Magnetoplasmadynamic Plasma Assisted Chemical Vapor Deposition of Diamond Films

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Abstract

Diamond possesses a combination of properties which makes it uniquely suited to a number of scientific, military, and industrial applications. One promising approach to large scale production of chemically vapor deposited diamond is the use of plasma discharges to create the required chemical environment growth. DC-arcjet sources have been successfully used in the synthesis of diamond and have demonstrated higher rates of deposition than other sources using different gas activation processes. Materials processing with DC-arcjets represents an effective dual use of this technology which has benefited from extensive studies characterizing arcjet thrusters performed over the years. Other electric propulsion technologies may also possess unique advantages for materials processing. Although the magnetoplasmadynamic thuster may be particularly well suited to diamond synthesis, its potential has not been explored. This paper outlines a proposed research activity to assess the feasibility of using an MPD plasma source in the chemical vapor deposition (CVD) of diamond films. After reviewing properties and applications of diamond films, the MPD and arcjet discharges are compared, highlighting some of the important differences which may result in higher growth rates and facilitate scale up of the process. Finally, a specific set of tasks are outlined which would assess the viability of this approach and establish a basic understanding of the relevant chemical processes.

Background and Motivation

Diamond has a wide range of scientific and engineering applications because of its unique combination of thermal, electronic, mechanical, and chemical properties. Diamond and other covalent solids are among the hardest know materials making them particularly attractive in the form of thin film coatings for components subject to chemical exposure or mechanical wear. Diamond is transparent in the visible and infrared wavelengths which has led to the fabrication of windows and coatings for sensors required to operate in corrosive or high temperature environments. Diamond has a thermal conductivity fifteen times that of silicon and five times that of copper at room temperature as well as a very low coefficient of thermal expansion[1]. This has resulted in widespread interest in its use a heat sink for high power electronic components. Heat sinks require the capability of fabrication in the form of a thin film, either bonded to or directly deposited on the component. The relatively recent development of low pressure chemical vapor deposition of diamond over areas of many square centimeters has made this possible. Wide application of these materials will require successful scaling of the relevant processes to industrial production levels through some form of batch processing.

In the last decade there has been a significant increase in the amount of research directed towards understanding the synthesis of diamond and diamond-like materials at low pressures from a gas phase carbon precursor. Although first demonstrated in the 50s in the former Soviet Union and the United States, the number of laboratories actively investigating this technique increased rapidly in the 1980s as a result of Japanese advances in identifying a variety of gas activation schemes[1]. The essential requirement for any gas activation technique is the production of adequate amounts of the key radical species needed for growth. While a definitive chemical pathway has yet to be agreed upon, there is widespread consensus that the presence of atomic hydrogen, and various hydrocarbon radicals, particularly methyl, play a key role[3,4]. Some of the numerous activation schemes which have been experimentally investigated are hot filament, oxygen-acetylene flame, RF and microwave induced plasma discharges, and the DC-plasma arc[2]. For opto-electronic device applications, the quality of the film with respect to defects and impurities, rather than the thickness is particularly important. For other applications such as wear resistant coatings and heat sinks, the thickness, area and adhesion are most important. The highest growth rates to date have been obtained from the DC-plasma discharge assisted synthesis.

DC- Plasma Arc Assisted CVD

Plasma activated species include relatively large number densities of atomic hydrogen and methyl radicals, two key components to growth. Atomic hydrogen is believed to play a key role in terminating dangling carbon bonds during growth of successive layers on the diamond lattice. In addition the graphite etch rate of activated hydrogen is several orders of magnitude higher than that of diamond resulting in higher growth rates and less graphite co-deposition[1]. Much of our understanding of DC-plasma arc assisted chemical vapor deposition is due to the work of Cappelli using arcjets originally developed for electric propulsion[5]. Using arcjets for gas activation represents an effective dual use of previously developed technology which has been optimized over many years to achieve high efficiency and low wear. Furthermore, there is a wide body of data available on the performance and plume characteristics of these devices available to support ongoing efforts to understand the reaction kinetics and growth chemistry of diamond synthesis. A logical extension of this is the assessment of other electric thruster technologies which could enhance growth rates even further. One such technology is the magnetoplasmadynamic (MPD) thruster. As a thruster, this device suffered from poor efficiency at low power levels (tens of kW). However, certain characteristics of the discharge and plume suggest it may be well suited to high growth rate synthesis of diamond over larger areas.

Potential Advantages of MPD Plasmas

To the best the author's knowledge, no work has been published to date describing use of an MPD plasma source for diamond CVD. Table 1 lists some relevant discharge characteristics for both arcjets and MPD discharges. Both of these devices have been operated over a wide range of discharge currents and voltages over the years. The values listed in Table 1 are intended to be representative of arcjet operating parameters used in previous diamond CVD[5]. Those for the MPD are the anticipated parameters for the proposed investigation. Three characteristics in particular suggest the possibility that one could obtain significant enhancements in growth rate and deposition area using an MPD. These are the inherently higher level of dissociation and ionization of the gas species in the plume core, the higher jet velocity, and the scaleability to higher power and growth areas. These are discussed in detail below.

Higher Dissociation/Ionization Fraction: Because MPD discharges utilize electromagnetic forces to achieve plasma acceleration they are not limited by thermal constraints at a physical nozzle throat. For this reason they are capable of operation at significantly higher power levels than arcjects. The proposed operating point for these initial experiments is an order of magnitude higher than previous arcjet power levels used in diamond CVD. One consequence of operating at a higher power is the production of a high enthalpy plume with significant dissociation and ionization. Higher levels of dissociation will increase the number densities of species required for growth and suppression of graphite. While dissociation of the hydrocarbon precursor gas and the hydrogen diluent gas is essential, it is not clear whether the higher ionization level will affect growth. Experiments will include evaluation of the effect of biasing the substrate to see if this affects the area over which material is deposited.

High Jet Velocity: In an electromagnetic thruster, the thrust level scales approximately with the square of the current. As a result the mean gas velocities in the plume are expected to be higher than the arcjet. While the anticipated discharge currents are 1 - 2 orders of magnitude higher than the arcjet, this increase is offset somewhat because the corresponding mass flow rate will also be higher due to the need for argon flow through the discharge as well. The consequence of higher jet velocity will be a higher stagnation temperature, higher mach number, and correspondingly thinner stagnation boundary layer at the substrate surface. It is anticipated this will result in sharper concentration gradients over the growth region and a higher flux of activated radicals tothe surface.

	ARCJET	MPD
Type of discharge	Localized	Diffuse
Centerline jet velocity (km/s)	10 - 14	20 - 30
Degree of dissociation (%)	> 50	> 75
Discharge Voltage (V)	50 -200	15 - 35
Discharge Current (A)	5 - 20	700 - 1000
Chamber Pressure (Torr)	0.15 - 0.35	5 - 35
Power (kW)	1 - 3	15 - 25

Table 1. Comparison of Arcjet and MPD Discharge for Diamond Synthesis

Scaleability: Because the MPD is an electromagnetic device, it is more easily scaled up to higher power and/or larger electrodes to achieve deposition over a larger region of the substrate than a thermal arcjet. Electrode geometry can be scaled to maintain a manageable cathode current density while increasing the overall power and exhaust plume cross sectional area. Such scale-up could have significant commercial potential if the overall chemistry of the MPD plume is found to be effective for achieving growth.

Facility Description

The facility (Figure 1) to be used for the proposed work is the Cathode Test Facility at JPL originally developed and used extensively to investigate the behavior of high current, thermionic cathodes for high powered Lorentz Force Accelerators. The 0.5m x 2.4 m stainless steel chamber consists of four water cooled segments. The system is pumped by a 610 l/sec Roots blower backed by a 140 l/sec Stokes mechanical capable of provided a vacuum of less than 0.13 Pa pressure with no gas flow and 80 Pa with an 0.75 g/sec flow of Argon. Figure 2 is a cutaway diagram of the first two segments of the chamber. A

Figure 1. Test Facility used for Plasma Assisted Materials Processing Experiment

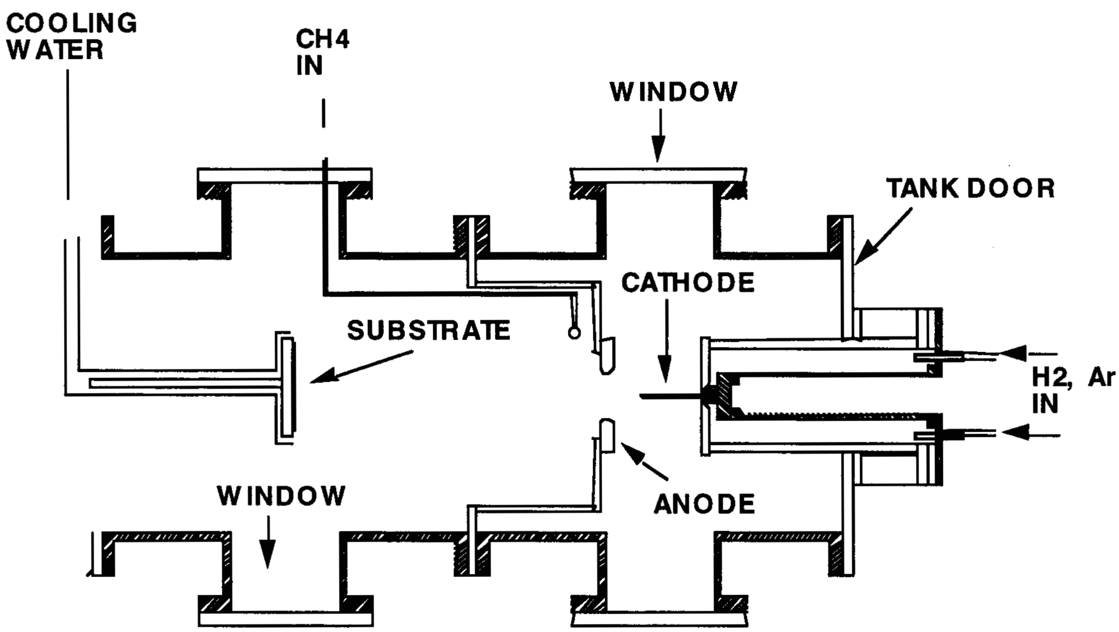

Figure 2. Diagram showing discharge chamber, cathode, anode, water cooled substrate, methane injector, and windows for optical access.

76 mm long, 9.5 mm diameter thoriated tungsten cathode is mounted on a water cooled electrode and supported on a sliding door which provides access to the discharge chamber. A separate electrode located downstream supports a ring shaped, water cooled anode with an orifice of approximately 2.75 inches. The methane gas which provides the carbon precursor is injected just downstream of the anode plane through a ceramic tube, and further downstream a water cooled copper mount supports a removable molybdenum disk which serves as the substrate for the growing film.

A number of windows on the chamber provide optical access at different locations for optical diagnostics. A McPherson monochromator will be used for all emission spectroscopy in the plume and an optical pyrometer and thermocouples for measurements of the substrate surface temperature.

Proposed Tasks

The proposed effort includes a combination of experimental and numerical analysis of the MPD plasma assisted CVD process designed to assess its feasibility and also to provide measurements of gas species in the plume which can be compared with existing data for arcjet based systems. This work is divided into five specific tasks which are described below.

<u>1. Parametric Sensitivity:</u> The effects of discharge power, gas mixture, substrate biasing, and background pressure on substrate temperature, film quality, area of deposition and deposition rate will be investigated. The primary goal will first be to demonstrate growth using the system. Once the process has been demonstrated, those independent parameters listed above will be varied over a limited range to determine process sensitivity.

<u>2. Estimate of Plume Properties:</u> Modeling the gas and surface chemistry at the substrate requires information on hydrodynamic characteristics of the plume such as mean gas velocity, pressure, and temperature. An experimental determination of gas velocity or temperature using Laser Induced Fluorescence or other optical methods is beyond the scope of the this activity. Therefore estimates will be made of mean gas velocity normal to the substrate, static temperature, static pressure, and degree of ionization/dissociation at the substrate. These estimates will be based on actual experimental operating conditions, data from similar discharges in the literature, and calculation.

3. Visible Optical Spectroscopy: Measurements of relative emission intensity of C, C2, CH, Hδ, Hβ, Hγ, lines will be made over several centimeters starting at the substrate surface and moving towards the gas exhaust plane. This data will be used to assess the degree of methane pyrolysis and compared with data published for arcjets. Also, estimates will be made of the mean free path in the plasma and compared with characteristic path lengths for methyl production. While no UV spectroscopy is planned as part of this activity, calculation of the characteristic path lengths for production will provide a qualitative indication of conditions favorable for methyl production.

4. Gas Phase Chemistry Modeling: The CHEMKIN (developed by Sandia Nat. Lab.) code will be used to model the methane pyrolysis from the point of injection to the substrate as a one dimensional reactor. Any additional ionized species reactions for which rate data can be found in the literature will also be incorporated. Predictions of relative concentrations of C, C2, and CH predicted with CHEMKIN will be compared with relative intensities observed spectroscopically. Also, relative concentrations of species predicted with CHEMKIN will be compared with those observed in other plasma reactors (arcjet, microwave).

5. Surface Chemistry Modeling: SURFACE CHEMKIN will be used using with a simplified heterogeneous mechanism from the literature to calculate film thickness as a function of methane to hydrogen gas ratio. Data from experiment and gas chemistry simulation (Task 4) will be used to set gas phase conditions above the substrate for the surface chemistry modeling. Estimates will be made of atomic hydrogen concentration above the substrate from experimental data and compared with calculations. The effect of atomic H concentration on predicted growth rate will be evaluated and compared with data.

References

1. Spear, K. "Diamond-Ceramic Coating of the Future", J. of the Am. Ceram. Soc. 72 (2), 1989, pp. 171 - 191.
2. Kazuaki, K., et. al. "High Rate Synthesis of Diamond by DC Plasma Jet Chemical Vapor Deposition", App. Phys. Lett. 52 (6), 8, February, 1988, pp. 437 - 438.
3. Coltrin M., and Dandy, D., "Analysis of Diamond Growth in Subatmospheric DC Plasma-Gun Reactors", J. of Appl. Phys. 74 (9), 1, November, 1993, pp. 5803 - 5820.
4. Coltrin M., and Dandy, D,"A Simplified Analytical Model of Diamond Growth in Direct Current Arcjet reactors", J. of Mat. Res., 10 (8), August, 1995, pp. 1993 - 2010.
5. Loh, M., and Cappelli, M., "Supersonic DC-arcjet Synthesis of Diamond", Diamond and Related Mat. 2 , 1993, pp. 454 - 461.

NOVEL TECHNOLOGY SUBMISSION - STATUS REPORT

March 11, 1999

To: John Blandino (125-224)

From: Technology Reporting and Communications (TRAC)

Subject: Item No. 0263b Docket No. 20668
MAGNETOPLASMADYNAMIC PLASMA ASSISTED CHEMICAL VAPOR DEPOSITION OF DIAMOND FILMS

The current status, or recent change in status, of the above-identified item of novel technology is given below:

[X] This case has been docketed for early preparation of a Novel Technology Report. Please refer to the above "Docket" number in all communications with our office regarding this case.

[ ] Requires additional information, but is being logged on our records and is being temporarily put on hold pending further development for the next 6-12 months.

[ ] Is being INACTIVATED. No future follow-up is expected.

If you have questions regarding this matter please refer them to the undersigned. Thank you for your cooperation in bringing this item to our attention. Your continued cooperation in achieving the reporting, patenting, utilization and transfer of novel technology will be sincerely appreciated.

TRAC Team Member C. Lewis Ext. 3-3421
Carla Lewis

Magnetoplasmadynamic (MPD) Accelerator Assisted Synthesis of Diamond

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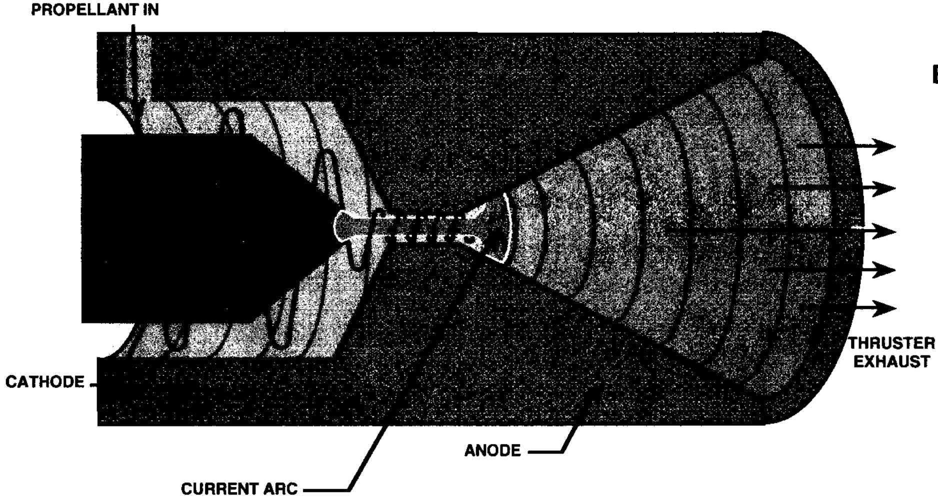
ICMCTF, April 12, 1999

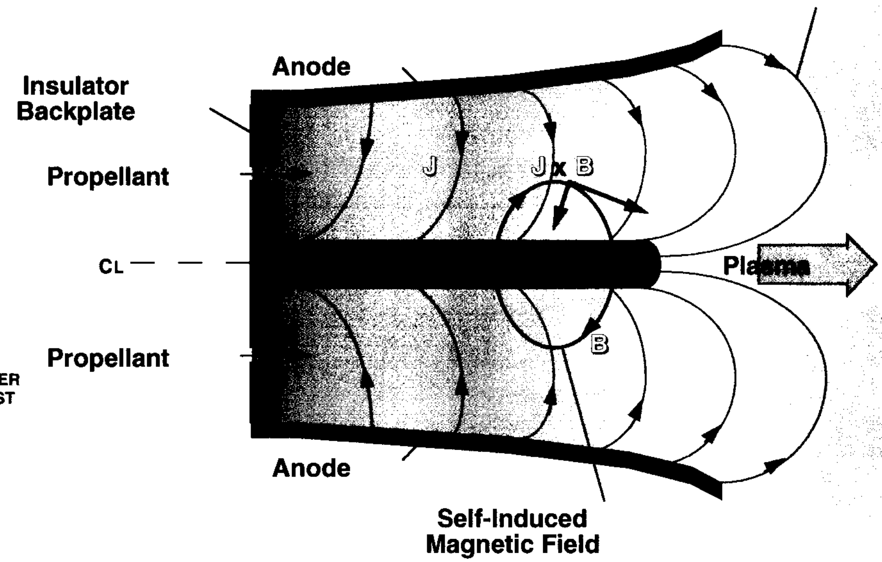
Arcjet vs. MPD Plasma Sources

Arcjet
1 - 10's kW



current	10's - 100's A
voltage:	100 - 200 V
jet velocity	5 - 10 km/sec

MPD
10's kW - 1 MW



current	100's - 10,000's A
voltage:	10's - 100's V
jet velocity	0.1 - 100 km/sec

Potential Advantages of MPD Sources

- Potential benefit of MPD sources for plasma assisted CVD are likely to be realized only at power levels > 100 kW

- Benefits for large scale commercial production:
  - Higher jet velocity (electromagnetic acceleration)
    > Factor of 2 -10 increase in jet velocity over hydrogen arcjet
      - Thinner b.l. -> sharper concentration gradients -> greater flux of active species to surface
  - High degree of dissociation and ionization (lower pressure discharge)
    > Factor of 2 - 7 increase in growth rates reported through substrate biasing or secondary discharge in boundary layer[1,2]
  - Scalability to large area sources (electromagnetic acceleration)
    > Electrode geometry more readily scaled to larger plume cross sections

1. Matsumoto, S., et. Al. Jap. J. of Appl. Phys. V 29, No 10, 1990, pp. 2082.
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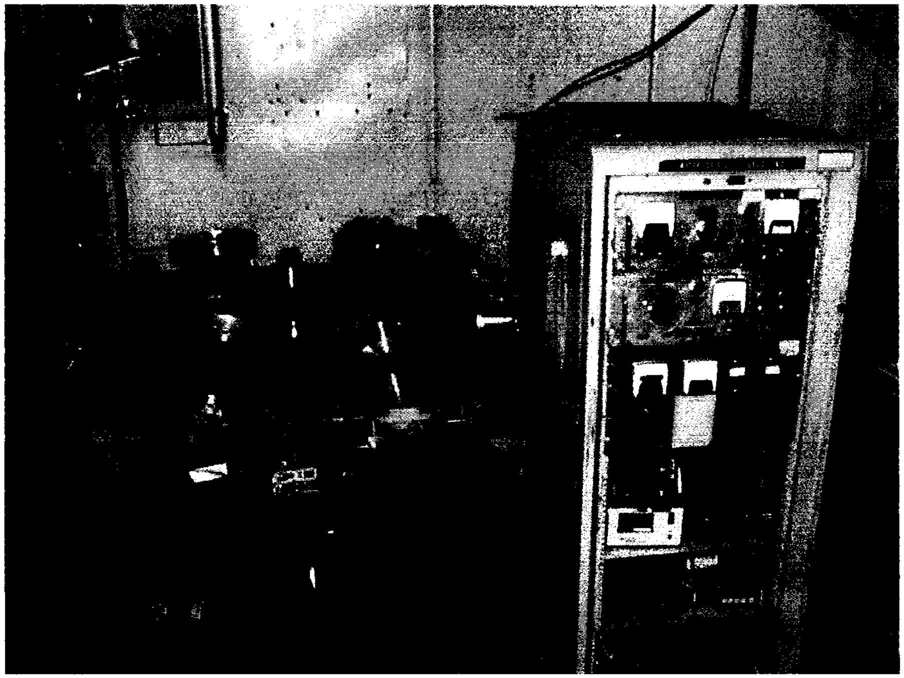
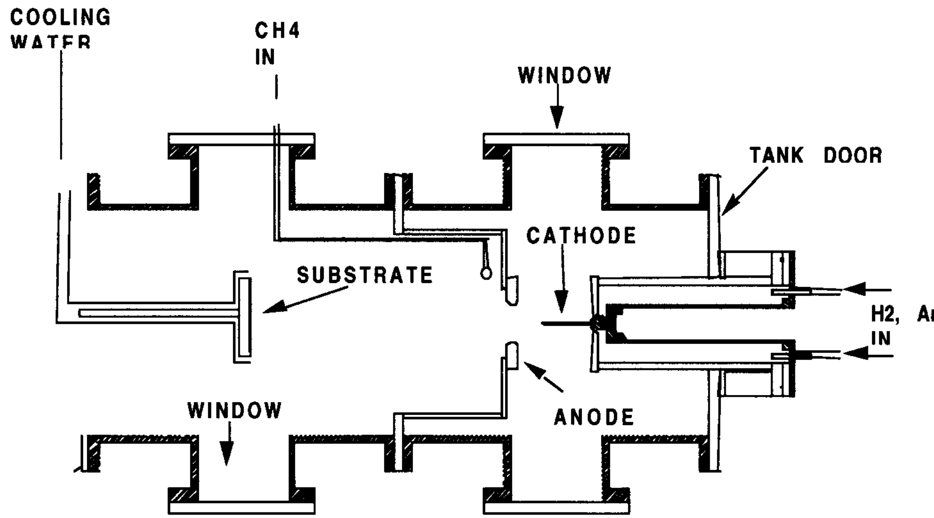
JPL Cathode Test Facility





0.5 m x 2.4 m facility designed for high current cathode research

Two 1500 A, 40V welding supplies (120 kW)

850 V, 4 A start supply

610 liter/sec blower backed by 140 liter/s mech. pump -> 150 mPa background press.

Discharge Conditions Used for Initial Trials

Discharge Voltage	15 – 20 V
Discharge Current	700 – 950 A
Discharge Power	10 – 16 kW
Chamb Press	1100 – 1200 Pa
Gas Velocity†	100 – 200 m sec^{-1}

† Estimated

- Purpose of low power tests (20 kW) was to assess capabilities and limitations of facility for diamond CVD
- Specific issues investigated:
  - Substrate placement, thermal control, and plume asymmetries
  - Injector location
  - Methane/Hydrogen ratio
  - Effects which limit film quality
    - > Contamination from residual gases and tungsten vapor
    - > Non uniform temp distribution (mechanical stresses) on substrate and film

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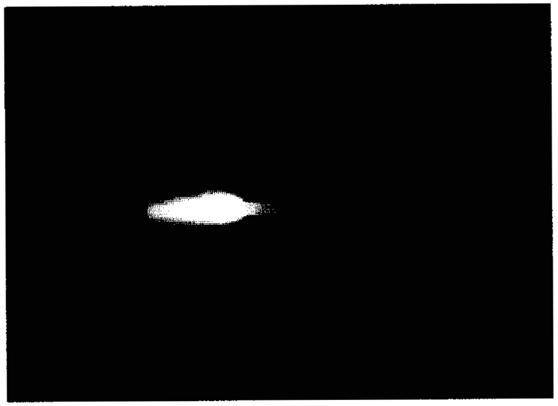
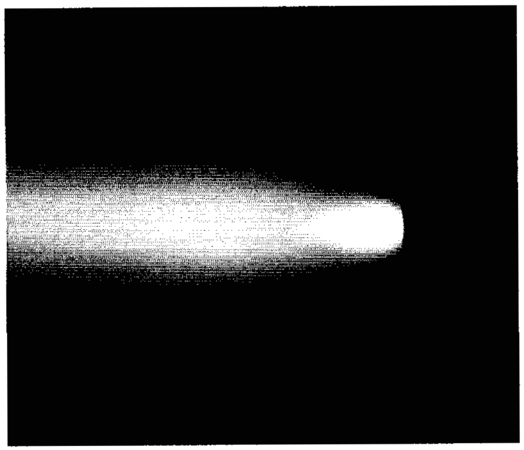
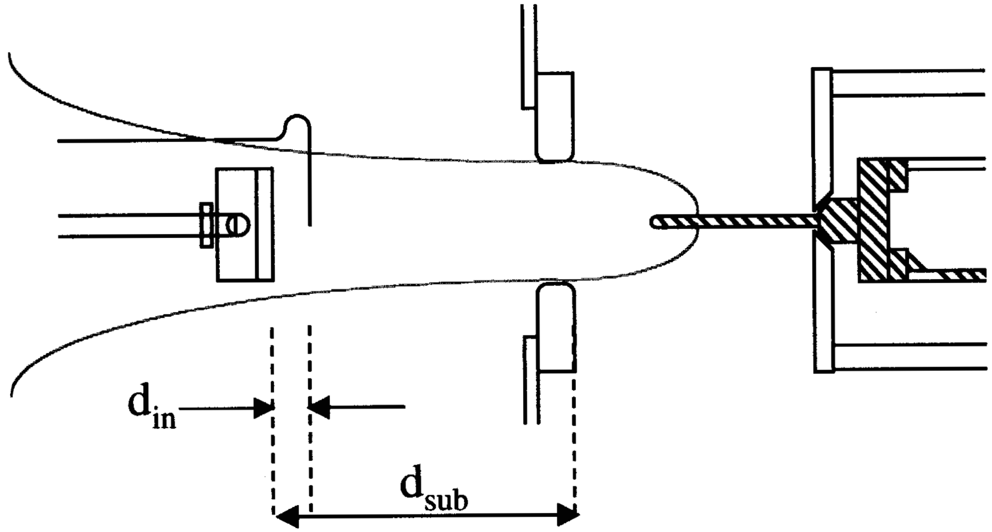
Setup for Initial CVD Experiments

Cathode, side view



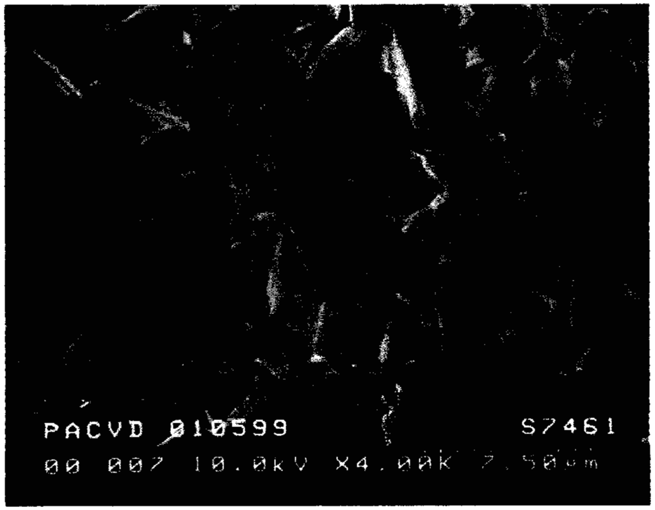
Anode, view of exit plane



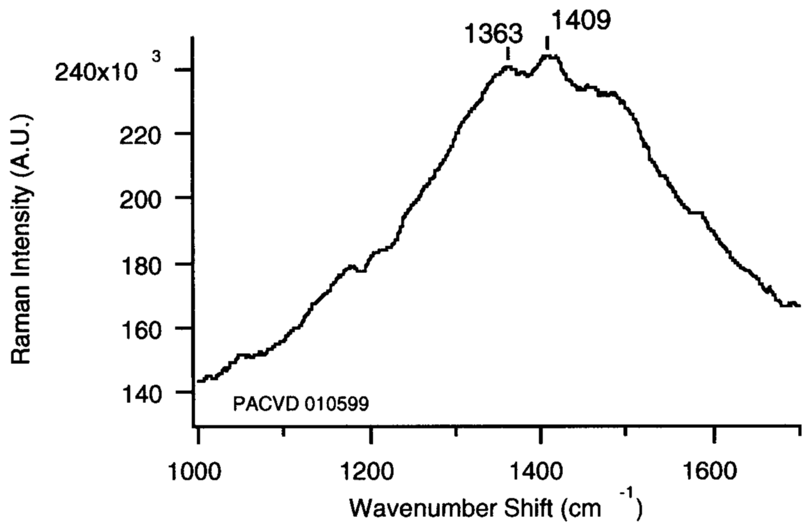


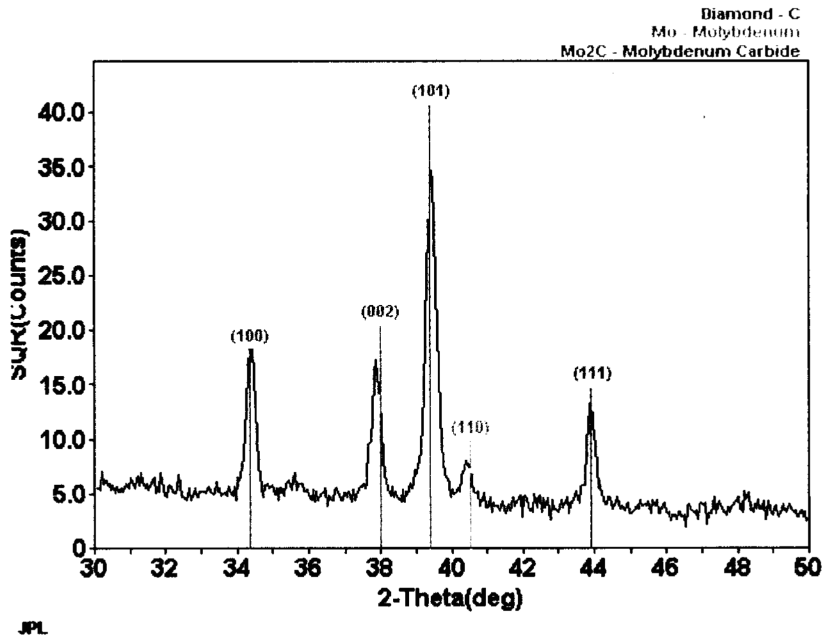
Substrate-Anode Dist (d_{sub})	14 cm
Injector-Substrate Dist (d_{in})	0.5 – 1.5 cm
Flowrates	Ar: 23 slm CH4: 0.013 -0.03 slm H2: 0.85 slm
Substrate	Molybdenum
Substrate Preparation	Polished with 1/4 μm diamond paste

Results: CH_4/H_2: 3.3%, d_{in}=1.3 cm

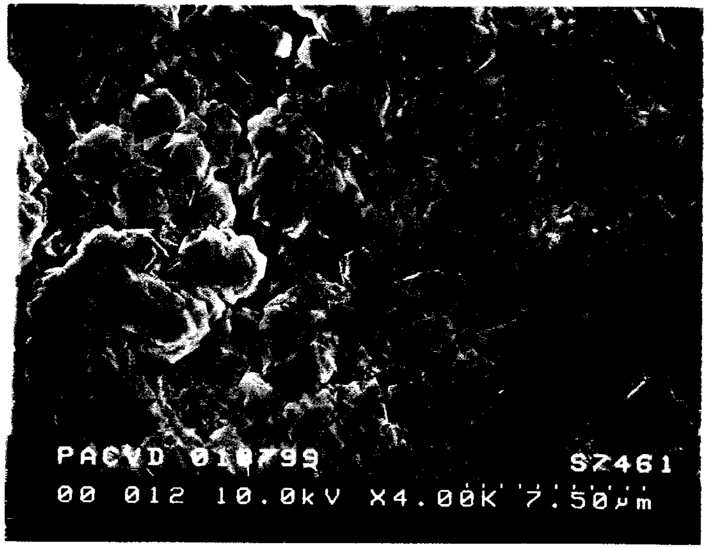


CH4/H2 Ratio (vol %)	3.3
Injector-Substrate Dist (cm)	1.3 (center)
Growth Duration (min)	77
Film Thickness (μm)	5.8
Substrate Temp (˚C)	860

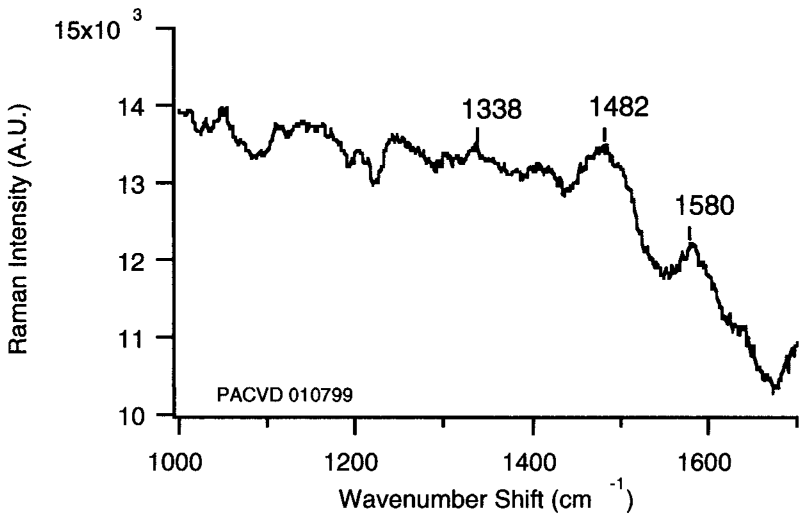


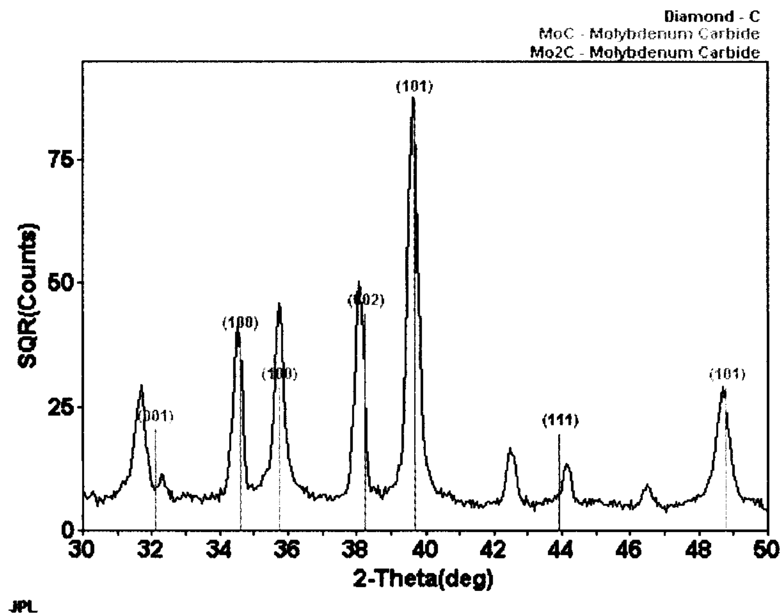


Results: CH_4/H_2: 3.4%, d_{in}=0.5 cm



CH4/H2 Ratio (vol %)	3.4
Injector-Substrate Dist (cm)	0.5 (center)
Growth Duration (min)	75
Film Thickness (μm)	2.7
Substrate Temp (˚C)	970





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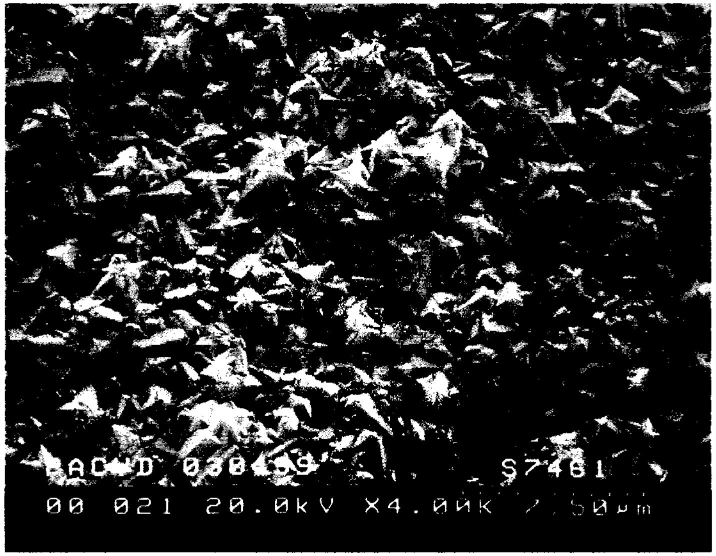
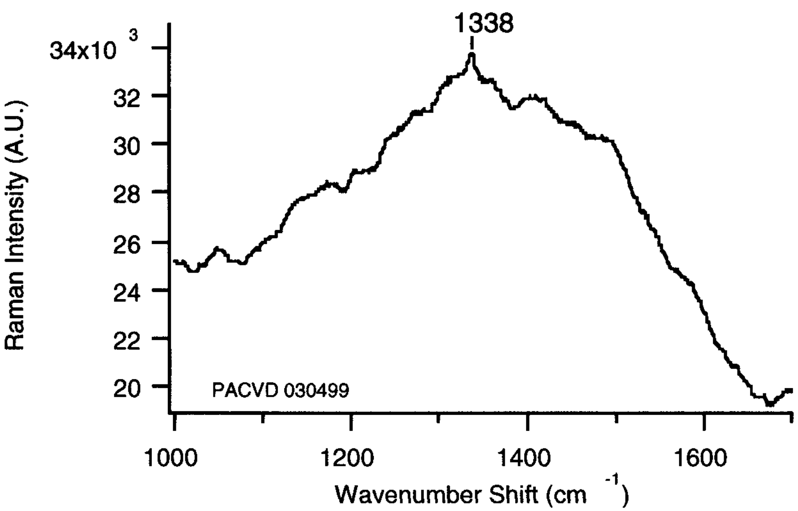
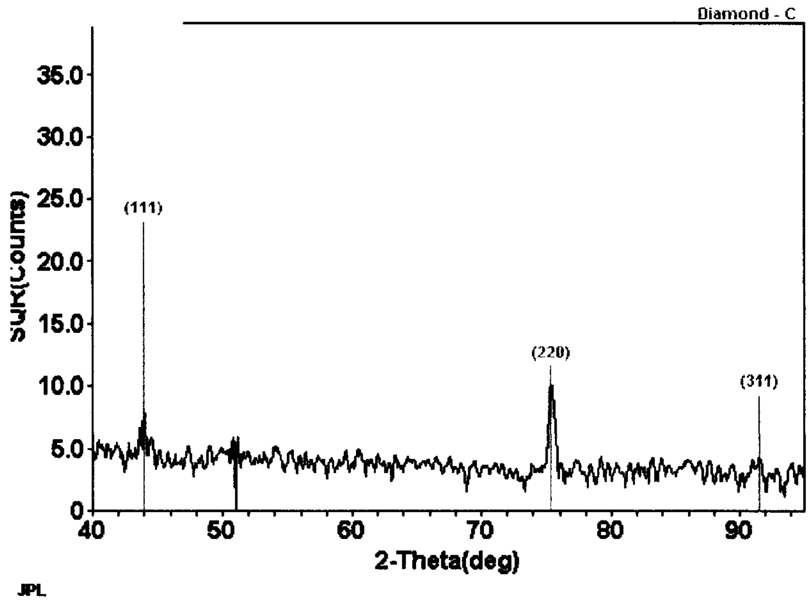
Results: CH_4/H_2: 3.4%, d_{in}=0.5 cm



CH4/H2 Ratio (vol %)	3.4
Injector-Substrate Dist (cm)	0.5 (side)
Growth Duration (min)	79
Film Thickness (μm)	4.9
Substrate Temp (˚C)	810





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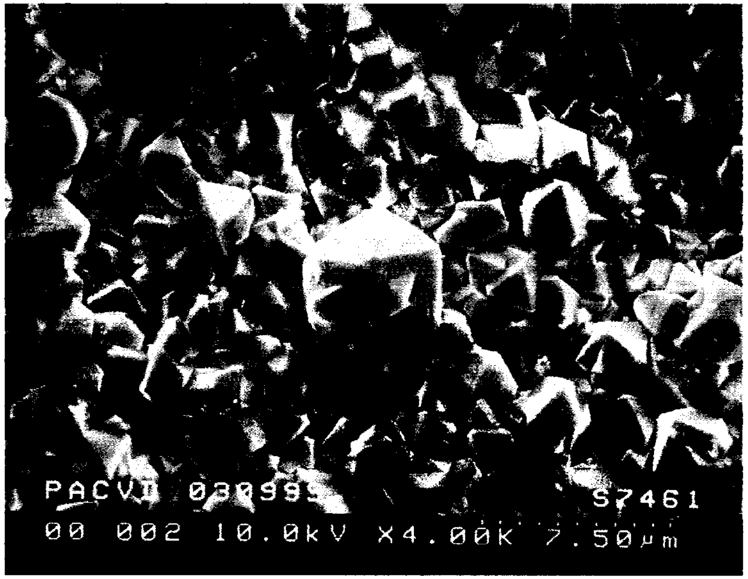
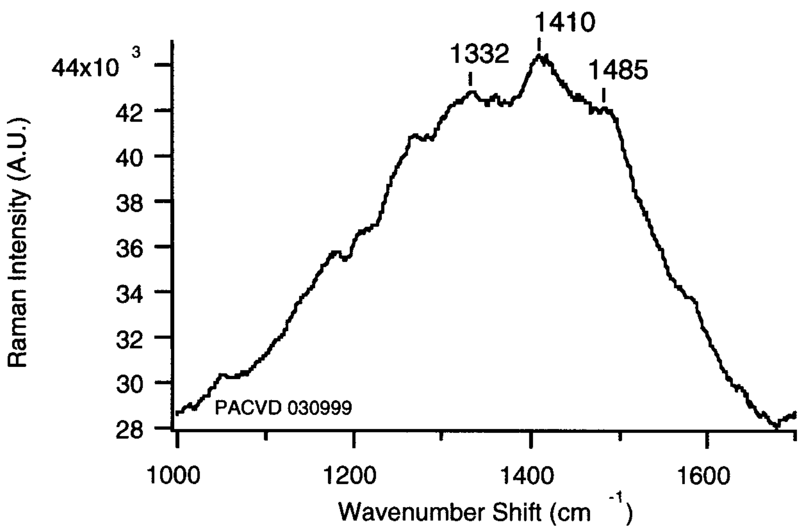
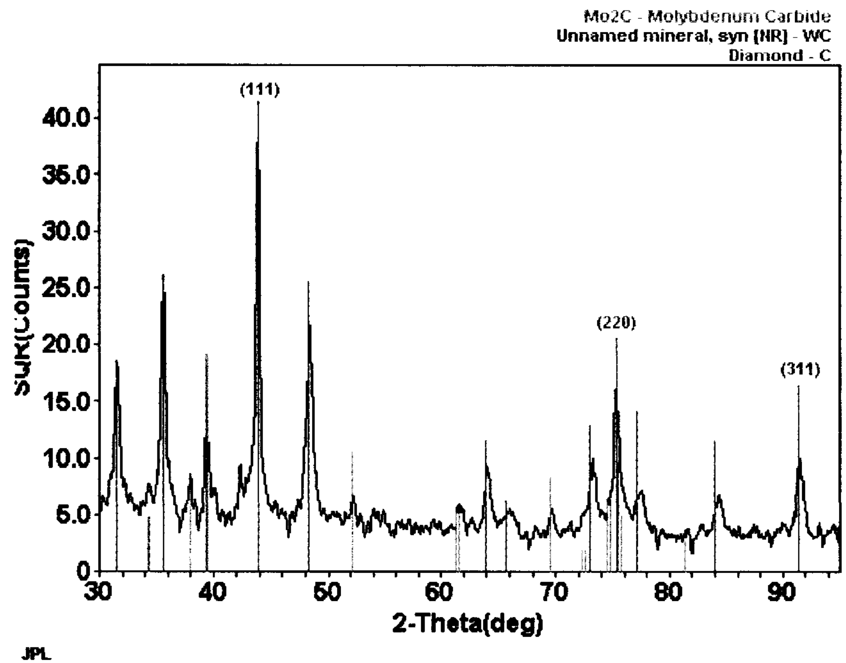
Results: CH_4/H_2: 1.5%, d_{in}=0.5 cm



CH4/H2 Ratio (vol %)	1.5
Injector-Substrate Dist (cm)	0.5 (side)
Growth Duration (min)	181
Film Thickness (μm)	2.5
Substrate Temp (˚C)	800





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Conclusions

- High power (>100's kW) MPD plasma sources could potentially benefit large scale commercial production as a result of higher ionization level, higher jet velocity, and ease of scaling.
- Of these potential benefits, the JPL Cathode Test Facility has the capability to evaluate benefits arising from low pressure, higher ionization level
- Initial tests have been performed to assess substrate thermal control and effects of gas composition and injector placement
  - Low film quality possibly due to a number of effects including contamination of system from residual gases, metal vapor, or stress induced defects
- Current work is focused on minimizing contamination and stresses from non-uniform heating
- Planned work will evaluate higher power, lower pressure operation with substrate biasing