Spectroscopic Determination of C₂ Densities in Ar/H₂/CH₄ and
Ar/H₂/C₆₀ Microwave Plasmas for Nanocrystalline Diamond Synthesis

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SPECTROSCOPIC DETERMINATION OF C2 DENSITIES IN AR/H2/CH4 AND AR/H2/C60 MICROWAVE PLASMAS FOR NANOCRYSTALLINE DIAMOND SYNTHESIS

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ABSTRACT

We have measured the steady state concentration of gas phase C2 in Ar/H2/CH4 and Ar/H2/C60 microwave plasmas used for the deposition of nanocrystalline diamond films. High sensitivity white light absorption spectroscopy is used to monitor the C2 density using the d^3II ← a^3Π (0,0) vibrational band of C2 as chamber pressure, microwave power, substrate temperature and feed gas mixtures are varied in both chemistries. Understanding how these parameters influence the C2 density in the plasma volume provides insight into discharge mechanisms relevant to the deposition of nanocrystalline diamond.

INTRODUCTION

In contrast with conventional hydrogen-rich methods of diamond chemical vapor deposition (CVD), nanocrystalline diamond films may be grown in environments where hydrogen comprises only a small percentage of the feed gas mixture. High quality, smooth nanocrystalline diamond films with exceptional frictional and wear properties and root-mean-square (rms) roughness on the order of tens of nanometers have been produced by the microwave dissociation of C60 or CH4 molecules in hydrogen-deficient argon (Ar) microwave plasmas [1-4]. Methyl, which is thought to be critical to diamond formation in conventional hydrogen-rich CVD environments is produced in very small quantities under these novel chemistries and alternative mechanisms for diamond growth must be considered. The carbon dimer, C2, is believed to be the primary growth species in both of these plasma chemistries.

High sensitivity white light absorption spectroscopy provides a non-perturbative, in-situ means of quantifying the densities of stable and free radical species in the gas phase of reactive plasmas [5].

EXPERIMENT

Apparatus

A commercial ASTeX PDS-17 microwave plasma-enhanced chemical vapor deposition (CVD) system is used for studies of diamond deposition. Premixed feed gases are introduced at the top of the chamber using a gas dispersion ring. Diamond typically is deposited on a mechanically polished Si (100) substrate. An rf-heated graphite susceptor, located in the
midplane of the water-cooled stainless steel vacuum chamber, maintains the Si substrate temperature. The introduction of 2.45 GHz microwave radiation through a quartz window at the top of the chamber initiates a nearly spherical discharge immediately above the substrate. A downstream throttle valve controls the total chamber pressure. Total mass flow into the chamber is maintained at 100 sccm.

For the deposition experiments using C_{60} as the source of carbon, a fullerene-containing soot is heated to a controlled temperature, causing C_{60} molecules and traces of higher mass fullerenes to sublimate from the soot. Ar is used as a carrier gas to introduce the sublimated C_{60} into the chamber through a side port. H_{2} is introduced via the dispersion ring. The C_{60} is collisionally dissociated in the plasma. Since the vapor pressure of C_{60} as a function of temperature is well known [6], the partial pressure of C_{60} in the chamber can be regulated.

Two viewports equipped with fused silica windows provide in-situ optical access to the plasma and near-substrate regions for the high sensitivity white light absorption spectroscopy. A stabilized high pressure Xe lamp serves as a continuum source for the white light absorption spectroscopy. Light from the Xe arc is focused to a 2 mm spot at the center of the chamber. The spot position is approximately 15 mm above the substrate in the radial center of the discharge. The continuum radiation is then re-imaged onto the entrance slit of a 0.5 m spectrometer. A narrow bandpass filter in front of the entrance slit rejects light not in the spectral region of interest. This helps eliminate stray or scattered light inside the spectrometer. A 1024 element photodiode array mounted at the output plane detects the dispersed light. The dispersion of the spectrometer is 8.3 Å/mm in the output plane and the resulting spectral limit of resolution is 0.2 Å per detection element. We are able to detect extremely small absorbances (< 1x10^{-4}) even in the presence of very intense emission from the microwave plasma in the same spectral region [7].

Measurement of C_{2} Density

To determine absolute densities of C_{2} in the a^3Π_{u} state, we use the (0,0) vibrational band of the Swan system. For each set of experimental parameters, a transmittance spectrum is obtained. The equivalent width of the bandhead is integrated over a wavelength interval containing 26 rotational lines. Prasad and Bernath list the frequencies of rotational lines for the three P and three R branches of this band [8]. For an optically thin homogeneous plasma, the equivalent width, \(W_{\nu}\), and the absolute density of the lower level, \(N_{\nu}\), are related by [9]

\[
W_{\nu} = \pi r_{e} c N_{\nu} f_{w} L
\]

where \(r_{e}\) is the classical radius of the electron, \(f_{w}\) the oscillator strength, \(c\) the speed of light and \(L\) the path length through the plasma. The absolute density is determined from each spectrum using the sum of the individual rotational line oscillator strengths. The line oscillator strengths, \(f_{\nu, jj'}\), are calculated from the band oscillator strength, \(f_{\nu, v'} = 0.027\), reported by Brewer and Hagan [10]. The line oscillator strengths and the band oscillator strength for a \(\Pi \rightarrow \Pi\) transition have the familiar relationship

\[
f_{\nu, jj'} \approx \frac{S_{jj'}}{2J'+1} f_{\nu, v'}
\]
where $S_{j',J'}$ is the appropriate Hönl-London factor. The small variation in frequency across the vibrational band is ignored in this approximation [11]. The line oscillator strengths are weighted by the ratio of Boltzmann factors over the partition function of molecules in the lower rotational level of the transition. We have used a spectroscopically determined neutral gas kinetic temperature of 1300 °C in determining the Boltzmann factors [7]. This statistical fraction includes the relative population distribution among the vibrational levels of the $a^3\Pi_u$ state. At a temperature of 1300 °C, the fraction of the $a^3\Pi_u$ population in the ground vibrational level is 0.77.

The Hönl-London factors $S_{j',J'}$ are normalized according to the sum rule:

$$\sum_{j'} S_{j',J'} = g(2J' + 1)$$

(3)

where the electronic degeneracy, $g$, incorporates both a spin degeneracy and the $\Lambda$-type doubling factor. The C$_2$ dimer is a homonuclear diatomic molecule, and the nuclear spin of $^{12}$C is zero. As a result, the antisymmetric energy levels do not exist. An orbital degeneracy in the $\Pi$ states does exist and the combined result of these two effects is that one of the two $\Lambda$-doublets is absent for each $J$ [8].

RESULTS

Comparison of Ar/H$_2$/CH$_4$ and Ar/H$_2$/C$_{60}$ Plasmas

Variations in chamber pressure and microwave power produce similar behavior in the C$_2$ density for both plasma chemistries. The steady state density of C$_2$ in the plasmas is empirically observed to scale as the cube of the chamber pressure. The C$_2$ molecule is produced collisionally in the plasma volume, with competing C$_2$ production and destruction processes controlling the steady state density of C$_2$ in the plasma. The steady state density of carbon dimers is the product of their production rate per unit volume, $P$, and their effective lifetime in the plasma, $\tau$:

$$n_{C_2} = P \tau.$$  

(4)

The C$_2$ production rate depends on both various collisional frequencies in the plasma and the total carbon content in the plasma, both of which increase linearly with chamber pressure. In addition, gas phase collisional destruction of C$_2$ scales with the chamber pressure. Conversely, the diffusion rate of C$_2$ out of the plasma volume scales inversely with chamber pressure. At lower pressures, the effective lifetime of C$_2$ in the plasma is limited by the diffusion of C$_2$ out of the plasma volume whereas at higher pressures collisional destruction of C$_2$ is likely to be the limiting factor. The processes mentioned are all independent of the particular chemistry employed. The observed variation of the C$_2$ density with chamber pressure results from a combination of these factors.

Increased microwave power has little discernible effect on the experimentally obtained C$_2$ densities in either chemistry. The spectroscopically measured gas temperatures were similarly insensitive to the microwave power. Calorimetry on the water used to cool the reactor walls indicates that the cooling water removes several hundred watts from the reactor walls. Not surprisingly, much of the microwave power deposited into the resonant cavity is transported to the walls. Direct thermal conduction through Ar from the plasma to the reactor walls is
calculated to be less than 10 watts. At the pressures used for these plasmas, thermal gradients between the hot plasma in the midplane of the reactor and cooler gas in contact with the water-cooled chamber walls are sufficient for the onset of free convection. Convective heat transport very efficiently cools the plasma, resulting in no appreciable change to the plasma gas kinetic temperature with additional power deposition. As a result, the plasma chemistry generally remains unaltered by changes in the microwave power.

The addition of H\textsubscript{2} to the feed gas mixture increases the rates of chemical reactions that convert C\textsubscript{2} to hydrocarbon species in both plasma chemistries. The spectroscopically measured gas temperatures do not differ significantly between the two plasma chemistries nor vary as the feed gas composition is altered. As a result, the rates for reactions converting C\textsubscript{2} to hydrocarbon species are expected to be similar for both plasma chemistries. In fact, the C\textsubscript{2} density decreases more sharply with increasing H\textsubscript{2} in the feed gas in Ar/H\textsubscript{2}/CH\textsubscript{4} plasmas than in Ar/H\textsubscript{2}/C\textsubscript{60} plasmas. This can be understood by considering the C\textsubscript{2} production rate per unit volume in both chemistries. Because the Ar/H\textsubscript{2}/CH\textsubscript{4} plasmas have a much higher total carbon content than the Ar/H\textsubscript{2}/C\textsubscript{60} plasmas, we suggest the C\textsubscript{2} production rate per unit volume is higher in Ar/H\textsubscript{2}/CH\textsubscript{4} plasmas, as is the rate of change of C\textsubscript{2} production rate per unit volume with additional H\textsubscript{2} in the feed gas. It is this difference in the rate of change of the C\textsubscript{2} production rate with H\textsubscript{2} content in the feed gas between the two plasma chemistries that causes the steady state C\textsubscript{2} density to decrease more sharply as H\textsubscript{2} in the feed gas is increased in Ar/H\textsubscript{2}/CH\textsubscript{4} plasmas than in Ar/H\textsubscript{2}/C\textsubscript{60} plasmas.

The C\textsubscript{2} production rate for a given chemistry is expected to scale linearly with the total carbon content of the plasma. Because the total carbon content in Ar/H\textsubscript{2}/CH\textsubscript{4} plasmas is adjusted through the percentage of CH\textsubscript{4} in the feed gas, the total carbon fraction in the feed gas cannot be adjusted independently of the total hydrogen fraction in the feed gas. We propose that the steady state C\textsubscript{2} density initially increases with the total carbon fraction in the feed gas in Ar/H\textsubscript{2}/CH\textsubscript{4} plasmas. This occurs despite the high total hydrogen content in the feed gas. The rates of chemical reactions converting C\textsubscript{2} into hydrocarbon species are initially insufficient to compensate the increased C\textsubscript{2} production rate from the increased carbon content of the feed gas. The C\textsubscript{2} density continues to increase with the carbon content of the feed gas until a critical hydrogen fraction in the feed gas is reached. We propose that at this critical hydrogen fraction, the rates of reactions converting C\textsubscript{2} to hydrocarbon species become sufficient to balance the increased C\textsubscript{2} production rate. Above this critical hydrogen fraction, the steady state density of C\textsubscript{2} decreases with increasing hydrocarbon content in the feed gas, as C\textsubscript{2} destruction rates from these chemical reactions dominate.

The steady state C\textsubscript{2} density decreases substantially with increasing substrate temperature in Ar/H\textsubscript{2}/CH\textsubscript{4} plasmas, whereas the effect is much less marked in Ar/H\textsubscript{2}/C\textsubscript{60} plasmas. Since the measured gas kinetic temperatures in the plasma do not vary significantly as a function of the substrate temperature, the C\textsubscript{2} production rate in either plasma is not expected to change significantly as a function of substrate temperature. Therefore, any observed variation in the steady state C\textsubscript{2} density must be attributed to a change in the effective lifetime of C\textsubscript{2} in the plasma. The growth rate of nanocrystalline diamond in Ar/H\textsubscript{2}/CH\textsubscript{4} plasmas has been observed to follow an Arrhenius-type dependence on substrate temperature [12]. Experiments are being conducted to determine what fraction of the observed decrease in the steady state C\textsubscript{2} density is directly attributable to the increased growth rate of the film. We suggest the difference in the degree of the functional dependence of steady state C\textsubscript{2} density on substrate temperature between the two plasma chemistries is similarly the result of the difference in the C\textsubscript{2} production rates per unit volume between the two plasma chemistries.
**C₂ Production Efficiency**

The C₂ production efficiency is defined as the ratio of the density of gas phase C₂ to the total carbon content in the plasma. In order to compare the C₂ production in both plasma chemistries, we use the experimentally determined C₂ density in an Ar/H₂/C₆₀ plasma for the lowest sublimator temperature for which the C₂ density was measured. At this low sublimator temperature, the partial pressure of C₆₀ delivered to the plasma is likely to be close to the C₆₀ vapor pressure inside the sublimator.

The measured steady state density of C₂ under these conditions is $2 \times 10^{10}$ molecules/cm³. At this temperature, the partial pressure of C₆₀ in the sublimator is only $9 \times 10^{-5}$ Torr. At a discharge temperature of 1300 °C, the density of carbon supplied by C₆₀ in the feed gas is at most $3.6 \times 10^{13}$ carbon atoms/cm³, assuming that the Ar carrier gas is saturated with C₆₀ molecules as it enters the chamber. Thus, for a sublimator temperature of 450 °C, the ratio of the C₂ density to the total density of carbon present in the chamber is $5.5 \times 10^{4}$.

Under standard operating conditions in an Ar/H₂/CH₄ plasma (100 Torr, 800 watts, 800 °C susceptor temperature and Ar:H₂:CH₄ = 97:2:1), the measured C₂ density in the plasma is $3 \times 10^{11}$ molecules/cm³. This is an order of magnitude greater than the C₂ density measured in an Ar/H₂/C₆₀ plasma for a sublimator temperature of 450 °C. However, the total carbon density in the chamber for an Ar/H₂/CH₄ plasma under these conditions is $6.7 \times 10^{15}$ carbon atoms/cm³. The ratio of the C₂ density to the total carbon density is then $4.5 \times 10^{5}$. Remarkably, this C₂ production efficiency for an Ar/H₂/C₆₀ plasma is approximately 12 times higher than that calculated for an Ar/H₂/CH₄ plasma. Because the total density of carbon in the feed gas for this calculation is based upon the assumed saturation of the C₆₀ vapor pressure in the sublimator, this factor is a lower bound estimate.

**CONCLUSIONS**

We have experimentally determined the steady state density of gas phase C₂ in Ar/H₂/CH₄ and Ar/H₂/C₆₀ microwave plasmas used in the deposition of nanocrystalline diamond films using high sensitivity white light absorption spectroscopy. The C₂ density was measured as chamber pressure, microwave power, feed gas composition and substrate temperature were varied. We have proposed explanations for the functional dependencies of C₂ density on these processing parameters. The C₂ production efficiency, defined as the ratio of the density of gas phase C₂ to the total carbon content in the plasma, was determined to be at least a factor of 12 higher in Ar/H₂/C₆₀ plasmas than in Ar/H₂/CH₄ plasmas.

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