

DIAGNOSTICS OF FILAMENT-ASSISTED DIAMOND GROWTH CHEMISTRY

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ABSTRACT

The use of in-situ optical diagnostics for probing the gas phase in the chemical vapor deposition (CVD) of diamond is described. Radical species (H and CH_3) as well as stable molecules (CH_4 , C_2H_2 , C_2H_4) have been detected with these techniques. We summarize here the results of resonance-enhanced multiphoton ionization (REMPI) studies and infrared diode laser absorption measurements made under filament-assisted diamond CVD conditions. The concentrations of two potential carbon-transport species, CH_3 and C_2H_2 , both increased as a function of the initial CH_4/H_2 fraction (F_0), whereas the H atom concentration decreased with increasing F_0 . In conjunction with known diamond film growth results, we interpret these observations as evidence for the *surface* role of atomic hydrogen in the diamond growth mechanism.

INTRODUCTION

Diamond has outstanding material properties, such as extreme hardness and high thermal conductivity.[1] The same properties make diamond exceedingly difficult to modify (*e.g.*, by machining or doping). Modification could in principle be more easily accomplished during vapor phase deposition, so the prospect of CVD-synthesized diamond is of great practical importance. Various diamond CVD techniques have already been demonstrated,[2] but development of improved deposition methods will be hindered without an understanding of the diamond formation mechanism. The fact that CVD diamond growth proceeds under temperature and pressure conditions at which graphite is the stable carbon form indicates that a delicate balance is needed for growth. Diamond deposition might be further manipulated once the mechanisms leading to this balance are understood.

Much insightful work has led to an empirical understanding of the diamond growth environment. Supersaturation of atomic hydrogen is crucial[3] for diamond deposition, although its exact role in the growth process is not clear. The postulated carbon-transport species have generally been hydrocarbon pyrolysis products, notably CH_3 , [3,4] CH and atomic carbon.[5] Other proposed mechanisms[6-8] find low calculated activation barriers based on C_2H_2 [6], or $\text{CH}_3^+/\text{CH}_3$ [7] as the active growth species. Only recently have in-situ gas phase measurements[9-11] been performed enabling testing of these hypotheses. We report here on determinations of the filament-assisted diamond growth chemistry made through the use of spectroscopic probes.

EXPERIMENTAL

The chamber used for both the deposition of diamond films and the infrared absorption measurements was described previously.[9] Briefly, a tungsten filament was suspended 1.5 cm above a substrate (*e.g.*, Si wafers or Ni foil) and mounted in the center of a stainless steel 6-way cross. Typical growth conditions included a slow flow (100 sccm) of <1.0% CH_4 in H_2 at 25 Torr total pressure, and a tungsten filament temperature (T_{fil}) of ~ 2000 C (measured with a 2-color pyrometer). The substrate, heated by radiation and convection, was maintained

in a temperature range necessary for diamond growth (~ 900 C).

Mirrors were mounted inside the chamber to provide a multi-pass geometry for the infrared absorption measurements. The diode laser beam passed ~ 20 times through the chamber, including a region located few mm above the substrate, before being focussed onto an infrared detector. Molecular species within the pathlength resonantly absorb the tunable IR light and are detected by the concomitant power loss at the detector. For the REMPI experiments, a focussed dye laser beam (1-15 mJ/pulse, $\Delta\nu \sim 0.2$ cm $^{-1}$), made 1 or 2 passes through the chamber. The substrate holder was biased (~ 150 V) to provide efficient collection of photoelectrons (generated by the MPI process) at a Pt probe wire inserted 2-4 mm above the substrate and 1-2 mm from the focal volume of the laser.[11]

RESULTS AND DISCUSSION

The films deposited in this chamber were analyzed with a variety of techniques which definitively established diamond deposition: SEM micrographs showed faceted crystallites, whether isolated or in polycrystalline films; Raman spectra exhibited an intense, sharp 1332 cm $^{-1}$ band, with little evidence for graphitic or amorphous carbon; small-spot Auger electron spectroscopy detected only carbon, with a lineshape similar to that of natural diamond; x-ray diffraction spectra yielded a diamond lattice constant.[9] All spectroscopic investigations were conducted under similar diamond growth conditions, although deposits were not always analyzed.

With $F_0 = 0.5\%$ and $T_{fil} = 2000$ C, the following gas phase species concentrations present during diamond CVD were determined from infrared absorption measurements: CH $_4$, $8 \pm 3 \times 10^{14}$ cm $^{-3}$ (~ 50 mTorr @ 300 C); CH $_3$, $2 \bullet 1.5 \times 10^{12}$; C $_2$ H $_4$, $6 \pm 2 \times 10^{12}$; and C $_2$ H $_2$, $2 \pm 1 \times 10^{14}$. No absorption lines due to C $_2$ H $_6$ or stable C $_3$ H $_y$ species were found. Experiments to follow the concentration of these species as a function of various growth parameters are currently in progress.

The IR observations can be qualitatively understood by consideration of the initial gas mixture at elevated temperatures ($1300 < T < 2500$ C), where C $_2$ H $_2$ is the thermodynamically-favored carbon-containing molecule. Various hydrocarbon fuels would be predicted to generate similar species by this technique. Detection of transient species (i.e., C $_2$, CH and C $_3$), which are predicted by the thermodynamic model to be present in detectable concentrations, was attempted using laser-excited fluorescence (LEF), but only C $_3$ was tentatively identified. The absence of ground state C $_2$ and CH in detectable concentration indicates that while these species may be produced at the hot filament, they are consumed by reactions occurring at lower temperature during transport to the surface. Both CH and C $_2$ have been detected from their excited-state optical emission spectrum during plasma-assisted diamond growth, but were not present in sufficient quantity to account for the observed rate of filament-assisted diamond growth. The observed concentrations of CH $_4$, CH $_3$, C $_2$ H $_2$ or C $_2$ H $_4$ could account for the diamond deposition rate.

Using in-situ mass spectrometric analysis, Harris, *et al.*[10] also observed significant conversion of CH $_4$ to C $_2$ H $_2$ in a filament-assisted diamond CVD chamber. The radical species concentrations predicted by their kinetic modeling study are in agreement with our observations. It was concluded that the probable carbon-transport species in this system are CH $_3$, C $_2$ H $_2$, CH $_4$ and C $_2$ H $_4$, with preference given to CH $_3$ and C $_2$ H $_2$ based on reactivity.[10]

The 2+1 REMPI band at 333.5 nm[12] was employed for in-situ detection of CH $_3$. The spatial resolution of the REMPI detection provides relative concentration measurements in a

volume directly above the growth surface. In Fig. 1, the C_2H_2 concentration derived from the IR absorption measurements is compared with the CH_3 REMPI signal. Note that for $F_0 = 0.5\%$ the average CH_3 concentration through the diode beam path is about 2 orders of magnitude lower than that of C_2H_2 . Both species concentrations increased for increased F_0 , with C_2H_2 growing at perhaps a faster rate.

To monitor the concentration of atomic hydrogen, the REMPI technique was employed, with specific detection provided by the 3+1 resonant transition at 364.7 nm.[13] An interference effect was observed in the single pass (travelling wave-TW) geometry due to the generation of third harmonic light, manifested by the absence of the resonant REMPI feature at 364.68 nm. The resonant REMPI peak was obtained using standing-wave (SW) excitation (a spherical mirror re-focussed the UV beam back along the optical axis). The observations are consistent with theoretical predictions[14] and experimental verifications (in rare gases)[15] of an interference effect between odd harmonics of the laser field (in this case, the first and third harmonics, at 364.7 nm and 121.6 nm, respectively).

The hydrogen atom concentration can be monitored using the intensity of the resonant REMPI signal from the SW excitation geometry. The T_{fil} dependence of the 365.68 nm feature for pure H_2 (Fig. 2(a)) agrees with the thermodynamics for H_2 dissociation. The signal attenuation at $F_0 = 0.5\%$ and 1.0% reflects a loss in H atom flux in a probed volume located 8 mm from the filament, probably due to gas-phase reactions. The $F_0 = 3\%$ curve (Fig. 2(d)) suggests a poisoning of the filament surface resulting in severely reduced H atom concentration for T_{fil} less than 2200 C. The poisoning, perhaps related to a tungsten carbide phase, might be avoided with the use of alternate filament materials, such as rhenium.

For CH_4 in H_2 , it has been shown that $F_0 < 1\%$ is necessary for growth of reasonable purity diamond. The diminished H atom flux for $F_0 > 1\%$ correlates with observations[16,17] of increased deposition of graphitic and amorphous carbon under these conditions; however, the measured concentration of CH_3 and C_2H_2 both increase with F_0 , even for $F_0 > 1\%$ (Fig. 1). We interpret these results as suggesting that the dominant role played by atomic hydrogen in diamond CVD is surface-related (e.g., dangling surface bond termination, preparation of active surface sites, and/or preferential etching of non-diamond forms of carbon), rather than generation of gas-phase intermediates.

SUMMARY

Our present model of the filament-assisted gas phase environment, in concert with that of Harris, *et al.*, [10] is one in which thermodynamically-favored species (e.g., C_2H_2 , CH_3) are formed at high temperature near the filament, followed by depletion of the more reactive species during transport to the diamond growth surface. The carbon-transport, or growth, species for this system may be CH_4 , C_2H_4 , CH_3 or C_2H_2 , but CH and C₂ do not appear to play a significant role in carbon deposition. Some aspects of polycrystalline diamond film growth correlate with hydrogen atom concentration, and we conclude that the interaction of hydrogen atom with the growing diamond surface is important, while the role of H atoms in gas phase chemistry appear to be less important.

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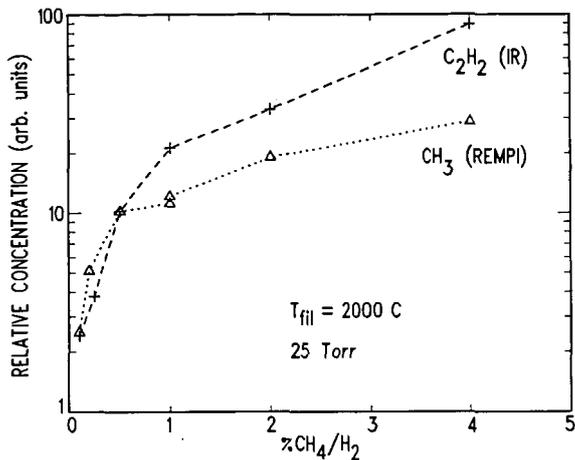


Figure 1: Relative concentrations of C₂H₂ (crosses, from infrared absorption), and CH₃ (triangles, REMPI data) vs. F₀. The IR measurements were not spatially resolved.

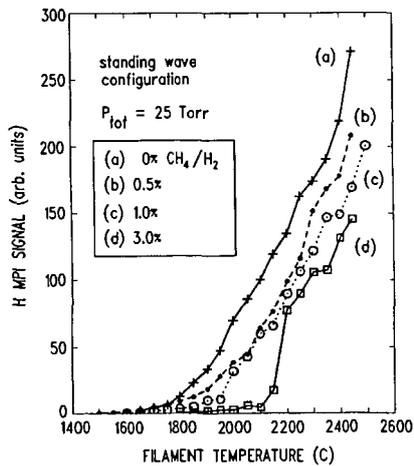


Figure 2: Relative H atom concentrations vs. filament temperature. The lines are merely to connect data points for each initial F₀ value, given in the figure. All data are for a filament-probe separation of 8 mm.