AD-A249 296

ON PAGE

1. A	April 1992	3. REPORT TYPE AND DATES COVERED Technical Rept. (Interim) 9/1/91-8/30/92

4. TITLE AND SUBTITLE Atomistic Simulation of the Nanoindentation of Diamond and Graphite Surfaces	5. FUNDING NUMBERS C: N00014-92-WX-24183 PE: 0601153N PR: RR013-01-01 RR022-03-02 TA: 4131062-03 WU: 61-3932-02

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7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Naval Research Laboratory Washington, DC 20375-5000 (Code 6170, D.L. Venezky)	8. PERFORMING ORGANIZATION REPORT NUMBER Technical Report #3

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) Office of Naval Research 800 N. Quincy Street Arlington, VA 22217-5000 (Code 1113PS, P.P. Schmidt)	10. SPONSORING/MONITORING AGENCY REPORT NUMBER

12a. DISTRIBUTION/AVAILABILITY STATEMENT This document has been approved for public release and sale; its distribution is unlimited.	12b. DISTRIBUTION CODE

13. ABSTRACT (Maximum 200 words)

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14. SUBJECT TERMS Nanoindentation, molecular dynamics	15. NUMBER OF PAGES
	16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT	18. SECURITY CLASSIFICATION OF THIS PAGE	19. SECURITY CLASSIFICATION OF ABSTRACT	20. LIMITATION OF ABSTRACT
Unclassified	Unclassified	Unclassified	

OFFICE OF NAVAL RESEARCH

CONTRACT # N00014-92-WX-24183

R&T Code 4131062

Technical Report No. 3

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April 15, 1992

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DTIC TAB	☐	
Unannounced	☐	
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Distribution /		
Availability Codes		
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92-11871

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ABSTRACT

Molecular dynamics simulations which make use of a many-body analytic potential function have been used to study the nanometer-scale indentation of diamond and graphite. We find that the simulation correctly reproduces experimentally determined trends in load versus penetration data. As a result, trends in mechanical properties, e.g. Young's modulus, are also reproduced.

I. INTRODUCTION

Microindention has long been used to characterize bulk properties of materials. An indentation curve plots the relationship between load and penetration depth, h, continuously measured and recorded during a hardness test.[1] A limitation of traditional indentation techniques is the need to image the surface after indentation to determine the penetration depth of the plastically deformed material. For microindentation, SEM and even TEM images are required.[1,2] Furthermore, shallow indents are often hard to find and difficult to image. As the interest in thin films has increased, so has the need for reliable characterization methods. This and other considerations have prompted the use of instruments such as the Nano-indentor[3] and the atomic force microscope (AFM)[2,4,5] to study the nanomechanical properties of solids and thin films.

Recently, the AFM has been used to measure the nanomechanical properties (e.g. elastic modulus and hardness) of an elastomer, graphite, gold films[2], and diamond surfaces,[5] and to examine the surface forces of monolayer films[6] with depth and force resolution superior to other methods. To better understand the strengths, limitations and interpretation of nanoindentation for characterizing materials and thin film properties, we have been using molecular dynamics (MD) to simulate indentation at the atomic scale. In this work we report initial studies of the indentation of hydrogen terminated (111) and (100) surfaces of diamond and the basal plane of graphite with a diamond tip. We find that the force on the simulated tip varies linearly with the penetration depth and that the slopes reflect the correct trends for the moduli of the various surfaces. We interpret the differences in moduli for the two diamond surfaces in terms of the relative displacement of bond angles and bond lengths during indentation.

Molecular dynamics calculations were carried out by integrating Newton's equations of motion with a third order variable time step Nordsieck predictor corrector.[7] The particle forces are derived from an empirical hydrocarbon potential that is capable of modeling intramolecular chemical bonding in both diamond and graphite lattices, as well as in a variety of small hydrocarbon molecules.[8] The potential used here is potential II of reference 8 with additional terms that better describe torsional forces[9] and short range repulsive terms which may prove important under high compression.[10] This potential has recently been used to model the compression of C_{60} between graphite planes,[9] the scattering of C_{60} from diamond surfaces,[11] and the compression and adhesion of diamond (111) crystals.[10,12] For the graphite simulations, interactions between graphite sheets were modeled by a pair-additive exponential-6 potential that had been fit to the experimental interplanar distance and compressibility of graphite.[13]

The initial atomic positions for the tip-substrate systems are shown in Fig. 1. The tip contains 10 layers of carbon atoms and two layers of hydrogen atoms (325 total atoms). It was constructed by removing atoms from a (111) crystal until it looked approximately like an inverted pyramid with a flattened apex. Hydrogen atoms were added to the edge carbon atoms, i.e. the sides of the tip, to satisfy their valency. During the simulation the top two layers of the tip are held rigid, the four layers closest to the substrate have no constraints, and frictional forces are applied to the middle six layers to control the temperature of the tip.[14] The diamond (111) substrate has 10 carbon layers and two hydrogen layers (one on top and one on bottom), each with 64 atoms per layer. The initial surface before indentation has the structure of the truncated bulk, in agreement with recent experimental studies.[15] The diamond (100) surface contains 16 carbon layers, each with 64 atoms per layer, and one layer of hydrogen atoms at the top surface. At present there is no general agreement regarding the structure of the (100) diamond surface. Some experimental data[16] suggest that the bulk terminated (1 x 1) dihydride (two hydrogen atoms on each carbon atom) is the most stable structure. By comparison, there are experimental[17] and theoretical[8,18] data which suggest that the dimer reconstructed (2 x 1) monohydride (one hydrogen atom on each carbon atom) is the most stable structure. Thus, we start with the (2 x 1) monohydride structure. The graphite lattice is composed of five carbon atom layers of 128 atoms each. The bottom two layers of the diamond substrates and the bottom layer of the graphite substrate are held rigid. Frictional forces are applied to the next six layers of the diamond (111) substrate, the next seven layers of the diamond (100) substrate, and the next four layers of the graphite substrate. The remaining top layers of the substrates have no constraints. Periodic boundary conditions are applied in the x-y plane which contains the (111) and (100) surfaces of the diamond lattices and the graphite sheets in order to simulate an infinite indentation surface. The temperature of the system is maintained at 300K throughout the simulation.

Indentation is performed in the following way. The rigid layers of the tip are moved toward the substrate in steps of 0.15 Å . The tip-substrate system is then allowed to equilibrate for 200-500 time steps of the order 0.1 femtoseconds. (Although these indentation rates are orders of magnitude faster than typical experimental values, they are sufficiently slow to allow equilibration of the system.) Once the system equilibrates, the load on the tip in the z direction (parallel to the indentation) is calculated by summing the z forces on all the tip atoms. This number is then averaged over the next 100-250 time steps. The rigid layer of the tip is then moved another 0.15 Å closer to the surface and the above process is repeated. Penetration depth is defined as the original z position of the substrate surface minus the average z position of the tip surface. In these simulations the load is
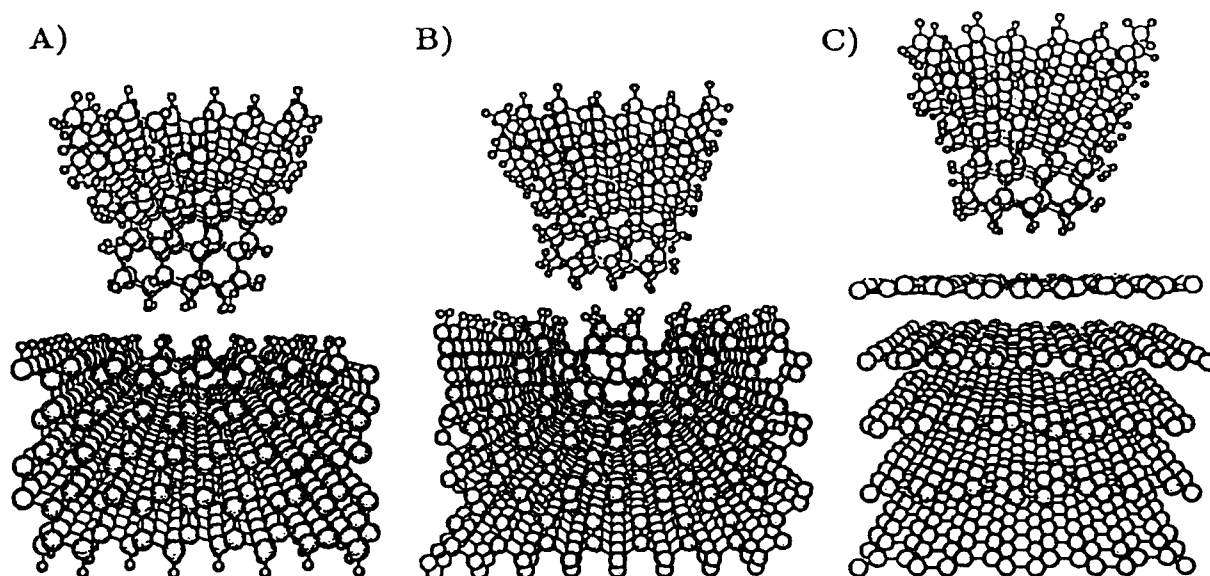
Figure 1. Initial tip-substrate configurations: A) a hydrogen terminated (1 x 1) diamond (111) surface; B) a hydrogen terminated (2 x 1) diamond (100) surface; and C) the basal plane of graphite.

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increased by decreasing the distance between the rigid layers of the tip and the rigid layers of the substrate.

III. RESULTS

Fig. 2 shows simulated indentation (loading) curves for each of the substrates. The curves are approximately linear, with slopes $S_{111} > S_{100} >> S_{Graphite}$. For the purposes of this discussion only the loading portion of the curves are shown. It should be noted that for all cases examined here the interactions are elastic, i.e. no irreparable damage has occurred to the substrate. For comparison we show in Fig. 3 experimental indentation curves for diamond[5] and for graphite[2] measured with an AFM. (A tungsten tip was used to indent the graphite and a Berkovich diamond tip was used to indent the diamond (100) substrate.) Although the scale of the two sets of data is much different, they show similar trends in that both are approximately linear, and the curve for diamond has a larger slope than graphite.

Classical elasticity theory predicts that the slopes of the indentation curves should be proportional to the modulus of the material.[19] For cubic systems, Young's modulus for a (111) face, E(111), and a (100) face, E(100), is related to the elastic constants, c_{ij}, of the substrate via the following relationships[20]

$$E(111) = 6c_{44}(c_{11} + 2c_{12})/(c_{11} + 2c_{12} + 4c_{44}) \qquad (1)$$

$$E(100) = c_{11} + c_{12} - 2c_{12}^2/c_{11}. \qquad (2)$$

For hexagonal substances such as graphite, Young's modulus is given by[19]

$$E = [s_{11}sin^4\theta + s_{33}cos^4\theta + (2s_{13} + s_{44})cos^2\theta sin^2\theta]^{-1} \qquad (3)$$

where s_{ij} are the compliance coefficients and θ is the angle between the long axis and the hexagonal axis. (See reference 22 for the relationship between compliance coefficients and elastic constants.) Substituting the elastic constants for the potential used here[21] into the Eqs. 1-3 give values of 1364 GPa for E(111), 482 GPa for E(100) and 17.3 GPa ($\theta = 78.7°$) for graphite. Therefore, in agreement with continuum theory, the differences in the slopes of the simulated indentation curves yield the same qualititative trend as that given using the elastic constants.
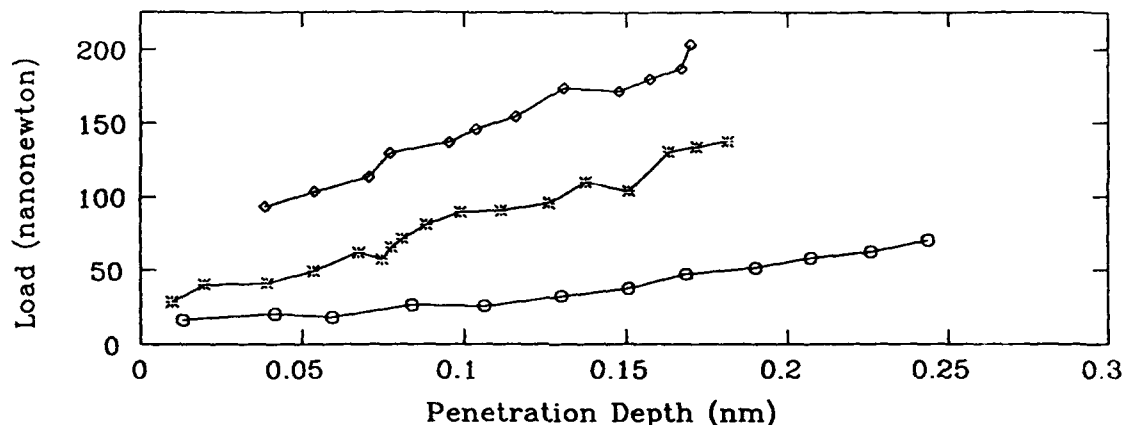

Figure 2. Simulated indentation curves for a diamond tip indenting graphite and diamond. Open diamonds are for the hydrogen terminated (1 x 1) diamond (111) substrate, asterisks are for the hydrogen terminated (2 x 1) diamond (100) substrate, and open circles are for the graphite substrate.
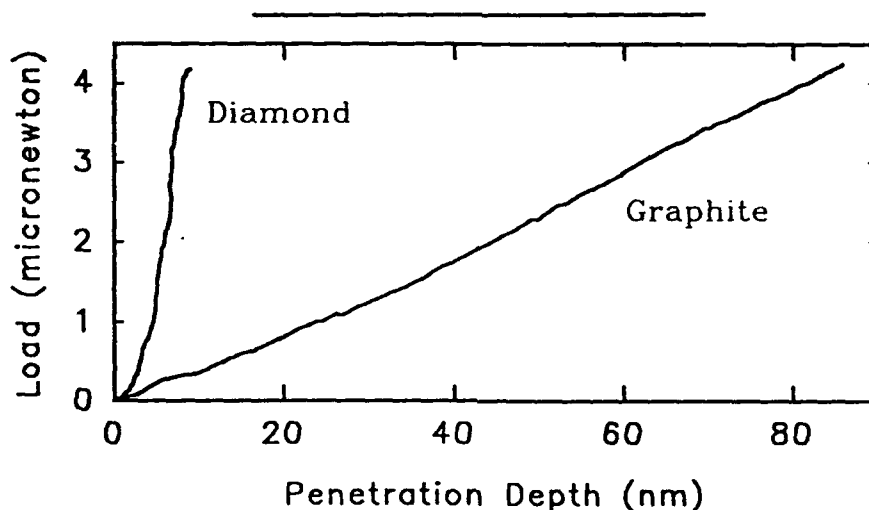

Figure 3. Experimental load versus penetration depth for the indentation of the basal plane of graphite and the (100) surface of diamond. These data were obtained with an AFM.[5]

It is encouraging that these simulations predict the proper trend in stiffness for the diamond faces. Because MD simulations allow the atomistic mechanism of compression to be examined, they can yield insight into the stiffness difference between the diamond (111) and (100) surfaces. Compare, for example, the typical bulk layer structure for diamond (111) and diamond (100) shown in Figure 4. For the (111) surface, the first layer atoms are directly above the second layer atoms whereas for the (100) surface, the first layer atoms are over holes in the lattice. Our previous compression studies of diamond slabs[10] showed

that it is easier to bend a carbon-carbon bond than to compress it. Therefore, the stiffness of the (111) surface is expected to be greater than the (100) surface. Experimentally, this trend in Young's modulus is also present (E(111)=1274 GPa and E(100)=1179 GPa), however these values are much different than those produced by our potential.
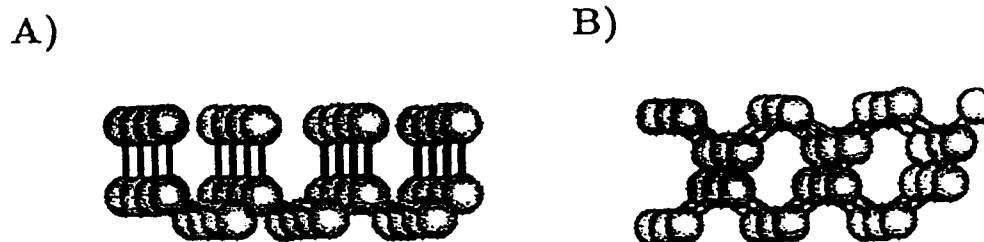
A)

B)

Figure 4. Side view of the bulk lattice structure for A) for the diamond (111) lattice and B) the diamond (100) lattice.

In summary, it appears that molecular dynamics simulations of indentation hold promise for understanding mechanical properties obtained by nanoindentation. The empirical potential used here yields elastic constants which are, in general, too soft. Improving the potential energy function so that the elastic constants are better described should allow for a direct comparison of calculated mechanical properties with those obtained experimentally. These simulations should also allow us to compare simulated indentation curves with analytic models derived from classical continuum theory. Work in both areas is currently under way.
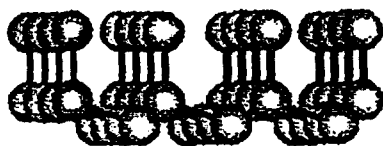
ACKNOWLEDGEMENTS

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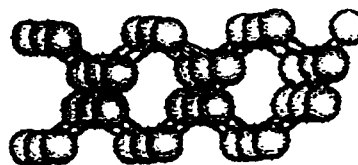
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