Radial Distribution of Hydrogen in Chemical Vapor Deposited Diamond

Karen Mary McNamara[†] and Karen K. Gleason[*]

Department of Chemical Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

At the center of a ⟨100⟩ oriented microwave plasma diamond film, a hydrogen concentration of 0.120 at. % was measured by solid-state nuclear magnetic resonance (NMR) spectroscopy. Somewhat lower contents were found for the central regions hot-filament and dc arc-jet materials, 0.031 and 0.023 at. %, respectively. However, the NMR line shapes are similar in all three cases, indicating similar bonding environments for the hydrogen. Radial variations in hydrogen content in the hot-filament and dc arc-jet samples were also observed by NMR. Regions with higher hydrogen contents also gave rise to increased absorption in the CH stretch region of the IR spectra and an increased background signal in the Raman spectra. Similarities in hydrogen content and distribution in these films indicates that a common mechanism for hydrogen incorporation at the growing diamond surface. Understanding such mechanisms is important for producing diamond films with uniform properties over large areas.

Introduction

The unique properties of diamond, such as its high thermal conductivity, mechanical characteristics, optical transmission, and electronic properties, make it an attractive material for many applications.[1-4] Recent advances allowing the production of high-quality diamond films have generated substantial interest in research laboratories throughout the world. These high-quality materials are produced by a variety of methods including microwave plasma, hot-filament, and dc arc-jet chemical vapor deposition (CVD). Although large differences in growth rates exist between these methods, all seem capable of producing highly faceted polycrystalline films with little evidence of non-diamond carbon.

The primary difference between most of the CVD techniques used to deposit diamond is the method by which energy is introduced into the gas phase. The reactant mixture is typically quite similar consisting of dilute hydrocarbon species (0.5–2.0%) in hydrogen.[2-4] Energy is introduced in order to dissociate and excite these gases, allowing hydrocarbon fragments and hydrogen atoms to reach the growth surface which is maintained at 800–1000 °C. Hot-filament and dc discharges have maximum gas-phase temperatures of ~2500 K, yielding growth rates on the order of 1 μm/h. Dc arc-jet plasmas have gas-phase temperatures of 4500 K or more and can yield deposition rates of >100 μm/h.[4] The properties of the diamond, from run to run and also spatially within the sample, should be effected by the conditions and species which prevail at the surface of the growing film. Due to the relatively high pressure and light emission in diamond growing environments, it is difficult to examine the state of the growing

surface in situ. Differences observed by ex situ detection, however, may give some insight into the differences in growth mechanisms in various systems.

This paper examines the hydrogen content of hot-filament, dc arc-jet and microwave plasma CVD diamond films by solid-state nuclear magnetic resonance (NMR) spectroscopy. This extends our early work using ^{1}H NMR, which focused only on hot-filament materials.[5,6] In addition, variations of hydrogen content as a function of radial position in the sample will be measured for the dc arc-jet and hot-filament films. Hydrogen content was chosen as a useful indicator of diamond quality because it correlates well with IR transmission[5,6] and is also proposed to effect electrical properties, such as resistivity.[7] In addition, the quantitative NMR measurements will be related to the results of more commonly employed diamond characterization techniques.

Experimental Section

Three free-standing diamond films were produced from CH_4 and H_2 by microwave plasma (MW), dc arc jet (DC), and hot-filament (HF) CVD, respectively. Further details of the MW and DC depositions are propriety. The HF CVD sample was deposited at a rate of 1.87 μm/h from 1% CH_4 in H_2 onto a thick, rotating, 1-in.-diameter silicon wafer substrate at a pressure of 100 Torr. The tantalum filament was maintained at a temperature of 2375 K, at a distance of 4 mm from the substrate.

The microwave film was obtained from the center of a >500-μm-thick dark film. The dc arc-jet material was ~400-μm-thick and also appeared dark. Samples from this film were obtained at 0.5-in. intervals across the 4.0-in. disk. Finally, the hot-filament sample was only ~50 μm thick with a gray-white appearance, and samples were obtained at 0.25-in. intervals across the 1.0+ in. disk.

All of the films were analyzed using Raman spectroscopy, infrared (IR) spectroscopy, X-ray diffraction, scanning electron microscopy (SEM), and solid-state nuclear magnetic resonance

---

(1) Geis, M. W.; Angus, J. C. *Sci. Am.* 1992, *267*, 84.
(2) Angus, J. C.; Hayman, C. C. *Science* 1988, *913*, 241.
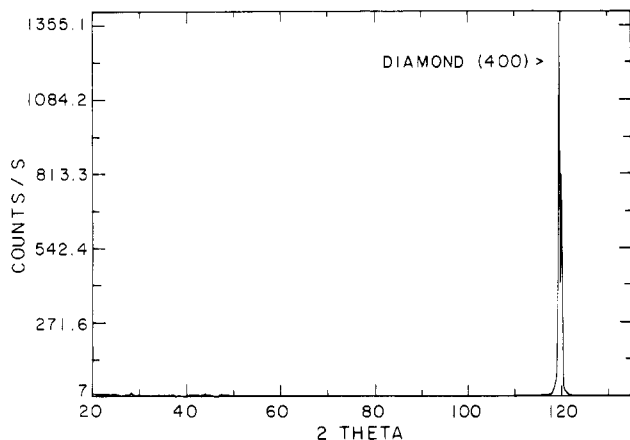(3) DeVries, R. C. *Annu. Rev. Mater. Sci.* 1987, *161*, 161.
(4) Bachman, P. K.; D. Leers, D.; Lydtin, H. *Diamond Relat. Mater.* 1991, *1*, 1.

(5) McNamara, K. M.; Levy, D. H.; Gleason, K. K.; Robinson, C. J, *Appl. Phys. Lett.* 1992, *60*, 580.
(6) McNamara, K. M.; Gleason, K. K.; Robinson, C. J. *J. Vac. Sci. Technol. A* 1992, *10*, 3143.
(7) Landstrass, M. I.; Ravi, K. V. *Appl. Phys. Lett.* 1989, *10*, 975.

Figure 1. X-ray diffraction pattern for the microwave CVD film, showing predominant orientation in the ⟨100⟩ direction.
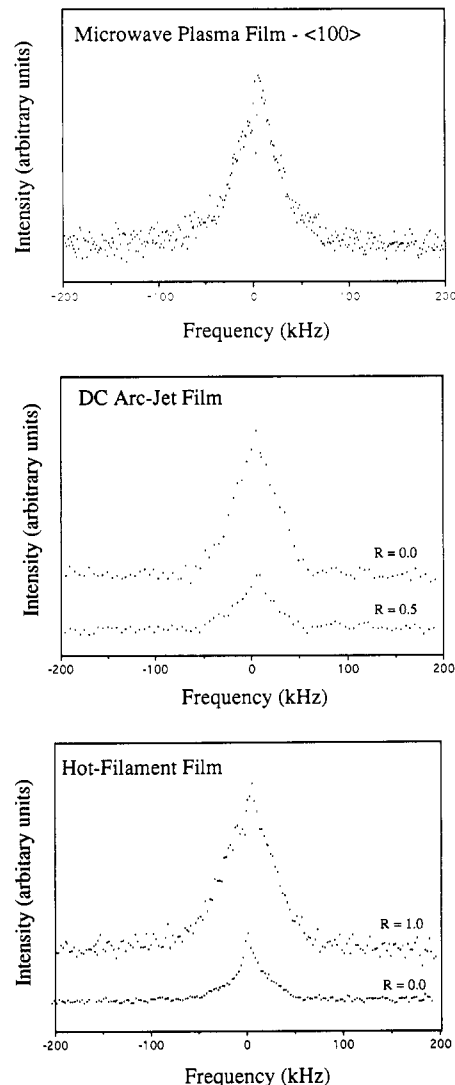
(NMR) spectroscopy. The dc arc-jet and hot-filament films were examined for radial variations by these techniques. Since NMR measures average bulk concentration of the material residing in the sample probe, this radial resolution was achieved by sectioning these samples for individual measurements. Thick diamond samples were prepared for analysis by laser cutting, while thinner samples could be sectioned by hand. All samples were free standing and examined intact without crushing. No polishing of the interface exposed upon substrate removal was performed. We cannot distinguish if this region of initial growth has a different hydrogen content from subsequently grown material because NMR does not provide depth resolution. However, our previous work[5,6] does not show a strong relationship between film thickness and total hydrogen content, indicating that such an initial region does not contribute significantly to the overall hydrogen content measured by NMR.

Solid-state ^{1}H NMR spectra were obtained at a static magnetic field of 6.7 T, giving a [1]H Larmor frequency of 270 MHz, as described previously.[5,6] Approximately 1500 signal averages were performed at room temperature. A delay of 5 s between averages allows for complete spin–lattice relaxation of the protons. Comparison of the total integrated area under the spectrum obtained from a diamond film of a given weight with that of a poly(methyl methacrylate) (PMMA) standard yields quantitative hydrogen contents for the samples.[8]

Results and Discussion

As anticipated based on previous reports,[9,10] SEM micrographs of the microwave film showed a relatively smooth surface with an average grain size of ~5 μm, predominantly oriented in the ⟨100⟩ direction, as confirmed using X-ray diffraction (Figure 1). The SEM micrographs of the hot-filament and dc arc-jet prepared samples show significantly higher surface roughness with average grain sizes of 10–15 μm and ~70 μm, respectively. The SEM and XRD analysis also show a smaller degree of orientation, primarily along the ⟨110⟩ direction.

The solid-state ^{1}H NMR spectra of the films deposited by each method are shown in Figure 2a–c. For the dc-arc jet (Figure 2b) and hot-filament films (Figure 2c), spectra for both the central (R = 0.0) and one of the outer regions (R > 0) are shown. For the microwave sample (Figure 2a), only a single spectrum was obtained. To facilitate line-shape comparison, each of the three parts of Figure 2, has a different normalization factor. However, within Figure 2b, the ratio of intensities of the two spectra equals the

(8) Levy, D. H.; Gleason, K. K. *J. Vac. Sci. Technol. A* **1993**, *11*, 195.

(9) Wild, C.; Koidl, P.; Muller-Sebert, W.; Walcher, H.; Kohl, R.; Herres, N.; Locher, R.; Samlenki, R. *Diamond Relat. Mater.* **1993**, *2*, 158.

(10) Dischler, B.; Wild, C.; Muller-Sebert, W.; Koidl, P. *Physica B* **1993**, *185*, 217.

Figure 2. Solid-state ^{1}H NMR spectra from (a) microwave, (b) dc arc-jet, and (c) hot-filament CVD diamond films. All spectra show similar line shapes. For the dc arc-jet film (b), the integrated intensity of the spectra from the center (R = 0.0) versus that at a radius of 1 in. (R = 0.5) of the dc arc-jet film, indicates a decrease in the hydrogen content by a factor of ~2.5. For the hot-filament film (c), the intensity difference between the integrated area for the center (R = 0.00) and the outer edge (R = 1.00) indicates an ~7-fold increase.

ratio of their hydrogen contents. The same is true for the spectra in Figure 2c.

Each line shape in Figure 2 contains two components, a narrow Lorentzian and a broad Gaussian, consistent with the observations of earlier NMR studies.[5,6] In that work, the narrow Lorentzian component of the line shape is associated with motionally averaged hydrogen. The Gaussian component, on the other hand, is attributed to static, densely packed hydrogen. Here, as in the earlier investigations, a majority of the hydrogen is associated with the broad component (i.e., static hydrogen) and only a small fraction is motionally narrowed. Previously, multiple-quantum NMR has shown the static, densely clustered hydrogen to be primarily distributed on two-dimensional surfaces rather than on three-dimensional lattices.[11] Hydrogen passivation of grain boundary and growth surfaces in the polycrystalline films could account for observed hydrogen incorporation levels. Indeed, films

(11) Levy, D. H.; Gleason, K. K. *J. Phys. Chem.* **1992**, *31*, 8125.

Table 1. Summary of Radial Variation for Dc Arc-Jet Diamond Film

| normalized radial position	$R = 0.00$	$R = 0.25$	$R = 0.50$	$R = 0.75$
at. % H	0.023	0.020	0.009	0.026
fwhm$_G$ NMR (kHz)	58.4	56.4	57.0	60.1
fwhm$_L$	6.6	8.0	9.6	7.0
fwhm$_{1332}$ Raman (cm^{-1})	17.3	13.5	9.3	9.3

with larger grain boundary areas (i.e., smaller crystallite sizes) have higher hydrogen contents.[6] However, hydrogen decoration of surfaces associated with defects internal to the crystallites cannot be ruled out. In films with higher hydrogen contents (>1 at. %) than those previously examined by multiple-quantum NMR, additional types of hydrogen incorporation may also exist. It is interesting that the characteristics of the NMR line shape, and thus the local hydrogen bonding environment, do not change significantly with deposition technique. This may indicate a common surface process occurs under these different conditions.

Integration of the NMR line shapes show that the hydrogen content of the microwave sample is approximately an order of magnitude higher (0.120 at. %) than those observed in the center of the hot-filament (0.031 at. %) and dc arc-jet (0.023 at. %) samples. Although hot-filament films with such high hydrogen contents have been previously observed by NMR, they are not common.[5,6] For hydrogen contents of >0.1 at. %, the concentrations measured by NMR are somewhat lower than calculated from the CH stretch IR region, although good agreement between the two techniques was found at lower concentrations.[6] Between 0.4 and 0.9 at. % H has been measured by IR spectroscopy for ⟨100⟩ textured microwave films,[10] in rough agreement, although slightly higher, than the NMR measurement of the textured microwave sample used in this study. There are several possible explanations for this relatively high hydrogen concentration of this sample. First, the surface area available for hydrogen passivation could be larger. In support of this hypothesis, its 5-μm crystallite size is relatively small compared to films previously studied by NMR. In addition, crystallite size evolves with film thickness.[10] This evolution may lead to more grain boundary area in a strongly ⟨100⟩ textured film as compared to the more commonly weakly ⟨110⟩ textured material. Another possibility is that the ⟨100⟩ texture exposes surfaces which allow a higher hydrogen packing density or that additional locations for hydrogen incorporation exist, such as a non-diamond phase. However, such changes are not apparent in the NMR line width which is determined by the distribution of proton spacings.

Radial variations in hydrogen content were observed for both the hot-filament and dc arc-jet diamond. Samples from the dc arc-jet material were laser cut 5-mm diameter disks cut at 0.5-in. intervals along the 2-in. radius of the film. Labeling from center to edge and normalizing, samples are taken at $R = 0.00$, $R = 0.25$, R = 0.50, and R = 0.75. Note that no sample was obtained from the outer edge of the film. The hydrogen concentrations obtained from the total integrated area under the NMR line shape are listed in Table I. Also listed are the full-width at half-maximum (fwhm) of both the Gaussian and Lorentzian components of the NMR line. A comparison of the ¹H NMR line shapes obtained at the center of the sample ($R = 0.00$) and 1.0 in. from the center ($R = 0.50$) are shown in Figure 2b. The integrated area under the line shapes
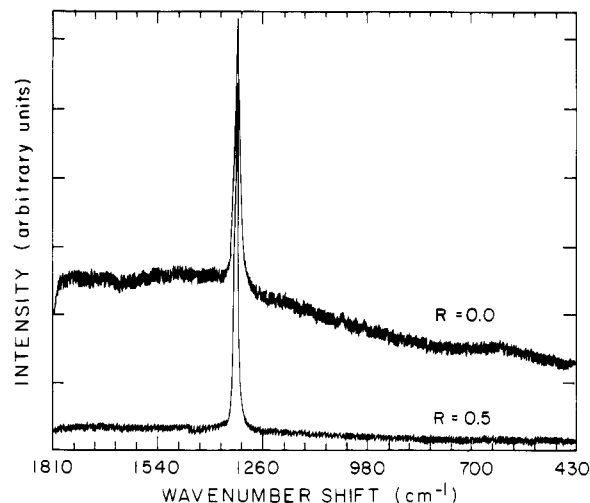
Figure 3. Raman spectra taken from the dc arc-jet sample at $R = 0.00$ and $R = 0.50$. No artificial offset imposed on these spectra, indicating a larger background signal at $R = 0.00$. The linewidth of the 1332 cm^{-1} peak (Table 1) is also broader at this central position.
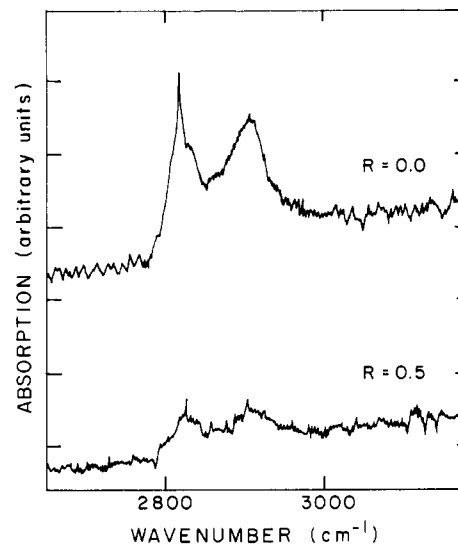
Figure 4. Infrared spectra of samples taken from the dc arc-jet sample at $R = 0.00$ and $R = 0.50$. The absorption in the CH stretch region is larger at $R = 0.00$, consistent with the ¹H NMR results (Figure 2b). Also, a strong mode at ∼2820 cm^{-1} is apparent in the $R = 0.0$ spectrum.

indicate that the center piece contains more than twice the amount of hydrogen (0.023 at. %) found in the sample obtained 1 in. from the center (0.009 at. %). The shape of the NMR line, however, does not change significantly.

Comparison of the two corresponding Raman spectra (Figure 3) shows a larger fwhm for the 1332-cm^{-1} peak (Table I) and an increase in background signal intensity for the central ($R = 0.0$) region. Note that the offset between the two Raman spectra in Figure 3 is real and not artificially produced.

In addition, the IR spectrum (Figure 4) of the dc arc film show an increase in the CH-stretch absorption in the center of the film, in agreement with the higher hydrogen observed by NMR. These IR spectra also shows a strong absorption at 2820 cm^{-1}, from the central region of the film ($R = 0$). This absorption occurs at lower wavenumbers than CH$_x$ bonding configurations in polycrystalline diamond and diamond-like carbon films and has previously been observed in CVD diamond films.[6,10] A tentative assignment of this mode as monohydride species at

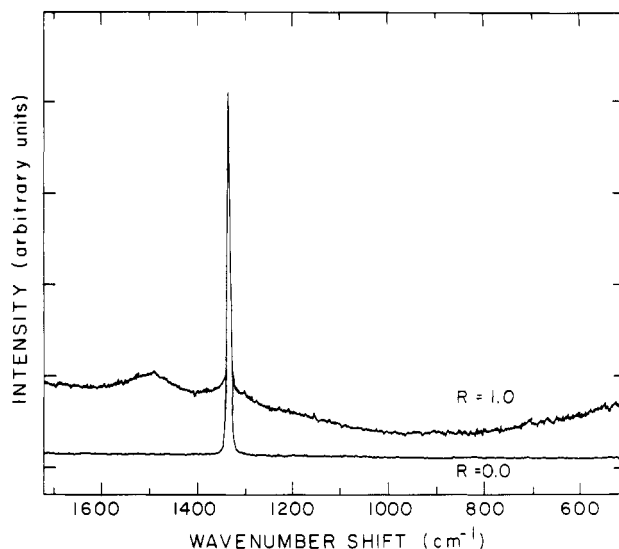**Table 2. Summary of Radial Variation for Hot-Filament Diamond Film**

normalized radial position	$R = 0.00$	$R = 0.50$	$R = 1.00$
at. % H	0.031	0.039	0.229
fwhm$_G$ NMR (kHz)	62.2	69.6	72.9
fwhm$_L$ NMR (kHz)	10.5	17.6	8.8
fwhm$_{1332}$ Raman (cm^{-1})	6.1	6.1	5.5

dislocations or similar defect sites has been suggested.[10] Another possibility is related to IR studies of organic molecules where stretching frequencies between 2810–2820 and 2805–2870 cm^{-1} have been cited for a –OCH$_3$ and –NCH$_3$ groups, respectively.[12] The prevalence of oxygen and nitrogen as impurities or as intentionally introduced components in the gas phase of diamond deposition environments suggests that –OCH$_3$ or –NCH$_3$ groups might account for the 2820-cm^{-1} absorption in polycrystalline diamond. Further work is required before a definitive assignment of this mode is made and its relationship to the diamond growth process is established.

Results for the radial variation of the hot-filament CVD diamond were obtained from sections broken from the sample at 0.25 inch intervals along the 0.5+ inch radius of the film and are recorded in Table 2. Labeling from center to edge and normalizing, samples are taken at $R = 0.00$, $R = 0.50$, and $R = 1.00$. The variations in the fwhm of both NMR components and the 1332-cm^{-1} peak in the Raman spectra are also recorded in Table 2. A significant increase in hydrogen content from 0.031 at. % to 0.229 at. % is observed in the ^{1}H NMR spectra (Figure 2a) obtained from diamond located near the edge ($R = 1.00$) as compared to the center ($R = 0.00$) of this sample. Although there is an increase of almost an order of magnitude in hydrogen concentration, little variation is observed in either the fwhm or the NMR line shapes.

The central and edge samples from the hot-filament film have similar 1332 cm^{-1} peak fwhm in the Raman spectra (see Table 2). Thus, higher hydrogen content does not relate to increased broadness of the Raman one-phonon mode, as was seen in the dc arc-jet film (Figure 3). However, the background in the $R = 1.0$ Raman spectra of the hot-filament material is larger than for the $R = 0.0$ spectra (note that no artificial offset was introduced in Figure 5). In both the dc arc-jet (Figure 3) and hot-filament (Figure 5) samples, a larger Raman background was noted for regions of higher hydrogen content. This observation may only be a coincidence and does not necessarily indicate a cause-and-effect relationship. However, higher hydrogen contents are expected as grain boundary area and the fraction of non-diamond-bonded phases increases. These two trends could also influence phenomena which might give rise to the Raman background signal such as luminescence, scattering or absorption of non-diamond phases. Indeed, a peak at ~1500 cm^{-1} is observed at $R = 1.0$ (Figure 5) indicating the presence of non-diamond carbon in this region of relatively high hydrogen content.[13]

The larger CH stretch absorption observed at $R = 1.0$ in Figure 6 indicates a significantly higher hydrogen content at the edge of the hot-filament film, in agreement with the NMR results (Figure 2c). As previously observed,[6,10] the characteristic symmetric and asymmetric stretching modes of CH$_2$ groups at ~2850 and ~2920 cm^{-1} are clearly visible in the $R = 1.0$ IR spectra. The

(12) Bellamy, L. J. *The Infrared Spectra of Complex Molecules*; Chapman and Hall Ltd.: London, 1980; Vol. 2.
(13) Knight, D. S.; White, W. B. *J. Mater. Res.* **1985**, *4*, 5873.

Figure 5. Raman spectra taken from the center ($R = 0.0$) and outer edge ($R = 1.0$) of the hot-filament film. Increased background is observed in the $R = 1.0$ sample, which contains no artificial offset.
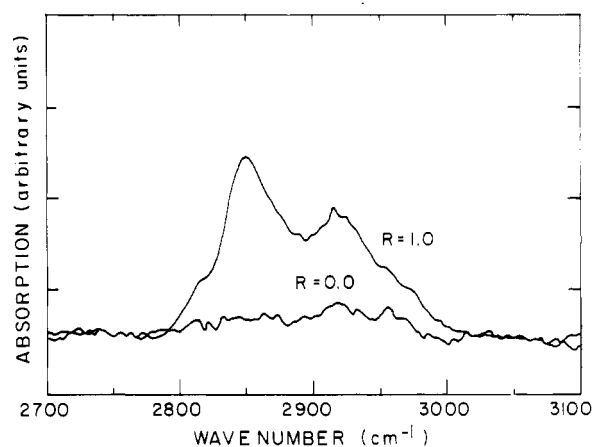
Figure 6. IR spectra taken from the hot-filament samples at $R = 0.00$ and $R = 1.00$. The sharp increase in absorption in the CH stretch region at $R = 1.00$ is consistent with the ^{1}H NMR results (Figure 2c). Strong stretching modes from CH$_2$ groups dominate the $R = 1.0$ spectrum.
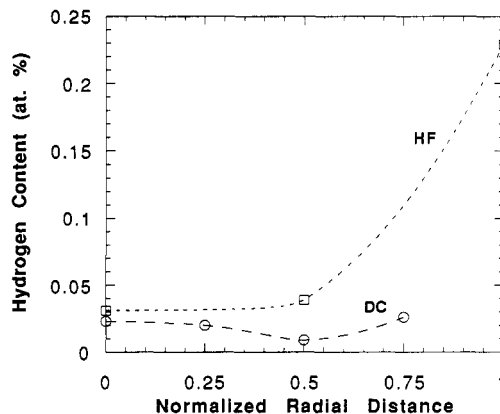
Figure 7. Hydrogen content of the dc arc-jet and hot-filament CVD diamond films as a function of normalized radial position.

mode at ~2820 cm^{-1} is also apparent in Figure 6, although less intense than for the dc arc-jet film (Figure 4).

Figure 7 shows a plot of the variation in hydrogen content as a function of normalized radial position for the hot-filament and dc arc-jet samples. The material located away from the edges of both samples have surprisingly

similar hydrogen contents, ~0.01–0.04 at. %, despite the difference expected for the growth rates in dc arc-jet and hot-filament environments.[4] Thus, the similarity in hydrogen content in the two films may indicate that hydrogen incorporation is controlled by surface processes which are similar in both systems. The results, however, are not identical. The hot filament diamond film shows a significant increase in hydrogen with radial position, while the trend in the arc-jet film is unclear. A slight increase is observed in the outermost region, but no samples were obtained less than $1/2$ in. from the edge. There is also a minimum in the hydrogen content at the position halfway between the center and edge of the sample ($R = 0.50$).

The fact that similar hydrogen contents are observed in the center of the growth region on both samples may indicate a similar mechanism for diamond formation in both processes. The variations in hydrogen content, on the other hand, may result from fluctuations in the gas-phase concentrations above the growth surface, nonuniformities in surface temperature, orientation of the crystallite growth surface, and surface area of these crystallites. The importance of these factors may differ between the two growth environments and even between different reactors of the same type, which serves to highlight the importance of understanding surface chemistry and controlling local reactor conditions in these systems in order to control film properties. This becomes particularly important for large area samples.

It is important to consider the effects of these variations in hydrogen content on the properties of diamond films. As an example, it has been demonstrated that hydrogen content can be quantitatively correlated with absorption in the CH stretch region in the IR spectrum (see Figures 6 and 9).[5,6] In addition, there is a qualitative correlation between hydrogen content and the film's absorption in the 8–10-μm region.[14] This absorption is particularly important in the application of CVD diamond for infrared windows. Significant variations in this absorption would not permit the use of such large area diamond films in these applications. These nonuniformities also raise questions about the definition of specifications on diamond samples. One might expect to see specifications developed which include both the maximum absorbance or other characteristics of interest and the maximum tolerable variation in that parameter.

Conclusions

Low hydrogen contents, as measured by ^{1}H NMR, were observed at the centers of three polycrystalline diamond films deposited by distinctly different processes: microwave plasma (MW, 0.120 at. %), dc arc-jet (DC, 0.023 at. %) and hot-filament (HF, 0.031 at. %) CVD. This result is in agreeement with a previous study of a series of hot-filament films, all of which contained <0.25 at. % H. Thus, the three CVD methods studied here (MW, DC, and HF), may have a similar mechanism for hydrogen incorporation despite their expected differences in growth rate and gas-phase composition. Hydrogen incorporation at internal surfaces such as grain boundaries could account for this similarity. This would support the hypothesis of hydrogen termination of the growing surfaces in these three differnt CVD environments. In addition, the hydrogen contents of the diamond films are extremely low compared to those for typical hydrogenated amorphous carbon films prepared

by radiofrequency plasma CVD (~10 to >50 at. %).[15] Thus, very little of such a heavily hydrogenated amorphous carbon can exist in polycrystalline diamond.

The distribution of surfaces available for hydrogen passivation should vary with the texture of a polycrystalline diamond films and thus produce changes in the ^{1}H NMR line shape. However, the MW film, which displays ⟨100⟩ oriented crystals at the surface, has a similar proton NMR line shape to the DC and HF films which have a weaker ⟨110⟩ preferred orientation. If only surfaces from the large oriented crystallites were being observed, the expected hydrogen content of the MW would be quite low. However, the highly textured MW film has an order of magnitude higher hydrogen content than the central regions of the DC and HF materials. Thus, other surfaces, such as from smaller crystallites which are covered over during growth or from internal void surfaces within crystallites, most likely dominate the NMR spectra of the MW film.

The CH stretch region of the IR spectra allows observation of the distribution of covalent bonding environments for hydrogen in polycrystalline diamond. Clear differences are seen between films and spatially within a single film. In particular, the CH_2 stretching modes can be well defined. In addition, some film regions contain a distinct mode at ~2820 cm^{-1}, which lacks a defined assignment. This mode is not observed in hydrogenated amorphous carbon films and represents a distinct configuration of hydrogen in polycrystalline diamond. A one-to-one correspondence exists between the remaining absorptions in the CH_x stretching region of diamond and those of hydrogenated amorphous carbon films.[6,10] If these environments represent the growing diamond surface, there is a large heterogeneity of surface sites during polycrystalline film growth.

Using ^{1}H NMR, significant radial hydrogen concentrations variations were observed in the HF film, from 0.031 at. % at the center to 0.229 at. % at the edge. Regions with higher hydrogen contents also gave rise to increased background signals Raman spectra, although no cause-and-effect relationship may exist. Thus, despite the high diffusivities of gas-phase species HFCVD diamond reactors and steps taken to minimized thermal gradients at the growth surface (thick substrates and sample rotation), variations in hydrogen content can occur. Such differences in hydrogen content are known to affect the optical quality of diamond and will likely impact other properties, as well. Better understanding of the surface kinetics, gas-phase kinetics and mass transport is required to reduce spatial variations in film quality, particularly in large area films.

(14) Hartnett, T. M.; Miller, R. P. *SPIE Proc.* **1990**, *1307*, 60.

(15) Dischler, D.; Budenzer, A.; Koidl, P. *Solid State Commun.* **1983**, *48*, 105.