REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1a. REPORT SECURITY CLASSIFICATION	1b. RESTRICTIVE MARKINGS
Unclassified/Unlimited	

AD-A216 090

DTIC
ELECTE
DEC 21 1989
S D
D C8

2a. SECURITY CLASSIFICATION AUTHORITY	3. DISTRIBUTION/AVAILABILITY OF REPORT
	Approved for Public Release
2b.	Distribution Unlimited

4. PERFORMING ORGANIZATION REPORT NUMBER(S)	5. MONITORING ORGANIZATION REPORT NUMBER(S)
Number 2	N00014-89-J-1197

6a. NAME OF PERFORMING ORGANIZATION	6b. OFFICE SYMBOL (If applicable)	7a. NAME OF MONITORING ORGANIZATION
Stanford University		Office of Naval Research Dr. R. Schwartz

6c. ADDRESS (City, State, and ZIP Code)	7b. ADDRESS (City, State, and ZIP Code)
Mechanical Engineering Dept. Bldg. 520 Stanford, CA 94305-3032	Code 373 Naval Weapons Center China Lake, CA 93555-6001

8a. NAME OF FUNDING/SPONSORING ORGANIZATION	8b. OFFICE SYMBOL (If applicable)	9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER
Office of Naval Research		

8c. ADDRESS (City, State, and ZIP Code)	10. SOURCE OF FUNDING NUMBERS			
800 N. Quincy Street Arlington, VA 22217-5000	PROGRAM ELEMENT NO.	PROJECT NO.	TASK NO	WORK UNIT ACCESSION NO.

11. TITLE (Include Security Classification)
High Growth Rate Diamond Synthesis in a Large Area Atmospheric Pressure Inductively Coupled Plasma

12. PERSONAL AUTHOR(S)
M. A. Cappelli, T. Owano, M. Gordon, C. H. Kruger

13a. TYPE OF REPORT	13b. TIME COVERED	14. DATE OF REPORT (Year, Month, Day)	15. PAGE COUNT
Technical	FROM ____ TO ____	1989, December 12	11

16. SUPPLEMENTARY NOTATION
Submitted to Applied Physics Letters

17. COSATI CODES			18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)
FIELD	GROUP	SUB-GROUP	Diamond Synthesis, Thermal Plasma, Raman spectroscopy of Diamond.

19. ABSTRACT (Continue on reverse if necessary and identify by block number)

Diamond synthesis is demonstrated in an atmospheric pressure inductively coupled argon-hydrogen-methane plasma. The plasma generated has a free stream active area of 20 cm^2 and has an equilibrium electron temperature T_e, of approximately 4000 K. Growth rates are typically in the range of 25-50 μm/hour and are found to depend on the processing condditions and position on the substrate. Individual crystallites are analyzed by micro-Raman spectroscopy. Large (50 μm) size well-faceted crystallites are found to be under a state of compression, displaying shifts in the principal phonon mode as great as 3 cm^{-1} from that of smaller polycrystalline diamond clusters or secondary nucleation sites. These shifts are shown to be expected within the framework of linear thermal expansion theory and the assumption of negligible stress relief at the crystallite-substrate interface.

20. DISTRIBUTION/AVAILABILITY OF ABSTRACT	21. ABSTRACT SECURITY CLASSIFICATION
☐ UNCLASSIFIED/UNLIMITED ☒ SAME AS RPT ☐ DTIC USERS	

22a. NAME OF RESPONSIBLE INDIVIDUAL	22b. TELEPHONE (Include Area Code)	22c. OFFICE SYMBOL

DD Form 1473, JUN 86
Previous editions are obsolete

89 12 20 074

HIGH GROWTH RATE DIAMOND SYNTHESIS IN A LARGE AREA ATMOSPHERIC PRESSURE INDUCTIVELY COUPLED PLASMA

Submitted by

M. A. Cappelli, T. Owano, M. Gordon and C.H. Kruger
High Temperature Gasdynamics Laboratory
Stanford University
Stanford, California 94305-3032

December 12, 1989

HIGH GROWTH RATE DIAMOND SYNTHESIS IN A LARGE AREA ATMOSPHERIC PRESSURE INDUCTIVELY COUPLED PLASMA

M. A. Cappelli, T. Owano, M. Gordon and C.H. Kruger

High Temperature Gasdynamics Laboratory

Stanford University,

Stanford, California 94305-3032

Abstract

Diamond synthesis is demonstrated in an atmospheric pressure inductively coupled argon-hydrogen-methane plasma. The plasma generated has a free stream active area of 20 cm^2 and has an equilibrium electron temperature T_e, of approximately 4000 K. Growth rates are typically in the range of 25-50 μm/hour and are found to depend on the processing condiditions and position on the substrate. Individual crystallites are analyzed by micro-Raman spectroscopy. Large (50 μm) size well-faceted crystallites are found to be under a state of compression, displaying shifts in the principal phonon mode as great as 3 cm^{-1} from that of smaller polycrystalline diamond clusters or secondary nucleation sites. These shifts are shown to be expected within the framework of linear thermal expansion theory and the assumption of negligible stress relief at the crystallite-substrate interface.

High growth rate synthesis of polycrystalline diamond using atmospheric pressure plasmas and flames is a promising alternative to the more conventional synthesis techniques[1-3]. It has already been demonstrated that growth rates as high as 200 μm/hour can be achieved in direct current (DC) plasma arcs[4,5], with a noticeable improvement in quality when compared to microwave plasma deposited diamond film. In DC plasma arc deposition, diamond growth occurs primarily over the region where the arc is in contact with the substrate (usually the anode in the transferred arc mode) and the deposit is highly irregular and non-uniform[4]. High power transferred arcs suffer from additional disadvantages such as cathode material contamination, which suggests that applications of such synthesis strategies may be limited to production of industrial grade polycrystalline powder for abrasive applications. There has been some limited study of the use of inductively coupled thermal plasmas for diamond synthesis[6]. Such a plasma is electrodeless and is therefore preferred over the DC arc in the synthesis of diamond coatings with a minimum level of impurities. In addition, inductively coupled atmospheric plasmas can be generated over larger volumes than their DC counterparts. This makes it attractive for large area coating applications. Such plasmas however, have a number of disadvantages for laboratory investigation and some industrial applications

in that they are intrinsically noisy, generating RF interference at the operating frequency, and can establish relatively high (1-3 kV) plasma potentials[7].

Perhaps most important to the understanding of the deposition chemistry is the fact that these plasmas are close to thermal equilibrium, and an analysis of the reacting stream is complicated solely by the presence of finite rate chemistry. In essence, the problem reduces to that of hot filament assisted chemical vapor deposition of diamond, and is free of the nonequilibrium features associated with low pressure (< 50 torr) microwave and DC discharge sources. A great deal of progress has been made in the modelling of reacting flows (with transport)[8], and we may soon expect to see a one-dimensional transport code that incorporates surface chemsitry[9]. In diamond synthesis at atmospheric pressure, supersaturation of hydrogen in the gas phase adjacent the substrate or growing surface is believed to be responsible for diamond synthesis. This supersaturation is established as a result of rapid diffusion and finite recombination rates through the thermal boundary layer adjacent the growth surface. Atomic hydrogen is known to preferentially "etch" or gasify non-diamond carbon[10,11], and is believed to play a role in producing an "active site" (through adsorbed hydrogen abstraction) in which a gas phase hydrocarbon monomer (of the type C_2H_x) can be inserted to propogate the crystal growth plane[12,13].

In this paper, we report on results of our investigation of diamond synthesis, in an atmospheric pressure inductively coupled plasma flow reactor. In the course of this investigation, we have studied nucleation and growth on a variety of substrates, and report here only our results of a set of experiments involving diamond growth on polycrystalline molybdenum. Our diamond films are grown under conditions similar to that of Matsumoto et al[6] and Koshino et al[4]. No parametric study however, has been performed to investigate the range of optimum processing conditions, and we suspect that this range can be considerably different than that observed in low pressure PECVD of diamond[14].

The plasma deposition facility includes a 50 kW RF generator operating at 4 MHz, and a comercially available inductive load coil torch h. ' vhich acts as an antenna, coupling as much as 20 kW into the gas stream. For the re: '' resented here, an energy balance on the system indicated that approximately 6 kW of power was coupled into a gas stream comprising a mixture of argon, hydrogen and methane with relative volumetric flow ratios of 210:32:1. The total volumetric flow was approximately 120 l/min. A specially designed water cooled quartz cylinder, 5 cm in diameter, surrounded the plasma flow and minimized air entrainment. A water cooled molybdenum substrate holder is mounted in stagnation point flow within this quartz envelope (see Fig.1). A molybdenum foil acts as the substrate, and is fastened by molybdenum clamps to achieve good thermal contact.

The plasma emission is monitored with a 3/4 meter scanning monochromator. Analysis of the relative intensity of hydrogen spectral lines permitted a measurement of the electron temperature which under these conditions is expected to be equal to the gas temperature. For the runs reported here, the line emission was well represented by a straight line on a Boltzmann plot and the free steam electron temperature was measured to be approximately 4000K, 2 cm below the substrate. A dissappearing filament pyrometer is used to measure the surface brightness temperature. For the results presented here, the substrate surface is approximately 3x3 cm in dimension and is maintained at approximately 900 °C. The surface temperature did not appear to vary substantially across the substrate face (although this measurement was a diificult task) however, there may be a slight increase in the surface temperature (approximately 100 °C) from the center stagnation line to the substrate edge.

Results of numerous runs of 2 hours in duration indicate that the deposit is pattern is very reproducible and that the deposit varies substantially across the substrate surface. Nucleation and growth occurs primarily in the outer regions of the substrate surface. There is no nucleation in the central core (r < 1 cm). A low resolution scanning electron micrograph of the area near the interface between the region of no growth (center stagnation region) and the region where a continuious film is established, is depicted in Fig. 2. As one moves radially out from the centre, the nucleation density increases rapidly, with first a region of nicely faceted crystallites followed by a region of dense film. The crystallites appear to adhere very well to the substrate whereas the film can be physically detatched from the substrate with some effort.

The larger well-facetted crystallites display a growth habit yet unreported in low pressure diamond CVD. Fig. 3a is a representative electron micrograph, showing that the (100) facets appear to form a "hollow" twinned structure with three fold rotational symmetry. Fig. 3b depicts a similar structure, again very typical for the deposit, only this crystallite may have reached a later stage in growth, having a more completed crystal habit. The twinned crystallites of the type illustrated in Fig. 3b usually show evidense of secondary nuceation on the completed (100) facets. The individual crystals and secondary nucleation sites were large enough for miro-Raman analysis. The Raman spectrum of the well-faceted crystallites (Fig. 4) contain the characteristic peak associated with the first order phonon mode of diamond althogh shifted somewhat to longer wavelengths (1335 cm^{-1}). This shift is significantly greater than the resolution and accuracy of the instrument (approximately 0.5 cm^{-1}) and is attributed to a compressive stress in the crystallite. This stress arises from the mismatch in thermal expansion between the diamond crystal and underlying interlayer (likely to be MoC or Mo_2C). Substantial shifts in the Raman peaks of CVD diamond grown on sapphire have been reported in the past[15]. The shifts observed here correspond to a compressive stress of approximately 1GPa, based on the pressure dependence of the first order Raman peak as

measured by Boppart et al[16]. A compressive stress of such magnitude is expected if one assumes that the interlayer is Mo_2C with a linear expansion coefficient of approximately 7×10^{-6} °C^{-1} [17] over the temperature range of interest. Upon cooling, $\Delta T \sim 1000$ K, and assuming negligible stress relief at the interface, this translates to a linear compression in diamond of about $a/a_o = 0.9993$ (here a is the bond length and a_o the bond length at atmospheric pressure). Theoretical shifts calculated by Sherman[18] for this compression are in the 2-3 cm^{-1} and hence in agreement with our observations. It should be pointed out that Raman analysis of secondary nucleation sites present on (100) facets show a substantial non-diamond component usually attributed to disordered sp^2 structure[15] and an unshifted Raman peak (Fig. 5). The unshifted Raman peak of diamond is frequently observed when a substantial non-diamond contribution is evident in the Raman spectra, and may be indicative of stress relief by the amorphous matrix.

Growth rates on the order of 25-50 µm/hour have been observed for well faceted crystallites and are more than an order of magnitude greater than that observed in low pressure microwave plasma deposition strategies[14]. This difference is attributed to the higher carbon and atomic hydrogen flux associated with such thermal plasmas at these temperatures. This growth rate is based on an estimate of the crystallite size and the run duration, and may be substantially higher if one takes into account the "induction" time necessary for nucleation[19]. The absence of diamond growth in the region near the stagnation point of the flow is attributed to too high an atomic hydrogen flux, and is the subject of a future publication.
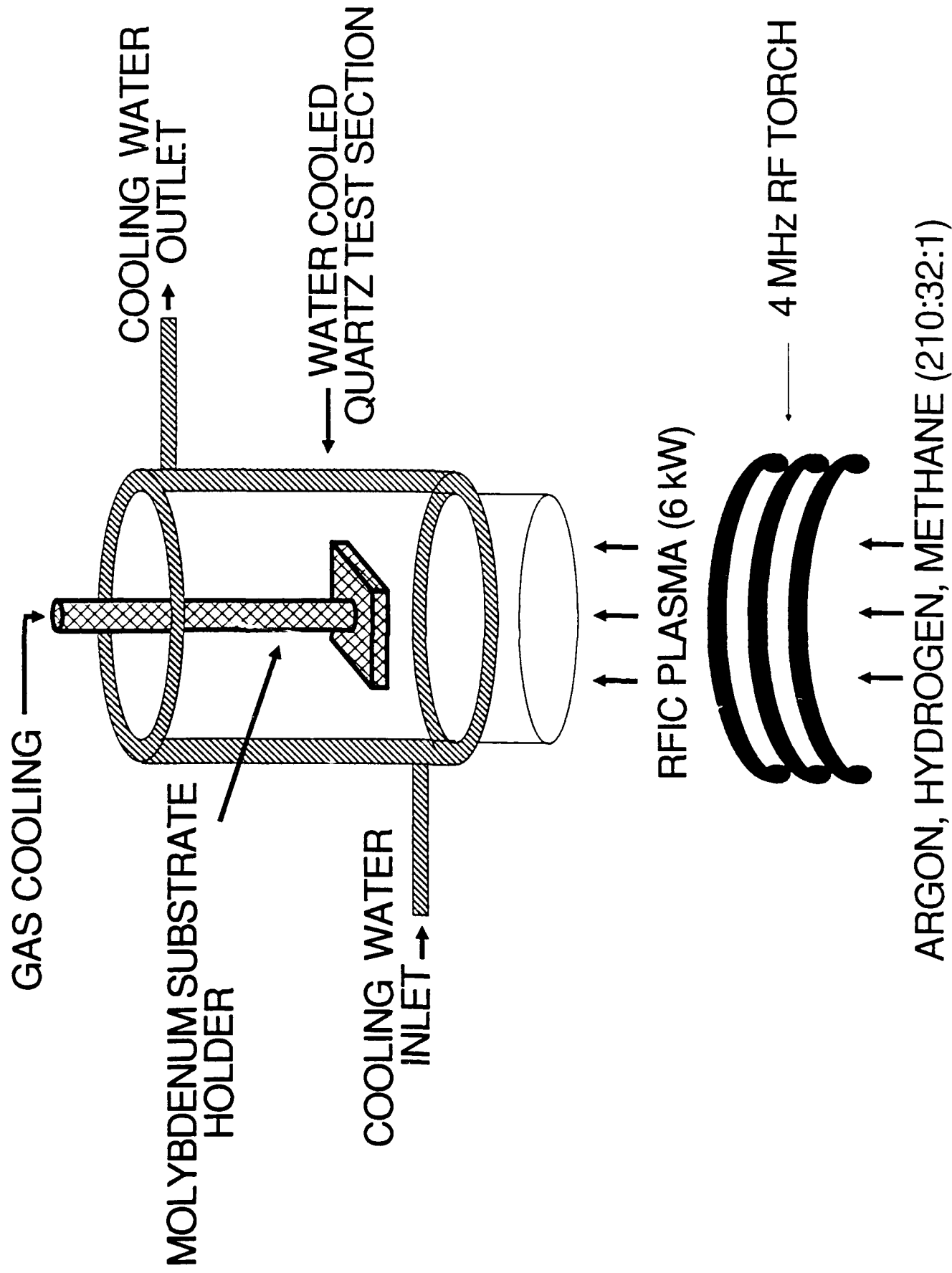
References

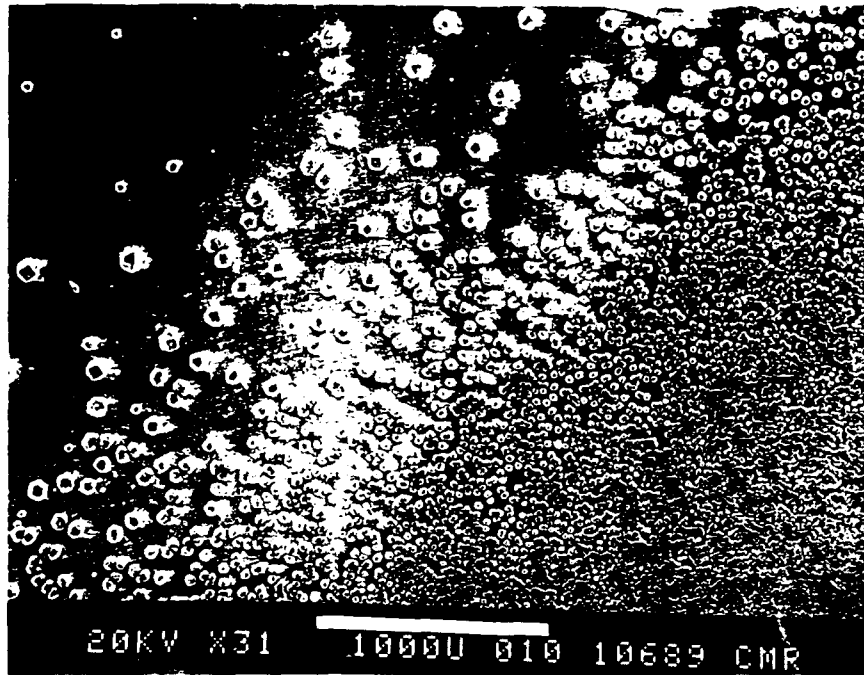1. F.P. Bundy, H.T. Hall, H.M. Strong, and R.H. Wentorf Jr., Nature **176**, 51 (1955).

2. H. Liander and E. Lundblad, Arkiv. Kemi. **16**, 139 (1960).

3. P.S. DiCarli and J.C. Jamieson, *Science* **133**, 182 (1961).

4. N. Koshino, K. Kurihara, M. Kawarada, and K. Sasaki, Extended Abstracts from the Spring Meeting of the Materials Research Society, p. 85, April 5-9, Reno, Nevada (1988).

5. S. Matsumoto, Extended Abstracts from the Spring Meeting of the Materials Research Society, p. 119, April 5-9, Reno, Nevada (1988).

6. S. Matsumoto, T. Kobayashi, M. Hino, T. Ishigaki, and Y. Moriyoshi, Proc. 8th Int. Symp. on Plasma Chem., p. 2458, August 31-Sept. 4, Tokyo, Japan (1987).

7. T. Owano and M. Gordon, unpublished.

8. R.J. Kee, J.A. Miller, and T.H. Jefferson, CHEMKIN: A General-Purpose, Problem Independent, Transportable Fortran Chemical Kinetics Code Package, Sandia Report SAND 80-8003, July (1987).

9. R.J. Kee, private communications.

10. D.E. Rosner, Annual Rev. Mat. Sci. **2**, 573 (1972).

11. W.L. Hsu, J. Vac. Sci. Technol. **A6**, 1803 (1988).

12. M. Frenklach and K.E. Spear, J. Mat. Res. **3**, 133 (1988).

13. D. Huang, M. Frenklach, and M. Maroncelli, J. Phys. Chem. **92**, 6379 (1988).

14. Y. Mitsuda, Y. Kojima, T. Yoshida, and K. Akashi, J. Mat. Sci. **22**, 1557 (1987).

15. D.S. Knight and W.B. White, J. Mat. Res. **4**, 385 (1989).

16. H. Boppart, J. van Straaten, and I.F. Silvera, Phys. Rev. B **32**, 1423 (1985).

17. In Engineering Properties of Selected Ceramic Materials, edited by J.F. Lynch, C.G. Ruderer, and W.H. Duckworth, published by the American Ceramic Society, Inc., Columbus, Ohio (1966).

18. W.F. Sherman, J. Phys. C: Solid State Phys. **18**, 1973 (1985).

19. P.O. Joffreau, R. Haubner, and B. Lux, to be published in J. Ref. Hard Metals.
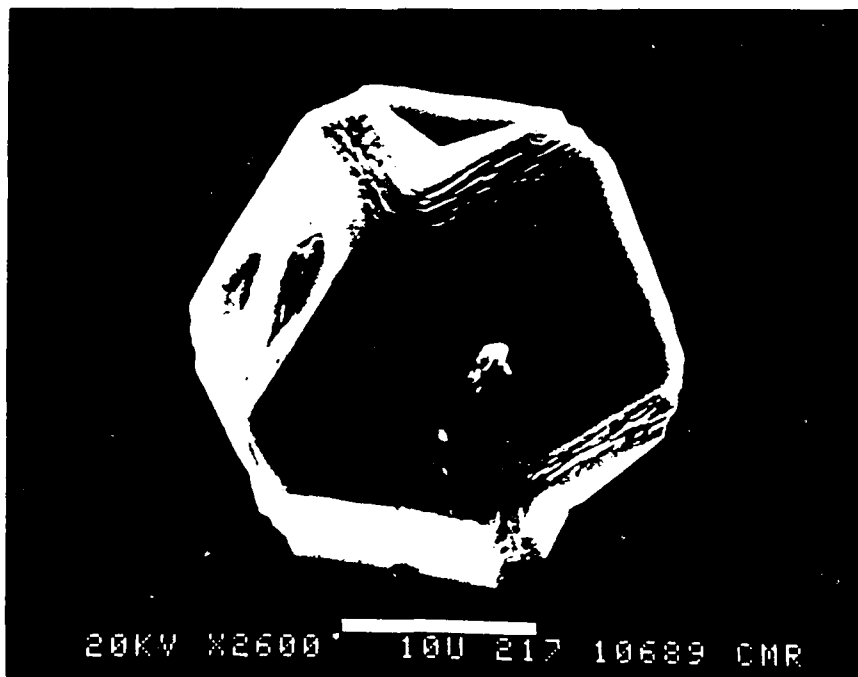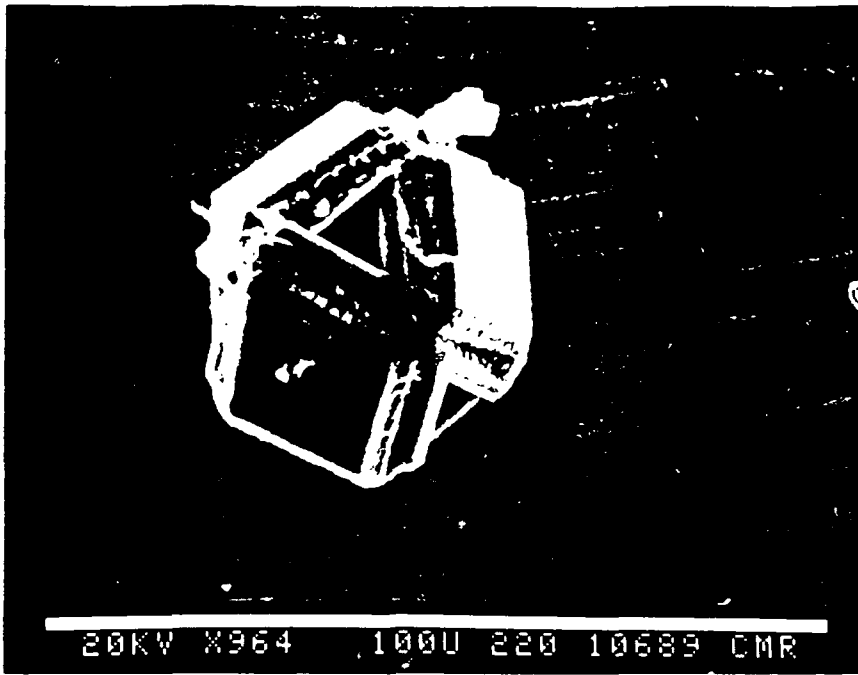
Figure Captions

Fig. 1.   Experimental Schematic of the thermal atmospheric pressure induction plasma deposition facility.

Fig. 2.   Low resolution scanning electron micrograph of region between discrete particle growth and growth of a continuos film.

Fig. 3.   Electron micrographs of a) twinned "hollow" structure and b) similar structure believed to be in a more complete stage of growth.

Fig. 4.   Raman spectrum of a typical well faceted crystallite. The Raman peak associated with the principal phonon mode (normally at 1332 cm^{-1}) is shifted by approximately 3 cm^{-1}.

Fig. 5.   Typical micro-Raman analysis of secondary nucleation sites on well facetted crystallites. The Raman peak asociated with diamond is evident above a background amorphous signiture, and is unshifted, centered at approximately 1332 cm^{-1}.
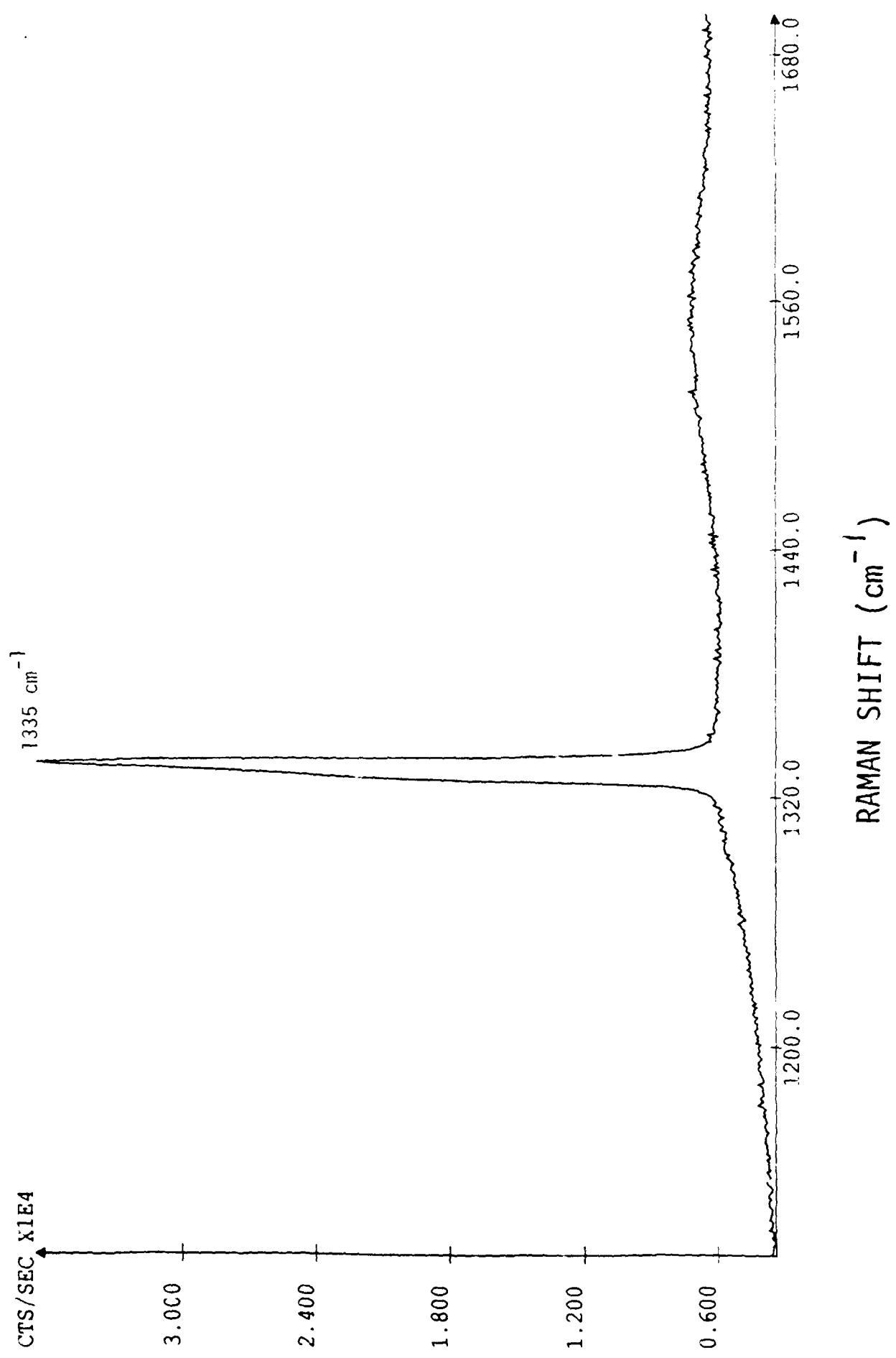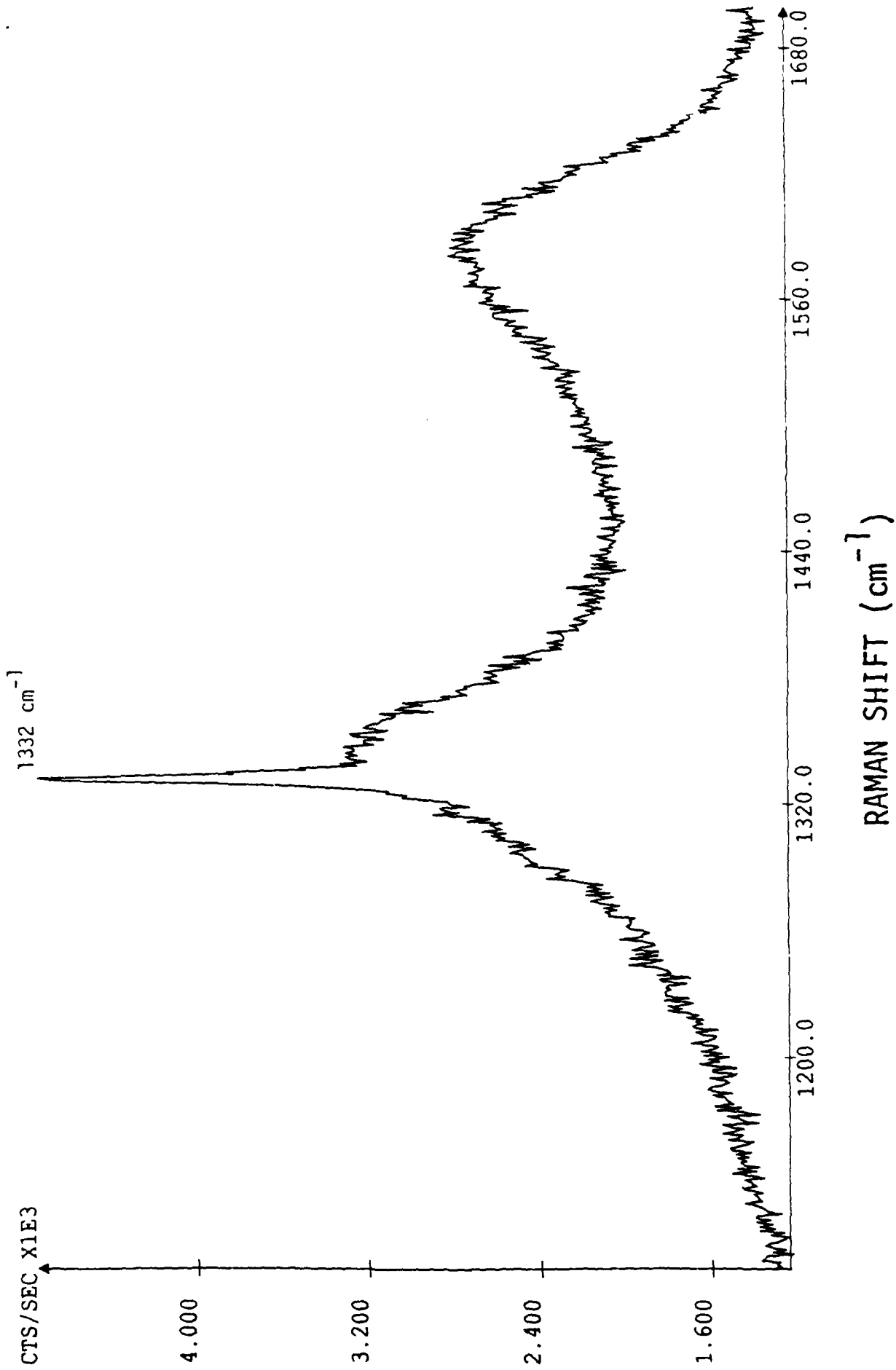
THERMAL PLASMA DEPOSITION OF DIAMOND

GAS COOLING

MOLYBDENUM SUBSTRATE HOLDER

COOLING WATER INLET

COOLING WATER OUTLET

WATER COOLED QUARTZ TEST SECTION

RFIC PLASMA (6 kW)

4 MHz RF TORCH

ARGON, HYDROGEN, METHANE (210:32:1)

20KV X31 1000U 010 10689 CMR

20KV X964 100U 220 10689 CMR

20KV X2600 10U 217 10689 CMR

Dr. W. Adler
General Research Inc.
P. O. Box 6770
Santa Barbara, CA 93160

Dr. Mufit Akinc
Mat'ls Science & Eng. Dept.
Iowa State University
110 Engineering Annex
Ames, IA 50011

Dr. H. E. Bennett
Code 38101
Naval Weapons Center
China Lake, CA 93555

Dr. S. Block
Group Leader
Structural Chemistry
National Bureau of Standards
Gaithersburg, MD 20899

Dr. J. Burdett
Chemistry Department
University of Chicago
Chicago, IL 60637

Dr. Mark A. Cappelli
Mechanical Engineering Dept.
Stanford University
Stanford, CA 94305

Dr. J. A. Cox
Honeywell Systems & Research
Dept. MN 65-2600
3660 Technology Drive
Minneapolis, MN 55418

Dr. B. Dunn
Materials Science & Eng. Dept.
Univ. of California, Los Angeles
Los Angeles, CA 90024

Dr. A. Harker
Rockwell International
P. O. Box 1085
1049 Camino Dos Rios
Thousand Oaks, CA 91360

Dr. D. C. Harris (Code 3854)
Naval Weapons Center
China Lake, CA 93555
(1 copy for distribution)

R. A. Heinecke
Standard Telecommunication
Laboratories, Ltd.
London Road
Harlow, Essex CM17 9MA
England

Dr. Lisa C. Klein
Center for Ceramics Research
College of Engineering
Rutgers University
P. O. Box 909
Piscataway, NJ 08854

Dr. P. Klocek
Texas Instruments
P. O. Box 660246
Dallas, TX 75266

Dr. R. Messier
Pennsylvania State University
Materials Research Lab
University Park, PA 16802

Dr. G. Messing
Materials Research Department
Pennsylvania State University
University Park, PA 16802
(1 copy for distribution)

Dr. S. Musikant
General Electric Company
P. O. Box 8555
Philadelphia, PA 19101

Dr. Dale Perry
U.S. Army Missile Command
Redstone Arsenal
Huntsville, AL 35807

Dr. W. Pittman
AMSI-RD-AS-PM
Redstone Arsenal
Huntsville, AL 35898

Dr. R. Raj
Materials Science&Eng. Dept.
Cornell University
Ithaca, NY 14853

Dr. W. Rhodes
GTE Laboratories
40 Sylvan Road
Waltham, MA 02134

Mr. D. Roy
Coors Porcelain Co.
Golden, CO 80401

Dr. D. Roy
Mat'ls Science Lab
Pennsylvania State Univ.
University Park, PA 16802

Dr. J. Savage
Royal Signals & Radar Establishment
St. Andrews Road
Great Malvern, WORCS, WR14 3PS
ENGLAND

Dr. A. Stacy
Chemistry Departament
Univ. of Calif. Berkeley
Berkeley, CA 94720

Dr. I. G. Talmy, Code R31
Naval Surface Weapons Center
White Oak Laboratory
Silver Spring, MD 20903

Dr. R. Tustison
Raytheon Co., Research Div.
131 Spring Street
Lexington, MA 02173

Dr. W. White
Materials Research Lab
Pennsylvania State Univ.
University Park, PA 16802

Dr. A. Wold
Chemistry Department
Brown University
Providence, RI 02912

Capt. Ken L Yates
AD/AFATL/AGA
Eglin AFB, FL 32542

Defense Documentation Center
Cameron Station
Alexandria, VA 22314
(12)

Naval Surface Weapons Ctr
10901 New Hampshire Ave
White Oak Laboratory

Office of Naval Research
800 N. Quincy Street
Arlington, VA 22217
Attn:Code1113(H.Guard)
• • • • • • • • "(D.Nelson)

Dr. R. W. Schwartz
Code 373
Naval Weapons Center
China Lake, CA 93555-6001

Naval Air Systems Cmd
1411 Jeff Davis Hwy.
Arlington, VA 22202
Attn:Code 931A (L.Sloter)

Scientific Advisor
Commandant of the
MarineCorps(CodeAX)
Washington,DC 20380

Office of Naval Technology
800 N. Quincy Street
Arlington, VA 22217
Attn:Code 0712(1) Code 0725 (1)