②

OFFICE OF NAVAL RESEARCH

Grant N00014-91-J-1550

R&T Code: 413w003

Technical Report No. 7

Homoepitaxial growth rate studies on diamond (110), (111), and (100) surfaces in a hot-filament reactor

by

C. J. Chu, B. J. Bai, N. J. Komplin, D. E. Patterson, M. P. D'Evelyn,
R. H. Hauge, and J. L. Margrave

Prepared for publication in

Materials Research Society Symposium Proceedings

Rice University
Department of Chemistry
Houston, TX 77251-1892

May 29, 1992

REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1. AGENCY USE ONLY *(Leave blank)*

2. REPORT DATE May 1992

3. REPORT TYPE AND DATES COVERED Technical

4. TITLE AND SUBTITLE
Homoepitaxial growth rate studies on diamond (110), (111), and (100) surfaces in a hot-filament reactor

5. FUNDING NUMBERS
Grant #:
N00014-91-J-1550

6. AUTHOR(S)
C. J. Chu, B. J. Bai, N. J. Komplin, D. E. Patterson, M. P. D'Evelyn, R. H. Hauge, and J. L. Margrave

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
Rice University
Department of Chemistry
Houston, TX 77251-1892

8. PERFORMING ORGANIZATION REPORT NUMBER
Technical Report
#7

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:
Materials Research Society Symposium Proceedings (in press).

12a. DISTRIBUTION / AVAILABILITY STATEMENT
Approved for public release; distribution is unlimited.

12b. DISTRIBUTION CODE

13. ABSTRACT *(Maximum 200 words)*

Growth rates of homoepitaxial (110), (111), and (100) diamond films were experimentally determined, for the first time, in a hot filament reactor using methane and carbon tetrachloride as the carbon source. Methane concentrations from 0.07% to 1.03% in H_2 were studied at a substrate temperature of 970 °C. Growth rates were found to be crystal-face dependent with respect to methane concentration, being linear or first order for the (100) orientation, sublinear for (110), and sigmoidal for (111). The observed growth kinetics of (111) suggest the viability of an acetylene mechanism for (111), along with the methyl radical mechanism at methane concentrations above 0.73%. CCl_4 concentrations from 0.06% to 0.69% in H_2 were also investigated at a substrate temperature of 970 °C. Growth rate behavior was similar to that of methane for all three crystal faces. The temperature dependence of the growth rates was also crystal-orientation dependent. At substrate temperatures above 730 °C, growth rates are thought to be mainly transport limited, yielding effective activation energies of 8 ± 3, 18 ± 2, and 12 ± 4 kcal/mol for (100), (110), and (111) orientations, respectively. At substrate temperatures below 730 °C, growth rates are thought to be surface reaction rate-limited, with an overall effective activation energy of 50 ± 19 kcal/mol for the three crystal-orientations studied.

14. SUBJECT TERMS
Diamond, chemical vapor deposition, homoepitaxy, 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
Unclassified	Unclassified	Unclassified	

HOMOEPITAXIAL GROWTH RATE STUDIES ON DIAMOND (110), (111), AND (100) SURFACES IN A HOT-FILAMENT REACTOR

C. JUDITH CHU*, BENJAMIN J. BAI, NORMA J. KOMPLIN, DONALD E. PATTERSON*
MARK P. D'EVELYN, ROBERT H. HAUGE, AND JOHN L. MARGRAVE*
Rice University, Department of Chemistry, P. O. Box 1892, Houston, TX 77251
*also affiliated with Houston Advanced Research Center, 4802 Research Forest Dr.,
The Woodlands, TX 77381

ABSTRACT

Growth rates of homoepitaxial (110), (111), and (100) diamond films were experimentally determined, for the first time, in a hot filament reactor using methane and carbon tetrachloride as the carbon source. Methane concentrations from 0.07% to 1.03 % in H_2 were studied at a substrate temperature of 970°C. Growth rates were found to be crystal-face dependent with respect to methane concentration, being linear or first order for the (100)-orientation, sublinear for (110), and sigmoidal for (111). The observed growth kinetics of (111) suggest the viability of an acetylene mechanism for (111), along with the methyl radical mechanism at methane concentrations above 0.73%. CCl_4 concentrations from 0.06% to 0.69% in H_2 were also investigated at a substrate temperature of 970°C. Growth rate behavior was similar to that of methane for all three crystal faces.

The temperature dependence of the growth rates was also crystal-orientation dependent. At substrate temperatures above 730°C, growth rates are thought to be mainly transport limited, yielding effective activation energies of 8±3, 18±2, and 12±4 kcal/mole for (100), (110), and (111) orientations, respectively. At substrate temperatures below 730°C, growth rates are thought to be surface reaction rate-limited, with an overall effective activation energy of 50±19 kcal/mole for the three crystal-orientations studied.

Introduction

It is well known in the chemical vapor deposition of polycrystalline diamond films that the final film morphology is very sensitive to growth conditions such as substrate temperature and methane concentration. There have been reports of changes in the crystal faces from (111) to (100) as well as from (100) to (111) with increasing substrate temperature.[1-3] With increasing methane concentration, the morphology changes from predominantly (111) at low concentrations, to cubo-octahedron ((111) and (100)), to predominantly (100) at high concentrations (3-6% CH_4).[1-2,4-6] Clearly a detailed study of the growth kinetics is needed. Due to the complexity of polycrystalline diamond growth, and the fact that the modeling of diamond growth has all been performed on single faces of diamond such as (110),[7] (111),[8-10] and (100),[11-12] a study of the growth kinetics of homoepitaxial (100), (111), and (110) diamond films is therefore warranted. We have previously reported the growth of homoepitaxial (111), (100), and (110) diamond films in our hot filament reactor in identifying the precursor for diamond growth.[13] We now present the results of our growth rate studies on (110), (111), and (100) diamonds.

Experimental

The hot-filament chemical vapor deposition chamber used for these studies has been described in detail previously.[14] A diagram detailing the position of the diamond substrates relative to the filaments, the methane injection port, and the gas sampling port is illustrated in Figure 1. The experimental conditions are listed in Table I. Five strands of 5 mil tungsten wire at 2160°C (measured by optical pyrometry) were used for hydrogen activation. Methane was injected either with the hydrogen above the hot filaments or below the filaments near the substrate, with 10 sccm of H_2. The experiments with CCl_4 were performed by injection under the filaments with 10 sccm of H_2. The (110), (111), and (100) diamond substrates were type 2A natural diamond windows from Dubbledee Harris, 1.5 x 1.5 x 0.1 mm in dimension. The diamonds were mounted side-by-side on a 6 mil-thick platinum ribbon which functions as a holder and heater. Circular holes, 0.05 mm in diameter, were cut in the platinum ribbon under the diamond windows which enabled the platinum ribbon to function simultaneously as an IR holder. During growth, the holes were covered with thin-foil platinum (3 mil thick) to prevent growth on the bottom side of the diamond substrates. The temperature of the substrates were measured by a Pt/Pt13%Rh thermocouple spot-welded on the platinum ribbon between the diamonds. The growth rate measurements were performed by growing the diamond films at a given CH_4 concentration and substrate temperature for 1 hour (0.5 hr for CCl_4), then removing the platinum ribbon and measuring the changes in thickness of the diamond windows from the interference fringes in transmission FTIR with the equation $d = (2n)^{-1}[(1/\lambda_2) - (1/\lambda_1)]^{-1}$ where

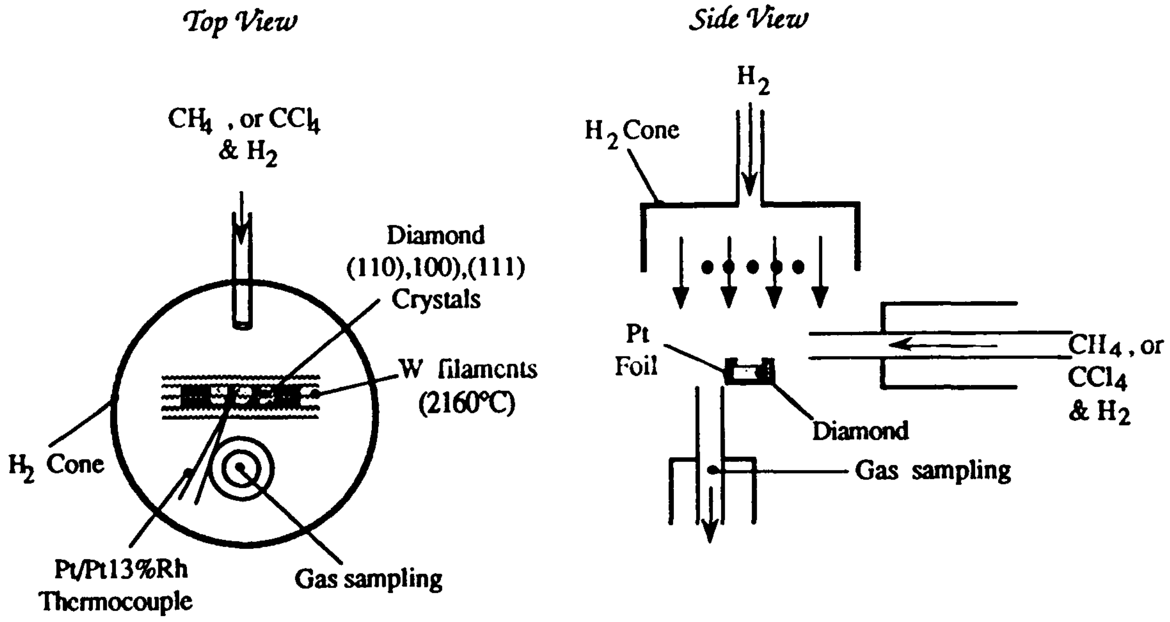
d = thickness of the diamond,
λ= frequency,
n = index of refraction of diamond.

The thickness measurements were averaged from 1000 to 600 cm-1 and a 0.1 mm accuracy in the thickness calculations was obtained.

Table I. Experimental Conditions

Concentration study:	
H_2 (over filaments)	150 sccm
H_2 (below filaments) (when injecting CH_4 below the filaments)	10 sccm
CH_4 flow	0.1 - 1.3 sccm
CCl_4 flow	0.1 - 1.1 sccm
chamber pressure	25 torr
substrate temperature	970°C
filament temperature	2160°C
substrate to filament distance	10 mm
Substrate temperature study	
hydrogen gas (over filaments)	150 sccm
CH_4 flow	0.6 sccm
chamber pressure	25 torr
substrate temperature	1000-600°C
filament temperature	2160°C
substrate to filament distance	10 mm

Figure 1. Diamond substrates in the CVD chamber

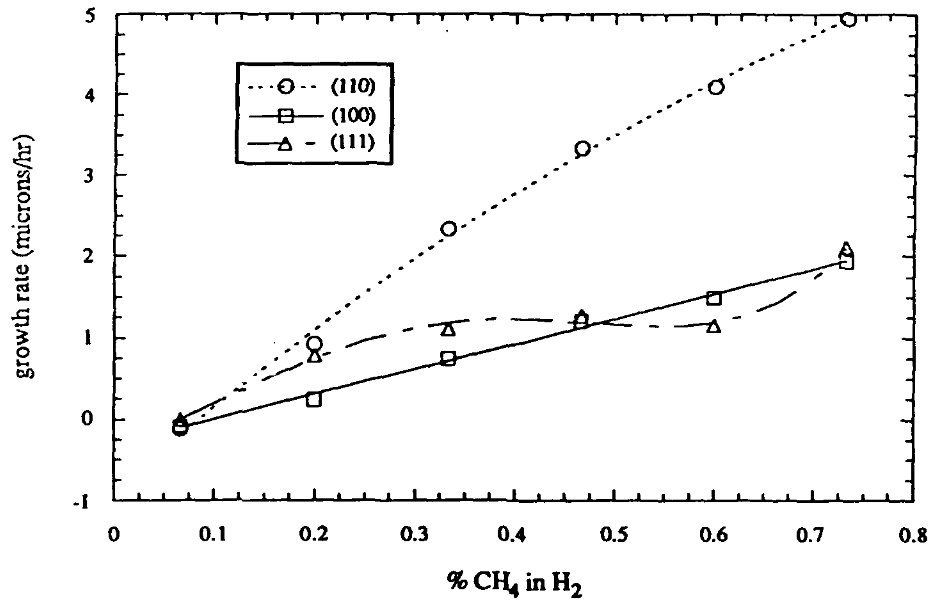


Results and Discussion

Dependence of growth rates relative to concentration

The dependence of (110), (111), and (100) diamond growth rates on CH_4 concentration is shown in Figure 2 where CH_4 and H_2 were introduced above the filaments. Methane concentrations from 0.07% to 1.03 % in H_2 were studied at a substrate temperature of 970°C. Growth rates were found to be crystal-face dependent. Linear or first order growth rates were observed for (100) diamond films with respect to methane concentration. (110) was the fastest growing crystal-face, exhibiting a sublinear functional dependence on methane concentration. A sigmoidal dependence was observed for (111)-oriented diamond films where the growth rate became relatively insensitive to methane concentration from 0.33% to 0.60%. This insensitivity to methane concentration implies a saturation of CH_3 radical coverage on the (111) surface, presumably due to the large steric effects in achieving clusters of CH_3 on (111).[15] Small variations in methane concentration can change the relative growth rates of (111) and (100). At very low methane concentrations (below 0.48%), the growth rate of (111) is faster than (100); from 0.48% to 0.72 %, (100) is faster than (111); and above 0.72 %, (111) becomes again the faster growing orientation. This phenomena is consistent with polycrystalline film growth where it is widely known that small changes in the growth conditions can change the final film morphology either from (111) to (100) or from (100) to (111).

Figure 2. Diamond homoepitaxy growth rate study
CH_4 introduced above the filaments



The observed relative insensitivity of (111) to methane or methyl radical concentration, coupled with a linear rise in growth rates at higher methane concentrations, imply the existence of another growth mechanism besides the methyl radical mechanism for the (111) crystal face. It can be postulated that acetylene may become equally as important as the methyl radical for (111) film growth at high methane concentrations. From gas phase analysis, we have observed a near second-order dependence of acetylene on methane concentration, where at high methane flow rates, the relative concentrations of acetylene becomes greater than that of methane. These simultaneous increases in (111) growth rate and acetylene concentration suggest a complex growth mechanism for the (111) crystal face.

Results from growth rates studies with CH_4 and CCl_4 injected below the filaments are illustrated in Figures 3 and 4, respectively. Figure 3 is a combined plot of the above-filament and below-filament CH_4 injection where the CH_4 concentrations for below-filament injection have been multiplied by 1.4. This is an experimentally derived factor to compensate for the higher localized CH_4 concentrations for below-filament injections. Similar results and interpretations of diamond growth mechanisms are obtained for the below-filament studies as for the above-filament methane studies. Homoepitaxial diamond film growth with CCl_4 appears to be similar to that of CH_4 under the experimental conditions related in this study.

Figure 3. Diamond homoepitaxy growth rate study of CH_4 injected above (open symbols) and below (filled symbols) the filaments

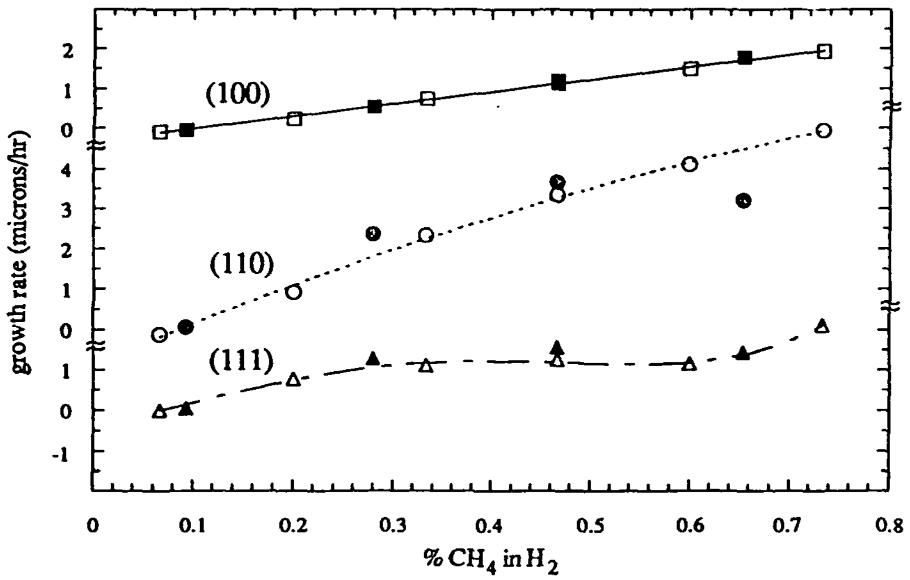
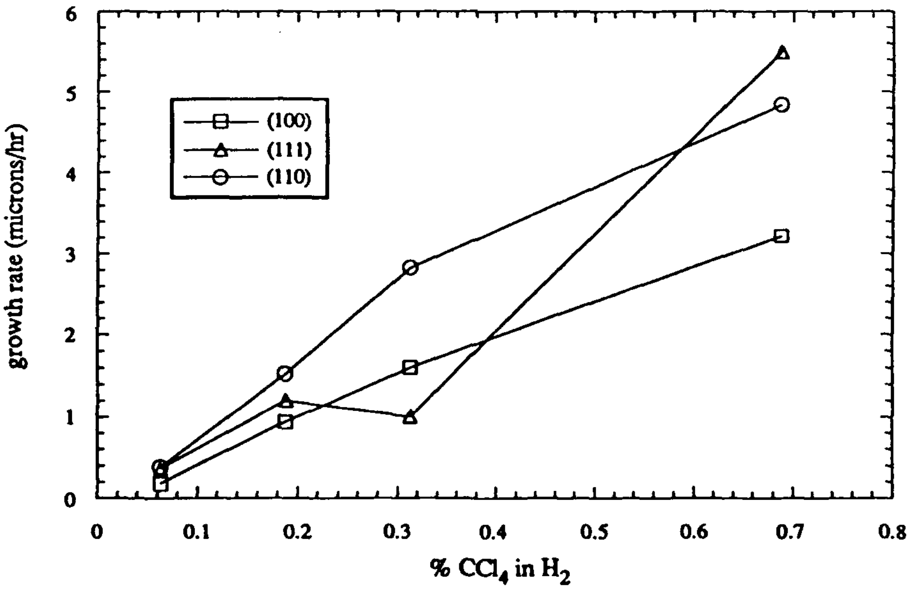


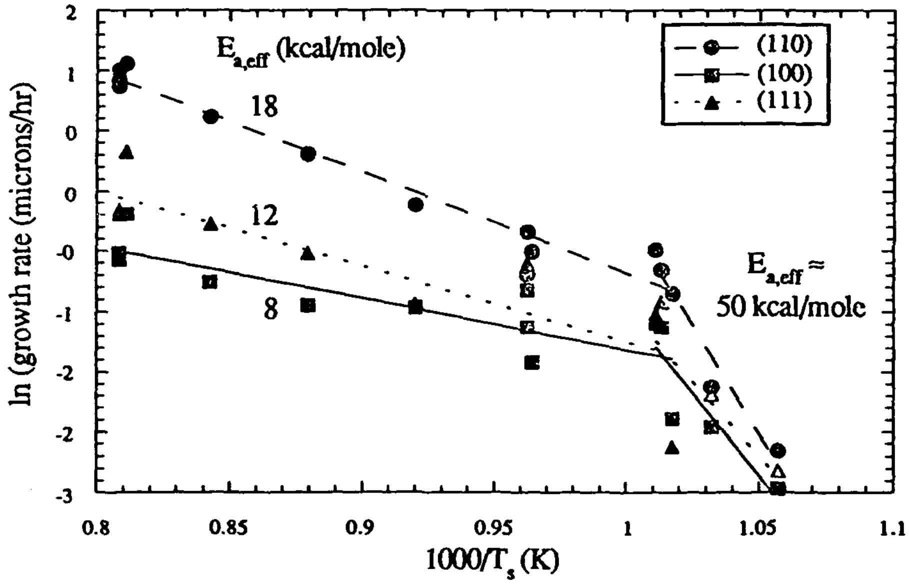
Figure 4. Diamond homoepitaxy growth rate study with CCl_4 as the carbon source



Dependence of growth rate on substrate temperature

The effects of substrate temperature on growth rates were studied at a CH_4 concentration of 0.4%. The results are illustrated in Figure 5. Two temperature dependent regions were observed. At substrate temperatures above 730°C, growth rates are weakly temperature dependent. This behavior is typical of that observed for the chemical vapor deposition of single crystal silicon.[16] When surface reaction rates are fast relative to the transport of reactants to the growth surface, transport becomes the rate-limiting step, thus growth rates are not as sensitive to temperature. In this transport-limited region, the temperature dependence of the growth rates

Figure 5. Temperature dependence study of growth rates



was found to be somewhat crystal-face dependent. Different effective activation energies of 8±3, 18±2, and 12±4 kcal/mole were calculated for the (100), (110), and (111) orientations, respectively. These differences suggest that reaction rates are not enirely determined by transport limitations.

At substrate temperatures below 730°C, growth rates are highly temperature dependent. At the lower substrate temperatures, surface reactions becomes slow relative to transport, thus growth rates become strongly temperature dependent, yielding an overall effective activation energy of 50±19 kcal/mole for the three crystal-orientations studied. Due to the high scatter of the data, the relative activation energies for (110), (111), and (100) can not be differentiated.

Conclusions

To summarize, growth rates of homoepitaxial (110), (111), and (100) diamond films were experimentally determined for the first time. Methane and carbon tetrachloride were used as the carbon source in a hot filament reactor. Growth rates were found to be crystal-face dependent with respect to methane concentration, being linear or first order for the (100)-orientation, sublinear for (110), and sigmoidal for (111). The behavior of (111) growth rates suggests a viable acetylene-methyl radical mechanism for the (111) crystal-face. Growth rate behavior with CCl_4 was similar to that of methane for all three crystal faces.

Two rate-limiting temperature regions were found in the temperature dependent growth rate studies. At substrate temperatures above 730°C, growth rates are thought to be transport limited and crystal-orientation dependent, yielding effective activation energies of 8±3, 18±2, and 12±4 kcal/mole for (100), (110), and (111) orientations, respectively. At substrate temperatures below 730°C, growth rates are thought to be surface reaction rate-limited, with an overall effective activation energy of 50±19 kcal/mole for the three crystal-orientations studied.

Acknowledgement

The authors wish to acknowledge the support of the National Science Foundation, DARPA, and the Office of Naval Research for this work.

References

1. B.V. Spitsyn and L. L. Bouilov, Diamond and Diamond-Like Materials Synthesis, MRS Extended Abstracts, EA-15, edited by G.H. Johnson, A.R. Badzian, M.N. Geis (Materials Research Society, Pittsburgh, PA, 1988) pp. 3-14.
2. W. Zhu, R. Messier, A.R. Badzian, Proceedings of the First International Symposium on Diamond and Diamond-Like Films, edited by J.P. Dismukes et. al. (The Electrochemical Society, Los Angeles, 1989) pp.61-79.
3. S. Matsumoto, Y. Sato, M. Tsutsumi, N. Setaka, J. Mater. Sci. 17, 3106 (1982).
4. K. Kobashi, K. Nishimura, Y. Kawate, and T. Horuchi, Phy. Rev. B38, 4067 (1988).
5. Y. Sato, C. Hata, M. Kamo, First International Conference on the New Diamond Science and Technology Program and Abstr., 50-51 (JNDF, Tokyo, 1988)
6. W.A. Yarbrough and R. Messier, Science 247, 688-696 (1990).
7. W.A. Yarbrough, Diamond Optics IV, SPIE Proc. 1534, edited by S. Holly and A. Feldman, 1991) p. 90.
8. M. Frenklach and K.E. Spear, J. Mater. Res. 3, 133 (1988).
9. D. Huang, M. Frenklach, and M. Maroncelli, J. Phys. Chem 92, 6379 (1988).
10. S.J. Harris, D.N. Belton, and R.J. Blint, J. Appl. Phys. 70, 2654 (1991)
11. S. J. Harris, Appl. Phys. Lett. 56, 2298 (1990).
12. D.G. Goodwin, Appl. Phys. Lett. 59, 277 (1991).
13. C.J. Chu, M.P. D'Evelyn, R.H. Hauge, and J.L. Margrave, J. Appl. Phys. 70, 1695 (1991).
14. C.J. Chu, M.P. D'Evelyn, R.H. Hauge, and J.L. Margrave, J. Mater. Res. 5, 2405 (1990).
15. S.M. Valone, M. Trkula, and J.R. Laia, J. Mater. Res. 5, 2296(1990).
16. J.M. Jasinski, B.S. Meyerson, and B.A. Scott, Ann. Rev. Phys. Chem. 38, 109-40 (1987).