

AD-A265 530



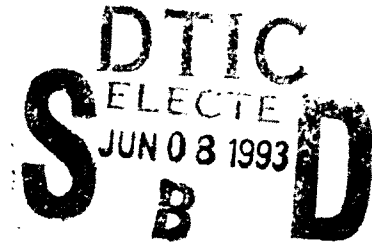
2

OFFICE OF NAVAL RESEARCH

Grant N00014-91-J-1550

R&T Code: 413w003

Technical Report No. 16



Progress toward atomic layer epitaxy of diamond:
Diamond films grown one layer at a time

by

R. Gat, T. I. Hukka, R. E. Rawles, and M. P. D'Evelyn

Prepared for publication in

36th Annual Technical Conference Proceedings, Society of Vacuum Coaters

Rice University
Department of Chemistry
Houston, TX 77251-1892

May 4, 1993

Reproduction, in whole or in part, is permitted for any purpose of the United States Government.

This document has been approved for public release and sale; its distribution is unlimited.

93 6 07 116

93-12751



REPORT DOCUMENTATION PAGE

Form Approved
OMB No 0704 0188

Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302, and to the Office of Management and Budget, Paperwork Reduction Project (0704-0188), Washington, DC 20503.

1. AGENCY USE ONLY (Leave blank)	2. REPORT DATE <p style="text-align: center;">May 1993</p>	3. REPORT TYPE AND DATES COVERED <p style="text-align: center;">Technical</p>	
4. TITLE AND SUBTITLE <p style="text-align: center;">Progress toward atomic layer epitaxy of diamond: Diamond films grown one layer at a time</p>		5. FUNDING NUMBERS <p style="text-align: center;">Grant #: N00014-91-J-1550</p>	
6. AUTHOR(S) <p style="text-align: center;">R. Gat, T. I. Hukka, R. E. Rawles, and M. P. D'Evelyn</p>			
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Rice University Department of Chemistry Houston, TX 77251-1892		8. PERFORMING ORGANIZATION REPORT NUMBER <p style="text-align: center;">Technical Report #16</p>	
9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES) Office of Naval Research 800 N. Quincy Street Arlington, VA 22217-5000		10. SPONSORING / MONITORING AGENCY REPORT NUMBER	
11. SUPPLEMENTARY NOTES <p style="text-align: center;">Prepared for publication in: <i>36th Annual Technical Conference Proceedings, Society of Vacuum Coaters</i></p>			
12a. DISTRIBUTION / AVAILABILITY STATEMENT <p style="text-align: center;">Approved for public release; distribution is unlimited.</p>		12b. DISTRIBUTION CODE	
13. ABSTRACT (Maximum 200 words) Diamond would be the ultimate coating for many applications: it is the hardest material known, is chemically inert in most environments, has a thermal conductivity five times that of copper, and is optically transparent from the ultraviolet through the mid- and far-infrared. However, conventional CVD methods for diamond have important limitations—many substrates of interest cannot withstand the 500-1000 °C temperatures commonly employed, and the typically low nucleation density generates films with large crystal grains and rough morphologies. We are developing a novel low-pressure method for atomic layer epitaxy of diamond which should enable high-quality film growth at modest temperatures with very high nucleation densities. The method uses alternating fluxes of halocarbon radicals and atomic hydrogen, generated by reaction with atomic fluorine. Under suitable conditions, carbon atom additions to the growing film and subsequent re-hydrogenation of the surface should each be self-limiting reactions, resulting in deposition of one atomic layer of diamond per cycle. To date we have obtained evidence for diamond growth at rates up to 0.1 microns/hr from continuous flows of hydrogen and CHCl ₃ , CH ₄ , or C ₂ H ₂ at reactor pressures between 10 ⁻⁴ and 10 ⁻² Torr. In order to perform cost-effective measurements of the growth rate per cycle to optimize the ALE process, we have applied Fizeau laser interferometry as an <i>in situ</i> probe of diamond homoepitaxy with nanometer sensitivity.			
14. SUBJECT TERMS <p style="text-align: center;">Diamond, chemical vapor deposition, atomic layer epitaxy, radical precursors</p>		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

PROGRESS TOWARD ATOMIC LAYER EPITAXY OF DIAMOND: DIAMOND FILMS GROWN ONE LAYER AT A TIME

ROY GAT, TERTTU I. HUKKA, ROBIN E. RAWLES, AND MARK P. D'EVELYN

Department of Chemistry and Rice Quantum Institute, Rice University, Houston, TX
77251-1892

ABSTRACT

Diamond would be the ultimate coating for many applications: it is the hardest material known, is chemically inert in most environments, has a thermal conductivity five times that of copper, and is optically transparent from the ultraviolet through the mid- and far-infrared. However, conventional CVD methods for diamond have important limitations—many substrates of interest cannot withstand the 500-1000 °C temperatures commonly employed, and the typically low nucleation density generates films with large crystal grains and rough morphologies. We are developing a novel low-pressure method for atomic layer epitaxy of diamond which should enable high-quality film growth at modest temperatures with very high nucleation densities. The method uses alternating fluxes of halocarbon radicals and atomic hydrogen, generated by reaction with atomic fluorine. Under suitable conditions, carbon atom additions to the growing film and subsequent re-hydrogenation of the surface should each be self-limiting reactions, resulting in deposition of one atomic layer of diamond per cycle. To date we have obtained evidence for diamond growth at rates up to 0.1 microns/hr from continuous flows of hydrogen and CHCl_3 , CH_4 , or C_2H_2 at reactor pressures between 10^{-4} and 10^{-2} Torr. In order to perform cost-effective measurements of the growth rate per cycle to optimize the ALE process, we have applied Fizeau laser interferometry as an *in situ* probe of diamond homoepitaxy with nanometer sensitivity.

INTRODUCTION

The extreme properties of diamond and myriad of applications for diamond thin films have motivated the rapid growth of chemical vapor deposition (CVD) growth technology [1,2]. Besides being the hardest material known, diamond has the highest thermal

conductivity at room temperature of any material and is chemically inert under most conditions. Diamond film applications which are already in commercial production include heat sinks and hard abrasive coatings.

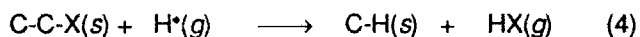
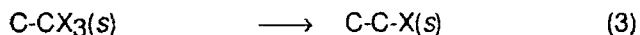
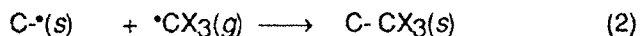
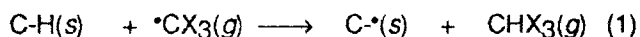
Many challenges remain, however, for diamond CVD technology. The rather modest nucleation densities typically achieved lead to grain sizes in the micron range and films which are too rough and strongly scattering to be useful for optical coatings for visible light. Typical growth temperatures range from 500 to 1000 °C. This temperature range is too high for many substrates and produces highly stressed films due to the mismatch in thermal expansion coefficients. Considerable effort is being devoted to reduction of growth temperatures, control of nucleation and film morphology, and better understanding of the growth mechanism(s).

We are developing a method for atomic layer epitaxy of diamond which may solve several of the problems mentioned above. Atomic layer epitaxy (ALE) is a powerful technique for growing materials one atomic layer at a time [3]. ALE involves alternating, cyclic exposures to different gas-phase reactants, with approximately one monolayer of material being deposited per cycle. Originally developed for growth of II-VI materials, ALE has been widely applied to growth of GaAs and other III-V semiconductors [3], and methods for ALE of silicon are being developed.

Our method for diamond ALE involves selectively-produced radicals in medium vacuum and should have a number of advantages over more conventional diamond growth techniques. The surface dangling bonds remain capped by hydrogen or halogen atoms throughout the process cycle, stabilizing the diamond surface. Because radical reactions typically have low activation energies, the process should remain viable

at relatively low substrate temperatures. There is no obvious nucleation requirement and therefore extremely high nucleation densities may be achievable.

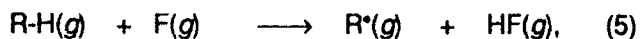
As described in detail elsewhere [4], our ALE method involves alternating cycles of halocarbon radicals and atomic hydrogen:



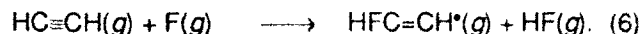
where X is a halogen atom (F or Cl). The cycle begins with a hydrogenated substrate surface. Surface hydrogen is abstracted by a CX₃ radical, and then a second CX₃ radical adsorbs on the resulting dangling-bond site. Adsorbed halocarbon species then undergo surface decomposition or rearrangement reactions to produce a halogen-terminated surface. Reactions (1)-(3) should be self-terminating because activation energies for abstraction of halogen atoms by carbon- and silicon-centered radicals are much higher than for abstraction of hydrogen. In the final step of the cycle, the surface halogen atoms are stripped off by abstraction reactions of incoming hydrogen atoms and replaced by hydrogen. Because etching of diamond by atomic hydrogen is very slow, reaction (4) should also be self-terminating.

EXPERIMENTAL DETAILS

Growth experiments were performed in an ultrahigh-vacuum-compatible CVD/ALE reactor that has been described previously [4]. Briefly, atomic fluorine is produced by thermal dissociation in a hot tube. As tube materials we have used both Ni and Ni-heated MgO, which are heated to 650-800 °C in order to produce a high degree of dissociation. Precursor molecules are injected into the stream of F atoms, undergoing gas-phase hydrogen abstraction reactions to produce radicals with nearly complete chemical specificity:



where R = H, CH₃ or CCl₃, corresponding to injection of H₂, CH₄, or CHCl₃. We have also performed some experiments using C₂H₂ as a precursor, which probably reacts primarily via an addition reaction, generating a fluorovinyl radical:



The radicals (and HF) formed downstream of the F-atom source flow under nearly molecular flow conditions to the substrate. F-atom-based secondary generation of radicals has previously been used to perform *etching* of semiconductor substrates (at rates up to 1000 Å/min) [5].

Because only a handful of groups in the world have successfully demonstrated diamond growth at pressures below 1 Torr [6] and because this growth method is completely new, our initial goal was to achieve diamond growth using *continuous* flows of precursor plus hydrogen, that is, by CVD rather than by ALE. Typical flow rates were 0.1-3 sccm of F₂, 2-6 sccm of H₂, and 1-10 sccm of CH₄, CHCl₃, or C₂H₂. The chamber pressure rose to 10⁻⁴ - 10⁻² Torr during growth. As substrates we have used natural diamond (100) and polycrystalline copper and nickel wires seeded with natural diamond grit, held at temperatures between 500 and 900 °C.

Films were characterized by Raman spectroscopy, scanning electron microscopy, and electron-beam microprobe. Film thicknesses on the diamond (100) substrates were determined by measuring the total thickness of the substrates before and after growth from the fringe pattern in Fourier transform infrared transmission spectra [7].

RESULTS AND DISCUSSION

In experiments on diamond (100) substrates, we have observed evidence for growth from both CH₄ and CHCl₃--thickness increases of 0.3-0.9 μm in 10-12 hours [4,8]. In the case of CH₄ evidence for etching of diamond was also seen--etch pits were visible in SEM photographs and in some cases a thickness decrease was observed. Raman spectroscopy indicated that any graphite deposition was below the sensitivity limit. In the case of growth from CHCl₃,

ledge features located at 90° angles were observed, also indicative of growth of the cubic diamond lattice.

Preliminary evidence of *de novo* diamond growth was obtained using C₂H₂ as the precursor and a copper substrate. Platelets with square faces and ledge features, several microns in size, were observed by SEM [9]. Energy-dispersive x-ray fluorescence analysis indicated that no elements were present except for carbon, and wavelength-dispersive (WDX) spectra indicated that the particles are diamond [9]. Graphite and diamond exhibit slightly shifted WDX spectra due to the different bonding arrangement, and the spectrum of the particles was identical to that of a natural diamond standard and significantly shifted with respect to the spectrum from a graphite standard.

Further diamond growth experiments are underway in our laboratory to define the appropriate parameters for ALE growth of diamond. In order to optimize the ALE process, it is necessary to determine the growth rate per cycle and adjust the process variables so as to reach a plateau in parameter space, that is, where the growth rate per cycle is relatively insensitive to flux, temperature, etc., characteristic of self-limiting growth [3]. Clearly, a sensitive, *in situ* thickness monitor would greatly facilitate this optimization process.

We have applied Fizeau interferometry [10] to *in situ* growth rate measurements of diamond on diamond (100) substrates [11]. Light from a HeNe laser is reflected from the back of the sample, passes through a concave lens, and impinges on a videocamera CCD array detector. Interference between light beams reflected from the front and back faces of the sample produces a spatial fringe pattern which is imaged by the detector and acquired by a videocassette recorder. The fringe pattern constitutes a real-space image of the local thickness of the sample. The fringe spacing is determined by the wedge angle between front and back faces and, at a wavelength of 633 nm and a refractive index of 2.4, corresponds to a lateral thickness difference of 132 nm. Growth causes the fringes to propagate laterally. The propagation rate is directly proportional to the growth rate, and a lateral movement of one fringe corresponds to a thickness increase of 132 nm. In addition, changes in the fringe spacing or contour shape indicate changes in the surface orientation or smoothness, respectively, and

therefore the method also provides a sensitive measure of the *uniformity* of growth.

ACKNOWLEDGMENTS

The authors gratefully acknowledge the Office of Naval Research for support of this work and the Academy of Finland for a stipend supplement for TIH.

REFERENCES

1. J. C. Angus and C. C. Hayman, *Science* **241**, 913 (1988).
2. K. E. Spear, *J. Am. Ceram. Soc.* **72**, 171 (1989).
3. T. Suntola, *Mater. Sci. Reports* **4**, 265 (1989).
4. T. I. Hukka, R. E. Rawles, and M. P. D'Evelyn, *Thin Solid Films* **225**, 212 (1993).
5. J. E. Spencer, J. H. Dinan, P. R. Boyd, H. Wilson, and S. E. Buttrill, Jr., *J. Vac. Sci. Technol.* **A 7**, 676 (1989).
6. (a) J. Suzuki, H. Kawarada, K. Mar, J. Wei, Y. Yokota, and A. Hiraki, *Jpn. J. Appl. Phys.* **28**, L281 (1989); (b) Y. H. Shing, F. S. Pool, and D. H. Rich, *Thin Solid Films* **212**, 150 (1992); (c) W. Tsai, G. J. Reynolds, S. Hikido, and C. B. Cooper III, *Appl. Phys. Lett.* **60**, 1444 (1992); (d) R. A. Rudder, J. B. Posthill, G. C. Hudson, D. P. Malta, R. E. Thomas, R. J. Markunas, T. P. Humphreys, and R. J. Nemanich, *Mater. Res. Soc. Symp. Proc.* **242**, 23 (1992); (e) S. Jin and T. D. Moustakas, *Dia. Rel. Mater.* (in press).
7. C. J. Chu, M. P. D'Evelyn, R. H. Hauge, and J. L. Margrave, *J. Appl. Phys.* **70**, 1695 (1991).
8. T. I. Hukka, R. E. Rawles, and M. P. D'Evelyn, *Mater. Res. Soc. Symp. Proc.* **282**, 671 (1993).
9. R. Gat, T. I. Hukka, R. E. Rawles, and M. P. D'Evelyn, *Proceedings of the 3rd International Symposium on Diamond Materials*, edited by J. P. Dismukes *et al.*, The Electrochemical Society, Pennington, NJ (submitted).
10. For example, S. Tolansky, *An Introduction to Interferometry*, Longman Press, London, 1973.
11. R. E. Rawles, C. Kittrell, and M. P. D'Evelyn, *Proceedings of the 3rd International Symposium on Diamond Materials*, edited by J. P. Dismukes *et al.*, The Electrochemical Society, Pennington, NJ (submitted).

DTIC QUALITY INSPECTED 2

Library Codes
Serial and/or
Dist Special

A-1