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R&T Code: 413w003

Technical Report No. 15

Low-pressure diamond growth using a secondary radical source

by

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Prepared for publication in

Materials Research Society Symposium Proceedings

92-32886

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December 11, 1992

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REPORT DOCUMENTATION PAGE			Form Approved OMB No. 0704-0188	
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1. AGENCY USE ONLY (Leave blank)	2. REPORT DATE December 1992	3. REPORT TYPE AND DATES COVERED Technical		
4. TITLE AND SUBTITLE Low-pressure diamond growth using a secondary radical source		5. FUNDING NUMBERS Grant #: N00014-91-J-1550		
6. AUTHOR(S) T. I. Hukka, R. E. Rawles, and M. P. D'Evelyn				
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Rice University Department of Chemistry Houston, TX 77251-1892		8. PERFORMING ORGANIZATION REPORT NUMBER Technical Report #15		
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 Prepared for publication in: <i>Materials Research Society Symposium Proceedings</i>				
12a. DISTRIBUTION / AVAILABILITY STATEMENT Approved for public release; distribution is unlimited.			12b. DISTRIBUTION CODE	
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14. SUBJECT TERMS Germanium, hydrogen, pairing, HCl, HBr, surface chemistry, kinetics			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	

LOW PRESSURE DIAMOND GROWTH USING A SECONDARY RADICAL SOURCE

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ABSTRACT

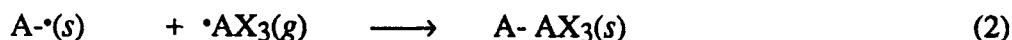
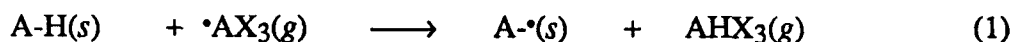
A novel method for chemical vapor deposition and atomic layer epitaxy using radical precursors under medium vacuum conditions is being developed. Fluorine atoms are generated by thermal dissociation in a hot tube and abstract hydrogen atoms from precursor molecules injected immediately downstream of the source, generating radicals with complete chemical specificity. The radical precursors are then transported to the growing substrate surface under nearly collision-free conditions. To date we have grown diamond films from CCl_3 or CH_3 radicals together with atomic hydrogen, generated by injecting CHCl_3 or CH_4 and H_2 into the F atom stream at reactor pressures between 10^{-4} and 10^{-2} Torr. This approach should be ideal for low-temperature growth and atomic layer epitaxy: growth rates remain relatively high because activation energies for radical reactions are typically small and because the cycle times for atomic layer epitaxy can be reduced to the msec range by fast gas-stream switching, and contamination and segregation are minimized by keeping the surface "capped" by chemisorbed intermediates.

INTRODUCTION

Radical chemistry offers a number of potentially very important advantages for chemical vapor deposition and atomic layer epitaxy¹ of thin films but has been largely ignored. The attainment of low growth temperatures is a major goal of current research—interdiffusion is greatly reduced and the effects of differential thermal expansion coefficients in complex layered materials are minimized. Radical precursors enable the dangling bonds on the substrate surface to remain capped during the entire growth process—reducing contamination, segregation, interdiffusion, and three-dimensional island formation—since radicals can create vacant surface sites by simply abstracting the capping adsorbed atoms. Maintaining a terminated surface appears to be absolutely essential to the growth of diamond films.² Once a radical precursor has chemisorbed on the substrate surface, the resulting surface species is more likely decompose (yielding growth) than to simply desorb (yielding nothing). This preference for decomposition over desorption is the most likely reason why CH_3 is a more effective growth precursor for diamond than is C_2H_2 .^{3,4} A further consequence of the "stickiness" of radical precursors is that nucleation densities may be greatly enhanced, particularly for materials with extreme properties such as diamond. Finally, radical precursors may specifically enhance atomic layer epitaxy (ALE) processes. ALE involves alternating exposures to different gas-phase reactants, with approximately one monolayer deposited per cycle.¹ Development of ALE processes for group IV materials such as silicon and diamond has proved to be very challenging,^{1,5} and radical reactants may provide the key to the development of a commercially-viable process. Also, the use of radical precursors in medium vacuum in principle allows cycle times to be reduced from typical values of 10 sec and more⁵ to the msec range, greatly improving the cost-competitiveness of ALE processes. The cycle time should be

limited by gas-flow switching times rather than reactor evacuation times since wall collisions will consume the radicals by chemical reaction.

We are developing a method for achieving ALE growth of group IV materials using radical reactants generated in a chemically-specific way in medium vacuum. As described in detail elsewhere,⁶ the method involves alternating cycles of halogenated precursor and atomic hydrogen:



where A = C, Si, or Ge and X is a halogen atom. The cycle begins with a hydrogenated substrate surface. Surface hydrogen is abstracted by an AX₃ radical, and then a second AX₃ radical adsorbs on the resulting dangling-bond site. Reactions (1) and (2) will be self-terminating because activation energies for abstraction of halogens by carbon- and silicon-centered radicals are much higher than for abstraction of hydrogen.^{7,8} Abstraction of halogen atoms adsorbed on Si(100) by atomic hydrogen has been shown to be facile,⁹ and abstraction reactions are also believed to play a dominant role in surface reactions in diamond CVD.^{2,10}

EXPERIMENTAL

Our radical CVD/ALE reactor, illustrated schematically in Fig. 1, is ultrahigh-vacuum-compatible and is evacuated by a corrosive-service turbomolecular pump with an integral molecular drag stage and oil-free diaphragm backing pump. F₂ is injected into a MgO tube which is wrapped by Ni foil. The Ni foil acts as a furnace for the MgO tube and is resistively heated to a temperature of 700-800 °C, in principle yielding fluorine dissociation in the range of 96-98% at a pressure of ≈1 Torr. MgO is chosen as the wall material because MgF₂, which will form on the inside wall of the tube, is among the least volatile of all the fluorides (lower than NiF₂, for example), with a vapor pressure of 10⁻⁸ to 10⁻⁶ Torr in this temperature range. The principal advantages of a thermal source relative to a discharge source are simplicity, low cost, and flexibility in the choice of gas pressures and flow rates (maintenance of a plasma discharge requires a substantial pressure and flow rate). For a scaled-up reactor, a plasma F-atom source would probably be preferable. The fluorine atoms abstract hydrogen atoms quantitatively from precursor molecules injected in excess downstream from the F source where the gas density is high enough for collisions. The extreme reactivity of fluorine atoms toward hydrogen drives the reaction to completion, producing HF (135 kcal/mol bond energy), which is nonreactive to hydrogen-terminated diamond, silicon, and germanium in the absence of water. The radicals (and HF) formed downstream of the F-atom source flow under nearly collision-free 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).¹¹

Our initial film growth efforts have focused on diamond, which has been successfully grown at pressures less than 1 Torr by only a handful of groups.¹² The reagents F₂ (Air Products, 97%), CHCl₃ (Aldrich, 99.9%), CH₄ (Matheson, 99.99%) and H₂ (Air Products, 99.9995%) were used without further purification. The CHCl₃ was carefully outgassed before use by numerous freeze-evacuate-thaw cycles. Typical flow rates were 0.1-1.5 sccm of F₂, 4-6 sccm of H₂, and 2-6 sccm of CHCl₃ or CH₄. The chamber pressure rose to 10⁻⁴ - 10⁻² Torr during growth.

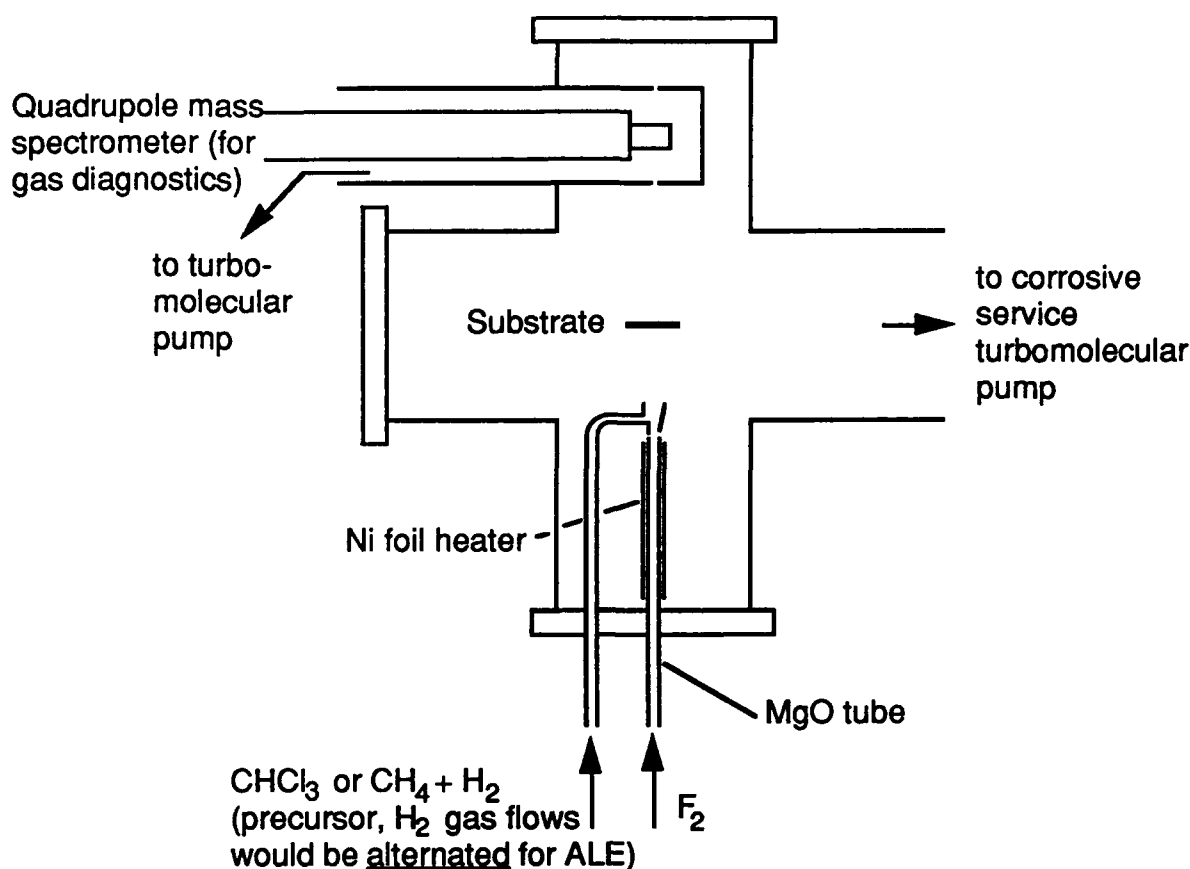


FIG. 1. Schematic of ultrahigh-vacuum-compatible radical ALE/CVD growth apparatus.

Natural diamond (100) substrates, $3.0 \times 3.0 \times 0.22 \text{ mm}^3$ in dimension, were supported by resistively-heated 0.025-mm-thick Pt foil or, alternatively, between two 1.6-mm-diameter graphite rods. The samples were held at 850-950 °C during the growth experiments, as measured by a chromel-alumel thermocouple.

Films were characterized by Raman spectroscopy, scanning electron microscopy, and electron-beam microprobe. Film thicknesses were determined by measuring the total thickness of the diamond (100) substrates before and after growth from the fringe pattern in Fourier transform infrared transmission spectra.^{4(b)}

RESULTS AND DISCUSSION

To date the best evidence we have obtained for diamond growth using the new method is a film grown using CHCl_3 as the precursor which increased in thickness by $0.9 \text{ }\mu\text{m}$ in 12 hours, corresponding to a modest growth rate of $0.08 \text{ }\mu\text{m/hr}$. We estimate the uncertainty in the thickness measurements to be $\pm 0.4 \text{ }\mu\text{m}$, so the thickness increase appears to be real. A scanning electron micrograph of this film is shown in Fig. 2, and a Raman spectrum obtained after growth is shown in Fig. 3. The SEM image also suggests that growth has occurred: the linear features arranged by 90° with respect to one another on the left-hand portion of the image are highly suggestive of $[011]$ - and $[0\bar{1}1]$ -oriented ledge features arising from growth, as no such features were present on the as-polished substrate and ledges do not normally occur upon etching.



FIG. 2. Scanning electron micrograph of 0.9- μm -thick film grown from CCl_3+H on diamond (100).

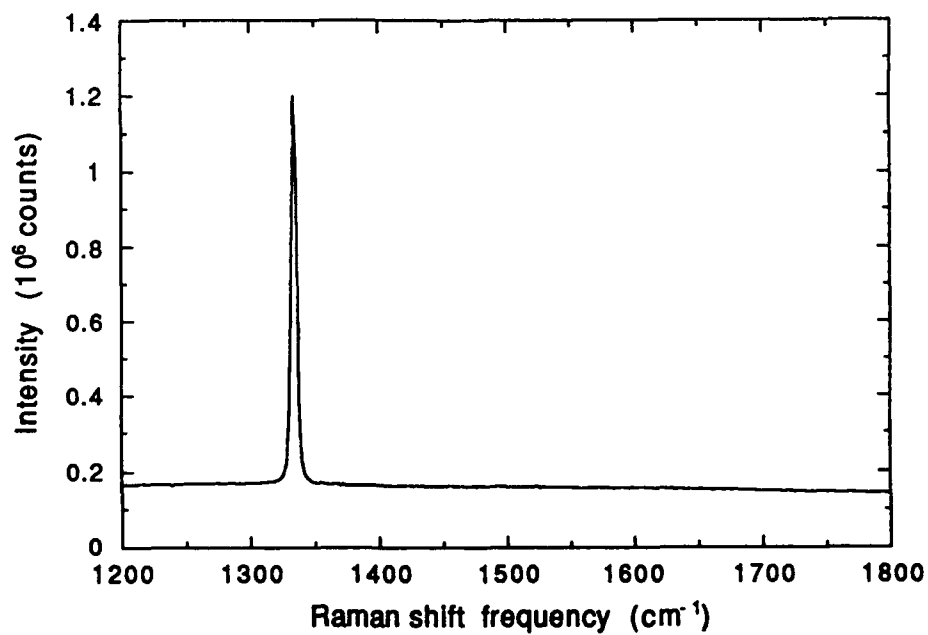


FIG. 3. Raman spectrum of 0.9- μm -thick film grown from $\text{CCl}_3 + \text{H}$ on diamond (100).

A scanning electron micrograph of a film grown for 10 hours from $\text{CH}_4 + \text{H}_2$ is shown in Fig. 4. The thickness increase is measured to be only $0.3\text{ }\mu\text{m}$, which is within our estimated uncertainty for the thickness measurements. The SEM image suggests that both growth and etching have occurred: the central feature appears clearly to be an etch pit and the region around the periphery with a rough morphology presumably resulted from growth. Another diamond sample grown with a smaller CH_4 flow and larger H_2 flow exhibited larger and more numerous etch pits and smooth regions where neither growth nor etching appear to have taken place; the infrared transmission measurements indicated a thickness decrease of $0.3\text{ }\mu\text{m}$.



FIG. 4. Scanning electron micrograph of $0.3\text{-}\mu\text{m}$ -thick film grown in 10 hours from $\text{CH}_3 + \text{H}$ on a diamond (100) substrate.

Deposits of metal fluorides (NiF_2 , MgF_2 , AlF_3 , CaF_2 , and SiF_2) were sometimes observed on portions of the samples, the sample holder and on the chamber walls, and may have played a role in forming the globular features on the right-hand portion of Fig. 3. Areas of the sample which were free of visible particulates appeared to be contamination-free at the sensitivity of the electron-beam microprobe. Surface contamination may nonetheless have reduced the growth rate. We believe that initial designs for the gas injector and sample holder were responsible for most of the impurities, as modification of the apparatus eliminated the deposits. It is presently unclear whether the observed etching of diamond (Fig. 4) resulted primarily from atomic hydrogen or unreacted F_2 and whether metal fluoride contaminants play an important role. The Raman spectrum (Fig. 3) indicates that no non-diamond carbon was deposited, to within our sensitivity limit, as no feature near 1550 cm^{-1} associated with graphitic carbon is visible.

Further diamond growth experiments are underway in our laboratory. Presently we are attempting to grow polycrystalline diamond films on copper substrates, which would bypass the potential ambiguities in the infrared thickness measurements. We hope to improve several aspects

of the experiments, including the reliability of the radical source and the sensitivity of the growth rate measurements. Once incontrovertible evidence for diamond growth has been achieved and the approximate parameter values for optimal growth have been identified, we hope to be able to achieve ALE by cycling the reactant fluxes.

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. We also thank Dr. Dan Callahan for assistance with the scanning electron microscopy, and Benjamin Bai, Judy Chu, and Yitao Ren for assistance with the Raman spectroscopy.

REFERENCES

1. T. Suntola, *Mater. Sci. Reports* **4**, 265 (1989); *Proceedings of the Second International Symposium on Atomic Layer Epitaxy, Thin Solid Films* (in press).
2. (a) W. A. Yarbrough and R. Messier, *Science* **247**, 688 (1990); (b) F. G. Celii and J. E. Butler, *Annu. Rev. Phys. Chem.* **42**, 643 (1991); (c) J. C. Angus, Y. Wang, and M. Sunkara, *Annu. Rev. Mater. Sci.* **21**, 221 (1991).
3. (a) L. R. Martin and M. W. Hill, *J. Mater. Sci. Lett.* **9**, 621 (1990); (b) S. J. Harris and L. R. Martin, *J. Mater. Res.* **5**, 2313 (1990); (c) L. R. Martin, *J. Mater. Sci. Lett.* (in press).
4. (a) C. J. Chu, M. P. D'Evelyn, R. H. Hauge, and J. L. Margrave, *J. Mater. Res.* **5**, 2405 (1990); (b) *J. Appl. Phys.* **70**, 1695 (1991); (c) M. P. D'Evelyn, C. J. Chu, R. H. Hauge, and J. L. Margrave, *J. Appl. Phys.* **71**, 1528 (1992).
5. J. Nishizawa, K. Aoki, S. Suzuki, K. Kikuchi, *J. Electrochem Soc.* **137**, 1898 (1990).
6. T. I. Hukka, R. E. Rawles, and M. P. D'Evelyn, *Thin Solid Films* (in press).
7. J. A. Kerr, in *Free Radicals*, ed. J. K. Kochi (Wiley, New York, 1973), p. 1.
8. J. W. Wilt, in *Reactive Intermediates*, Vol. 3, ed. R. A. Abramovitch (Plenum, New York, 1983), p. 113.
9. C. C. Cheng, S. R. Lucas, H. Gutleben, W. J. Choyke, and J. T. Yates, Jr., *J. Am. Chem. Soc.* **114**, 1249 (1992).
10. (a) S. J. Harris, *Appl. Phys. Lett.* **56**, 2298 (1990); (b) M. Frenklach and H. Wang, *Phys. Rev. B* **43**, 1520 (1991); (c) B. J. Garrison, E. J. Dawnkaski, D. Srivastava, and D. W. Brenner, *Science* **255**, 835 (1992); (d) M. Zhu, R. H. Hauge, J. L. Margrave, and M. P. D'Evelyn, *Mater. Res. Soc. Symp. Proc.* (in press).
11. J. E. Spencer, J. H. Dinan, P. R. Boyd, H. Wilson, and S. E. Buttrill, Jr., *J. Vac. Sci. Technol. A* **7**, 676 (1989).
12. (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) S. Jin and T. D. Moustakas, *Dia. Rel. Mater.* (in press).