substrate temperature; and incorporating impurity elements in the film. These methods to reduce stress and improve adhesion may also reduce certain qualities of the coatings, so tradeoffs will need to be made.

We have identified four areas where the extraordinary properties of a:D can have a large impact. The first is the coating of tool bits for use on diamond turning machines to exploit the toughness, adhesion, hardness, and wear resistance of a:D. If successful, this process will lead to cost savings where the surface finish and precision required is less than that produced by diamond turning, yet better than can be produced by conventional cutting bits. At present, the finish obtained on a part is limited by the edge quality of our coated carbide bits, which in turn is limited by current polishing methods. If a better method can be found to form the tip radius of a coated bit, geometries and precision not practical with natural diamond could be achieved.

Second, the surfaces of metrology blocks, caliper faces, and precision slides can be coated and polished to provide hard, smooth, and wear-resistant surfaces that will not change dimensions or scratch the parts under test. This will allow more confidence in the continued accuracy of the tools, save re-calibration time, and prolong the life of the equipment.

Third, there are applications that would benefit from the tribological properties of a:D, in air and in vacuum. The friction coefficient for a:D is measured to be 0.2 or less in all conditions. There are several important areas where a long-life solid lubricant could have prevented the failure of mechanical systems on spacecraft, and would enable new mechanisms to be practical in spacecraft. A representative example is the Galileo probe's main antenna that failed to deploy due to the failure of the MoS_2 lubricant on its opening mechanism. Coating both disk surface and heads will reduce the damage caused by 'head crashes' and may enable magnetic recording media of higher density by allowing smaller head-to-disk distance.

Finally, there are several applications of a:D in the medical field. Due to the wear resistance and biocompatibility of a:D, the potential is great for coating scalpels, replacement-joint wear surfaces, and other implanted parts. If a suitable technique is developed to allow a coated blade to achieve the sharpness of a natural diamond scalpel, the potential benefits would be tremendous. Incisions made by diamond scalpels heal up to five times faster than those made with steel blades, reducing recovery times (and hospital costs) for many surgical procedures. The high cost of diamond scalpels (several thousand dollars each) is now the main limit to their use.

Progress

In FY-92, we produced carbon films with our filtered cathodic-arc system, which was developed in previous years. The cathodic-arc source produces a carbon ion beam from a graphite target, in a high vacuum environment.[1] Our goals for the year were to investigate the conditions under which a:D is formed, to improve adhesion to various substrate materials, to model the deposition process using molecular dynamics (MD), and to reduce residual stress in the films, which is required to deposit greater thicknesses.

We installed a cooled and biasable holder to control the substrate temperature during deposition. Initially, the holder was cooled by liquid nitrogen, but we found that water cooling produced equivalent results. By using a high-voltage bias for the first few seconds of coating, we have produced coatings on cemented carbide tool bits with adhesion above 10 kpsi (limit of the Sebastian pin-pull tester). We are investigating methods that will measure adhesion to higher values.

We were able to achieve hard carbon coatings that are low in hydrogen content. The hardness of carbon films is inversely related to the hydrogen content; e.g., 10 to 20% hydrogen in a carbon film (known as diamond-like-carbon, or DLC) reduces the hardness by a factor of four. The hydrogen content of our coatings was measured to be less than 0.1%, using forward recoil scattering (FRS). We determined the density of our films from the areal density obtained, using Rutherford backscattering (RBS) and the film thickness. We measure the density of a:D to be 2.7 $\pm$ 0.3 g/cc, which is between graphite at 2.26 g/cc and diamond at 3.5 g/cc.

One of the most appealing properties of amorphous diamond is its extraordinary hardness. However, standard hardness tests made by indenting are generally difficult to interpret when the coating is thin and harder than the substrate material. To get a true measurement of the coating hardness, the indent depth must be less than 7 to 20% of the coating thickness.[2] Quantitative hardness tests are in progress with an ultra-microhardness tester, which uses such a small indent that the measurement is not influenced by the substrate. A standard Vickers indent of a tungsten carbide tool bit coated with 8 μm of a:D with loads up to 500 g gives a hardness of 10,000 $\pm$ 10%, the same as

natural diamond. At 500 g, the indent depth is 17%. To put the severity of this test in perspective: the stress put on the film at the 500-g load is over 17 × 10⁶ psi. For thinner coatings, the Vickers test gives a hardness above 5000 at low indent loads (25 g) and then decreases, as the load increases to roughly the substrate hardness value (hardness of tungsten carbide is ~ 2000 Hv). To get another assessment of the hardness, we used an abrasion test. We assessed the hardness of the a:D coatings that we produced, by abrading various hard materials against a coated plate. We were able to polish facets in all materials attempted, including natural and synthetic diamond, indicating that the coating is approximately as hard as diamond. This may point to yet another application, i.e., the surfacing of ceramic, or even diamond tools.

The greatest difficulty with a:D films is their high intrinsic stress. Our filtered cathodic-arc source produces a fully ionized beam of carbon with a mean energy of 22 eV³, and produces stress levels of 6 to 10 GPa. This can be reduced by increasing the incident ion energy impinging on the substrate. We used a 13.56-MHz rf supply to provide a bias during deposition. Since the films produced are non-conductive, rf bias is required to maintain the potential at the film surface during coating. We have reduced the intrinsic stress in a:D films by a factor of two using bias alone, and by a factor of five using a combination of bias and the incorporation of 7% nitrogen in the films. A plot of the residual stress vs bias voltage on the substrate (DC level) is shown in **Fig. 1**. Coatings with and without nitrogen are shown. Although residual stress is reduced by the addition of nitrogen, the measured hardness of the films is reduced to ~ 6000 Hv, as noted above. Residual stress was inferred from the bowing of two-inch silicon wafers. On carbide-forming materials, the adhesion is sufficient to produce thick coatings, without delamination of the coating caused by the compressive stress, as long as the bias voltage is kept above 150 V during deposition. The 8-μm-thick coating produced on a tungsten carbide tool bit was limited only by source material depletion.

The fine structure of a:D was characterized by TEM and electron diffraction. TEM showed no evidence of any ordered structure down to 10Å, indicating its amorphous nature. Unlike natural diamond or DLC, a:D has a flat transmission spectrum from 0.8 to > 50 μm, which is due to its amorphous nature and the lack of hydrogen. The transmission of a free-standing film was measured using a FTIR spectrophotometer. From the interference between the front and back surfaces and
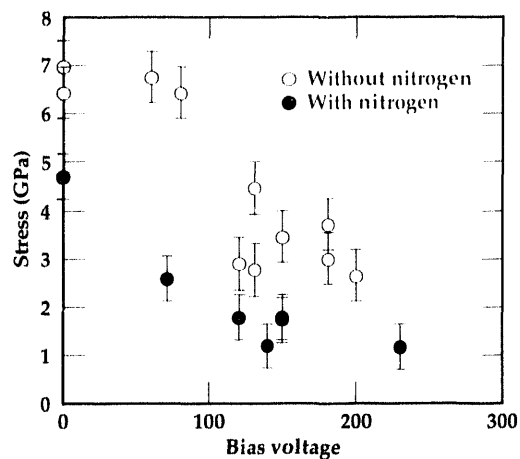

Figure 1. *The intrinsic stress in amorphous diamond films vs bias voltage. Stress is reduced substantially by the addition of bias during deposition, and even further by the addition of nitrogen. Data taken with no nitrogen during deposition are in open circles; data taken with a nitrogen background are in solid circles. In both cases, the stress reaches its lowest value around 150 V and is roughly constant above that value.*
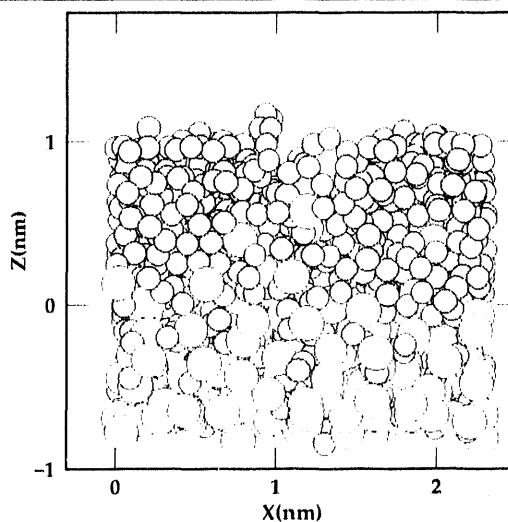

Figure 2. *A molecular dynamics simulation of 20 eV carbon (880 atoms) impinging on a silicon surface. Substantial mixing occurs at the interface. The carbon atoms are shown as dark gray circles; the silicon atoms are light gray. The view is parallel to the original silicon surface.*

the measured thickness of the films, we determined the index of refraction of our a:D to be in the range 2.47 to 2.57. This is close to 2.42, the refractive index of natural diamond.

Using MD simulations, we have modeled the condensation of carbon atoms onto a silicon substrate to see the effects of deposition energy on coating structure and stress. **Figure 2** shows carbon deposited on a silicon surface. Even at the deposition energy of 20 eV, there is substantial

mixing at the interface. We are now using the code results to interpret the electron diffraction measurements. By Fourier transforming the atom positions in the simulation, we were able to closely match the observed positions of diffraction rings.

Future Work

We have described only a few of the possible applications of a:D, with others to be realized as the material becomes better characterized. The combination of extreme hardness, low friction, smoothness, and low deposition temperature make amorphous diamond a unique and very promising material.

The next step in the development of this material would be to test our amorphous diamond films in practical applications. However, we have not yet obtained continued funding for this project.

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Laser-Assisted Self-Sputtering

Peter J. Biltoft,
Steven Falabella,
Steven R. Bryan, Jr., and
Ralph F. Pombo
Materials Fabrication Division
Mechanical Engineering

Barry L. Olsen
Materials Division
Chemistry and Materials Science Department

Our goal for FY-92 was to demonstrate laser-assisted self-sputtering as a method for sputter deposition of thin film coatings in a high vacuum environment.

Introduction

Our experimental program was designed to investigate merging the technology of magnetron sputtering[1] and laser ablation[2] to create a well-controlled deposition process free of the need for a process gas. Self-sputtering of copper, using a conventional magnetron sputter gun, has been reported.[3] In this process, a glow discharge plasma was initiated by operating a magnetron in the conventional manner, with argon as the process gas at a pressure in the range of from 5 to 20 mTorr. After the plasma was well established, the process gas pressure was slowly reduced. As this was done, sputtering was maintained by ionization of sputtered copper atoms in close proximity of the cathode. We hope to demonstrate self-sputtering initiated by a laser-induced plasma in the absence of any process gas.

Progress

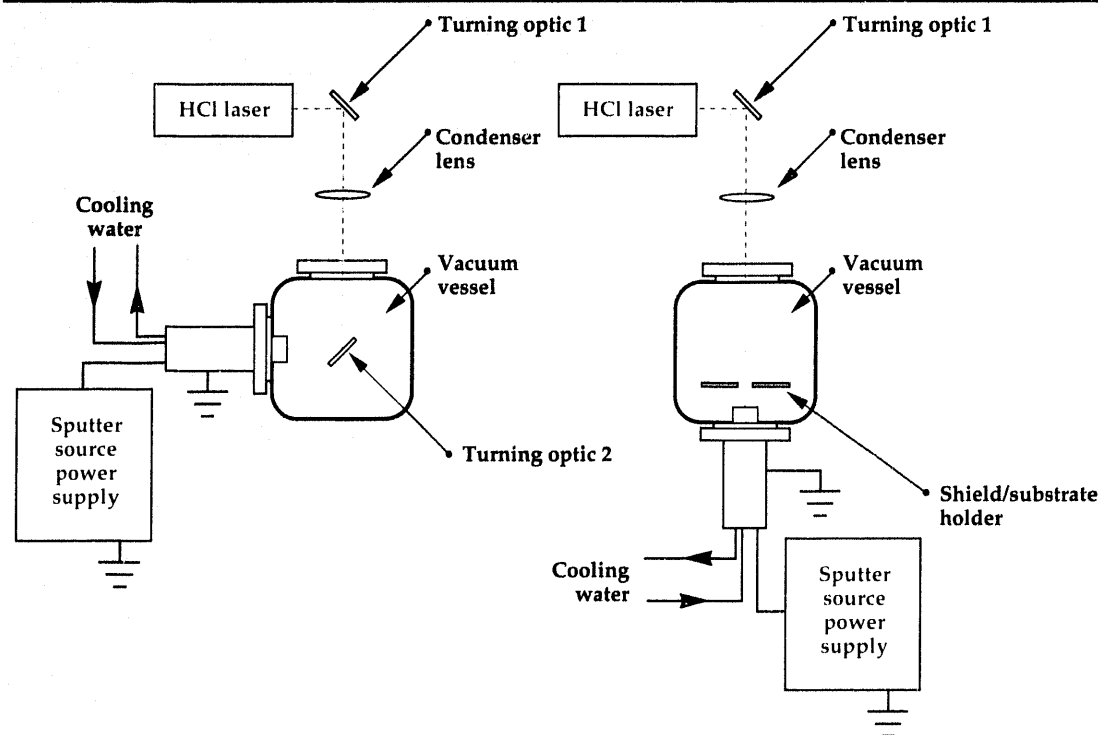Our first goal was to design and build a fixture that would accommodate installation of a

Figure 1. Initial (left) and final (right) configuration of the laser-assisted self-sputtering apparatus.

conventional magnetron sputter gun into an existing vacuum vessel designed for thin film growth by laser ablation. We selected a small, commercial, sputter-deposition source (2-in. US gun) for our first evaluation. A schematic of the experimental apparatus is presented in **Fig. 1** (left). Initial deposition runs were conducted at pressures below 5×10^{-5} Torr, as measured using a hot cathode ionization gauge on the vacuum vessel. We used a pulsed-output HCl laser operating at a wavelength of 308 nm to initiate the plasma. Typical operating parameters for the laser were 1- to 10-Hz repetition rate and 160- to 320-mJ pulse power. The laser beam was de-magnified using a 500-mm focal length, plano-convex lens external to the vacuum vessel. Power density at the sputter source cathode was between 21 and 42 J/cm². A high-output power supply designed for magnetron sputtering was used to bias the cathode to -5000 V. While we were able to briefly maintain a plasma at the sputter source, we discovered that the laser damaged turning optic 2 rapidly, reducing the power density we were able to deliver to the cathode. To rectify this problem, we reconfigured the apparatus as shown in **Fig. 1** (right). In the second configuration, we were able to initiate and maintain indefinitely a toroidal plasma at the sputter target. The color of the plasma for the copper target was bright green, indicating the presence of high concentrations of copper species in the plasma.[4] Using this setup, we deposited several thin films of copper. During 10-minute deposition runs, the magnetron power supply outputs indicated that the peak voltage was 5000 V, and average current was 0.1 A.

Using a storage oscilloscope, we observed that the voltage output of the magnetron power supply was reduced almost to zero following every laser pulse. In an effort to deliver higher current to the sputter source, we installed a 0.1 μF capacitor capable of operating at > 5 kV, between the magnetron sputter supply and the sputter source. No appreciable benefit was realized through this modification.

Results

We have deposited thin films of copper, aluminum, and tantalum by laser-assisted self-sputtering in a high vacuum environment. Deposition rates for the copper films were observed to be greater than 0.1 nm/s. This represents an increase in deposition rate of greater than a factor of 50 compared to pulsed-laser deposition of copper under identical circumstances.

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Simulation of Diamond Turning of Copper and Silicon Surfaces

David B. Boercker and
James Belak
Condensed Matter Physics Division
Physics Department

Irving F. Stowers
Precision Engineering Program
Engineering Directorate

We have applied molecular dynamics modeling to the diamond turning of a ductile metal (copper) and a covalent material (silicon). On the nanometer-length scale, both materials show ductile behavior, but the atomistic mechanisms that allow the behavior are significantly different in the two cases. In addition, we studied the wear of small diamond asperities while they machined a silicon surface.

Introduction

Diamond turning is, by now, a well established technique for machining high-quality surfaces with dimensional tolerances of a few tens of nanometers. This technique is particularly successful when applied to non-reactive, ductile metals such as copper. It is less useful when applied to carbide-formers, like iron, or to brittle materials. Tribochemical reactions can cause excessive tool wear, while brittle fracture produces surface damage. Recently, there has been interest in diamond turning silicon to obtain precisely shaped optical substrates. In this case, both problems occur. Silicon is a strong carbide former, and it is a covalently bonded, hard material that is prone to fracture.

To gain insight into the atomistic mechanisms of importance to diamond turning and to diamond tool wear, we have performed molecular dynamics (MD) simulations of the machining of both copper and silicon surfaces with diamond tools. The basic MD method is the same as that used previously[1] to simulate orthogonal cutting and nano-indentation. The simulations are performed in the rest frame of the cutting tool and follow the detailed, microscopic motions of the atoms, both in the tool and in the work piece, as it moves under the tool. Such simulations give good qualitative descriptions of chip formation and dislocation propagation.

The central input to the simulations is an appropriate interatomic force law. In the copper simulations, we use the embedded atom potential[2] for the interaction between two copper atoms, while the atoms in the diamond tool are assumed to interact with the metal atoms through a Lennard-Jones potential. For the silicon simulations, we have implemented interatomic potentials for silicon and carbon,[3] which include angular-dependent forces that are very important in covalent materials with low coordination. Interactions between like and unlike atoms are included in this model.

Progress

We have performed two types of simulations, each designed to look at a different aspect of the problem. One class is designed to simulate orthogonal cutting and to focus on chip formation and mechanisms of plastic flow. The other looks in detail at possible wear mechanisms, such as graphitization and carbide formation, for the tool.

In both types of simulation, the work piece is a large slab containing tens of thousands of atoms oriented with a specific crystal direction face up. Most of the atoms in the work piece move freely according to Newton's laws. Relatively few atoms near the upstream boundary and the lower boundary have additional constraint forces that maintain their temperature at a constant value,[4] allowing heat generated at the tool tip to flow out of the system. Finally, a constant velocity boundary condition is imposed on the lowest atoms in the slab. Atoms leaving the simulation cell at the 'downstream' end are destroyed, and new ones are periodically produced at the 'upstream' boundary. Performing the calculation in the rest frame of the

Figure 1. Contrasting behavior of copper and silicon under orthogonal cutting: (a) copper chip remains crystalline but reorients to slip along the easy (111) plane; (b) silicon amorphizes and then 'flows.'
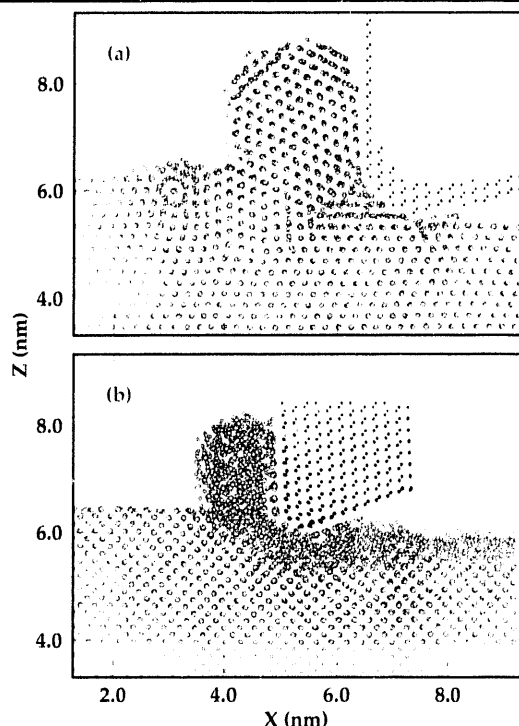
tool allows the simulation of cutting over lengths that are many times the computational cell dimension, without having to follow the motion of a prohibitively large number of atoms.

Orthogonal Cutting

We simulated diamond turning in the orthogonal cutting geometry by creating a wedge-shaped tool with a close-packed (111) cutting face, and imposing periodic boundary conditions in the direction parallel to the surface and normal to the cutting direction. In the case of copper, the diamond tool comprised a rigid array of atoms with about a 2 nm radius of curvature. The work piece contained 36,000 copper atoms with the (111) face up, and moved under the tool at a speed of about 100 m/s from left to right. A cross-sectional 'snapshot' of the simulation is shown in **Fig. 1a**. From this picture, we notice that the chip has remained crystalline, but it has been reoriented to form a (111) slip plane in the primary shear zone in front of the tool.

In contrast to the copper simulation, the silicon calculation allows the lower atoms in the tool to move according to their force laws, and only the uppermost atoms are held rigid. Atoms just below the rigid layers are maintained at constant temperature. The work piece consisted of 20,160 atoms with the (001) plane face up, moving at about 540 m/s, left

to right. A cross-sectional 'snapshot' of this simulation is shown in **Fig. 1b**. The first thing to notice is that both the chip and the cut surface are amorphous. In addition, there appears to be a boundary layer of silicon clinging quite tightly to both the rake and clearance faces of the tool.

Tool Wear

Tool wear was simulated by suspending two small carbon asperities from a flat diamond surface and observing their interaction with the silicon work piece. The asperities differed in size, but were both shaped as square pyramids with the four triangular faces being (111) surfaces. The square base of the larger pyramid contained 64(= 8×8) atoms, while the base of the smaller one contained 36(= 6×6) atoms. All of the atoms in both asperities were free to move as Newton's equations dictate. The bases of the pyramids were (001) planes attached to the bottom (001) plane of rectangular diamond slab, four atomic layers thick. The atoms in the bottom two layers of the slab also moved according to Newton's equations, but their temperature was controlled. The atoms in the top two layers were kept in a rigid lattice that initially moved downward at a constant velocity, but stopped after the desired penetration was obtained. After that time, these atoms were held fixed in space. Soon after the asperities made contact with the silicon, the atoms in their tips began to break away, and some were replaced by silicon.[5] Later in the simulation, a graphitic cluster of six carbon atoms appeared at the surface on the downstream side of each asperity. No other damage to the asperities, except for a build-up of silicon on the pyramid faces, was visible during the simulation time of about 10 ps.

The central result of this work is the contrasting behavior of our prototype materials, copper and silicon, under orthogonal cutting. Copper forms a face-centered-cubic (fcc) crystal with a single-atom basis. As a result, slip along the close-packed (111) planes is analogous to sliding stacks of marbles over each other, and as seen in **Fig. 1a**, the copper chip remains crystalline, but reorients and slips along the easy plane. In contrast, silicon forms a diamond lattice that is also fcc, but contains a two-atom basis. Consequently, sliding along the (111) plane is hindered by the strong angular forces, and **Fig. 1b** shows that silicon amorphizes and then 'flows.' This suggests that the surface selects the state that minimizes the work done by the tool.

Our simulation of the wear of small diamond asperities while cutting silicon showed evidence

of both 'graphitization' and carbide formation. Six carbon atoms broke off the asperities and formed hexagonal rings, while silicon atoms filled the resulting vacancies by bonding strongly to the diamond.

Future Work

The ability to understand and control the ductile-brittle transition in glass is critical to improving the economic viability of the state-of-the-art machining capabilities being developed at Lawrence Livermore National Laboratory (LLNL). Our next objective is to define the mechanisms of microplasticity and damage initiation in fused silica by using MD techniques, to follow changes in the structural properties and the dynamic interactions of the atomistic glass network. We hope that an explicit demonstration of the ability to model these processes will greatly enhance the competitive-

ness of LLNL's materials fabrication efforts within the Department of Energy and elsewhere.

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