DIAGNOSTICS OF DIAMOND FILM DEPOSITION PLASMAS

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### Diagnostic Methods

Diagnostic methods were developed and applied toward understanding the gas phase processes occurring in diamond film deposition plasmas. Diagnostics were applied in plasma arcjet environments, hot filament systems and in radio frequency plasma systems. The diagnostic methods included optical emission spectroscopy, surface Raman spectroscopy, scanning electron microscopy, laser-induced fluorescence, and surface analysis by laser ionization. The parameters that were measured included radical concentrations and temperatures, ground-state and excited-state temperatures of C2 and CH molecules, electron temperatures and energy distribution functions, ion densities, and the observation of acetylene and other hydrocarbon species. Some modeling and comparison of experimental results to model predictions were also performed.
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1. EXECUTIVE SUMMARY

Under contract to the Army Research Office (ARO), SRI International has conducted research on the development and application of diagnostic methods to analyze diamond-forming plasmas. Our research concentrated on the plasma arcjet approach, which we and others have shown to provide a high growth-rate environment for producing polycrystalline diamond films. Smaller diagnostic development efforts have been applied to hot-filament chemical vapor deposition (CVD) systems as well as radio frequency (rf) plasma discharges. The diagnostics that we have applied include in situ time- and space-resolved optical emission spectroscopy, laser induced fluorescence (LIF), Langmuir probes, and mass spectroscopy. In addition, we have used ex situ Raman spectroscopy and surface analysis by laser ionization (SALI) to characterize the diamond films that we produce. The physical and chemical information we have obtained by the gas-phase diagnostic techniques include ground-state temperatures of several radical species, excited-state temperatures of C₂, electron temperatures and ion densities in the arcjet plasma, relative measurements of impinging fluxes of hydrocarbons produced in the arcjet during diamond growth conditions, and temperature measurements of OH radicals in hot-filament systems. Surface enhanced Raman spectroscopy indicates the spatial variation in diamond quality, and the SALI measurements indicate the degree of surface contamination found on arcjet-deposited diamond films.

This final report describes our research findings over the last three years as well as recommendations for further research. Our work on developing diagnostic techniques for diamond deposition plasmas has been very successful. Our findings have been incorporated into modeling efforts of other scientists involved in diamond CVD and many of our findings and techniques have been employed by other experimentalists engaged in diamond deposition research and technology.
2. PRINCIPAL RESEARCH FINDINGS

Most of our research findings have been discussed in the text of our semiannual reports. This research has resulted in ten published papers and sixteen presentations at scientific conferences. In this section, we review the principal findings as discussed in those reports and in our publications.

2.1 DC ARCJET PLASMAS

We first achieved experimental confirmation of diamond growth with a 1-kW DC arcjet plasma.\(^1,2\) Effluent from the plasma arc was directed at a water cooled silicon substrate where diamond grew at rates in excess of 60 \(\mu\)m/hr. Unlike other diamond deposition methods, no pretreatment of the silicon was required. However, significant damage to the substrate from the high energy jet sometimes manifested itself in the form of localized cracking or melting. Raman spectra of the film confirmed the presence of diamond, and scanning electron micrographs (SEM) enabled us to determine the growth rate.

The light emission from the luminous jet emanating from the plasma arc was spectrally resolved, and emissions from CH, C\(_2\), and C\(_3\) were identified and analyzed to obtain a gas temperature. The spectral shape of C\(_2\) emission in the \(d^3\Pi_g - a^3\Pi_u\) Swan bands could be fit with a spectral simulation and a vibrational and rotational temperature near 5,000 K just beyond the exit orifice. Because DC arc plasmas are often quite hot, with temperatures in excess of 10,000 K, this high temperature seemed quite reasonable. However, emission temperatures from molecules in a chemically reactive environment can be misleading, so we undertook laser-induced fluorescence (LIF) measurements to compare with emission measurements.

The rotational and vibrational distribution observed from molecular electronic transitions depends strongly on the excitation mechanism. There are three possible excitation mechanisms: (1) thermal equilibrium by energy transfer collisions, (2) electron-impact excitation, and (3) chemiluminescent chemical reaction.

If the electronic excited state is in thermal equilibrium with the ground state, the energy transfer collisions that produce rotational and vibrational distributions in the excited state will reflect the gas temperature. However, there is evidence that the population of the d-state of C\(_2\) in the arcjet effluent is greater than thermal. In the luminous region of the plasma arcjet, we expect the concentration of atomic hydrogen to be larger than that of any carbon containing molecule,
given the large dissociation fraction in the arc and the incoming gas ratio of 99% hydrogen and 1% methane. The lack of Balmer $\alpha$ and $\beta$ emission from the atomic hydrogen, which has excitation energies in excess of 12 eV from the ground state but only 2 eV above the metastable 2S state suggests that the electronic emission from H atoms was strongly quenched.

LIF interrogates the ground-state molecules, which have a much longer chemical lifetime than the quenching dominated lifetime of the electronically excited molecules. The rotational distribution of these molecules is expected to reflect the gas temperature. These measurements are the first comparison of emission and LIF in DC arcjet plasmas.

Using an experimental configuration shown in Figure 1, we observed LIF from both CH and $C_2$ in the plasma effluent from the exit orifice (anode) to 1 cm downstream of the anode, the position of the stagnation point of the arcjet during diamond growth. This was the first observed LIF of any molecule in a diamond CVD environment. We found a rotational distribution of CH near 2,100 ± 200 K, and for $C_2$ a $^3\Pi_u$ a less precise temperature of 2,000 ± 500 K. Thus, the LIF measurements indicate that the gas temperature is significantly cooler than indicated by the emission from the arcjet.

The electron temperature was measured with a Langmuir probe and found to be 0.9 eV, somewhat hotter than the apparent temperature deduced from the optical emissions. Such relatively high electron temperatures are capable of exciting significant fractions of $C_2$ to the upper level, with subsequent emission of Swan-band radiation. If the excitation mechanism is due to electron impact of ground-state molecules, we expect a vibrational distribution in the excited state dominated by Franck-Condon vertical transitions and little change in the rotational distribution from that in the ground state. For electron-impact excitation, we expect the rotational distribution to reflect the gas temperature but not the vibrational temperature. The gas from the arcjet 1 cm downstream from the anode has a 5- to 10-μs transit time from the orifice, and the hard-sphere collision frequency is approximately $10^8$ s$^{-1}$. With an approximately 100-ns radiative lifetime, the Swan band excitation must occur near or within the observation volume. Thus, the observation that the excited-state temperature is larger than the LIF-determined ground-state temperature suggests that another possible excitation mechanism is chemiluminescent chemical reaction, although electron-impact excitation coincident with collisional thermalization cannot be ruled out.

The rotational and vibrational distribution of the products from chemiluminescent reactions can be quite nonthermal. If the reaction has a barrier in the exit channel, the lifetime of the collision complex is sufficient for product molecules to have a thermal rotational and vibrational distribution that reflects the sum of the gas temperature and the excess energy of the reaction. For example, since the exothermic energy of the reaction $C + CH \rightarrow C_2^* + H$ is 2.6 eV (see Reference 3), the
product molecules can have highly excited rotational and vibrational distributions if a significant fraction of the exothermicity goes into vibrational and rotational states of the product molecule. Details of how the excess energy is partitioned among the translational, vibrational, and rotational degrees of freedom of the reaction products pose interesting research questions. At the pressures used here, the rate for collisional quenching of the excited state is competitive with the collision rate of rotational and vibrational relaxation; thus, the emission may be affected by molecules that have not collisionally relaxed from the nascent product distribution. Such differences between emission measurements and actual gas temperatures are common in flames: chemiluminescent Swan band emission is observed in flames with rotational and vibrational distributions of 5,000 K, which is several thousand degrees above the adiabatic flame temperature. Recently, similar chemiluminescent temperatures were observed in ultrasonic cavitation at pressures of many kilobars. The 5,000 K distribution from Swan emission may indicate that the same reaction produces the product C₂ d-state in all these systems.

Chemical reaction rates vary exponentially with gas temperature, which means that the difference between the emission and LIF temperatures makes an enormous change in the predicted composition of the plasma-arc effluent with a chemical model. For example, the equilibrium mole fraction of atomic hydrogen varies from 0.90 at 5,000 K to 0.01 at 2100 K; our finite rate model with the actual residence time and measured temperatures predicts a dissociation fraction of 0.42.

2.2 COMPARISON OF EXPERIMENTAL MEASUREMENTS WITH PREDICTIONS OF GAS-PHASE KINETIC MODELS

Using the measured temperature, we modeled the chemical composition of the gas in the arc effluent. We have assembled a computer model of the gas chemistry of the small molecular weight species (less than 3 carbon atoms) in the gas jet and constrained the conditions to the measured gas temperature and gas flow rates. The predictions of this model at the position in the gas jet where diamond grows best indicate that the chemistry is far from chemical equilibrium. We find a methyl radical concentration that is too low to account for the observed growth rate when the growth mechanism of Harris is assumed. We collaborated with Dr. David Goodwin at California Institute of Technology and combined our chemical model with his more complete model of the fluid mechanics. Even with this more complete calculation, the predicted methyl radical concentration is marginal for the observed growth rate. In all these calculations, a surprising superequilibrium of atomic carbon (five orders of magnitude) was found. We speculated that perhaps atomic carbon could play a role in diamond growth. Recently, Dandy and Coltrin have assembled a diamond growth model for arc-jet plasmas that has contributions from atomic carbon, methyl radical, and acetylene. They find that the atomic carbon predicted is also high and quite
Figure 1. Diagram of dc-arc-jet plasma showing water-cooled substrate and luminous gas jet. The optical collection column is limited by a spatial filter. Some experiments use a monochromator to disperse the signal light; others used an interference filter to select the desired fluorescence wavelength.
dependent on the hydrogen dissociation function in the plasma arc. Thus, arcjet-grown diamond may have contributions from several different diamond growth mechanisms, depending on operating conditions.

We have also observed LIF from a large polyatomic hydrocarbon radical in the center of the luminous gas jet. Although we have not yet fully identified this polyatomic species, our tentative determination is a polycyclic aromatic hydrocarbon with four or five rings. Species of this variety are quite important to chemical models of soot formation in flame chemistry, and they may play an important role in gas chemistry related to diamond formation.

We also found a large spatial variation in the quality of the diamond film grown by our arcjet deposition system. Our diamond films grown on silicon were analyzed with spatially resolved micro Raman spectrometry, which showed the diamond growth to be localized in a circular region below the stagnation point of the impinging arcjet plasma. The arcjet thus presents a unique, yet challenging, environment for studying the mechanism of diamond growth. The rapid flow of the feedstock gas through the arc to the substrate provides a well-defined gas residence time, which greatly simplifies the chemical modeling. The gas temperature and composition can be characterized with spatially resolved measurements at the exit plane of the arc and at the top of the stagnation point of the effluent flow, and the variations correlated with diamond film quality. During diamond growth on a single substrate, we can probe the arc effluent that leads to varying quality by radial translation of the observation region from the center of the flow. During this contract we made such spatially resolved LIF temperature and radical measurements. To determine the gas composition at the growing substrate, we have begun to use molecular-beam-sampled mass spectroscopic methods.

2.3 MASS SPECTROMETRIC MEASUREMENTS

Mass spectrometric sampling of the core of the plasma-arc effluent presented some technical difficulties. The fundamental idea is to sample the gases striking the substrate surface through a small hole in the substrate. Our arcjet reactor produces diamond films at pressures near 200 Torr. The mass spectrometer requires pressures no higher than $10^{-4}$ Torr. Thus, significant differential pumping is needed right behind the substrate orifice. We built our system to achieve this pressure drop in just 1 cm with a two-stage pumping system. Since arcjet plasmas are commercially used for metal machining and cutting, significant water cooling of the deposition substrate was required to avoid erosion or melting of the sampling surface.

These problems were solved, and we have begun experiments to mass analyze the arcjet plasma. Gas from the arc impinges on a tantalum substrate and some of the gas that diffuses
through the boundary layer is sampled through a hole in a water cooled substrate. The gas flowing through this hole is formed into a beam by a second skimmer before entering the high-vacuum analysis chamber. A tuning fork chopper modulates the beam so that signals from background gas in the mass spectrometer chamber can be distinguished from the arc effluent in the beam. Diamond growth around the high-pressure sampling hole in the substrate has been confirmed by ex situ Raman analysis and microscopic observation of the crystalline deposit.

As predicted by our model, we found a significant hydrogen dissociation fraction and a large acetylene production from 99% hydrogen and 1% methane feedstock. We found that the acetylene was linearly proportional to the amount of methane in the feedstock; however, the observed methyl radical variation was erratic. Surprisingly, we did not originally observe significant concentrations of atomic carbon. Perhaps this finding indicates that the atomic carbon is chemically lost in the boundary layer. Also, we found some quantity of M/e = 29, which we identify as HCO, COH, or C_2H_5. Production of HCO or COH obviously requires a source of oxygen in our reactor. Oxygen is most likely due to small leaks of air, cooling water, or a virtual leak outgassing in our reactor. Such a leak may modify the chemistry to remove the atomic carbon expected. Persistent mass peaks at M/e = 32, 28, and 18 are evidence of such a leak or significant outgassing from arcjet components.

Because of these persistent questions relating to oxygen contamination, and the importance of oxygen in diamond deposition, we decided to rebuild the arcjet test stand with additional funds provided by a separate project utilizing the arcjet for studies of fullerene production. This new, upgraded reactor was used in the last stages of our research and gave much better mass spectrometric measurements that were free of air-leak effects. We now observe clear evidence of significant acetylene production, and the M/e peak at 29 is clearly C_2H_5. Even larger peaks at M/e = 27 and 28 suggest that C_2H_3 and C_2H_4 are being produced, although we are currently determining whether they are produced in the arcjet or are fragmentation products in the quadrupole mass spectrometer. Atomic carbon is also observed in small quantities, but the same fragmentation issues apply to these observations.

2.4 RF PLASMAS

We performed a short series of experiments on an rf plasma deposition apparatus that was fitted with external heaters for better control of the substrate temperatures. Observed visually, the films produced under certain discharge conditions appeared to be of very high quality. The films were analyzed in a Raman spectrometer, and only high-quality diamond-like carbon was detected. Since few reports exist on diamond CVD with rf deposition techniques, on either rf-biased or unbiased electrodes, we would like to understand the differences between this plasma
environment and t\textsuperscript{icrowave, hot-filament, and DC arcjet plasmas where diamond readily grows. Glass at North Carolina State University is now attempting nucleation of diamond by rf-biased ion bombardment in microwave plasmas,\textsuperscript{12} so these types of plasmas are becoming important in diamond CVD. Glass notes that prolonged DC biasing beyond the nucleation stage in a microwave discharge results in poor diamond growth, so ion bombardment may be desirable in nucleation but not in the growth stage. Since rf plasmas discharges are inherently scalable to larger sizes, unlike some of the other diamond deposition reactors, they would be desirable if suitable process conditions could be determined.

In similar rf plasma discharges, we correlated electron energy distribution function (EEDF) measurements and rf phase-dependent optical emission data. This work was performed in collaboration with Dr. W. G. Graham of Queen's University, Belfast, Northern Ireland, who is supported by British SERC funding for diagnostics of diamond deposition processes. Dr. Graham and his students visited our laboratory. This work resulted in one publication.\textsuperscript{13}

This brief effort was terminated after no significant $sp^3$ diamond deposition was found.

2.5 HOT-FILAMENT DIAMOND CVD

We measured spatially resolved absolute concentration and rotational temperature of the OH radical by LIF in our hot-filament diamond CVD reactor. The calibration of LIF measurements to provide absolute number density of molecules is a complex task that is seldom done properly. We must know the absolute number density of OH to assess the importance of OH etching of the growing diamond/graphite surface. Gas temperature measurements are crucial to absolute concentration measurements because the LIF signal depends on temperature to determine both the collisional quenching rate and the Boltzmann fraction in the quantum state excited by the laser.

Calibration of LIF signals for absolute measurements requires consideration of three different quantities. First, the response and transmission of the optical detection system to a known number of photons per solid angle per optical bandwidth must be measured. This was accomplished by measuring the system response to Rayleigh scattering in the reactor in 1 atm nitrogen and comparing the Rayleigh signal intensity to the OH LIF intensity. Second, the collisional quenching of the excited state must be determined as a function of temperature and pressure. For these data we combined our current gas temperature measurements with the temperature-dependent quenching measurements made in our laboratory five years ago. Third, we determined the fraction of ground state molecules excited by the laser from our spatially resolved temperature measurements for the Boltzmann fraction and spectroscopic data on OH line strengths determined some ten years ago in our laboratories. Thus, we were uniquely qualified by our
previous work on OH to determine the absolute number density of the radical. The values varied with process parameters and distance from the filament over the range of 0.1 to 15 ppm.
3. SUMMARY AND RECOMMENDATIONS

Our work on developing diagnostic techniques for diamond deposition plasmas has been very successful. Our findings have been incorporated into modeling efforts of other scientists involved in diamond CVD, and many of our findings and techniques have been employed by other experimentalists engaged in diamond deposition research and technology.

The advances in the technology of diamond CVD over the last three years have been remarkable. Commercial products ranging from thermal management substrates to optical windows are now available at reasonable costs. Military applications of diamond film technology now include monolithic microwave integrated circuits (MMICs). Many of these diamond devices are made by the deposition techniques that we study. For example, the Norton Diamond Film Company deposits diamond with a variant of our plasma arcjet technology. Diagnostics based on our research are being used by this company to optimize and develop controls for their deposition processes.

We recommend the following research areas to improve our understanding of diamond thin film formation.

1. Develop and apply laser-based, mass spectroscopic and other measurement techniques to plasmas that are depositing diamond thin films, including the following tasks:
   
i. In a hot filament diamond reactor, determine spatial gradients of gas temperature versus different operational parameters including filament temperature, total energy dissipated, substrate temperature, and reactant flow rates.
   
ii. Determine the feasibility of probing the boundary layer region above the growing diamond surface with laser-induced fluorescence.
   
iii. Characterize the major species in the arc effluent with mass spectrometric sampling as a function of operating conditions and diamond film quality.
   
iv. For selected operating conditions from (iii), characterize the spatial variation of gas temperature along the arcjet, from as close to the orifice as possible to as close to the substrate as possible with laser-based diagnostics.
   
v. Investigate the role of species such as HCO, C2H2, CH3, and C in the chemical mechanism of diamond growth.
2. Investigate deposition of diamond films with a molecular beam derived from the arcjet plasma source. Study the deposition as a function of beam flux, composition, and substrate type and temperature.

Based on the recent rapid improvement in diamond technology, we believe that continued development and application of these advanced plasma diagnostic techniques will enable producers of both military and commercial diamond CVD products to speed the delivery of diamond-based devices to market.
4. PUBLICATIONS, REPORTS, AND ABSTRACTS SUPPORTED BY THIS CONTRACT

4.1 REFEREEED PAPERS


4.3 CONFERENCE PRESENTATIONS


5. LIST OF PARTICIPATING SCIENTIFIC PERSONNEL

1. Dr. K. R. Stalder, Co-Principal Investigator
2. Dr. J. B. Jeffries, Co-Principal Investigator
3. Dr. G. P. Smith, Senior Chemist
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5. Dr. G. A. Raiche, Postdoctoral Fellow
6. Dr. D. E. Heard, Postdoctoral Fellow
7. Mr. W. Homsi, Undergraduate Student, University of San Francisco
8. Mr. L. Hunziker, Undergraduate Student, University of California at Berkeley.
8. Professor W. G. Graham, Visitor from Queen's University, Belfast, Northern Ireland
6. INVENTIONS

No inventions were discovered during this project.
7. BIBLIOGRAPHY

11. A. W. Phelps, private communication.
12. J. Glass, private communication.