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14. ABSTRACT

This project developed atomistic and microstructural models for the growth of polycrystalline thin films. The atomistic simulations were based upon the kinetic Monte Carlo method and employed experimental and first-principles data for different surface reactions. The models predict the atomic structure of the film, the surface structure, point defect incorporation and the growth rate of different surfaces. The microstructural models employ the atomistic simulation predictions of growth rate for different surfaces to track the evolution of an ensemble of 1000 grains during film growth under a wide range of growth conditions. This model predicts the grain structure, grain size, surface roughness, crystallographic texture, etc. Both of these models were also used to show how to optimize diamond film growth.

15. SUBJECT TERMS

diamond thin films, chemical vapor deposition, kinetic Monte Carlo, microstructure, morphology, texture, growth optimization

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March 20, 2000

Dr. James Butler
Code 6174
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Dear Jim:

Enclosed, please find a copy of the final report for my NRL contract N00014-97-1-G013, *Molecular and Microstructure Scale Models of CVD Diamond Growth.* It outlines our main results and contains a summary of our publications and invited presentations on this topic.

Sincerely,

David J. Srolovitz

Edward deMille Campbell Professor of
Materials Science & Engineering
Professor of Applied Physics

Dr Butler:

Professor Srolovitz is now at Princeton University and that is the phone # given in Block 19B.

You can also contact me if there are questions & I can direct you to the appropriate person.

Bonnie Lietz
Administrative Assistant
(704) 936-0174

Final Project Report on Grant N00014-97-1-G013

Molecular and Microstructure Scale Models of CVD Diamond Growth

Submitted by:

Professor David J. Srolovitz

Department of Materials Science and Engineering
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Ann Arbor, MI 48109-2136

Project terminated: 9/10/2000

During the course of this NRL/DARPA program, we developed a novel, kinetic Monte Carlo (kMC) simulation code capable of modeling diamond growth on the atomic scale. We also developed a two-dimensional simulation code capable of predicting the evolution of faceted polycrystalline diamond films as a function of diamond growth conditions.

We developed a kinetic Monte Carlo technique for simulating thin film growth by chemical vapor deposition which is inherently atomistic and three dimensional, and incorporates known reaction kinetics. The kinetics of the relevant surface processes and the effects of surface atomic structure and morphology are included within this model. Processes which involve cooperation between adjacent surface atoms, such as reconstruction and growth of {100} faces of diamond, are handled explicitly and atomistically. The temporal evolution of the system is simulated using an N-Fold Way Monte Carlo scheme which employs a variable time increment, allowing the consideration of processes that occur on widely different time scales. The model is efficient enough to handle the growth of hundreds of atomic planes on substrates containing thousands of surface atoms, using only a desktop workstation. Because the model is inherently atomistic, it is useful not only for studying the evolution of film morphology and defect incorporation, but also as a tool for examining and verifying proposed atomic growth mechanisms. The growth of {111}-oriented diamond films was simulated for several substrate temperatures ranging from 800 to 1500 K. Under typical CVD conditions, the growth rates vary from about 0.1 to 1.2 μm/hr between 800 and 1500 K, and the activation energy for growth on the {111} surface between 800 and 1100 K is 11.2 kcal/mole, in agreement with experiment and other simulations. The concentrations of incorporated point defects are low at substrate temperatures below 1300 K, but become high above this temperature. While the growth rates are controlled by the combined contributions to growth from CH_3 and C_2H_2, the incorporation of point defects depends on competition between C_2H_2 and CH_3 growth. Therefore, in the growth environment simulated here, optimal {111} growth efficiency, defined as the ratio of growth rate to point defect concentration, can be achieved between approximately 1100 and 1200 K.

The growth of {001}, {011}, and {111} diamond films was simulated in various gaseous environments containing H, H_2, CH_3, and C_2H_2 concentrations typical of hot filament CVD reactors. The effects of surface chemistry is incorporated in the model through conventional reaction rate coefficients, and surface atomic structure and morphology are included by representing the films atomistically in three dimensions. The formation of dimer bonds between surface atoms is handled explicitly, allowing arbitrary dimer surface reconstructions of {001} facets. The concentrations of H, CH_3, and C_2H_2 were varied independently over six decades, and the effects of these variations on growth rate and film morphology were ascertained. Changes in H concentration affect growth rates the most, since the rate of formation of radical sites on the diamond surface is proportional to H concentration. Rates of growth of all facets are comparable at each gas composition, except when the concentration of C_2H_2 is low (below approximately $1x10^{-}$

2%). The disparity in growth rates at low C_2H_2 concentrations is due to the coordination that adsorbed C atoms must assume to form a diamond cluster on a flat surface. The {001}, {011}, and {111} films require that one, two, and three neighboring adsorbed C atoms, respectively, bond together in order to initiate a monolayer on a flat face. However, the chemisorption of C_2H_2 contributes two carbon atoms, and thus this effect is only significant at low C_2H_2 concentrations. The growth of {111} films in C_2H_2-deficient atmospheres is controlled by the nucleation of diamond clusters on atomically smooth faces. Thus {111} films grow by step flow under these conditions, and are atomically smooth for extended periods (up to several minutes) during growth.

The growth of diamond films and the rate of incorporation of vacancies, H atoms, and sp^2 defects were simulated for several substrate temperatures and feed gas compositions. An efficient atomic-scale on-lattice kinetic Monte Carlo method was used to capture a simple yet physically meaningful representation of the atomic processes involved in defect trapping. Growth on (100)(2x1)- and (111)-oriented diamond surfaces was simulated for substrate temperatures from 600 °C to 1200 °C with 0.4% inlet CH_4, and for 0.4% to 7% inlet CH_4 concentrations with a substrate temperature of 800 °C. The simulations predict that H atom concentrations increase with substrate temperature as the relative contribution of C_2H_2 to deposition increases, simply because the larger C_2H_2 molecule can cover defect sites more easily than can CH_3. The concentrations of incorporated sp^2 bonds increase with the CH_4 content in the feed gas because the concentration of H, which is required to convert sp^2 bonds to sp^3 bonds at the surface, decreases with increasing inlet CH_4. Vacancy concentrations are low under all simulated conditions. The ratio of growth rate to H atom concentration is highest around 800-900 °C, and the growth rate to sp^2 ratio is maximum around 1% CH_4, suggesting that these conditions are ideal for diamond growth under the simulated conditions, as commonly observed experimentally.

Chemically vapor deposited (100)-oriented diamond is known to grow more slowly than (110)-oriented material and to contain smooth surface features. The existing self-consistent models for diamond growth, on the other hand, predict that (100)-oriented films grow fastest and are atomically rough. Surfaces which grow slowly and develop smooth features, such as (111), do so because the nucleation of new growth layers on these surfaces is much slower than growth at step edges,but there is no nucleation barrier for the formation of new growth layers on (100) surfaces. This suggests that the experimentally observed (100) growth behavior might be rationalized by the introduction of growth mechanisms that hinder layer nucleation and promote step-flow growth. One such mechanism is the preferential etching of monomolecular C islands. The thermochemistry of the (100) dimer insertion reaction, by which CH_2 species are incorporated at the surface, indicates that the incorporation reaction is reversible and that an etching mechanism might indeed exist. We have presented the results of coupled tight binding (TB) and density functional theory (DFT) quantum mechanical calculations that suggest that etching of isolated, monomolecular C islands occurs at an appreciable rate, while etching from larger C islands (i.e., step edges and

terraces) is not favorable. The TB/DFT calculations and the proposed etching mechanism were combined with previously determined hydrocarbon reaction rates on diamond surfaces and input to a kinetic Monte Carlo model of the chemical vapor deposition of diamond on (100), (110), and (111) surfaces. The simulation results clearly demonstrate that the inclusion of etching produces much smoother (100) diamond surfaces (as compared with calculations in which etching is omitted). Etching slows (100) growth considerably without substantially affecting (110) and (111) growth rates. The growth rates that are predicted when etching is included in the model are in very good agreement with a wide range of experimental evidence that suggest that (100) is slower than (110) growth and comparable to (111) growth under hot filament CVD reactor conditions. However, while etching is key to our understanding of diamond growth in general, and (100) growth in particular, several details of (100) growth remain unexplained.

We performed a series of simulations of the growth of polycrystalline, faceted films from randomly oriented nuclei in two spatial dimensions. The simulations track the motion of all corners where facets from the same grain and different grains meet. While earlier studies have employed this type of simulation method, this study provides the most complete analysis of the resultant microstructures performed to date. Examination of the microstructures showed that the grain boundaries are straight, but may turn abruptly when facet corners meet, and grains are annihilated when two grain boundaries meet (an observation made earlier by van der Drift). Much of the growth behavior may be understood in terms of the α-dependent idiomorphs (the shape found by convexifying a polar plot of growth velocity versus surface orientation). The surface morphology is sensitive to the value of α, especially for α's where idiomorphs suffer a change in topology. The mean grain size and RMS surface roughness were found to grow as $\sqrt{h}$ (where h is the film thickness) in agreement with experiment, theoretical and previous simulation results. The grain size distribution was found to be temporally self-similar when the grain sizes were scaled by the mean grain size. The grain size distribution is better fit by a gamma distribution than by a log-normal distribution. The crystallographic orientation distribution (i.e., texture) peaks at an α-dependent orientation and the peak sharpens during film growth. The orientation distribution is well described by a Gaussian, in agreement with theory. The α-dependent peak position may be derived directly from the orientation of the largest radius vector of the appropriate idiomorph in two and three dimensions. The volume of material grown from each facet type exhibits a cross-over at finite thickness to that predicted on the basis of the α-dependent idiomorphs, in agreement with experiments.

Several papers and a large number of invited talks were given based upon this contract work (although it is difficult to distinguish between those from this contract and the follow on). These include:

Published Papers

1. C. C. Battaile, D. J. Srolovitz and J. E. Butler, "A Kinetic Monte Carol Method for the Atomic Scale Simulation of Chemical Vapor Deposition: Application to Diamond", Journal of Applied Physics **82** [12] 6293-6300 (1997).

2. C. C. Battaile, D. J. Srolovitz and J. E. Butler, " Morphologies of Diamond Films from Atomistic Simulations of Chemical Vapor Deposition", Diamond and Related Materials **6** [9], 1198-1206 (1997).

3. C. C. Battaile, D. J. Srolovitz and J. E. Butler, "Molecular View of Diamond CVD Growth", Journal of Electronic Materials **26** [9], 960-965 (1997).

4. D. J. Srolovitz, D. S. Dandy, J. E. Butler, C. C. Battaile and Paritosh, "Integrated Multi-Scale Modeling of Diamond Chemical Vapor Deposition", JOM – J. Min. Met. Mat. S. **49** [9], 42-47 (1997).

5. C. Battaile, D. J. Srolovitz and J. E. Butler, "3-D Atomistic Kinetic Monte Carlo Simulations of Point Defects Incorporation During CVD Diamond Film Growth," Materials Research Society Symposium Proceedings **441**, 509-514 (1997).

6. C. Battaile, D. J. Srolovitz and J. E. Butler, "Atomic-Scale Simulations of Chemical Vapor Deposition on Flat and Vicinal Diamond Substrates," Journal of Crystal Growth **194**, 353-368 (1998).

7. I. I. Oleinik, D. G. Pettifor, A. P. Sutton, C. C. Battaile, D. J. Srolovitz and J. E. Butler, "Surface Chemistry of CVD Diamond: Linking the Nanoscale and Mesoscale Modelling Hierarchies," in "Multiscale Modelling of Materials," eds. Diaz de la Rubia, Kaxiras, Bulatov, Ghoniem, Phillips, Materials Research Society Symposium **538**, 275-284 (1999).

8. Paritosh, D. J. Srolovitz, C. C. Battaile, X. Li and J. E. Butler, "Simulation of Faceted Film Growth in 2-D: Microstructure, Morphology and Texture," Acta Materialia **47** [7], 2269-2281 (1999).

9. C. C. Battaile, D. J. Srolovitz and J. E. Butler, "Point Defect Incorporation During Diamond Chemical Vapor Deposition," Journal of Materials Research, **14** [8], 3439-3446 (1999).

10. C. C. Battaile, D. J. Srolovitz, I. I. Oleinik, D. G. Pettifor, A. P. Sutton, S. J. Harris and J. E. Butler, "Etching Effects during the Chemical Vapor Deposition of (100) Diamond," Journal of Chemical Physics **111** [9], 4291-4299 (1999).

Invited Talks

Computer Modeling of Materials Symposium, University of Pennsylvania, Philadelphia, PA 10/96
Oxford University, Oxford, UK 5/97
Multiple Length Scale Modeling Workshop, Argonne Nat. Lab, Argonne, IL 8/97
CCP5 Meeting, London, UK 9/97
University of Illinois, Champaign-Urbanna, IL 9/97
Pennsylvania State University, College Park, PA 9/97
Ohio State University, Columbus, OH 11/97
American Institute of Chemical Engineers, Los Angeles, CA 11/97
Case Western Reserve University, Cleveland, OH 2/98
Rice University, Houston, TX 2/98
RWTH, Aachen, Germany, 3/98
Knowles Atomic Power Laboratory, Schenectady, NY, 4/98
Materials Research Society Meeting, San Franciso, CA 4/98
Stanford University, Stanford, CA, 5/98
Diamond Synthesis Gordon Conference, Oxford, England, 8/98
University of Virginia, Charlottesville, VA 10/98
California Institute of Technology, Pasadena, CA 11/98
Princeton University, Princeton, NJ 11/98
Materials Research Society Fall Meeting, Boston, MA, 12/98
University of Toledo, Toledo, OH, 3/99
Materials Research Society Spring Meeting, San Francisco, CA 4/99
Princeton University, Princeton, NJ 1/99
University of Toledo, Toledo, OH, 3/99
Yale University, New Haven, CT 10/99
University of California - Berkeley, Berkeley, CA 10/99
Workshop on Microstructure Modelling, FOM Conference, The Hague, Netherlands 12/99
Dept. of Mechanical Engineering, University of Pennsylvania, Philadelphia, PA 2/00
Dept. of Materials Science & Eng., Rutgers University, Piscataway, NJ 2/00
Dept. of Chemical Engineering, Princeton University, Princeton, NJ 3/00
PMI Workshop on Computational Materials Science, Princeton, NJ 4/00