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Considerable empirical research has been performed in the field of diamond film growth over the past fifteen years. However, this approach has proven insufficient in optimizing the deposition process. Also, no deposition nechanism has become universally accepted.

A combination of *in situ* plasma diagnostic instruments, diamond film characterization, and computer nodeling has been used to produce a self-consistent model of diamond-producing DC plasmas and to optimize the leposition process in terms of bonding type (*i.e.*, graphite *vs.* diamond) and growth rate. The effects of mportant deposition parameters including methane concentration in hydrogen, current, electrode spacing, and ressure on both film and plasma characteristics have been analyzed.

The presence of a negative electric field at the anode (or substrate electrode) has been determined to be ecessary for the growth of high quality diamond films. The magnitude of this field is strongly dependent on ressure. Control of this field will be possible by monitoring with a Langmuir probe and controlling pressure, eading to *in situ* process control.

Acetylene appears to be responsible for the growth of graphite and methyl radicals for the growth of diamond.

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THERMOCHEMISTRY OF HYDROCARBON DECOMPOSITION AND RELATIONSHIP TO PROPERTIES OF PECVD DIAMOND FILMS

Executive Summary

LINDA PLANO

PRINCIPAL INVESTIGATOR
CRYSTALLUME
MENLO PARK, CA

MARCH 31, 1991

THERMOCHEMISTRY OF HYDROCARBON DECOMPOSITION AND RELATIONSHIP TO PROPERTIES OF PECVD DIAMOND FILMS

Objective

The objective of this program was to conduct coordinated research on DC plasma enhanced chemical vapor deposition of thin film diamond, emphasizing the interrelationships among externally controlled variables, plasma characteristics, and the structure and properties of the deposited films. This work will lead to an optimized deposition process with a working model of the critical physical processes and characteristics of the plasma.

Accomplishments/ New Results

- A DC plasma reactor based on production systems at Crystallume has been instrumented with three diagnostic instruments for *in situ* plasma analysis:
    - an optical emission spectrometer for qualitative chemical and plasma structure measurements;
    - a Langmuir probe for electrical and plasma structure measurements; and
    - a mass spectrometer with SIMS optics for quantitative chemical analysis.
- Bonding content and growth rate have been determined for over thirty carbon films grown according to a statistically designed set of experiments. Best results yielded growth rate of highly diamond-bonded material increased by up to a factor of five over earlier processes.
- Correlation of *in situ* diagnostic data with deposition parameters and film characteristics led to the following discoveries:
    - pressure and methane concentration are the most important deposition parameters in determining film bonding type (*e.g.*, graphite *vs.* diamond);
    - current and methane concentration are the most important parameters in determining film growth rate;
    - the presence of a significant negative electric field at the anode (substrate electrode) is essential to avoid the deposition of graphite films;
    - the magnitude of the anode field is a good predictor of film quality within certain limits, suggesting a potential *in situ* process control mechanism;
    - methyl radicals (and perhaps ethylene) are necessary for the growth of diamond;
    - acetylene appears to be responsible for the growth of graphite;
- A computer model based on *in situ* diagnostic data was developed. It is capable of qualitative prediction of ion and electron densities and fluxes, inelastic process rates, electric potential and fields, and electron temperature in diamond-producing DC plasmas.

Implications

In terms of diamond film production, this study has lead to significantly improved growth rate and film quality in terms of the extent of diamond bonding (Raman spectrum). Positive correlation between the electrical structure of the plasma and its effect on film bonding indicates that an *in situ* plasma monitor is feasible for diamond-producing DC plasmas.

From a basic research point of view, this research has provided considerable new insight into the relationship between plasma structure and chemistry and film bonding type. The importance of a significant negative electric field near the anode (substrate) has been established.

1. MOTIVATION FOR THE RESEARCH

Diamond films hold great promise in many fields, with potential application in electronic, optical, tribological, and ceramic products. However, in the fifteen years since the feasibility of the process was recognized internationally, only one product has reached the market to date. One of the main reasons for this delay is that, while deposition of diamond from the gas phase is relatively easily accomplished, reproducible production of a uniform, coalesced film with satisfactory growth rate over a substantial area and other characteristics has proven difficult. The most direct method of addressing these challenges is to develop a working model of the deposition system so that the critical parameters can be optimized and, ideally, controlled *in situ.*

2. APPROACH AND INSTRUMENTATION

The goal of this work was to deconvolute the relationships among deposition parameters, plasma characteristics, and film properties. This complex problem was approached by employing three separate methods: statistical design of deposition experiments to produce plasmas and films whose properties could then be correlated to deposition parameters, *in situ* chemical and electrical analysis of those plasmas by several instruments. and computer modeling of the system as a whole to develop a working theory of the physical processes responsible for the plasma assisted growth of diamond film.

DC plasmas were selected as the deposition system to be studied because it is a production process with which Crystallume has several years of experience and because DC plasmas are relatively well understood and straightforward to model, unlike microwave and RF-excited plasmas which contain an AC component. The deposition parameters determined to be of primary interest were methane concentration (in the reactant gas mix of hydrogen and methane), DC current, electrode separation, and pressure. The ranges of these parameters were as follows:

Methane Concentration	0.2 - 0.6% in H_2
DC Current	1 - 2 A
Electrode Spacing	1 - 3 cm
Pressure	18 - 38 torr

The controllable conditions held constant were:

Total Gas Flowrate	100 sccm
Substrate Temperature	725 °C
Substrate Material	Silicon

Two measures of film quality were taken for each film produced from the statistically designed set of deposition experiments. One was its growth rate, as determined by measuring its thickness by SEM, and the second was its bonding type(s), as detected by Raman spectroscopy. The plasma characteristics that were analyzed by *in situ* diagnostics were its electrical and chemical characteristics. Those species with radiative transitions were detected by optical emission spectroscopy as a function of interelectrode position. Charged species and electric potential were monitored by Langmuir probe, also as a function of interelectrode position. Charged and neutral molecules and radicals were sampled at the anode (substrate) and analyzed by mass spectrometer. The instruments are shown schematically in Figure 1.

The computer model was developed at U.C. Berkeley by M. Surendra and D. B. Graves. It is based on data from all three instruments and on the correlations among deposition parameters, plasma characteristics, and film properties. The model predicts electric potential, ion and electron densities, ion and electron fluxes, and inelastic process (such as electron-neutral impact dissociation and ionization) rates. The predictions agree qualitatively with experiment results.

3. EFFECT OF DEPOSITION PARAMETERS ON CARBON FILM CHARACTERISTICS

Correlations between the deposition parameters and the film characteristics of bonding type and growth rate were calculated by performing statistical regression with Edgework software [1]. Conditions were found which produced the best diamond film ever produced in a methane/hydrogen DC plasma (see Figure 2) at growth rates from two to three times higher than typical for a production process. Film quality in terms of diamond bonding was maximized by maximizing pressure and minimizing methane concentration within the ranges studied. Growth rate was maximized by maximizing methane concentration and DC current. To deposit a highly diamond bonded film at the highest growth rate possible, high pressure and current should be employed. It is necessary to compromise on the methane concentration since it has a positive effect on growth rate but a negative effect on diamond bonding.

The negative dependence of diamond bonding on methane has also been demonstrated in virtually every diamond deposition system throughout the world, although for most systems the methane concentration can reach 1 - 10% before adversely affecting bonding, as compared to the 0.3 - 0.5% limit for DC plasmas. This low tolerance for methane in DC plasmas strongly limits the maximum growth rate possible in these systems.

The strong positive dependence of bonding type on pressure has not been widely reported. It arises because of the effect of pressure on the electrical structure of the plasma and its chemistry, as is discussed in the following sections. The effect is so strong that under certain conditions, diamond could be grown at the maximum methane concentration (0.6%) provided the pressure was sufficiently high. Current and electrode spacing were both found to have limited effects on the bonding type.

Growth rate of nondiamond bonded films was found to be governed primarily by current, whereas the growth rate of diamond and diamondlike carbon was more strongly dependent on methane concentration. Some sacrifice in bonding type is needed to obtain the highest growth rates of diamond film, but if this compromise is acceptable, growth rates up to five times higher than normal can be achieved.

4. PLASMA STRUCTURE, DEPOSITION PARAMETERS, AND FILM PROPERTIES

"Plasma structure" is a term used to describe the spatial variations in a plasma of the emitted light intensity and the electric potential. The emitted light and potential are related to each other: electric fields accelerate the charged particles in the plasma; the resulting high energy electrons participate in inelastic electron-neutral reactions producing excited, ionized, and/ or dissociated species; when these species relax or recombine, energy can be released, often in the form of visible light.

Because of the interrelationship between emitted light and electrical structure, a combination of light detection and electrical measurements in the plasma can reveal much about the physical processes in the plasma. To determine the relationship between plasma structure and film characteristics, data from optical emission spectroscopy and Langmuir probe measurements were correlated with the deposition parameters. Since correlations were also made between deposition parameters and film characteristics (see previous section), it was possible to determine how the plasma structure affects the growing film. During data acquisition, particular attention was paid to the region adjacent to the anode since it is upon this electrode that diamond deposition occurs (energetic ion bombardment of the cathode prevents long range order in films grown there).

The emission intensity of excited molecular hydrogen as a function of interelectrode position is shown for two plasmas, one graphite-producing and the other diamond-producing, in Figure 3. The cathode region is similar for both plasmas (note that the plasmas were ignited at different electrode spacings), but there is a significant difference at the anode (Figure 3b). Where the diamond-producing plasma exhibits a distinct peak near the anode, the graphite producing plasma has none. The presence of a peak indicates that electron impact excitation of molecular hydrogen is occurring. In order to engage in inelastic collisions, electrons must be accelerated to energies above the threshold for these reactions. Thus, an electric field must be present near the anode. The field in the diamond-producing plasma (and its absence in the graphite-producing plasma) is shown in Figure 4. The data points are Langmuir probe measurements and the dashed lines are extrapolations to the known potentials of the electrodes (ground for the anode, about -350 V for the cathode).

Possible inelastic electron-neutral impact processes include dissociation, excitation, and ionization. As determined by the computer model, dissociation is the dominant process near the anode because the electron energies are so low that the activation energy of each process determines the probability of it occurring. At the cathode, electron energies are so high that it is the cross section for each process which is important so that ionization dominates. In the diamond-producing plasma, the electrons experience sufficient inelastic collisions after leaving the cathode region and before entering the field at the anode that their energy drops below the threshold for inelastic processes, resulting in a dark space.

An additional benefit of the anode field is that it is repulsive to positive ions which are thought to be disruptive to diamond bonding, particularly if accelerated to the growth surface, as would be the case for a substrate at the cathode. Thus, the anode field is beneficial to the growth of diamond film in several ways: it allows the production of methyl radicals and atomic hydrogen through electron impact dissociation near the growth surface; it repels potential damaging positive ions; and it supplies high energy electrons to the surface, possibly enhancing diamond growth kinetics.

The anode field could not be measured directly because of physical limitations of the probe. A reasonable approximation of the field magnitude could be obtained by monitoring the magnitude of the potential closest to the anode that it was possible to measure. This quantity was found to be a useful predictor of film quality, especially for electrode spacings of 1 - 1.5 cm, which tended to produce more stable plasmas than did the wider spacings. In Figure 5, floating potential profiles are grouped according to the bonding type they produced; the general trend is that the larger the magnitude of the potential measured nearest the anode (and to some extent, the greater the gradient in potential through the bulk of the plasma), the more diamond bonding was to be found in the resulting film. This trend suggests that an *in situ* process monitor and control system based on the Langmuir probe can be developed.

5. PLASMA CHEMISTRY

The Langmuir probe and optical emission measurements which revealed the electric field at the anode and the resulting anode glow provide a useful but incomplete description of the plasma. The missing factor is chemistry: the effect of different concentrations of different hydrocarbons; identification of the critical species for diamond depositions; the dominant gas phase reactions; and the relative and absolute concentration of atomic hydrogen. Hydrocarbon analysis was performed through mass spectrometry of species sampled through the anode. Atomic hydrogen measurements were also attempted but were unsuccessful due to probe malfunctions and low concentrations.

Four hydrocarbon species are present in detectable amounts in these plasmas. They are methane (the feed gas), methyl radicals, acetylene, and ethylene. Diamond growth theories have been developed proposing either methyl radicals [2, 3] or acetylene [4] as the critical diamond precursor. The concentrations of the four detectable hydrocarbons were monitored for the same statistically designed experiments as were used to grow carbon films. Since wide ranges of deposition parameters were explored, the films these plasmas produced varied from graphitic to diamond in bonding so that correlations among hydrocarbon concentrations and different bonding types could be explored. A drawback to this approach is that there are relatively few hydrocarbon concentration data points for each type of film bonding so that trends may be observed but firm conclusions can not necessarily be drawn due to interferences from other variables.

To determine which species is responsible for diamond deposition, growth rates of graphite and diamond as a function of methyl radical and acetylene concentration are compared in Figure 6. For graphite, growth rate shows a linear dependence on acetylene concentration and no apparent dependence on methyl radical concentration. Diamond growth rate exhibits a linear dependence on both methyl radical and acetylene concentration. These results suggest that acetylene is responsible for graphite growth under certain conditions, but that either its role changes under other conditions (*i.e.*, when there is a significant anode field) or its correlation with diamond growth rate is coincidental rather than causal (*i.e.*, the factors leading to increased diamond deposition may also lead to increased acetylene formation without there being a direct relationship between the presence of acetylene and the growth of diamond). Ethylene, which has not been proposed as a diamond precursor because its concentrations tend to be low (unlike acetylene) and it is not a very reactive molecule (unlike methyl radicals), also correlates linearly with diamond growth rate, further supporting the explanation for the role of acetylene.

Atomic hydrogen is known to play several critical roles in diamond deposition and, since it was not measured, it is not possible to develop a complete model of the plasma chemistry. Furthermore, those species which were detected were present in concentrations near the lower sensitivity limits of the mass spectrometer. This issue may be addressed by investigating plasmas which are more efficient at generating nonequilibrium species, such as microwave plasmas. Higher concentrations of all the critical species- atomic hydrogen, methyl radicals, and acetylene- could be detected more easily and with greater accuracy.

6. COMPUTER MODEL

The optical emission, Langmuir probe, and mass spectrometer data were used in the development of a self-consistent computer model at the University of California at Berkeley by M. Surendra and D.B. Graves. This work is an extension of their earlier computer model for low neutral gas density DC and RF plasmas [5].

The model predicts electric potential and field, electron and ion densities and fluxes, inelastic process rates, and electron temperature as a function of interelectrode position. The electrical and visible structure of the plasma can thereby be predicted and explained by the computer model, a very powerful tool. Several of these predictions are shown in Figure 7. Note the similarities between the predicted (Figure 7b) and measured (Figure 4, diamond-producing plasma) floating potentials and between the predicted inelastic process rates (Figure 7d) and the measured optical emission intensity (Figure 3, diamond-producing plasma). Thus, the actual data can be used to check the model predictions and the model can be used to explain the data. This synergistic relationship was essential to the development of an overall model of the physical processes involved in diamond-producing plasmas and the explanations of the plasma behavior in the two previous sections.

7. CONCLUSIONS

This work has resulted in new understanding of the diamond deposition process in DC plasmas and has resulted in a dramatic increase in system performance. These goals were accomplished through a combination of plasma analysis, film characterization, computer modeling, and statistical experiment design. The effects of major deposition parameters on two critical film characteristics have been determined, and, as a result, graphite-free diamond films can be grown at much higher rates than was previously possible. The plasma characteristics which are of importance in controlling film bonding type are also now known, as are the relationships among the deposition parameters and the plasma characteristics; thus, *in situ* process control is a possibility. A summary of the important results and their implications for diamond growth by DC plasma follows:

- a combination of plasma potential distribution and anode chemistry controls carbon bonding:
    - increased pressure leads to larger anode fields;
    - large, negative anode fields repel positive ions and encourage production of critical species;
    - anode field may aid surface kinetics through energetic electrons;
    - critical deposition species are hydrogen, methyl radicals, and possibly ethylene;
    - acetylene is responsible for the growth of graphite under certain conditions.
- diamond growth rate is determined primarily by methane concentration:
    - effects on bonding of increased methane concentration can be counteracted by increasing pressure

8. FUTURE WORK

Substantial improvements in DC plasma diamond deposition were achieved during this study. Similar process enhancement can be accomplished for other systems, such as microwave plasma diamond deposition, the most commonly used diamond deposition technique.

The plasma diagnostic facilities developed during execution of this contract are unique in diamond research today. They can be adapted to other types of plasmas (*e.g.*, microwave, RF), other deposition technologies (*e.g.*, hot filament), and other chemistries (*e.g.*, oxygen, boron, fluorine).

With the increased understanding of the plasma structure role in diamond deposition developed during this work, it can be seen that adding an intermediate electrode such as a wire mesh might provide additional control over the anode region, thereby enhancing the growth of diamond.

A final direction for future research would be the development of an *in situ* process control system based on the use of the Langmuir probe to measure the electric field distribution in the plasma which in turn determines the optimum diamond deposition conditions.

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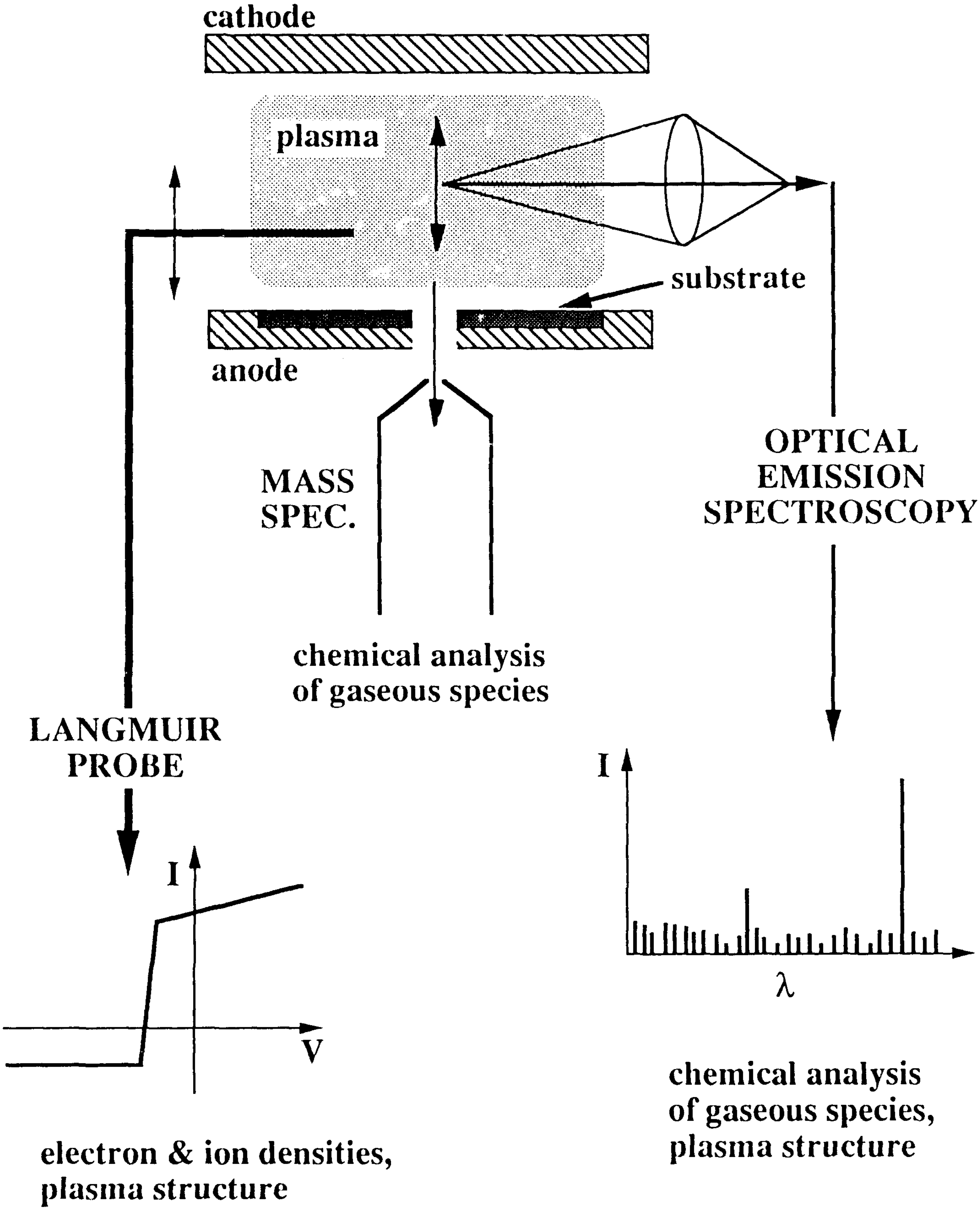


Figure 1: Schematic diagram of *in situ* diagnostics in Crystallume diamond reactor.

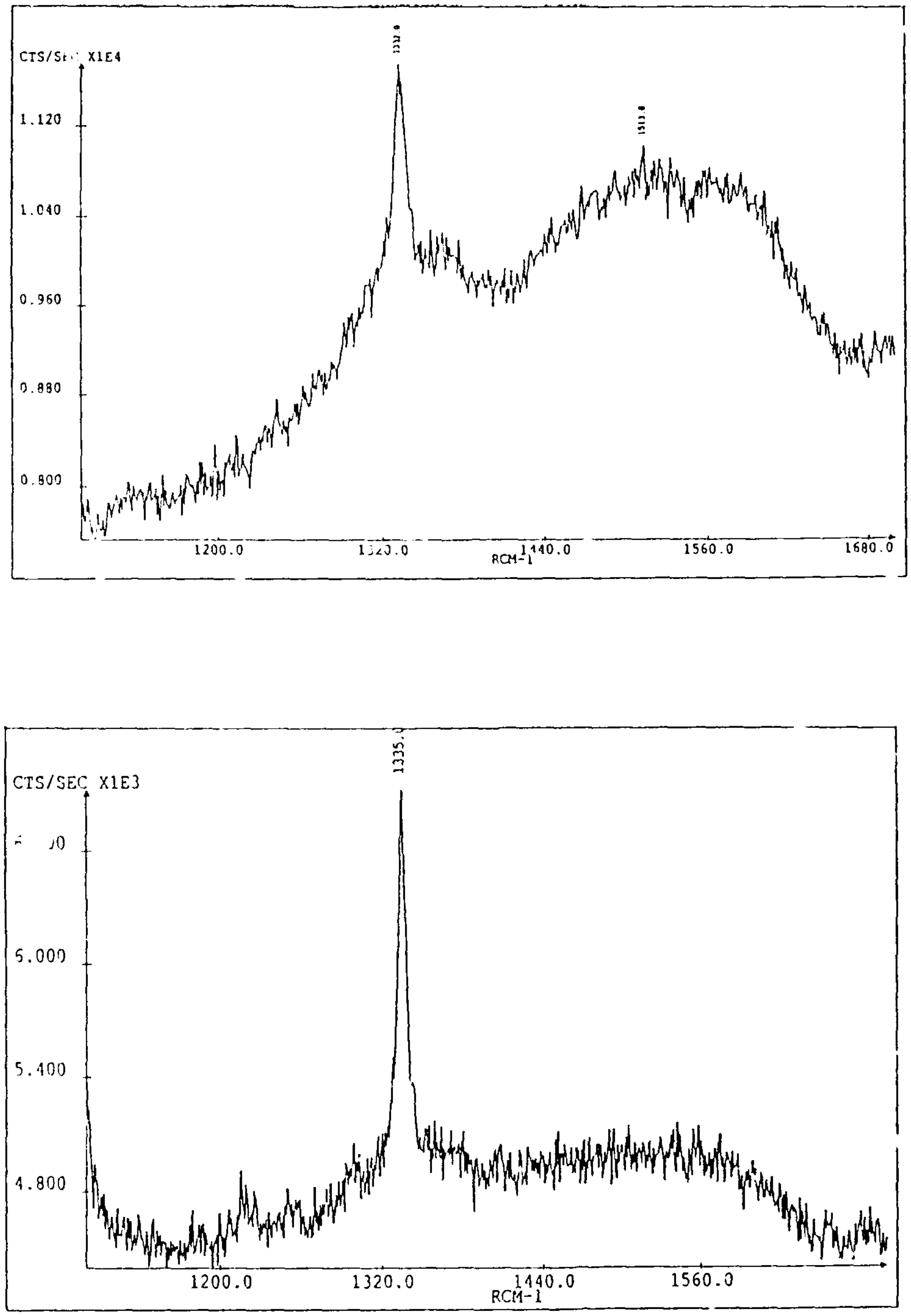
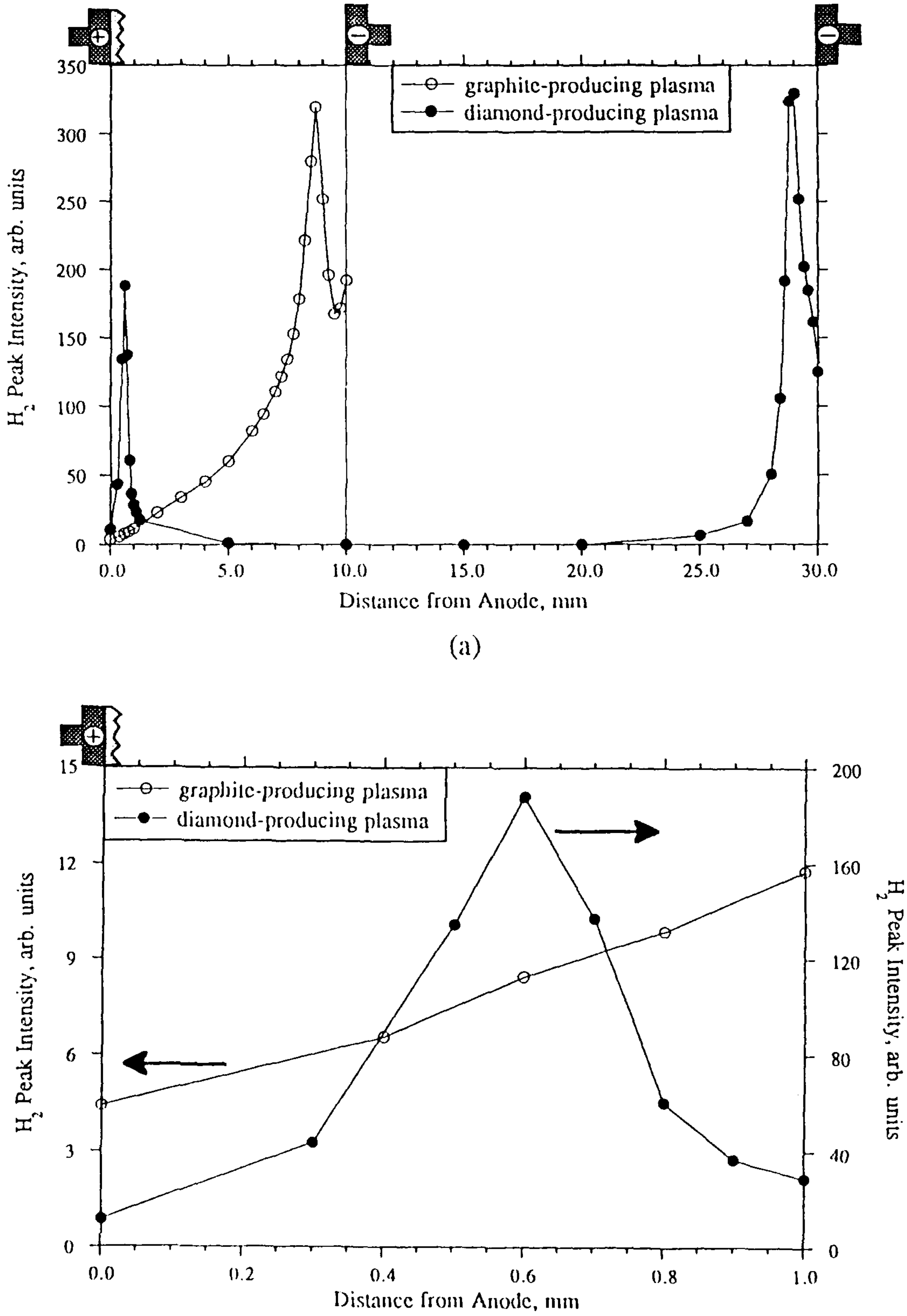


Figure 2: Raman spectra of diamond films grown using "standard" deposition conditions (top) and optimized deposition conditions developed during this work by statistical experiment design (bottom). Growth rate of bottom film is twice that of top film.



(a)

(b)

Figure 3: H_2 intensity profiles for diamond- and graphite-producing plasmas for (a) full plasma and (b) detail of anode region.

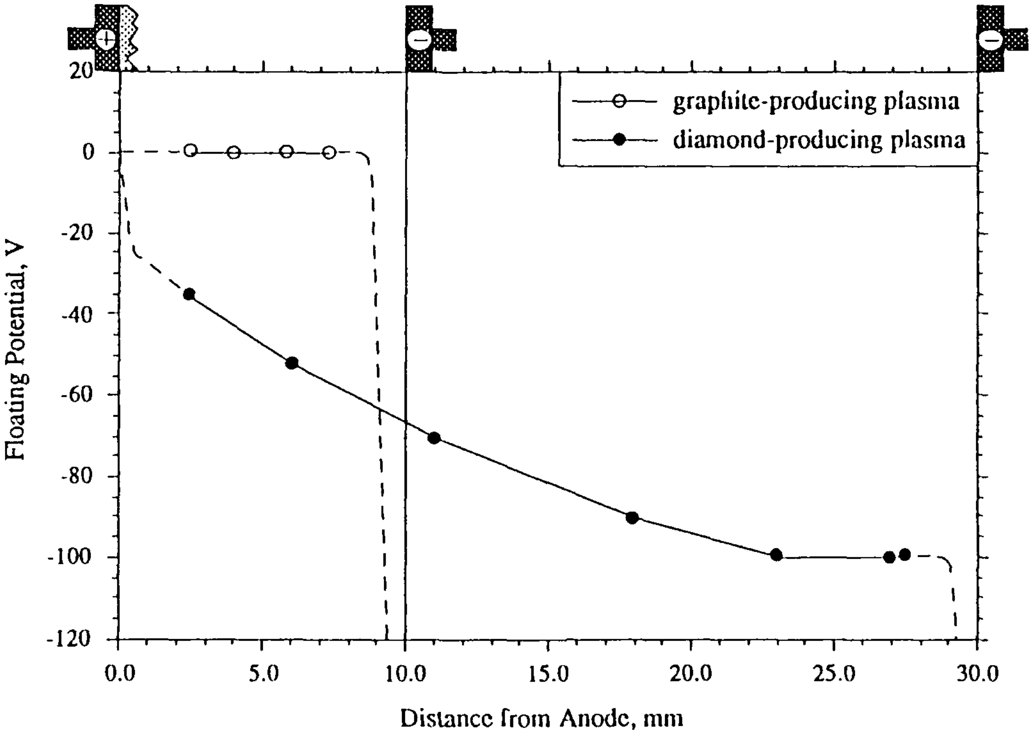


Figure 4: Electric potential profiles for diamond- and graphite-producing plasmas for full plasma. Data points are Langmuir probe measurements while dashed lines represent approximate profile extensions to the known potentials of the electrodes.

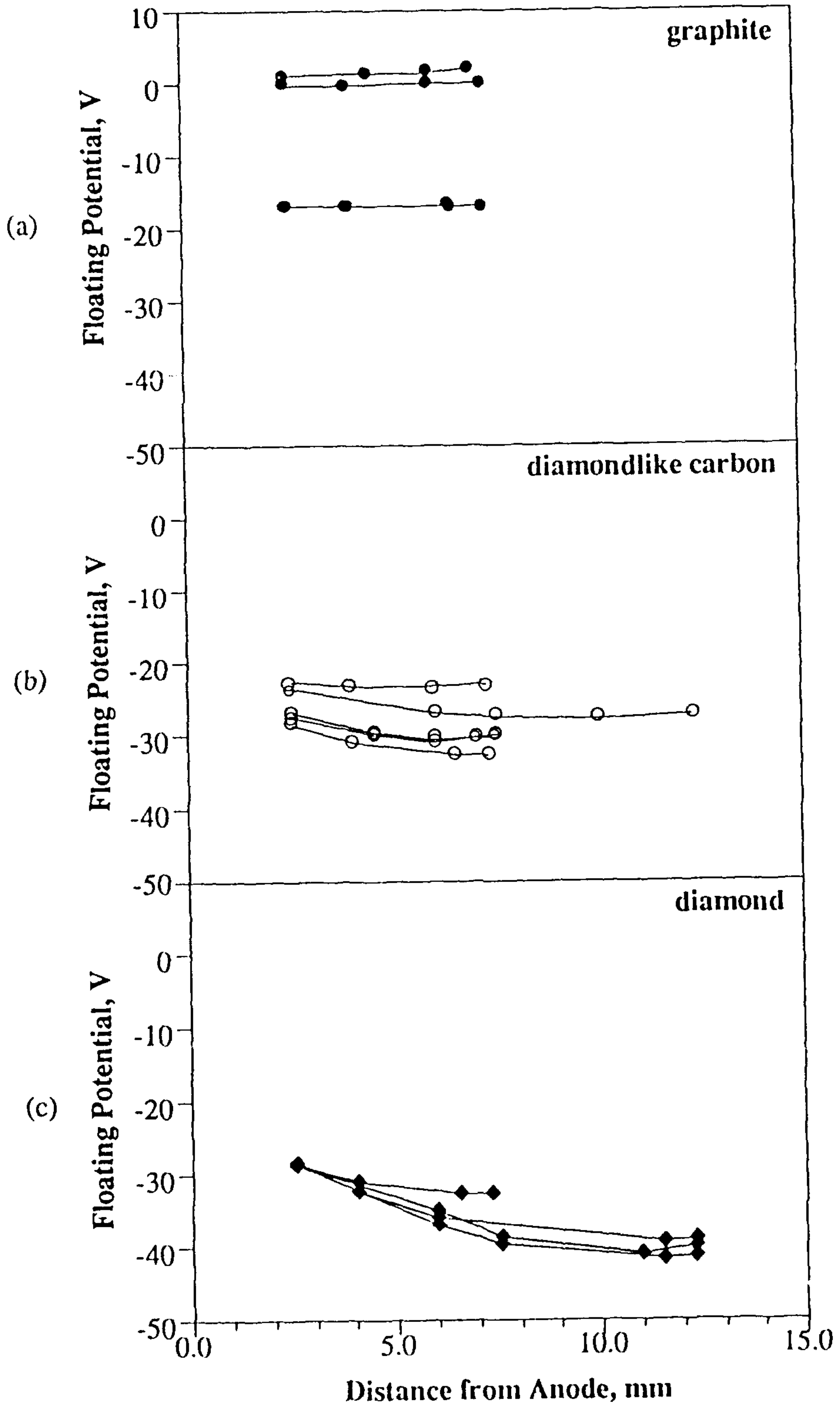


Figure 5: Floating potential profiles grouped according to the type of film produced by each plasma: (a) graphite, (b) diamondlike carbon, and (c) diamond films. Electrode spacings for all these profiles are ≤ 1.5 cm for maximum plasma stability.

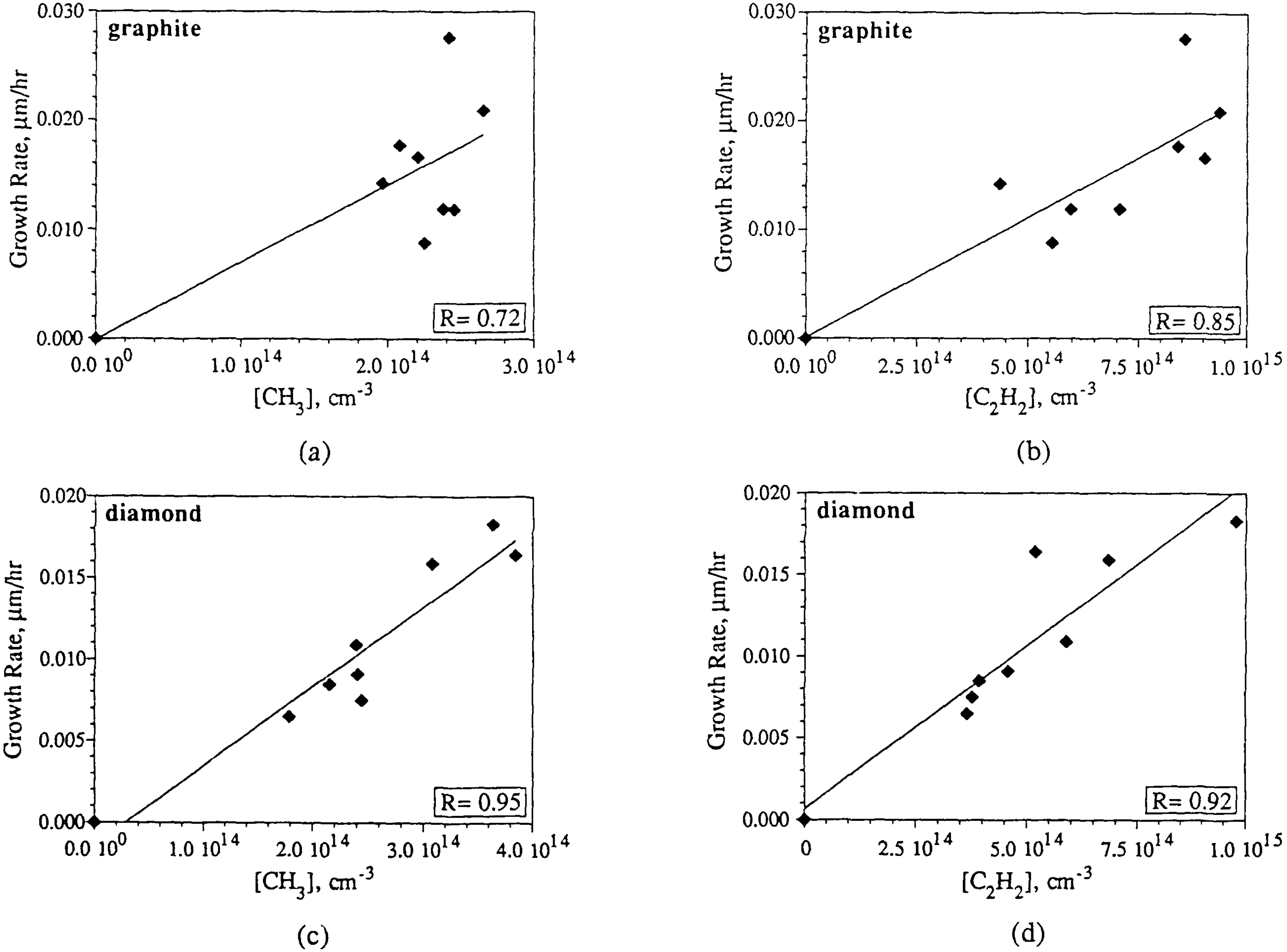


Figure 6: Growth rate of carbon films as a function of hydrocarbon concentration: (a) growth rate of graphite as a function of methyl radical concentration, (b) growth rate of graphite as a function of acetylene concentration; (c) growth rate of diamond as a function of methyl radical concentration; and (d) growth rate of diamond as a function of acetylene concentration.

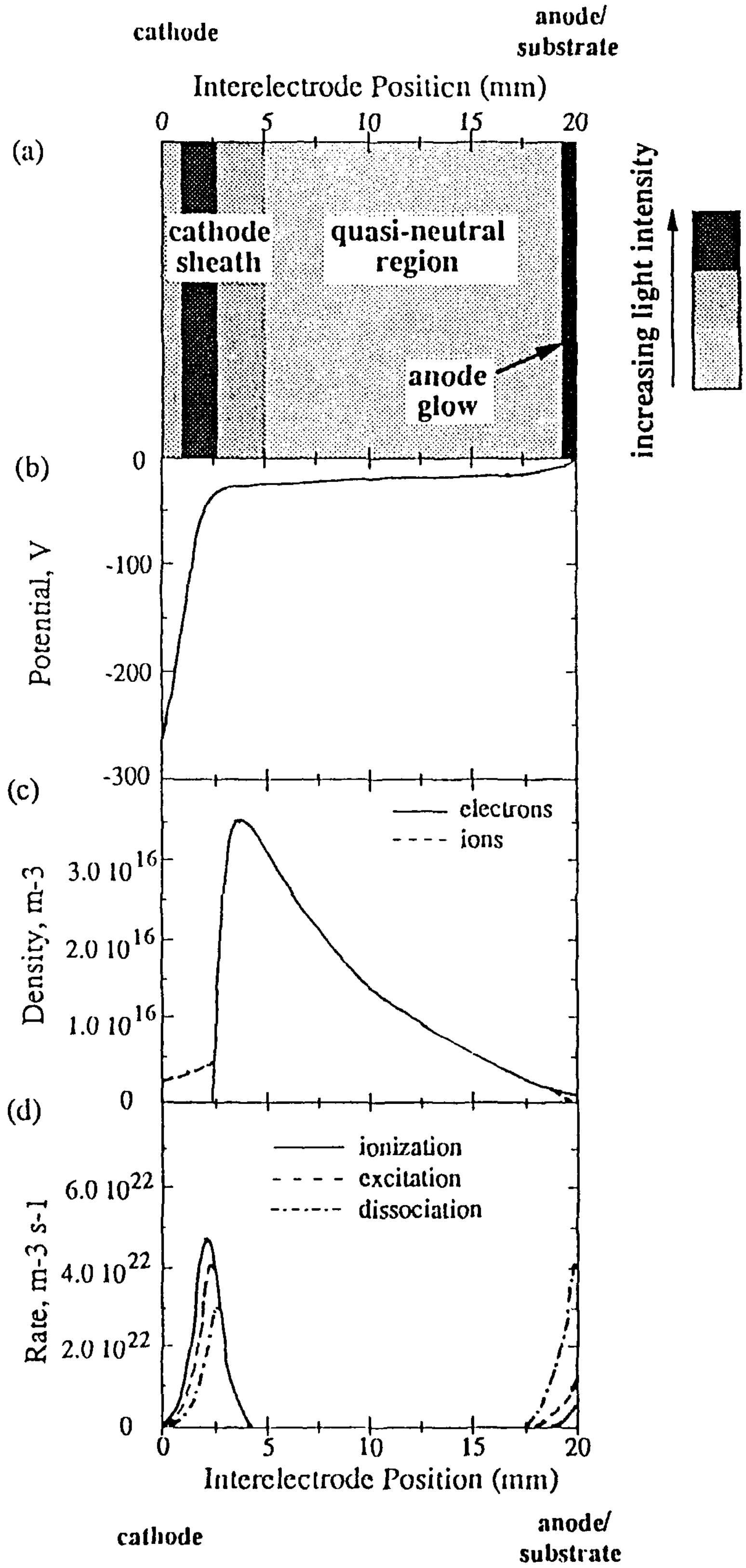


Figure 7: Computer model predictions for various diamond-producing DC plasma parameters: (a) schematic diagram of DC plasma, (b) predicted potential profile, (c) predicted charged particle density profiles, and (d) inelastic process rate profiles.

APPENDICES

A. Statement of Work

B. Subcontractors and Consultants

C. Ph.D. Thesis, Presentations, and Publications

APPENDIX A. STATEMENT OF WORK

1. Reactor Geometry

Crystallume has several years of experience in the design and construction of diamond deposition reactors. This expertise was utilized in the development of a reactor with state-of-the-art *in situ* plasma diagnostic capabilities. The reactor was designed to have maximum flexibility in terms of gas injection, plasma volume, substrate temperature, and plasma excitation mode. For this work, the simplest configuration was implemented to minimize complications in data interpretation: for example, DC plasma excitation was used instead of microwave. For the future work discussed in the text, the necessary changes can be made by modification of the top plate of the chamber, with no changes to the baseplate.

This design and implementation of the reactor is not discussed extensively in this report, but was a major undertaking, requiring extensive redesign of existing equipment, development of new vacuum seal technology, consideration of materials and thermal issues, and so on. A more complete description is given in the author's Ph.D. Thesis (June 1991).

2. Process Conditions

The process conditions with greatest effect on the diamond deposition process are known from empirical studies over the last five years. The known variables include methane concentration in the reactant gas mix, current, electrode spacing, pressure, total flowrate, substrate material, substrate temperature, cathode temperature, and identity and concentration of alternative precursor gases (such as carbon monoxide). Of these, the first four (methane concentration, current, electrode spacing, and pressure) were chosen for study. The values for each variable were set in each run according to a statistically designed set of experiments. This procedure allowed a much larger parameter space to be studied than would otherwise have been possible. It was also a very successful technique, leading to a greatly improved DC diamond deposition process.

3. Post-Deposition Characterization

After deposition, each film was characterized by Raman spectroscopy and SEM. Raman spectroscopy provided a measure of each film's quality in terms of the extent of diamond bonding while SEM yielded the morphology and growth rate (through measurement of the cross-sectional thickness across the center of the deposit). Transmission FTIR measurements were made on 15 membranes made from the films in Task 2, but no infrared active states were found, so these data are not presented.

4. Gas Phase Diagnostics

Three *in situ* diagnostic instruments were installed in the reactor described in Task 1. They are a mass spectrometer (with SIMS optics) for analysis of neutrals, radicals, and ions, an optical emission spectrometer for analysis of excited species, and a Langmuir probe for electrical measurements of the plasma. The optical emission spectrometer and Langmuir probe are both capable of mapping the plasma with micrometer controlled positioning. The plasmas specified by the statistical design of experiments described in Task 2 were analyzed by these instruments so that similarities in dependencies of film characteristics on deposition parameters and of plasma characteristics on deposition parameters could be observed. This comparison led to many of the results discussed in this report.

5. Computer Modeling of Plasma

Computer modeling was not included in the original proposal but added with the contract monitor's support during the first year. The purpose of this task was to develop a self-consistent model of the plasma, incorporating inelastic electron-neutral reactions, electron temperature, ion and electron densities and fluxes, and electric potentials and fields. Such a model had already been developed at the University of California at Berkeley by D.B. Graves and M. Surendra for low neutral gas density DC and RF plasmas. During the course of this contract, the model was expanded to high neutral gas density DC plasmas (*i.e.*, diamond-producing conditions). It was invaluable in describing the physical processes occurring in the plasma.

APPENDIX B. SUBCONTRACTORS AND CONSULTANTS

Subcontractors:

Professor D.B. Graves and M. Surendra of the University of California at Berkeley

Dr. Graves and M. Surendra developed the computer program used to model the high neutral gas density plasma employed for the deposition of diamond films. An example of their previous modeling of low neutral gas density DC and RF plasmas is given in the attached paper. Graves and Surendra also supplied considerable expertise in plasma processes.

Modeling was performed primarily through the second year of the contract. Expert advise on design, construction, and assembly of the diagnostic instruments was supplied throughout duration of the contract.

Consultants:

Dr. John R. Carruthers of Intel

Dr. Carruthers has supplied valuable support of this work through his expertise in materials and process development. He has been involved on a regular (weekly to monthly) basis throughout the execution of this contract.

APPENDIX C. PH.D. THESIS, PRESENTATIONS, AND PUBLICATIONS

PH. D. THESIS

Department of Materials Science and Engineering
Stanford University; Stanford, CA
Defense.....May 1991
Thesis...... June 1991

Linda S. Plano
STRUCTURE AND CHEMISTRY OF DIAMOND-PRODUCING DC PLASMAS

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App E Statistical Regression for Experiment Responses
- (a) Raman rating
- (b) Growth Rate (total)

App F Publications

PRESENTATIONS

Second International Conference on the New Diamond Science and Technology
Crystal City, VA
September 1990

1. Linda S. Plano, David A. Stevenson, and John R. Carruthers
   GAS PHASE CHEMISTRY IN DIAMOND-PRODUCING PLASMAS
2. M. Surendra, David B. Graves, and Linda S. Plano
   DC GLOW DISCHARGE MODELING APPLIED TO DIAMOND FILM GROWTH PLASMA REACTORS

Society for Photo-optical Instrument Engineers (SPIE) OE/LASE Conference
Los Angeles, CA
January 1991

3. Linda S. Plano
   OPTICAL EMISSION SPECTROSCOPY OF DIAMOND-PRODUCING PLASMAS

Electrochemical Society (ECS) Spring Conference
Washington, DC
May 1991

4. Linda S. Plano, Dave A. Stevenson, and John R. Carruthers
   CHARACTERIZATION OF DC PLASMAS FOR THE CONTROL OF DIAMOND DEPOSITION

American Chemical Society (ACS) Spring Conference
New York, NY
August 1991

5. Linda S. Plano
   GAS PHASE ANALYSIS OF DIAMOND-PRODUCING DC PLASMAS

PUBLICATIONS

No publications have been submitted to journals at this time. Planned publications include:

1. L.S. Plano, D.A. Stevenson, and J.R. Carruthers; "Effect of an Anode Field on Diamond Film Quality;" Electrochemical Journal Society Journal.
2. M. Surendra, D.B. Graves, and L.S. Plano; "Self-Consistent Model of Diamond-Producing DC Plasmas;" Journal of Applied Physics.

GAS PHASE CHEMISTRY IN DIAMOND-PRODUCING PLASMAS

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ABSTRACT

Most theories of diamond film growth point to either acetylene or methyl radicals as the critical diamond precursor hydrocarbon species. Investigations of chemical species in a low power (≤ 1 kW) DC diamond deposition reactor have been made with the goal of determining relationships between plasma-generated species and diamond film growth. Residual gas analysis (RGA) and SIMS techniques were used to identify gaseous species through the anode (the substrate electrode). Langmuir probe and optical emission spectroscopy data were taken as a function of interelectrode position to evaluate plasma structure and corroborate RGA data.

In a DC plasma, the majority of plasma-generated species are formed near the cathode. However, experience has shown that diamond will grow only at the anode, not the cathode. Thus, relative concentrations of candidate diamond precursors were monitored at the anode as a function of plasma power and of methane concentration. C_2H_2, CH_3, and growth rate were all found to vary linearly with plasma power. C_2H_2 was found to vary linearly with methane concentration as well. However, both CH_3 and growth rate were found to have a power law dependence on methane concentration with an exponent of approximately 0.45, indicating that methyl radicals are more directly related to diamond film growth than is acetylene.

INTRODUCTION

Most current theories of diamond film growth focus on two aspects of diamond deposition: The roles of atomic hydrogen and the identity of the carbonaceous precursor to diamond. The main roles of atomic hydrogen are generally thought to include surface stabilization of sp^3 bonding, surface hydrogen abstraction, graphite etching at the substrate and hydrogen abstraction in the gas phase. Methyl radicals [1] or cations [2] and acetylene [3] have all been suggested as possible diamond precursors. Experimental evidence is needed to verify these postulates so that the deposition process can be optimized for various applications.

The behavior of atomic hydrogen (excited and ionized), methyl radicals, and acetylene in the gas phase as influenced by the plasma parameters have been studied through residual gas analysis (RGA). The resulting measurements were compared to film growth rates under the same plasma conditions

In addition to *in situ* diagnostics, much can be learned about diamond growth through general observation. Diamond can be deposited by a wide range of CVD techniques, including both plasma- and thermally-assisted methods. This flexibility in deposition technology can yield information on the mechanisms controlling diamond film growth. For instance, hot filament is an efficient producer of diamond but produces almost no ions. Thus, the ions generated by plasma-assisted techniques apparently do not play a critical role in the growth process. A phenomenon peculiar to DC plasmas provides another set of clues: Diamond films grow only on the anode, not the cathode. Differences between the anode and cathode of this system were explored with Langmuir probe and optical emission spectroscopy.

EXPERIMENT DETAILS

Low power (≤ 1 kW) DC excitation was employed to generate the plasma studied in this work. DC excitation was selected because DC plasmas are fairly well understood, facilitating data analysis and system modeling [4]. The deposition conditions studied were in the ranges commonly used for low pressure diamond growth.

The reactor was equipped with three diagnostic instruments: A residual gas analyzer/ SIMS head (Hiden Analytical Ltd. MSPS), a Langmuir probe, and an optical emission spectrometer (EG&G PAR OMA III).

The MSPS was used for mass analysis of neutral species. It sampled the plasma directly through a 150 µm aperture in the bottom electrode, which could be biased either positive or negative with respect to the upper electrode. For this work, the bottom electrode was biased positive by holding it at ground while the upper electrode was driven negative. Double differential pumping was used to allow direct sampling of the plasma. The pressure in the first differential stage was typically in the range of 8 - 20 x 10^{-5} torr. The second stage was maintained at 1.5 - 3 x 10^{-6} torr.

The Langmuir probe consisted of a platinum wire in a quartz sheath which was inserted into the plasma, then biased to develop a current-voltage characteristic. The characteristic directly yielded ion saturation current and floating potential. Ion densities were estimated using theory developed by Kiel [4]. The optical emission spectrometer was used for qualitative structural and chemical analysis of the plasma. Both the Langmuir probe tip and the focal point of the optical emission spectrometer could be moved vertically between the two electrodes through micrometer control. The electrode spacing was externally variable.

RESULTS AND DISCUSSION

Langmuir probe and optical emission spectroscopy measurements were also made in pure hydrogen plasmas to facilitate data analysis. Hydrocarbon species were studied by mass spectrometry.

Optical emission spectroscopy was used to monitor the presence of excited hydrogen in the plasma. Specifically, the intensity of the $H\alpha$ Balmer line (produced by light emitted when an electron drops from the third to the second energy level in a hydrogen atom) was spatially resolved (Figure 1). This technique was only useful for qualitative analysis of plasma structure since there is no direct, stable relationship between the concentrations of excited and ground state atomic hydrogen. However, the presence of excited atomic hydrogen indicated that ground state atomic hydrogen was also present.

The most intense $H\alpha$ lines were found near the cathode, indicative of the dissociation occurring there. Thus, diamond might be expected to grow most quickly at the cathode. However, experience has shown that diamond films do not grow at the cathode. An explanation for this phenomenon can be found through analysis of Langmuir probe characteristics. The ion density of the plasma as a function of position is shown in Figure 2. As in the $H\alpha$ results, the maximum in ion density is found to occur near the cathode, in the cathode sheath. The spatial distribution of the potential is shown in Figure 3. Note that any positive ions would be repelled by the anode and driven into the cathode while electrons would be driven in the opposite direction, towards the substrate. Thus, ion bombardment (and possibly resulting heating) of the growth surface appears to be severely detrimental to film growth.

Diamond film has been routinely grown at the anode even when this electrode was well removed from the species generated in the cathode sheath. There is strong evidence that those species formed by dissociation (e.g., H_2 and

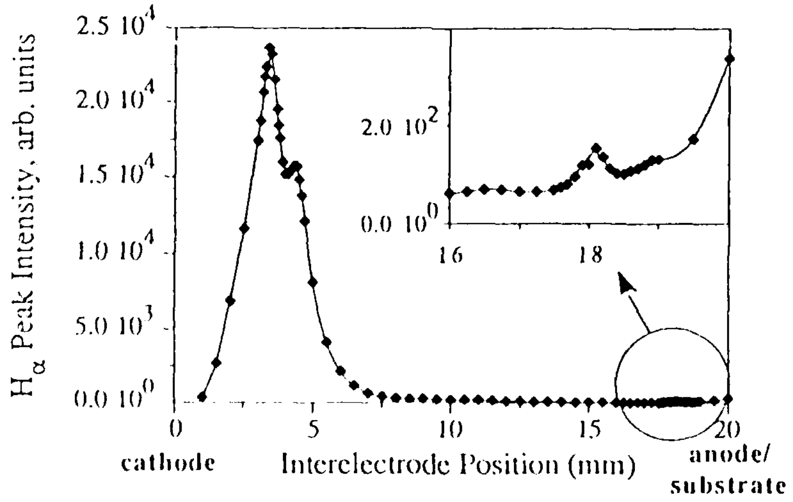


Figure 1: Intensity of $H\alpha$ Balmer line as a function of interelectrode position. Inset shows increase in $H\alpha$ intensity in proximity of anode.

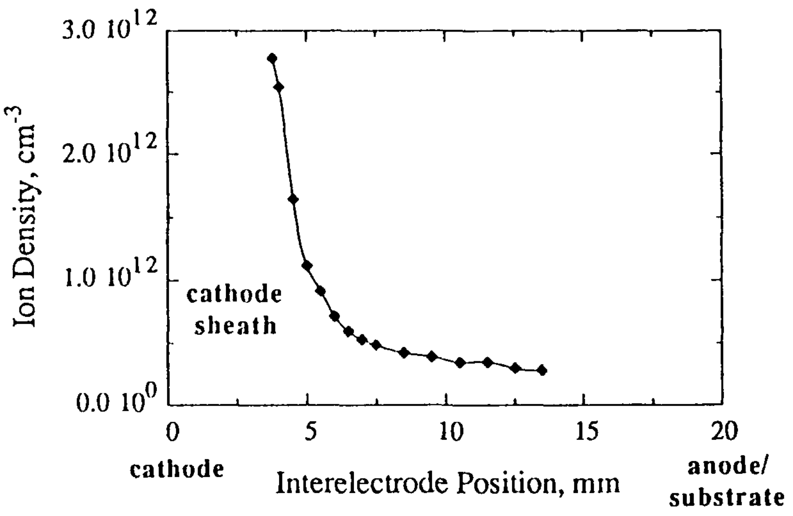


Figure 2: Ion density as a function of interelectrode position. Densities were calculated from Langmuir probe characteristics using theory developed by Kiel [4].

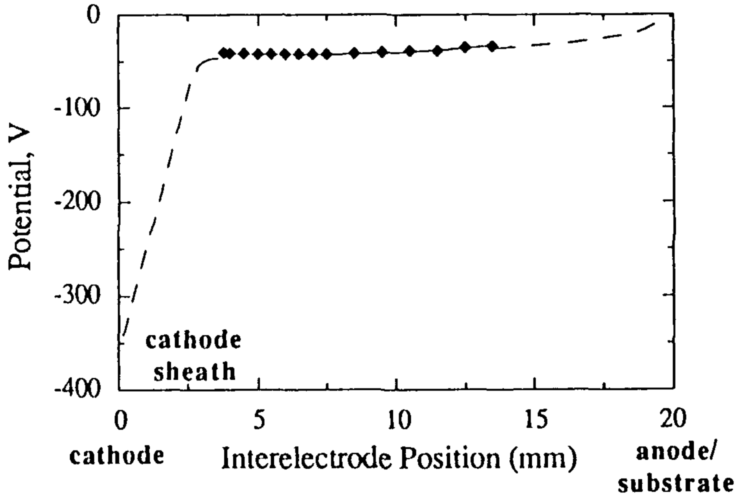
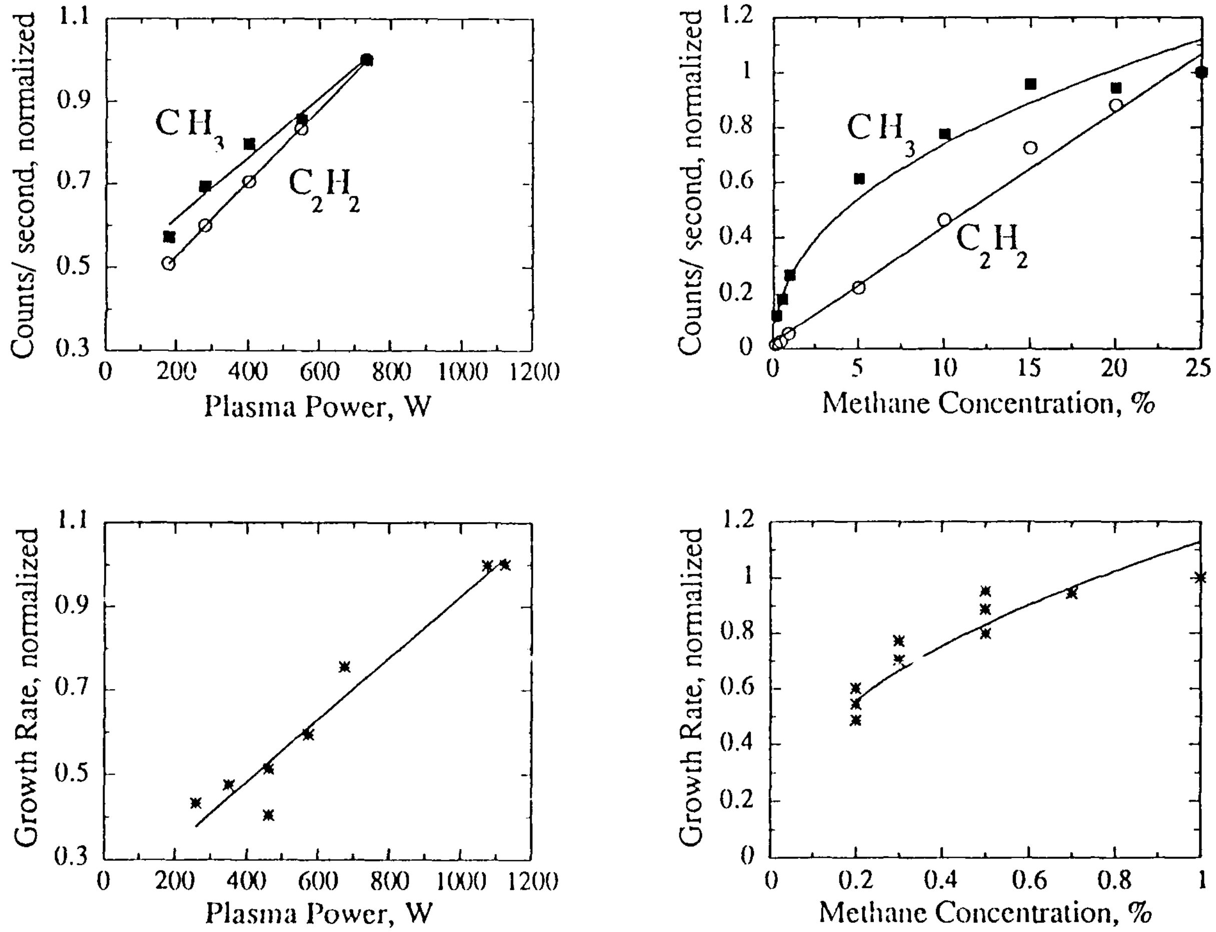


Figure 3: Potential as a function of interelectrode position. Potential was approximated by the floating potential in the bulk of the plasma and set to the electrode potentials at the appropriate boundaries.

CH_3) may be generated in the field near the anode [5], but for the purposes of this discussion, the creation mechanism will be ignored. Instead, direct measurement of the relative concentrations of the two most likely candidates for diamond precursor - acetylene and methyl radicals (as measured by RGA) - will be compared to diamond film growth rate with the goal of determining which has the more direct role in producing diamond.

Methyl radical and acetylene dependencies on plasma power are shown in the upper graph in Figure 4a. Both show a linear dependence on power. Growth rate, shown in the lower graph in Figure 4a, exhibits a similar dependence, suggesting that the three parameters are interdependent.

Methyl radicals were found to differ strongly from acetylene in their dependence on methane concentration. While acetylene again showed a linear dependence, methyl radicals showed a power dependence (top graph in Figure 4b). Preliminary measurements indicated that the power exponent value was approximately 0.45. Growth rate data were taken over a much smaller range of methane concentrations because graphitic bonding increases rapidly with methane concentration. However, over the range of methane concentration which produces good quality diamond films, the growth rate was also found to have a power law dependence on methane concentration. The power exponent was found to be about 0.44 (bottom graph, Figure 4b), quite close to that of the methyl radical dependence. This result indicates that methyl radical concentration and diamond growth rate are closely related. In addition, the linear increase in acetylene with methane concentration suggests that it may be responsible for the increasing graphitic bonding content of films deposited at higher methane concentrations. Further work is needed to more accurately establish these relationships.



(a) (b)

Figure 4: Dependencies of relative methyl radical and acetylene concentrations, and diamond film growth rates on critical plasma parameters. (a) Dependence on plasma power and (b) dependence on methane concentration. The power law dependencies for both methyl radical concentration and growth rate (b) have an exponent of approximately 0.45.

CONCLUSIONS

Diamond films do not grow on the cathode of a low power DC reactor in spite of the presence of large quantities of reactive species generated in the cathode sheath. Good films do grow at the anode, in spite of the much smaller electric field at this electrode. Ions bombard the cathode while only low energy electrons (1-2 eV) bombard the anode, suggesting that ions may be disruptive to diamond growth.

In this work, plasma-generated hydrocarbon species thought to be possible diamond precursors were observed at the anode. These species were studied as a function of plasma power and of methane concentration in the reactant gas mix. The results were compared to film growth rates for the same conditions.

Both acetylene and methyl radical concentrations appear to be related to film growth rate since all three have a linear dependence on plasma power. However, methyl radicals seem to be more directly related to diamond growth rate since both exhibit approximately the same power dependence on methane concentration, while acetylene concentration has a linear dependence.

ACKNOWLEDGEMENTS

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DC GLOW DISCHARGE MODELING APPLIED TO DIAMOND FILM GROWTH PLASMA REACTORS

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ABSTRACT

Low power (≤1 kW) DC plasmas have been successfully used to grow diamond films. An unusual aspect of these systems is that diamond will only grow at the anode, although most of the plasma-generated species are formed near the cathode. To understand the mechanisms responsible for this phenomenon, and to enhance DC deposition, a model used to describe processes in low neutral gas density DC plasmas has been adapted to diamond-producing DC plasmas. *In situ* diagnostics were used to supply necessary data for the adaptation and for testing the resulting model.

A mechanism for hydrogen dissociation near the anode has been developed. Near the cathode, the most common inelastic process was shown in the model to be ionization. Positive ions are driven by local fields to the cathode and away from the anode. As a result, the cathode is bombarded by ions, which may be responsible for the disruption of diamond growth on this electrode.

INTRODUCTION

Extensive research into the chemistry and kinetics of diamond film deposition has been undertaken by many researchers. The focus of most of this research has been to explore surface reactions [1,2] and gas phase chemistry [1,3] through *in situ* diagnostics and computer modeling of the growth surface. A comprehensive model of the plasma incorporating its electrical fields, inelastic reactions, and other physical processes would supply an important link between gas phase data and model predictions. To this end, a model developed for low neutral gas density DC plasmas has been adapted to diamond-producing, high neutral gas density DC plasmas.

Low power (≤ 1 kW) DC plasmas were selected for initial studies because they represent the simplest of plasma systems and have been successfully used for routine deposition of diamond films. In addition, there are several phenomena peculiar to DC plasmas that have assisted in developing a physical model of the deposition process. For instance, diamond grows only on the anode in these systems; DLC and graphite grow on the cathode. Also, if the anode does not exhibit a characteristic glow, DLC grows on the anode as well. These physical indicators of plasma parameters and behavior were found to be helpful in refining the model to its present state.

EXPERIMENT DETAILS

A DC plasma reactor based on production reactors was used for this work. The reactor was equipped with three diagnostic instruments: A residual gas analyzer/ SIMS head (Hiden Analytical Ltd MSPS), a Langmuir probe, and an optical emission spectrometer (EG&G PAR OMA III). These techniques were employed to establish the values of critical plasma parameters and to test predictions of the model.

The MSPS was used for mass analysis of neutral species. It sampled the plasma directly through a 150 μm aperture in the bottom electrode, which could be biased either positive or negative with respect to the upper electrode. For this work, it was held at ground while the upper electrode was driven negative so that the lower electrode was biased positively. Double differential pumping was used to allow direct sampling of the plasma. The pressure in the first differential stage was typically in the range of 8 - 20 x 10^{-5} torr. The second stage was maintained at 1.5 - 3 x 10^{-6} torr.

The Langmuir probe [4] consisted of a platinum wire in a quartz sheath which was inserted into the plasma, then biased to develop a current-voltage characteristic. The characteristic directly yielded ion saturation current and floating potential. Ion densities were estimated from probe characteristics using theory developed by Kiel [5]. The optical emission spectrometer was used for qualitative structural and chemical analysis of the plasma. Both the Langmuir probe tip and the focal point of the optical emission spectrometer could be moved vertically between the two electrodes through micrometer control. The electrode spacing was externally variable.

MODEL DETAILS

The model used here is an extension of the technique described in Ref. [6]. Briefly, the electrons are divided into two groups, 'slow' and 'fast' electrons. The fast electrons are electrons originating at the cathode due to secondary electron emission or created in the ionization avalanche in the cathode sheath, while slow electrons reside in the low field (or quasineutral) region. The fast electrons, being highly nonequilibrium, are treated as individual particles moving under the influence of the electric field. Collisions with neutral species are treated with a Monte Carlo method. The fast electron model provides inputs (such as ion and slow electron creation rates) to a fluid model for the ions and slow electrons. This model comprises conservation equations for ions and slow electrons, energy conservation for slow electrons together with Poisson's equations. The fluid model and fast electron model are solved iteratively until a fully self-consistent result is obtained.

RESULTS AND DISCUSSION

The DC plasmas used for this work were obtained at high neutral gas densities compared to those employed for many other common plasma processes, such as etching. Neutral gas density refers to the number density of unionized gaseous species. High neutral gas densities have a profound effect on plasma phenomena because of the short mean free paths and resulting high collision frequencies and low electron temperatures, as will be discussed more fully below.

A combination of computer modeling and experimental data was used to develop an overall representation of plasma phenomena. In Figure 1, model results are shown in the left hand column while comparable experimental data are displayed in the right hand column.

A schematic diagram showing principle structures in the high neutral gas density DC plasmas used for diamond deposition is shown in Figure 1a and b. The brightest region near the cathode results from relaxation of excited species which are created by the electron avalanche in the high field region next to the cathode. The anode is also brighter than the quasineutral region (where ion and electron densities are approximately equal), which makes up the bulk of the plasma.

Potential variation as a function of interelectrode position is shown in Figures 1c (model) and d (measured). The model shows the high field region next to the cathode and the smaller field region near the anode. Measured values for the floating potential are available only in the quasineutral region of the discharge. We have extrapolated this potential to the electrodes in a manner that is consistent with the model prediction. Note that the potential in the quasineutral region is quite negative with respect to the anode, which is in contrast to the potential in low neutral density discharges, where it is small and positive [6]. At the high neutral densities, the electrons experience many collisions (mean free path ranges from 0.01 - 0.1 mm) and, as a result, cool to near ambient temperatures. Because of the higher frictional forces, a field develops to assist electron motion towards the anode. At low neutral densities, electrons retain sufficiently high temperatures to easily diffuse against a potential barrier to the anode.

Charged particle density profiles are shown in Figures 1e (model) and f (estimated from Langmuir probe data). It is worthwhile to emphasize here that calculations made from probe data result in estimates, useful mainly for order of magnitude approximations. It is the shape of the experimental curve, rather than the absolute magnitudes, that are of interest here.

The species densities are at a maximum near the cathode sheath edge. This is not surprising since the ionization rate as predicted by the model (Figure 1g)

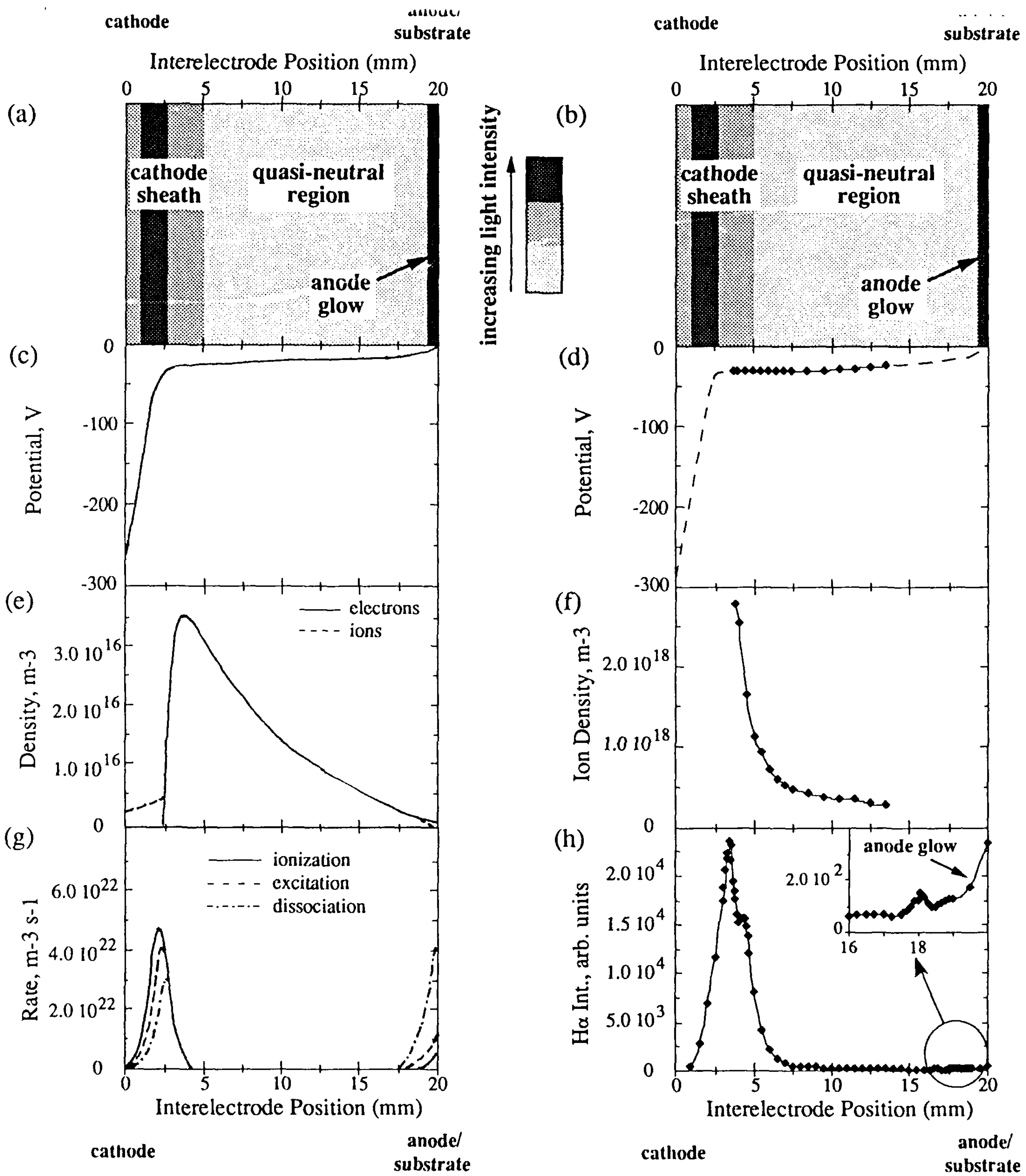

Figure 1: Computer model predictions (left) and comparable experimental data (right) for various diamond-producing DC plasma parameters.
(a) and (b): Schematic diagrams of DC plasmas.
(c) and (d): Predicted and measured potential profiles.
(e) and (f): Predicted and calculated charged particle profiles.
(g) and (h): Predicted inelastic process rates and measured H_α emission profile.

also peaks here. The concave shape of the species density profiles is due to the recombination between ions and slow electrons. The measured profiles (Figure 1f) decrease more rapidly than the predicted profiles, suggesting that recombination may play a greater role than assumed in the model. Note that the anode sheath is electron rich, which is consistent with the potential profile in Figure 1c (or d).

The anode sheath plays an important role in the discharge structure. From Figure 1g, it is apparent that inelastic rates (dissociation, excitation, and ionization) are sizeable at the anode. The peak in inelastic rates at the cathode sheath is typical of low neutral density DC glows [6]. The relative magnitude of the different inelastic rates at the cathode sheath and at the anode is interesting. At the cathode sheath ionization dominates, while at the anode dissociation dominates. In the cathode region, the electrons are very energetic (average energy ranges from 10 to 100 eV), leading to a substantial amount of ionization, since the cross sections for ionization are generally larger than the cross sections for the other inelastic process, even though the threshold for ionization is larger. The opposite is true at the anode, where the electron distribution has an average energy of about 2 eV as a result of heating by the small field. In this case the threshold for each process strongly influences the reaction rate constant.

No direct experimental evidence is available to confirm the predicted dissociation profile. However, according to the model results in Figure 1g, excitation occurs in the same regions as does dissociation. The light emitted by excited atomic hydrogen as it relaxes was monitored by optical emission spectroscopy. The profile of the H_α Balmer line intensity (Figure 1h) shows peaks in the same regions as the excitation peaks in the model (Figure 1g), suggesting that inelastic processes are indeed occurring where predicted.

Dissociation of molecular hydrogen leads to an increase in local atomic hydrogen concentration, known to be important to diamond deposition. Ionization is not thought to be a critical process since purely thermal, non-ion-generating systems have successfully produced diamond. In addition, ion bombardment of the substrate appears to have a negative effect on diamond growth. Thus, the combination of local atomic hydrogen formation at the anode, and the repulsion of any ions from the anode, appear to be the two factors allowing diamond deposition there, while ion bombardment and resultant heating of the cathode appear to retard diamond growth and/ or accelerate graphite growth.

CONCLUSIONS

Preliminary results indicate that modeling of diamond-producing DC plasmas can lead to a much improved understanding of the physical processes leading to diamond deposition. There are many significant differences between low neutral gas density plasmas (such as those used in etchers) and high neutral gas density plasmas (as used for diamond deposition). Specifically, the differences are as follows:

- The plasma potential is large (~ -30 V) and negative.
- The anode is the most positive part of the plasma.
- Ions are repelled at the anode while electrons are accelerated to it.
- As the electrons are accelerated to the anode, they gain sufficient energy to have inelastic collisions, leading to ionization, excitation, and, most importantly, dissociation near the anode.

One similarity between these two types of plasmas is that ions are strongly driven toward the cathode. These results, coupled with the fact that diamond grows at the anode while graphite and DLC grow at the cathode, suggest that diamond film can grow at the anode because of the presence of atomic hydrogen and the lack of ion bombardment. The growth of nondiamond-bonded carbon at the cathode is apparently a result of the overwhelming effects of ion bombardment on the sp^3 bonding.

ACKNOWLEDGEMENTS

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Optical emission spectroscopy of diamond-producing plasmas

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ABSTRACT

Diamond films grow on the anode of DC plasmas while only diamondlike carbon and graphite grow on the cathode. *In situ* plasma diagnostics were employed to investigate the plasma as a whole and the anode in particular. To this end, pure hydrogen and diamond-producing DC plasmas were studied with optical emission spectroscopy. The pure hydrogen plasmas were analyzed to determine the effect of critical deposition parameters on the visible structure of the plasma. Two methane/ hydrogen plasmas were also examined, one of which produced a graphitic film, the other a diamond film. The visible structures of these plasmas differed in that the diamond-producing plasma exhibited evidence of an anode (substrate) glow while the graphite-producing plasma had no glow.

1. INTRODUCTION

Plasma enhanced CVD of diamond films has become a routine deposition technique.[1,2,3] Although it is possible to control this process to the point that diamond film products are now available, the actual deposition mechanisms are not well understood.[4,5,6] *In situ* plasma diagnostics provide the most direct method of revealing some of these mechanisms.

Plasmas are inherently difficult to probe directly because they are chemically reactive and electrically active. Optical techniques such as laser enhanced fluorescence (LEF) are useful in that they minimize such interaction. Optical emission spectroscopy (OES) is ideal in that it is completely passive and so does not perturb the plasma.

OES is commonly used to identify various species in plasmas by the wavelength of their emitted light. This application is of limited use in determining the mechanisms of diamond growth since many critical species, such as methyl radicals and acetylene, do not have radiative transitions. Also, it is difficult to quantify the spectra of those species which are detectable since it is the excited rather than the ground states that are measured, and there is generally no simple and direct path between the two states. Instead, OES was used to spatially map the emitted light intensity as a function of interelectrode position. This data yields information on where critical inelastic electron-neutral reactions such as dissociation, excitation, ionization, and recombination are taking place.

An indication of the utility of analyzing spatially resolved emitted light intensity is shown schematically in Figure 1. Bright and dark regions of two types of DC plasmas are shown in conjunction with electric potential distributions, illustrating the relationship between these two plasma characteristics. The plasma in Figure 1a is a low neutral gas density DC plasma, ignited at a pressure of 1 torr and at room temperature, leading to a neutral gas density of 3.2×10^{16} cm^{-3}. It exhibits a visible and electrical structure that has been extensively researched. The second is typical of diamond-producing DC plasmas, with a high neutral gas density from high pressure at high temperature: 2.7×10^{17} cm^{-3}, nearly an order of magnitude higher than the previous case.

At low neutral gas densities, the plasma potential varies as shown in Figure 1a.[7] The diffusive flux of electrons is sufficiently high under these conditions that a small retarding field is necessary at the anode to reduce the electron current to an equilibrium level, generally as set externally. As neutral gas density is increased, electron mobility and diffusivity decrease and the diffusive flux becomes insignificant. An electric field must develop near the anode to compensate for the reduced diffusive flux to maintain a given current (Figure 1b). This field accelerates electrons out of the plasma and simultaneously imparts energy to them such that some may participate in inelastic processes.[8] These processes account for the anode glow in Figure 1b.

The effect of several important diamond deposition parameters, including DC current, pressure, and electrode spacing, on the visible structure of pure hydrogen DC plasmas was studied by OES. Two methane/ hydrogen plasmas, one which produced diamond film and one which generated graphitic material, were also analyzed. Striking differences between the visible structures of these two plasmas were observed.

2. EXPERIMENTAL INSTRUMENTATION

Experiments were performed in an aluminum bell jar vacuum chamber. The anode was attached to the baseplate and kept at ground while the cathode was mounted on a micrometer controlled tripod for *in situ* adjustment of electrode spacing. Hydrogen (and methane for the carbon film-producing plasmas) were introduced through the cathode, their flowrates controlled by mass flow controllers Substrate heating was accomplished with a resistance heater.

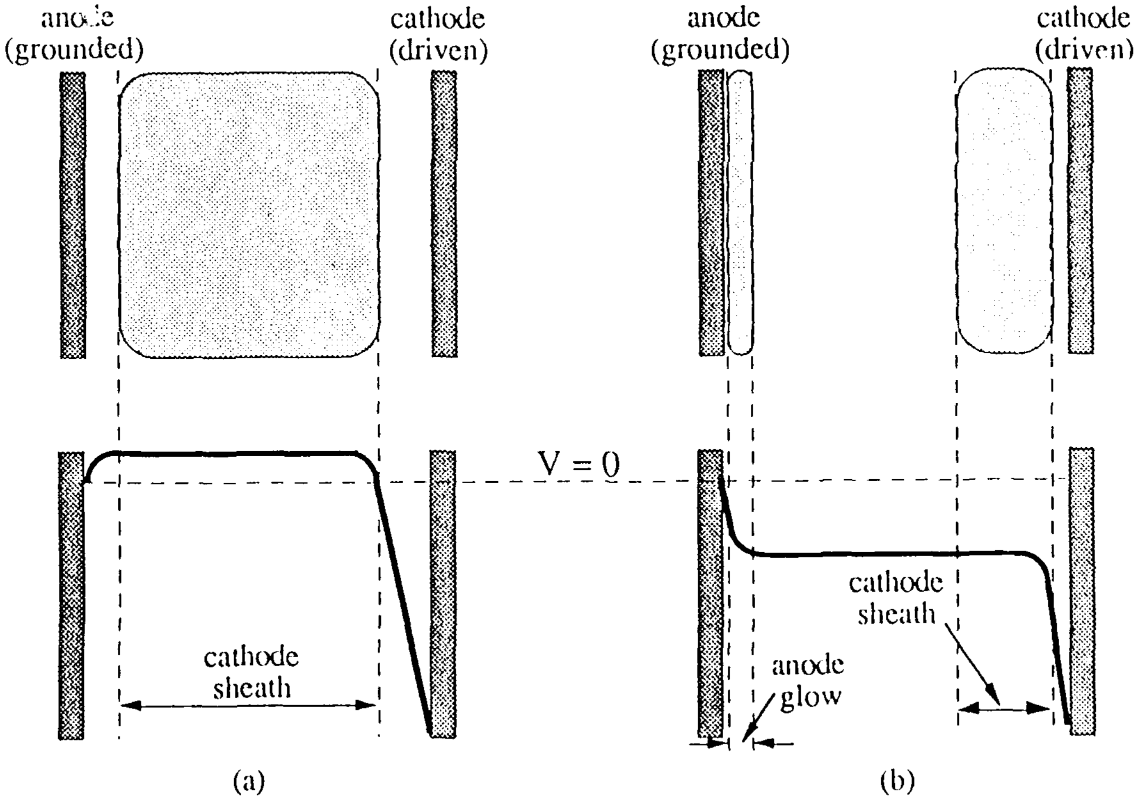


Figure 1: Visible and electrical structures of plasmas with (a) low neutral gas density and (b) high neutral gas density. Note anode glow and large negative plasma potential in (b).

Optical emission spectroscopy was performed with an EG&G Princeton Applied Research OMA III system with 0.25 meter monochromator. The optical train, which is shown in Figure 2 employs two fused silica lenses to allow ultraviolet radiation transmission. The port through which the plasma was sampled was of Suprasil quartz, also for enhanced ultraviolet transmission. The optical train had a movable focal point such that it was possible to map the presence of emitting species as a function of interelectrode position.

For each point measured, the OES produced a spectrum of peak intensity *vs.* wavelength. For the pure hydrogen plasmas, a wavelength range of 480 - 740 nm was used, while for the methane/ hydrogen plasmas the range was 350 - 610 nm. Atomic hydrogen peaks were present in all cases, indicating that this critical species is generated by these plasmas. However, a molecular hydrogen peak at 603 nm was used for this analysis since excited molecular hydrogen provides a more accurate indication of the inelastic process rates in the plasmas than does excited atomic hydrogen.

The effects of variations in diamond deposition parameters on emission spectra from both pure hydrogen plasmas and methane/ hydrogen plasmas were analyzed as a function of plasma position. Plasma structure was determined by recording emission intensities at various interelectrode points, then normalizing for the acquisition time.

During these experiments, the effects of four deposition parameters on visible plasma structure were studied. These parameters are methane concentration, DC current, electrode spacing, and pressure. For the pure hydrogen plasmas, methane concentration was held at zero and the other parameters were varied one at a time. For the carbon film-producing plasmas, the parameters were varied to produce diamond in one case, graphite in the other, based on results from a statistical process design. Nominal values of the deposition parameters were as follows:

Current	1.5 A
Spacing	2 cm
Pressure	28 torr

Total gas flowrate was held at 100 sccm, substrate temperature at 725 °C. Methane concentration was varied from 0.2 - 0.6% by volume for the two carbon film-producing plasmas.

3. RESULTS AND DISCUSSION

3.1 Hydrogen Plasmas

Pure hydrogen plasmas were studied as a prelude to carbon-film producing plasmas so that the role of chemistry in determining plasma structure would be minimized. The effects of current, pressure, and electrode spacing on the visible structure of a pure hydrogen plasma were studied individually and are discussed separately in the following sections.

3.1.1 Current Variation Effects.

To determine the effect of current on plasma structure, pressure and spacing were held constant at 28 torr and 2 cm, respectively, while the current was varied in three steps from 1 to 2 A. The higher the current, the more intense the radiation from the visible regions of the plasma. This behavior is shown in the H_2 profile in Figure 3. The relative intensity of H_2 radiation near both electrodes increases with increasing current. The widths of the cathode sheath and the anode glow are not affected.

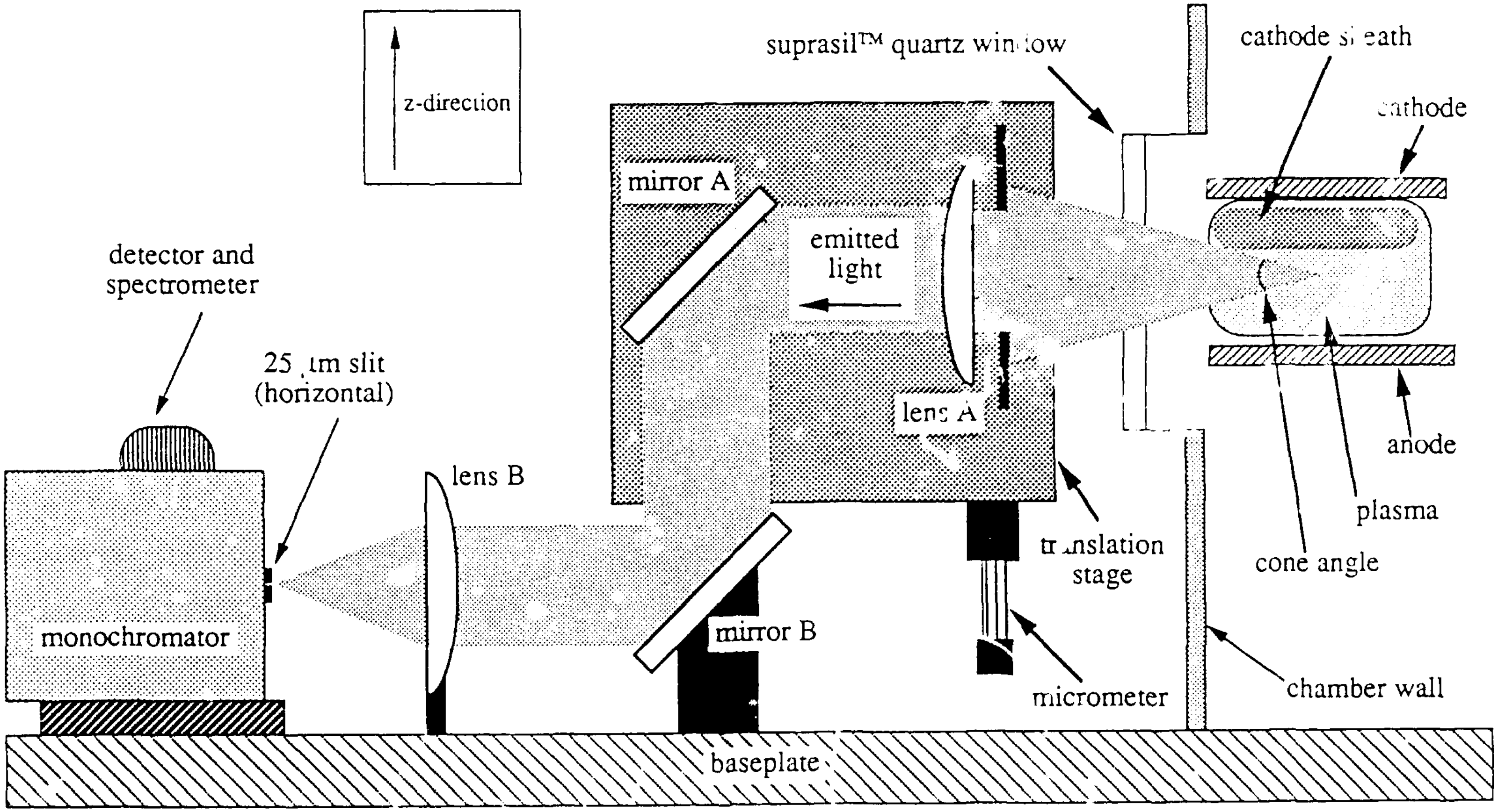


Figure 2: Schematic diagram of beam telescope used for detecting spatially-resolved emitted light from the plasma.

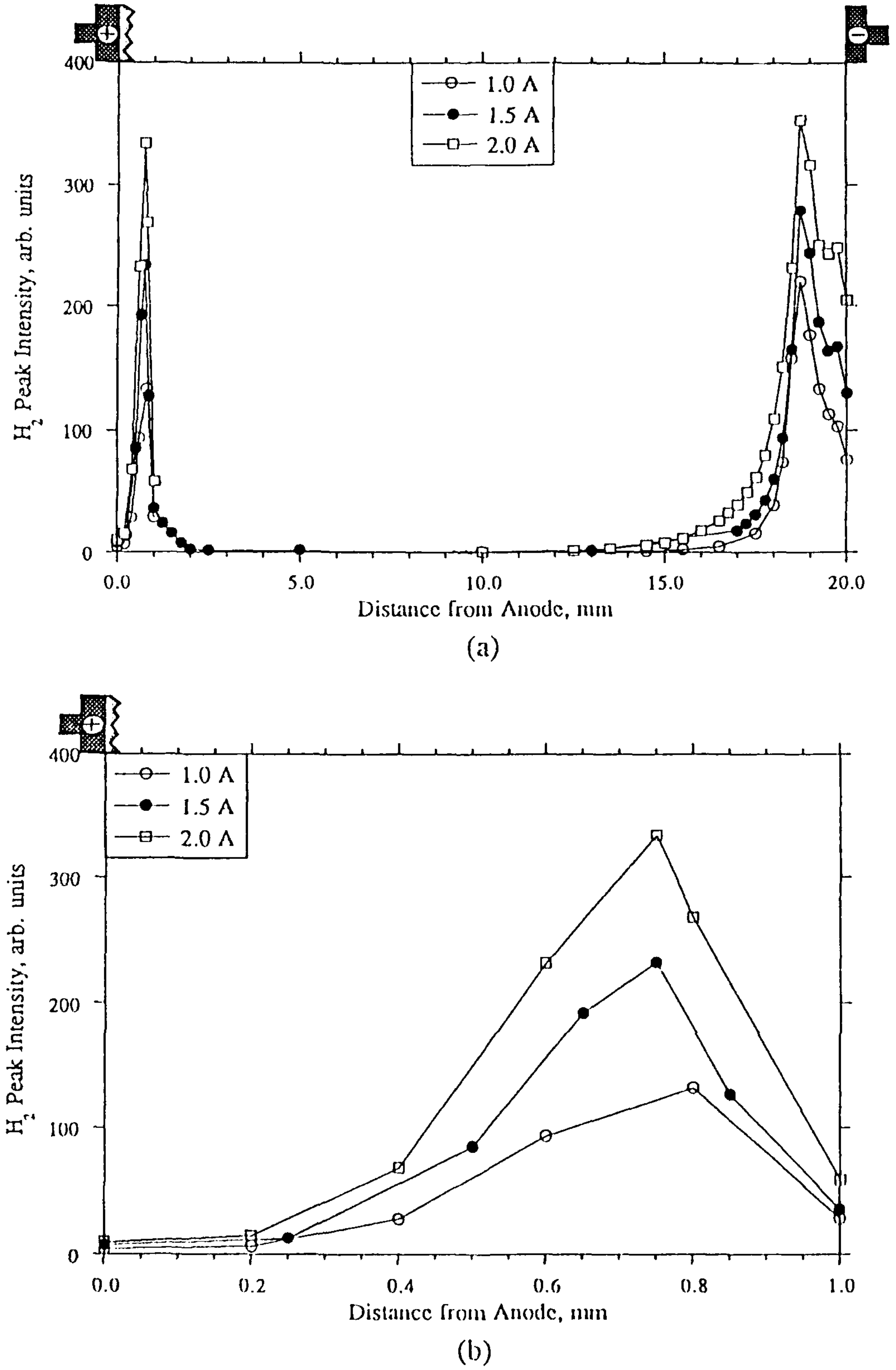


Figure 3: Effect of current variation on intensity of H_2 peak at 603 nm as a function of interelectrode position: (a) full plasma and (b) detail of anode region.

As current is increased, so must the density of charged particles be increased to carry the additional current between from cathode to anode. An increased driving voltage must be applied to create the additional carriers. Increased electron densities lead in turn to higher incidence of inelastic electron-neutral collisions, creating additional excited, dissociated, and ionized species, which leads to more intense emission spectra.

The width of the glow regions (the anode glow and the cathode sheath) is not affected by current variations because it is controlled by mean free path, *i.e.*, how far from an accelerating field an electron can retain sufficient energy to participate in inelastic collisions. Since variations in current do not affect neutral gas density, there is no effect on width.

3.1.2 Pressure Variation Effects

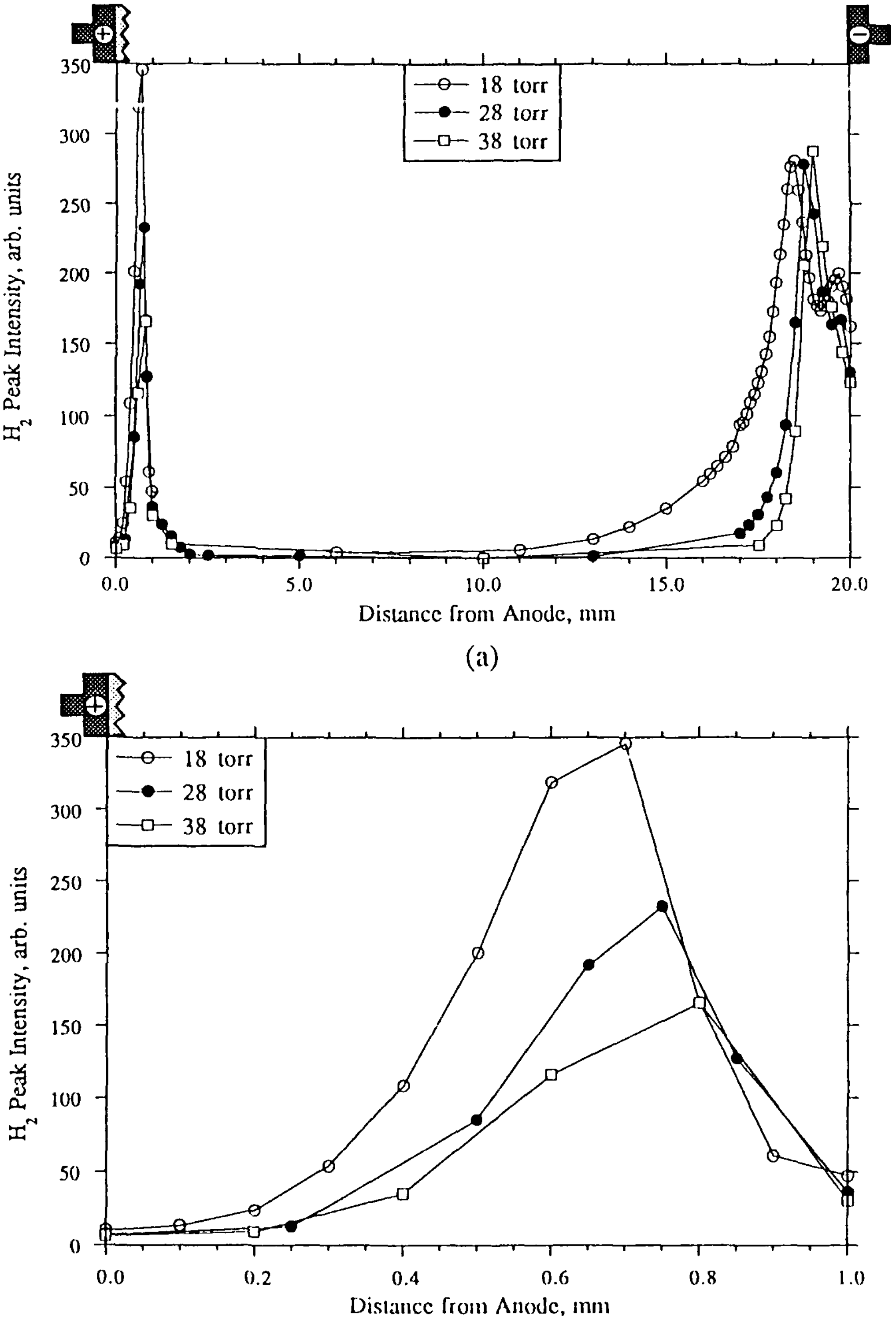
To explore the effect of pressure on plasma structure, current and electrode spacing were held constant at 1.5 A and 2 cm, respectively, while the pressure was varied from 18 to 38 torr in five steps. Data from only three steps are shown here for the sake of clarity.

The optical emission data in Figure 4 show a very strong dependence of the visible structure on pressure. Both the anode glow and the cathode sheath vary considerably in both intensity and width as a function of pressure. The width increases with decreasing pressure because the mean free path also increases, reducing the frequency of electron-neutral collisions. Interpretation of the variation in intensity is complicated by the change in inelastic electron-neutral collision frequency and, for increased neutral densities, the increased probability of trapping of emitted light by the excitation of a second species. For example, when the excited electron in a hydrogen atom drops from the third energy level to the second, the H_α radiation emitted may either escape the plasma and be detected by the optical emission spectrometer or it may excite an electron in another hydrogen atom from the second to the third energy level. The probability of the latter increases with increasing neutral density. Part of the increase in intensity with decreasing pressure may result from changes in driving voltage: as the pressure drops below a certain value, the driving voltage increases; for instance, a 10 torr drop from nominal pressure increases the voltage required to drive 1.5 A through the plasma by 50 V. In contrast, increasing the pressure by 10 torr has almost no effect on the driving voltage. Thus, at lower pressures, each electron, on average, will have more energy from acceleration by the increased field at the cathode, and will dissipate it more slowly because of the longer mean free path. The dependence of driving voltage on pressure is shown in Figure 5.

In short, it is not possible to deduce the direct effect of pressure on plasma structure from emission spectra alone. Other diagnostic techniques must be applied to determine the true effect of pressure. A study of this type using a Langmuir probe has been completed.[9]

3.1.3 Electrode Spacing Effects

To study the effects of electrode spacing on plasma structure, the current was set at 1.5 A and the pressure at 28 torr while the spacing was varied from 1 to 3 cm in three steps. The optical emission data do not exhibit significant changes as a function of spacing, as illustrated by Figure 6 (except for the position of the cathode sheath relative to the anode). The similarity in the widths of the glow regions is to be expected because there is no change in mean free path from one spacing to another. The similarities in intensities indicates that inelastic processes are occurring at approximately the same rate in all three cases.



(a)

(b)

Figure 4: Effect of pressure variation on intensity of H_2 peak at 603 nm as a function of interelectrode position: (a) full plasma and (b) detail of anode region.

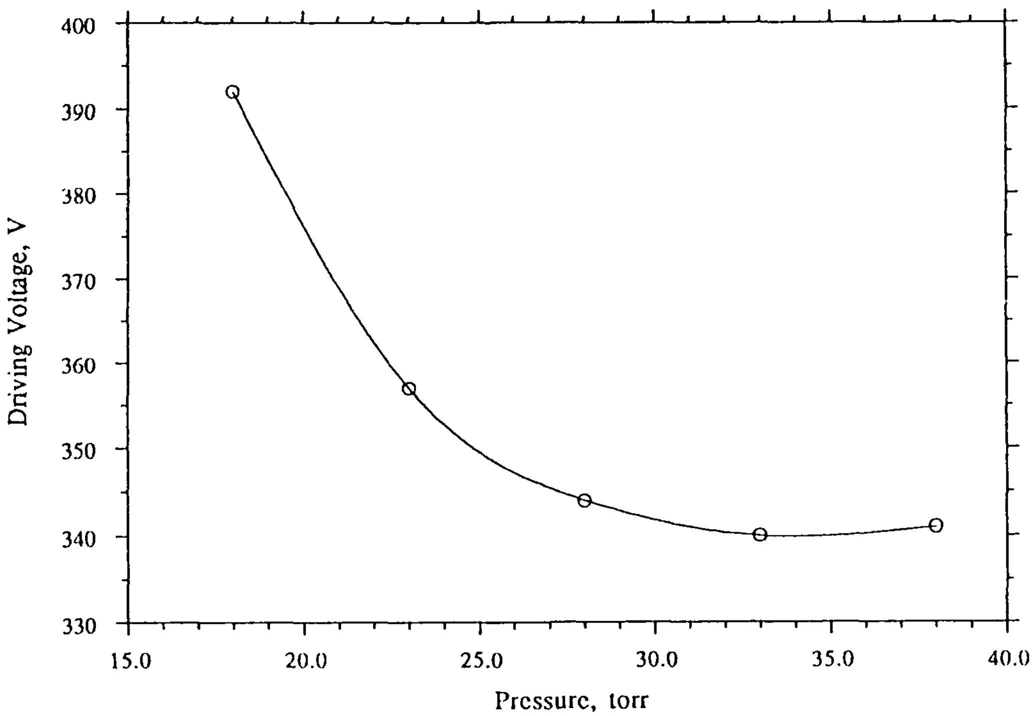


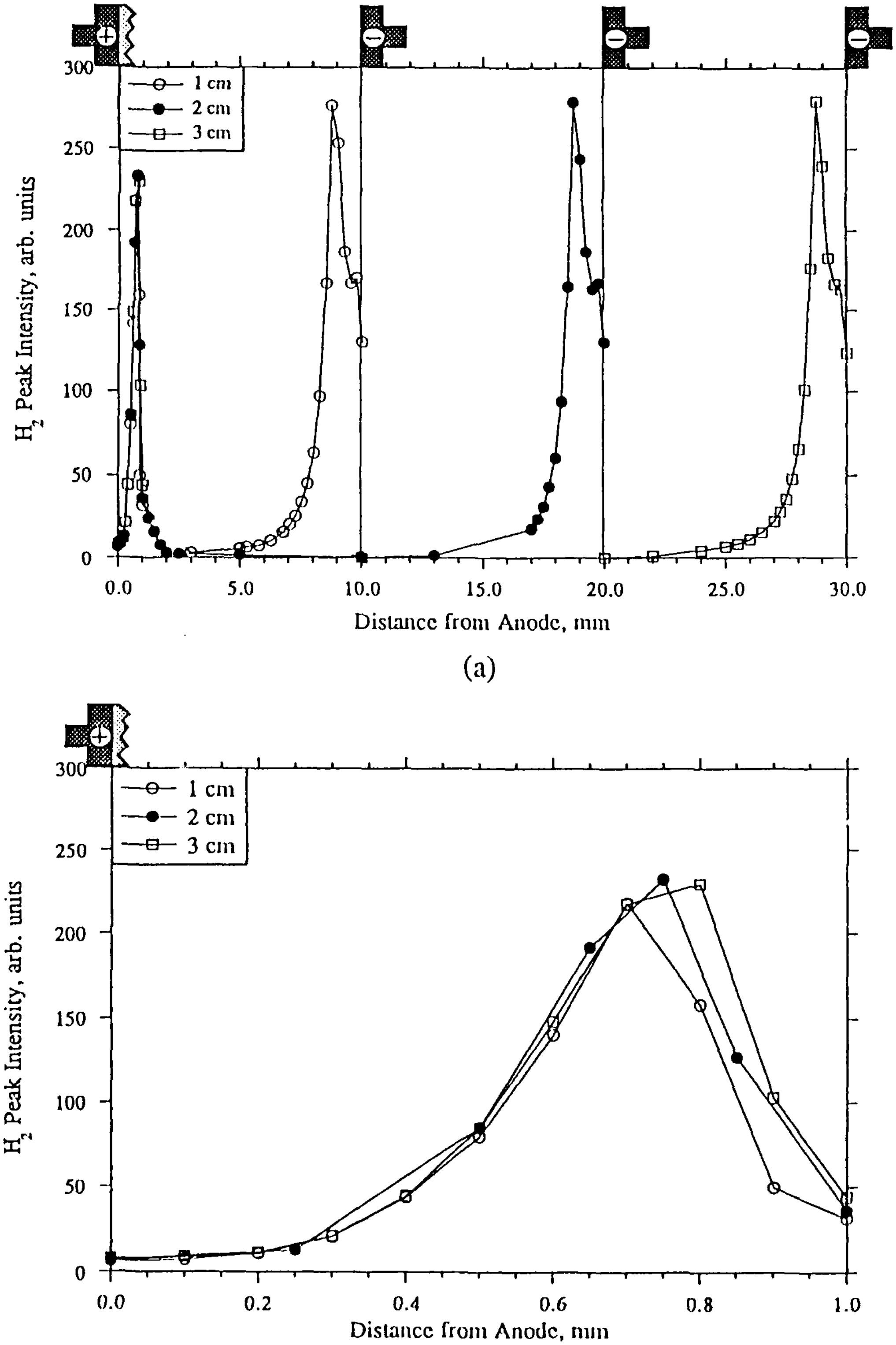
Figure 5: Plasma driving voltage dependence on process pressure.

Electrode spacing has minimal effect on the density of excited species because the critical components of the plasma- charged carrier density, electron mobility, and diffusivity- are relatively unaffected by electrode spacing. The driving voltage of the system increases with increasing spacing because the resistance of the plasma increases as well, due to the increased number of collisions the average electron experiences. However, this voltage increase does not appear to affect the electron energetics in either the anode or cathode regions, suggesting that the voltage is accommodated in the quasi-neutral region where it has relatively little effect.

3.2 Methane/ Hydrogen Plasmas

The individual effects of electrode spacing, pressure, and current provide insight into the physical processes controlling visible structures in plasmas similar to those which produce diamond. To illustrate the variation in plasma structure as a function of these factors plus that of methane concentration, the visible structure of a plasma which produced diamond bonded film was compared with that of a plasma which produced purely graphitic material. The plasma that generated the graphitic film was produced using low pressure, narrow spacing, high current, and high methane concentration while the plasma that grew the high quality diamond film was ignited at high pressure, wide spacing, high current and low methane concentration.

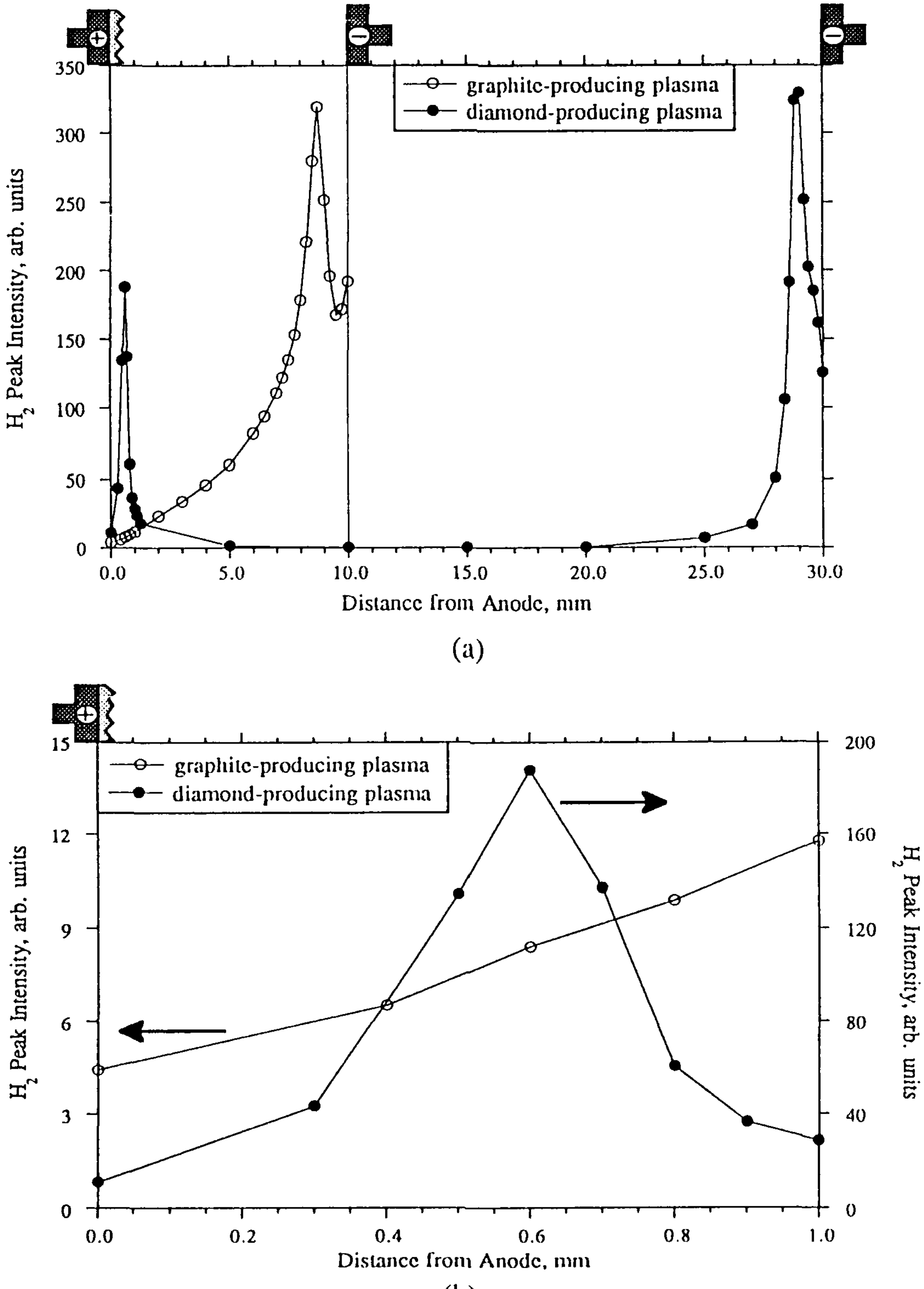
The H_2 emissions from these plasmas are plotted as a function of interelectrode position in Figure 7a. An expanded view of the anode region is shown in Figure 7b. The plasma that produced the high quality film exhibits the peak corresponding to the anode glow also found in Figures 3, 4, and 6. No such peak is apparent in the second plasma; in fact, the cathode sheath essentially extends from cathode to anode, as is apparent in Figure 7a. This condition results from the combination of low pressure and narrow spacing: the low pressure expands the cathode sheath width (Figure 4) and the narrow spacing brings the anode into the sheath region. Similarly, the high pressure and wide spacing of the diamond-producing plasma compresses its cathode sheath to a narrow region near the cathode.



(a)

(b)

Figure 6: Effect of electrode spacing on intensity of H_2 peak at 603 nm as a function of interelectrode position: (a) full plasma and (b) detail of anode region.



(a)

(b)

Figure 7: H_2 intensity profiles for diamond- and graphite-producing plasmas for (a) full plasma and (b) detail of anode region.

4. CONCLUSIONS

An anode glow, which is indicative of inelastic electron-neutral collisions occurring in the vicinity of the substrate, is of importance in determining the bonding type of carbon films produced by high neutral gas density DC plasmas. When it is not present, graphitic films are produced. This result suggests that the anode glow may be a source of gaseous species critical to the growth of diamond film. Alternatively, the energetic electrons implied by the presence of this glow may also be of use in the formation of diamond bonds on the anode surface.

From the data presented here, current has the strongest effect on the intensity of the anode glow, with electrode spacing having no effect and pressure an inverse effect. However, particularly in the case of pressure, it is important to analyze the same plasmas using different instruments because the true behavior of the plasma as detected by OES can be masked by secondary effects, such as light trapping. Such a study is discussed in Ref. 1.

Emitted light intensity is also great in the vicinity of the cathode so that diamond film deposition at either electrode might be expected. However, the ions which are also formed by inelastic electron-neutral collisions are accelerated by a large electric field into the cathode (Figure 1) where they can damage any growing film.

5. REFERENCES

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