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Spectroscopic Determination of C_2 Densities in $Ar/H_2/CH_4$ and $Ar/H_2/C_{60}$ Microwave Plasmas for Nanocrystalline Diamond Synthesis

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SPECTROSCOPIC DETERMINATION OF C_2 DENSITIES IN AR/H_2/CH_4 AND AR/H_2/C_{60} MICROWAVE PLASMAS FOR NANOCRYSTALLINE DIAMOND SYNTHESIS

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ABSTRACT

We have measured the steady state concentration of gas phase C_2 in Ar/H_2/CH_4 and Ar/H_2/C_{60} microwave plasmas used for the deposition of nanocrystalline diamond films. High sensitivity white light absorption spectroscopy is used to monitor the C_2 density using the $d\,^3\Pi \leftarrow a\,^3\Pi$ (0,0) vibrational band of C_2 as chamber pressure, microwave power, substrate temperature and feed gas mixtures are varied in both chemistries. Understanding how these parameters influence the C_2 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 C_{60} or CH_4 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, C_2, 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 ($< 1\times10^{-4}$) 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 $a\,^3\Pi_u$ 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_ν, and the absolute density of the lower level, N_l, are related by [9]

$$W_\nu = \pi r_e c N_l f_{lu} L \qquad (1)$$

where r_e is the classical radius of the electron, f_{lu} 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, $f_{v'v''J'J''}$, are calculated from the band oscillator strength, $f_{v'v''} = 0.027$, 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

$$f_{v'v''J'J''} \approx \frac{S_{J'J''}}{2J'+1} f_{v'v''} \qquad (2)$$

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:

$$\sum_{J''} S_{J'J''} = g(2J' + 1) \tag{3}$$

where the electronic degeneracy, g, incorporates both a spin degeneracy and the Λ-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 Π states does exist and the combined result of these two effects is that one of the two Λ-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, τ:

$$n_{C_2} = P\tau . \tag{4}$$

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_2 to the feed gas mixture increases the rates of chemical reactions that convert C_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_2 to hydrocarbon species are expected to be similar for both plasma chemistries. In fact, the C_2 density decreases more sharply with increasing H_2 in the feed gas in $Ar/H_2/CH_4$ plasmas than in $Ar/H_2/C_{60}$ plasmas. This can be understood by considering the C_2 production rate per unit volume in both chemistries. Because the $Ar/H_2/CH_4$ plasmas have a much higher total carbon content than the $Ar/H_2/C_{60}$ plasmas, we suggest the C_2 production rate per unit volume is higher in $Ar/H_2/CH_4$ plasmas, as is the rate of change of C_2 production rate per unit volume with additional H_2 in the feed gas. It is this difference in the rate of change of the C_2 production rate with H_2 content in the feed gas between the two plasma chemistries that causes the steady state C_2 density to decrease more sharply as H_2 in the feed gas is increased in $Ar/H_2/CH_4$ plasmas than in $Ar/H_2/C_{60}$ plasmas.

The C_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 $Ar/H_2/CH_4$ plasmas is adjusted through the percentage of CH_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_2 density initially increases with the total carbon fraction in the feed gas in $Ar/H_2/CH_4$ plasmas. This occurs despite the high total hydrogen content in the feed gas. The rates of chemical reactions converting C_2 into hydrocarbon species are initially insufficient to compensate the increased C_2 production rate from the increased carbon content of the feed gas. The C_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_2 to hydrocarbon species become sufficient to balance the increased C_2 production rate. Above this critical hydrogen fraction, the steady state density of C_2 decreases with increasing hydrocarbon content in the feed gas, as C_2 destruction rates from these chemical reactions dominate.

The steady state C_2 density decreases substantially with increasing substrate temperature in $Ar/H_2/CH_4$ plasmas, whereas the effect is much less marked in $Ar/H_2/C_{60}$ plasmas. Since the measured gas kinetic temperatures in the plasma do not vary significantly as a function of the substrate temperature, the C_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_2 density must be attributed to a change in the effective lifetime of C_2 in the plasma. The growth rate of nanocrystalline diamond in $Ar/H_2/CH_4$ 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_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_2 density on substrate temperature between the two plasma chemistries is similarly the result of the difference in the C_2 production rates per unit volume between the two plasma chemistries.

C_2 Production Efficiency

The C_2 production efficiency is defined as the ratio of the density of gas phase C_2 to the total carbon content in the plasma. In order to compare the C_2 production in both plasma chemistries, we use the experimentally determined C_2 density in an $Ar/H_2/C_{60}$ plasma for the lowest sublimator temperature for which the C_2 density was measured. At this low sublimator temperature, the partial pressure of C_{60} delivered to the plasma is likely to be close to the C_{60} vapor pressure inside the sublimator.

The measured steady state density of C_2 under these conditions is 2×10^{10} molecules/cm^3. At this temperature, the partial pressure of C_{60} in the sublimator is only 9×10^{-5} Torr. At a discharge temperature of 1300 °C, the density of carbon supplied by C_{60} in the feed gas is at most 3.6×10^{13} carbon atoms/cm^3, assuming that the Ar carrier gas is saturated with C_{60} molecules as it enters the chamber. Thus, for a sublimator temperature of 450 °C, the ratio of the C_2 density the total density of carbon present in the chamber is 5.5×10^{-4}.

Under standard operating conditions in an $Ar/H_2/CH_4$ plasma (100 Torr, 800 watts, 800 °C susceptor temperature and $Ar{:}H_2{:}CH_4 = 97{:}2{:}1$), the measured C_2 density in the plasma is 3×10^{11} molecules/cm^3. This is an order of magnitude greater than the C_2 density measured in an $Ar/H_2/C_{60}$ plasma for a sublimator temperature of 450 °C. However, the total carbon density in the chamber for an $Ar/H_2/CH_4$ plasma under these conditions is 6.7×10^{15} carbon atoms/cm^3. The ratio of the C_2 density to the total carbon density is then 4.5×10^{-5}. Remarkably, this C_2 production efficiency for an $Ar/H_2/C_{60}$ plasma is approximately 12 times higher than that calculated for an $Ar/H_2/CH_4$ plasma. Because the total density of carbon in the feed gas for this calculation is based upon the assumed saturation of the C_{60} vapor pressure in the sublimator, this factor is a lower bound estimate.

CONCLUSIONS

We have experimentally determined the steady state density of gas phase C_2 in $Ar/H_2/CH_4$ and $Ar/H_2/C_{60}$ microwave plasmas used in the deposition of nanocrystalline diamond films using high sensitivity white light absorption spectroscopy. The C_2 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 C_2 density on these processing parameters. The C_2 production efficiency, defined as the ratio of the density of gas phase C_2 to the total carbon content in the plasma, was determined to be at least a factor of 12 higher in $Ar/H_2/C_{60}$ plasmas than in $Ar/H_2/CH_4$ plasmas.

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