



DIAMOND FILM DEPOSITION BY CHEMICAL VAPOR TRANSPORT†

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Abstract—Chemical vapor deposition techniques for depositing diamond films at low pressure are reviewed, along with current and potential applications for these films. A new chemical vapor transport technique is described that is simpler and suitable for microgravity and centrifuge experiments. It was used to deposit diamond on silicon, molybdenum, graphite, glass, and carbon felt. Selective patterned deposition was achieved on a copper pattern on oxidized silicon. Centrifugation at only $\sim 2g$ greatly increased the nucleation density, area of deposition, and growth rate. The self-regulating behavior of this new technique is explained in terms of chemical and transport mechanisms. © 2001 Published by Elsevier Science Ltd.

1. INTRODUCTION

A variety of chemical vapor deposition (CVD) methods have been developed over the last 20 years for the deposition of diamond films at low pressure. These methods have led to many applications taking advantage of the exceptional properties of diamond. Although some of these have been commercialized, others await improved properties and lower costs.

Several years ago, we became curious about the influence of acceleration on diamond film deposition. The CVD techniques at that time utilized flowing hydrogen at ~ 0.1 atm containing a small amount of hydrocarbon gas. Either a hot tungsten filament or a plasma was used to generate atomic hydrogen, which was thought to be necessary for the nucleation and growth of diamond. We concluded that it was neither feasible nor safe to place a hydrogen cylinder, methane cylinder, vacuum pump, plasma generator, and accessories on our large, 1.6 m radius centrifuge. Consequently, we developed a simple, closed chamber technique in which an electrically heated graphite rod is placed near a substrate in ~ 0.1 atm hydrogen [1–5]. The hope was that the hot graphite rod would provide both the hydrocarbons and the hydrogen atoms necessary for diamond nucleation and growth. This

technique not only yielded high-quality diamond films, but also appeared to have several advantages over the prior art:

1. Simpler — no need for a hydrocarbon source, gas handling system or plasma generator.
2. Deposition rate much higher than the customary $\sim 1 \mu\text{m/h}$.
3. Able to deposit on a wide variety of substrates without the customary pre-treatment with diamond powder. Thus far, such substrates have included glass, graphite, carbon felt and molybdenum.
4. Self regulating, providing the ability for selective nucleation and growth to produce fine patterns [3].

Furthermore, centrifugation at only twice earth's gravity ($2g$) greatly increased the nucleation density, area covered, and growth rate. As described later, preliminary modeling of the chemistry and transport phenomena have revealed a very interesting system.

2. APPLICATIONS FOR DIAMOND FILMS GROWN BY CHEMICAL VAPOR DEPOSITION (CVD)

Because of its long list of exceptional properties and the relative ease of growing diamond films by low-pressure techniques, new applications for these films appear almost daily. Following is a partial list. Those already reported to be in commercial use are indicated with a \bullet in front of them. In other cases, commercialization awaits improvements in the deposition process, the properties of the product, or

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lower cost. (Throughout this paper, the cited references are intended to be illustrative and not comprehensive.)

- Heat spreaders for semiconductor devices, photonic devices, laser diodes for fiber-optic communication, high-power amplifiers, Multi Chip Modules, etc. [6–14].
- Hard coatings for tools for cutting, grinding, microdrilling, etc. [10,12–16].
- Highly transparent hard windows and coatings for windows, useful from the infrared to the ultraviolet and as a radome [10–12].
- Ultraviolet photodetectors [17–19]
- Chemically resistant coatings [9,20], e.g., for biomedical implants.
- Cold-cathode field emitters for flat panel displays, electron guns, amplifiers, oscillators, miniature X-ray sources for localized cancer treatment, etc. [6,12,20–23,152].
- High-frequency speaker diaphragms [6].
- Synchrotron X-ray beam-position sensors [6].
- Masks for X-ray lithography [6,14,24].
- Piezoresistive devices for pressure and acceleration sensors [25].
- Surface acoustic wave (SAW) filters for higher frequency cell phones and for high-power transmission [6,10,14,25].
- Electrodes for biomedical applications, in molten salts, and radioactive environments [26].
- Glucose sensor for implantable systems to control diabetes [27].
- Hydrogen and oxygen sensors [8].
- Secondary electron emission devices for single ion detection, crossed-field amplifiers, electron multipliers, photomultipliers [20,28,29].
- Semiconductor devices such as MESFETs [6,10], MOSFETs [30], high-power transistors and switches [10], Schottky diodes [31], and blue LEDs.
- High vacuum bearings and wear-susceptible parts.
- Strain gauges for microsensors for pressure and acceleration at high temperature [6,8].
- Microelectromechanical systems (MEMS) [32].
- Photoconductive detectors for high power soft X-ray flux measurements [33].

3. DIAMOND DEPOSITION METHODS

3.1. A brief history of diamond synthesis

The dream of synthesizing diamonds remained elusive until General Electric scientists announced in 1955 that they had succeeded by duplicating the high pressure and temperature conditions under

which natural diamonds form [34,35]. Their first process was too expensive for commercial applications, and so they sought ways to manufacture a cost-effective product. Subsequent research reduced the cost, permitting industrial diamonds to be produced commercially for abrasive and cutting applications — a business now in the range of \$1 billion/yr. High-temperature, high-pressure processes can also produce gem-quality diamonds.

Metastable growth of diamond at low pressure was, apparently, first achieved at Union Carbide Corporation in 1952 using diamond seeds and carbon monoxide [34,35]. Subsequently, other workers in the United States, Europe, and the former Soviet Union achieved some success in deposition of diamond from a variety of hydrocarbon gases. However, growth rates were low, diamond seeds were required, and there were serious problems with graphite formation. The surge in interest in diamond deposition began in the 1970s, when scientists in the USSR deposited high-quality diamond films from hydrocarbon–hydrogen gas mixtures at low pressure in the presence of a hot tungsten filament [34,36–41]. They achieved nucleation and growth of diamond at reasonable rates on non-diamond substrates without competing formation of graphite. By the early 1980s, Japanese workers had duplicated these results and added microwave and inductively coupled radio frequency-enhanced plasmas to the hot filament method [42]. Groups in the United States [43] and western Europe joined the race to produce diamond films commercially.

3.2. Techniques for chemical vapor deposition (CVD) of diamond films

It is generally believed that the following conditions are required for chemical vapor deposition of large-grain, high-quality diamond films (e.g. [9,35,44–51]):

1. A substrate on which diamond can nucleate and grow.
2. A substrate temperature of approximately 700–1000°C.
3. Atomic hydrogen at the growth surface.
4. A suitable hydrocarbon species at the growth surface.

Atomic hydrogen has been generated both by a hot filament and by a plasma at low pressure.

Diamond has also been deposited from rich oxy-acetylene flames at 1 atmosphere pressure (e.g. [52,53]). It has been said of combustion methods that: “While these flames have demonstrated high

growth rates of high-quality diamond, the deposition area is small and an approach for scale-up to large areas is not apparent" [54]. We concentrate here on hot filament chemical vapor deposition (HFCVD) and on the various plasma-assisted chemical vapor deposition processes (PACVD), because these are most relevant to our new technique.

Hydrocarbon gases are supplied as carbon sources in HFCVD and PACVD (but not in our new CVT technique). The most common gas mixture is hydrogen at 10–100 Torr containing on the order of 1% methane (CH_4). This gas mixture flows through the system, making it necessary to have a complete gas handling system with gas cylinders, control valves, exhaust facilities, and a continuously operating vacuum pump.

3.3. Plasma-assisted chemical vapor deposition (PACVD)

In the PACVD family of techniques, a plasma is used to generate hydrogen atoms and carbon-containing growth species. Microwave plasmas have higher densities and electron energies than isotropic plasmas. Turn-key microwave reactors are available commercially that can deposit diamond films over areas of up to 12 in in diameter [55]. The estimated cost was reported to be under \$10 per carat, or \$9 per tool coated. In magneto-microwave CVD, the microwave discharge is carried out in a magnetic field [56]. A DC arcjet reactor has also been used [57–59].

3.4. Growth from fullerene

After the discovery of fullerenes in 1985, some researchers became interested in using them as precursors for growing diamond films in argon microwave plasmas. Several experimental and theoretical papers were published on the study of diamond films grown from fullerene [50,60–64]. The resulting films were composed of very small diamond grains (10–300 nm). The average growth rate was 0.6 $\mu\text{m}/\text{h}$, and up to 10 μm thick films were grown. Because of continued nucleation during growth and the resulting small grain size, these films had a very low surface roughness, and 2–3 times lower friction coefficient than films of comparable thickness grown from the more usual H_2 – CH_4 mixtures. By observing the spectrum obtained from the intensely emerald-green plasma discharge, it was concluded that very extensive fragmentation of C_{60} occurred and that C_2 was the major product. It was speculated that C_2 may have been responsible for the exceptionally high nucleation rate. The

reaction of C_2 with the reconstructed monohydrated diamond (100) surface, which is expected in the presence of hydrogen atoms, was modeled in [64].

3.5. Hot-filament chemical vapor deposition (HFCVD)

In HFCVD techniques, electric current is passed through a filament in order to heat it to 2000–2500°C. Hydrogen at 10–100 Torr containing about 1% hydrocarbon is passed over the filament, which is believed to catalytically decompose hydrogen molecules into atoms. The most commonly used material is tungsten, although filaments also have been made from tantalum, molybdenum and rhenium. The filament is typically placed within 1 cm of the substrate, and often serves to heat the substrate as well.

Diamond has been deposited using a wide variety of hydrocarbon source gases, including methane, acetylene, alcohols and ketones. A large number of reactions occur on the filament surface and in the gas phase to produce many hydrocarbon species, including free radicals [44,46,47,65,66,141,143–151]. Theory and experiments showed that the species produced depend primarily on the atomic C/H and O/H ratios of the inlet gas, rather than which hydrocarbon source gas is used. Regardless of the inlet gas composition, methyl radical (CH_3) is believed to be the primary species responsible for growth of diamond, with some contribution from acetylene (C_2H_2), particularly for nucleation. The deposition rate is on the order of 1 $\mu\text{m}/\text{h}$.

3.6. Role of atomic hydrogen in diamond CVD

In previous CVD methods, hydrogen atoms were generated from hydrogen molecules either by a plasma or by catalytic decomposition on a hot filament. "It has been determined that atomic hydrogen is generated at the hot filament to about 60% of the concentration predicted for equilibrium dissociation of H_2 at that filament temperature" [67]. Although uncertainty remains as to the exact mechanisms involved in the metastable synthesis of diamond, it appears certain that atomic hydrogen plays a crucial role in the process (e.g. [35,42,46,47,65,66,68]). It has been proposed that atomic hydrogen preferentially attacks graphite if it forms, thermodynamically stabilizes diamond relative to graphite, reacts with other forms of carbon to form diamond nuclei, and plays a vital role in the growth mechanism. It is generally accepted that almost every carbon atom on the growing diamond surface is bonded to a H atom, yielding a configuration of carbon atoms closely resembling the interior

of the crystal lattice. According to Angus *et al.* [69–73], atomic hydrogen reacts with any graphite-like precursors to form molecular structures resembling the structure of diamond. Diamond is believed to nucleate on the edges of graphite basal planes because of hydrogenation.

Gat and Angus [74] demonstrated another important function of hydrogen during diamond deposition. Atomic hydrogen transports much of the energy reaching the substrate, via the highly exothermic hydrogen recombination reaction. This was demonstrated by the following experiment. The temperature of a tungsten or silicon substrate was set at 1062°C. A nearby tungsten filament was heated to 2000°C. The subsequent rise in the substrate temperature was measured with different reactor pressures and in different ambient gases: Ar, N₂, He, and H₂. Additional heating was found only in a hydrogen ambient.

3.7. Diamond nucleation

Control of nucleation is critical to obtaining the grain size, orientation, transparency, adhesion and other properties required for most applications. For example, smooth pinhole-free polycrystalline films for optics and X-ray lithographic masks require a high nucleation density and uniform crystal size. On the other hand, many semiconductor devices would function best with either single-crystal heteroepitaxial diamond or bulk single crystals. Wear and cutting applications need uniform deposition over large or irregularly shaped substrates such as tool bits.

Several questions in diamond nucleation have been subject to considerable investigation and debate over the years (e.g. [44,47,48,50–52,56–59,75–81]). How does nucleation of the diamond phase occur? How can one explain the induction time generally required before diamond can be detected? Why does application of an electric bias enhance nucleation and sometimes yield a preferred orientation? What is the role of the various carbon-containing species? How might one obtain hetero-epitaxial single-crystal growth?

Diamond films have been grown on many substrate materials, including diamond itself, graphite, amorphous carbon, fused silica, alumina, many metals, silicon, and several carbides and nitrides. Sometimes, as with deposition on steel [82], an interlayer of another material is required for successful diamond coating. The nucleation rate depends on the substrate material, its pre-treatment, and the deposition operating conditions. For example, the nucleation density on platinum was 10⁶ greater

than on adjacent SiO₂ [83]. We obtained similar results on copper and SiO₂ [3]. It is noteworthy that others [84] found it necessary to pretreat silica with a diamond powder slurry in order to obtain a continuous coating, while our new technique required no such pre-coating.

Butler *et al.* [51] wrote that “Diamond nucleation during CVD occurs as a result of some combination of suppression of graphite nucleus formation, stabilization of diamond nuclei and surfaces with respect to graphite nuclei and surfaces, and preferential etching of sp² carbon”. Prior to nucleation, it has been assumed that the substrate is covered with C or hydrocarbon radicals because hydrogen is completely desorbed from typical substrate surfaces above 800°C [72]. Nucleation might start even at a low concentration of adsorbed carbon species if the surface diffusivity is large enough for them to migrate and form critical clusters during their residence time. Alternately, it has been proposed that an induction period is necessary because a carbide or graphitic phase must form first. It is not clear whether the carbide or graphite provides heteronucleation sites, or if insufficient carbon is available to nucleate diamond until the surface is coated by carbide or graphite. Nucleation on non-carbide forming substrates is comparatively poor or non-existent unless carbide forming contaminants are present. The frequent occurrence of regularly shaped, twinned crystals is sometimes cited as evidence that a twinned nucleus forms from a high concentration of carbon-containing compounds adsorbed on the sample surface.

In one experiment, high-resolution transmission electron microscopy revealed a diamond-like amorphous carbon layer on copper, 8–14 nm thick, in which diamond microcrystallites about 2–5 nm across were embedded, prior to growth of diamond crystals [76]. A nucleation and growth model for diamond was proposed involving the following states: formation of carbon clusters, sp¹ → sp² → sp³ conversion of the bonding of the C atoms, crystallization of the amorphous phase, and growth of diamond crystals.

Several methods of substrate surface pretreatment enhance nucleation of diamond. Among these are scratching, seeding, chemical etching, ion implantation, pulsed laser irradiation, and carburization. The mechanisms causing enhanced nucleation are unclear. Nucleation on most non-diamond substrates is enhanced by scratching with diamond powder (or less effectively, with SiC or cubic boron nitride powder). The nucleation density on single-crystal substrates is lower than on corresponding polycrystalline materials. In

general, scratched carbide-formers nucleate better than scratched non-carbide formers, although there are some exceptions, such as Cu.

Oriented diamond particles were grown on cobalt by a multistep HFCVD, which involved seeding, annealing, nucleation, and then growth [85]. The substrates were seeded with diamond powders, graphite powders, or gaseous carbon species. In all cases, $\langle 111 \rangle$ oriented diamond particles were obtained on $\langle 0001 \rangle$ single-crystal cobalt substrates. The results were attributed to formation of a Co-C-H molten layer in which nucleation occurred.

The addition of O₂ and N₂ affected the nucleation and growth differently on carbon fibers than on other substrates such as polished Si [86]. On the fibers, the addition of N₂ led to a larger nucleation density and a smaller growth rate, while addition of O₂ resulted in a larger nucleation density, a lower growth rate, and a rougher surface.

3.8. Bias-enhancement of nucleation

Imposition of an electric bias on the substrate to enhance nucleation has become common in PACVD techniques [87–92]. This bias is thought to reduce and suppress oxide formation on the substrate surface, remove native oxides, and overcome the energy barrier for the formation of stable diamond nuclei by more effectively activating the substrate surface and/or increasing the flux and mobility of adatoms.

The influence of the process parameters on bias-enhanced nucleation of diamond on silicon (88) was studied using microwave plasma CVD [90]. A short bias duration (< 20 min) increased the diamond nucleation density and improved the film uniformity. The carbide that had formed on silicon via bias-enhanced nucleation was depleted after reaching a terminal thickness, resulting in a slightly carbon-rich surface. It was concluded that the carbon-containing species vital for nucleation differ from those required for growth.

One study on the effect of biasing on nucleation in PACVD used two joined chambers: a microwave CVD reactor and a multi-technique surface analytical chamber [87]. Biasing increased the nucleation density on unscratched silicon substrates by over five orders of magnitude. By changing the length of the bias pretreatment, the nucleation density was varied by over three orders of magnitude. After the biasing voltage was turned off, the diamond nuclei that were created during the pretreatment grew and negligible additional nucleation occurred. If the biasing voltage was left on until the end of the ex-

periment, the resulting diamond film was of much poorer quality than that produced with biasing followed by growth without bias. It was concluded that conditions ideal for diamond nucleation are not optimal for diamond growth. An interfacial layer of amorphous silicon carbide formed before significant diamond nucleation occurred. It was believed that when the silicon carbide layer reached a critical thickness, approximately 90 Å, the carbon on the surface became free to form clusters favorable for diamond nucleation. On the other hand, the significant nucleation enhancement on positively or negatively biased substrates has been attributed to an increase in the mobility of adatoms [77].

The same method as above was used to study nucleation on refractory metal substrates [88]. The effect of biasing pretreatment depended on the position of the substrate material in the periodic table, decreasing in the following order: IVB, VB and VIB. The nucleation density measured after 60 min increased with the heat of formation per metal atom. Thus hafnium, which has a more stable carbide than titanium, yielded a higher nucleation density than titanium. On the other hand, although silicon carbide has a heat of formation comparable to that of tungsten, it was much more effective as a substrate for diamond nucleation.

Polycrystalline diamond was deposited on Si and Mo substrates in a microwave PACVD reactor employing bias-enhanced nucleation [91]. The deposition process was subdivided into two steps: bias-enhanced nucleation and diamond growth. Between 680 and 750°C substrate temperature during pretreatment, the grain density on Si following the complete deposition cycle increased considerably with increasing substrate temperature. Continuous films formed at 770°C. Pretreatment above 770°C caused the appearance of an intense diamond plasmon at 34 eV, which is indicative of an increase in the concentration of diamond crystallites embedded in an otherwise amorphous C matrix. The same deposition parameters that gave a continuous diamond film on Si yielded only low nucleation densities on Mo. An increase in nuclei from $6 \times 10^6/\text{cm}^2$ to $2 \times 10^8/\text{cm}^2$ was achieved by raising the methane concentration in the gas phase during the pretreatment from 5 to 50% at 820°C. The C concentration in the pretreatment deposit determined by XPS also increased with increasing CH₄ concentration. From EELS analysis, the structure of the pretreatment deposit was comparable with disordered graphite or amorphous C; no diamond plasmon was observed. On the other hand, photoelectron spectroscopy showed that during biased-enhanced nucleation a molybdenum carbide interface formed,

followed by codeposition of graphitic carbon and diamond [92].

Bias pretreatment has also been applied to hot filament CVD [81,93–97]. For example, a four-step process, i.e. pretreatment, heating, bias nucleation and bias growth, was developed to enhance diamond nucleation and to grow textured (100) diamond on (100) Si [93]. In another study, application of a negative bias to a Si substrate resulted in enhanced diamond nucleation only along the edges of the Si wafer [94]. To obtain a deposit over the entire substrate, a metal wire-mesh was inserted between the filaments and the substrate to more uniformly distribute the impinging ion flux over the surface. The use of certain wire mesh sizes during biasing caused nucleation to occur in patterns. The nucleation enhancement was attributed to increased impingement of positive-charged carbon species on the substrate surface.

A hollow cathode technique was used for bias-enhanced nucleation prior to growth by HFCVD [95]. A large-area plasma above a Si substrate gave uniform nucleation even with a low bias voltage. Diamond films were deposited by conventional HFCVD after this pretreatment. Bias-enhanced nucleation of oriented diamond on Si (100) substrates using HFCVD was studied by ellipsometry [96]. A glow-discharge plasma was observed above the substrate on the Mo holder. This plasma appeared to play a critical role. Ellipsometry indicated that nucleation involved the following stages: carbonization, incubation, nucleation, nuclei growth and film growth. Biasing for too long induced twinning.

Bias-enhanced nucleation in HFCVD on single-crystal 6H-SiC substrates gave oriented diamond films [97].

3.9. Growth

Just as with nucleation, there have been many questions about growth that have interested the diamond community [9,35,44,46–48,50,51,66,76,78,98–102,146–150]. For example, what is the growth mechanism and how can one account for formation of {111} and {100} facets? What carbon-containing species are present and what are their roles in growth?

Experimental observations of smooth {100} faces with pronounced micro- and macro-steps suggest that growth on these surfaces might occur by step flow. However, the theories of {100} growth had been unable to account for these observations, and yielded {100} growth rates that did not correspond well with experimental mea-

surements. Consequently, an atomic simulation was carried out for the growth of diamond films on {110} : H and {111} : H surfaces in atmospheres containing H, H₂, CH₃ and various partial pressures of C₂H₂ [98,150]. Diamond was considered to form whenever an adsorbed C or cluster of C atoms bonded to the diamond film on neighboring sites. Atomic H stabilized the diamond phase by passivating radical sites on the growing surface and preferentially etching sp²-bonded carbon. Growth occurred by adsorption and subsequent incorporation of hydrocarbon species (primarily CH₃ and C₂H₂). Film growth rates and morphologies depended strongly on the concentration of C₂H₂ at the surface. Growth of {110} and {111} films in C₂H₂-deficient environments was controlled by the nucleation of diamond clusters on smooth faces. The {111} films grew by the flow of atomic-height steps at triangular islands on the surface, and were atomically smooth when the partial pressure of C₂H₂ was very low. These results suggested that C₂H₂ is important to growth because it controls the nucleation of growth layers. After a layer has been nucleated, the growth of a layer may be dominated by C incorporation from CH₃. Therefore, CH₃ might be responsible for the majority of growth events (e.g., at the steps bounding a growing layer), while C₂H₂ controls the growth rate by controlling layer nucleation.

It was shown experimentally [50] that C₂ is the dominant nucleation and growth species in 90–99% Ar (as described earlier for the extremely high nucleation rates observed with fullerenes). As Ar was added to the CH₄/H₂ system, the concentrations of CH₃ and C₂ changed. It was concluded that in 70–99% H₂, where the CH₃ concentration is 10¹⁴–10¹³/cm³, it is the predominant growth species. The rapid decline in CH₃ concentration as Ar was substituted for H₂, and the concomitant increase in C₂H₂, indicated that C₂H₂ becomes an important growth species in 20–70% H₂. When H₂ was decreased below 20% there was a sudden transition to nanocrystallinity, a lowered growth rate, and a 3–4 order of magnitude increase in C₂.

3.10. Quality of diamond films versus processing parameters

The criteria for quality of diamond films depend on the intended application. For example, for an abrasive coating, adherence, hardness and roughness are required. Ideally, semiconductor devices would be fabricated in a hetero-epitaxial single-crystal film on a readily available substrate

such as silicon. This has yet to be achieved, although highly oriented polycrystalline layers have resulted from biasing [31,89,93,94].

Defects within single crystal grains of CVD diamond include (111) twins, stacking faults, micro-cracks, low-angle grain boundaries and dislocations [44,102]. Vacancies and interstitial carbon are rare in as-grown material. Much of the graphitic carbon lies at grain boundaries. Common impurities are hydrogen, nitrogen, boron, silicon, tungsten, tantalum and phosphorus.

There has been considerable research on the effects of various process parameters on the quality of diamond films obtained by different techniques. For example, there seems to be a trade-off between rate and quality, but this relationship is not fully understood. Theory and experiment indicate that formation of sp^3 diamond bonds rather than sp^2 defects is favored by increasing hydrogen atom concentration and decreasing growth rate [44].

The crystallite grain size is a process-dependent parameter that determines the film surface roughness, chemical resistance and optical quality. Grains range in size from 100 Å to a few μm , and are often columnar extending through the entire film. Such a columnar structure is beneficial in tooling applications. Generally, the microstructure has a large impact on the properties of the finished film. As would be expected, the surface roughness depends on the initial nucleation density on the substrate [103], on the crystallographic orientation of the crystals relative to the surface, and on any continued nucleation on existing crystals.

A primary requirement in manufacturing diamond films is usually to promote the formation of diamond and inhibit the formation of graphite and other phases. The dependence of diamond quality and growth rate on source gas was addressed, for example, by Cassidy *et al.* [99]. To characterize the quality of diamond films by Raman spectroscopy, an empirical quality factor β was introduced, where $\beta = D/(D + ND)$, D is the diamond peak intensity, and ND is the average non-diamond peak intensity in the wavenumber range 1250–1650 cm^{-1} . Thus, β is an empirical measure of quality that ranges from 0 to 1; $\beta = 0$ when there is no detectable diamond and $\beta = 1$ when there is no detectable non-diamond carbon. They determined the influence on β of the source gas in HFCVD using methane, acetone, methanol, iso-propanol and t-butanol. Diamond did not grow from methanol. Iso-propanol gave the highest quality at a given growth rate. Ethanol and t-butanol gave similar results for both growth rate and diamond quality. At higher growth rates, the quality of diamond grown

using methane and acetone was similar and lower than that obtained using alcohols. At the lowest carbon concentrations and growth rates, the gases gave similar growth rates and Raman quality.

Kobayashi *et al.* [104] determined the dependence of diamond film quality on the source gas pressure and the voltage of the substrate during HFCVD with electron bombardment. A constant positive DC voltage of 140 V was applied to the substrate and the gas pressure was varied from 10 to 100 Torr. No diamond was synthesized under 10 Torr, while good crystallinity was obtained in the range of 30–50 Torr. When a constant gas pressure of 30 Torr was maintained in the system and the voltage applied to the substrate was varied from 0 to 140 V, the best results were obtained between 100 and 140 V. The substrate was not completely covered with diamond at 0 bias, and weak diamond peaks in the Raman spectra were obtained at 60 V.

4. NEW CHEMICAL VAPOR TRANSPORT REACTOR

Studies of the influence of acceleration should shed considerable light on the mechanisms of diamond deposition. Previous high- [158] and low-gravity experiments have shown that acceleration can have a significant influence on chemical vapor transport growth. In 1991, Regel suggested the study of the influence of high gravity on diamond film growth†. However, the prior methods for diamond CVD are unsuitable for flight experiments or for performance on our large centrifuge [140]. All require a flowing gas system for hydrogen-hydrocarbon mixtures at low pressure, with the attendant gas cylinders, flow controllers, vacuum pump, and waste gas disposal system. Many require a plasma or microwave generator.

4.1. Apparatus and technique

In 1996, we described a new closed chemical vapor transport (CVT) reactor that could deposit diamond films without continual addition of gas [105]. Graphite was used as a carbon source in the presence of hydrogen at low pressure, without a metal filament or plasma. As noted earlier, it was generally believed that one needs either a plasma or a catalytic filament in order to generate hydrogen atoms. It had been observed, for example, that tungsten ceases to catalyze the hydrogen dissociation reaction if it becomes coated with carbon [44,106]. Several years before, Spitsyn *et al.* [100,107] had grown diamond in a closed

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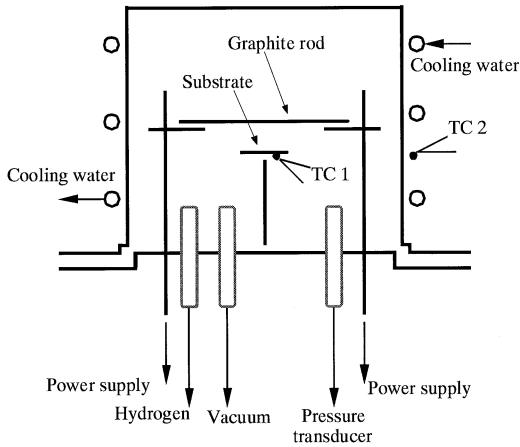


Fig. 1. First generation CVD reactor. During deposition, the hydrogen and vacuum outlets are closed.

system using a graphite rod, but only on a diamond seed. In 1991, good quality diamond was grown on diamond-scratched silicon using a microwave plasma, flowing hydrogen, and graphite as the carbon source [108]. In 1994, poor-quality material was deposited in a closed system using a DC discharge in hydrogen, with graphite used for both electrodes and the diamond-polished substrate cemented to the anode [109]. In 1995–1997, slow growth on diamond-roughened substrates was reported using a tungsten or rhenium filament with hydrogen and graphite in closed systems [110–113]. In 1998, oriented growth on silicon was achieved by first nucleating SiC during biasing in a closed chamber with tungsten filaments and a graphite carbon source in hydrogen [114].

For our new technique, we used a graphite rod at high temperature without a metal filament [1–5]. This proved to be successful, and under proper conditions could give diamond growth rates an order of magnitude larger than the $\sim 1 \mu\text{m/h}$ typical for CVD processes. An extensive series of experiments was performed in order to determine the optimal deposition conditions. These resulted in high-quality diamond on a wide variety of substrates, as demonstrated by Raman spectroscopy. The morphology ranging from isolated faceted crystals to continuous polycrystalline films. The deposits were not removed by the “scotch-tape test”.

Figure 1 shows a schematic diagram of the first generation apparatus. Basically, a graphite rod was held a few mm away from the substrate in a water-cooled stainless-steel chamber containing about 0.1 atm H_2 . The graphite rod was heated to $\sim 2000^\circ\text{C}$ by passing electric current through it. The substrate was heated by the graphite rod.

The substrate temperature was measured by a bare K-type thermocouple in contact with its back side.

Although satisfactory for testing the basic method, the first apparatus suffered from several limitations:

- Because of an inadequate cooling system for the chamber, deposition times were limited to about 45 min. By this time, the wall had become hot. If thicker deposits were desired, it was necessary to turn off the power to the heater, allow the chamber to cool, and then repeat the deposition process. This inadequate cooling also limited the size of the graphite rod and the power that could be supplied to it.
- The temperature of the graphite rod was known only approximately, and was in the neighborhood of 2200°C . Initially, the chamber had a quartz window that permitted a rough measurement of the graphite rod temperature by optical pyrometry. A calibration between heater power and temperature was obtained and optimal conditions determined for deposition on silicon. The window seal then developed a leak and had to be blanked off.
- Separate control of the substrate temperature was not possible. The substrate was heated primarily by radiation from the hot graphite rod and H atom recombination, with probably negligible contributions by convection and conduction. The temperature could be changed by changing the separation between the rod and the substrate, as well as by increasing the power to the rod. Unfortunately, changing these conditions also alters the rates of the chemical reactions as well as the transport of species to the substrate.
- The size of the chamber was small, limiting substrate sizes to about 4 cm^2 and heater rods to 2.5 cm long by 2 mm across.

Consequently, a new deposition chamber was constructed with an internal volume 2.5 times that of the first apparatus. With a water-cooled jacket, the operating time is now unlimited and the power requirement is only about 300 W. Larger graphite heaters and substrates can be used, with a substrate heater that permits independent control of the substrate temperature.

4.2. Experimental results

Several observations have been made that offer clues as to the performance of this new diamond deposition technique:

- For constant power to the graphite rod, the deposition of diamond decreased as the distance

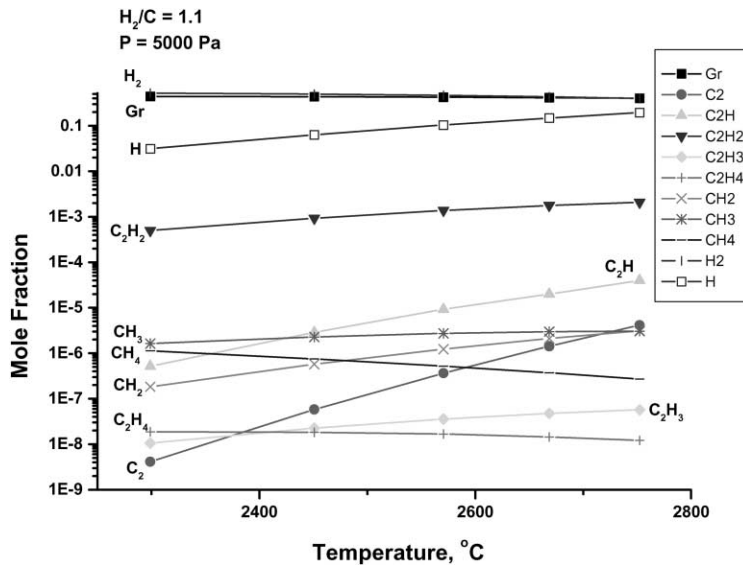


Fig. 2. Species formed at equilibrium between graphite and hydrogen, computed using FLUENT [142].

between the rod and the substrate was increased. Eventually, at large distance, only graphite deposited. Because the substrate could not be separately heated in the initial experiments, its temperature decreased as its distance from the heater increased. Consequently, a standard distance of 3 mm was used for most experiments. The optimal substrate temperature depended on the substrate used.

- The hydrogen gas pressure for optimal performance depended on the substrate, and ranged between 20 and 100 Torr.
- Deposition was obtained on fused silica using essentially the same conditions that gave no deposition on oxidized silicon when most of the surface was covered with a pattern of copper, on which deposition occurred readily [3].
- Somewhat better deposition was obtained with the substrate located below the graphite than with the substrate above the graphite.
- Centrifugation of the chamber at a total acceleration of twice earth's gravity ($2g$) caused a notable increase in nucleation density, growth rate, and area covered.
- Holding all other parameters fixed, use of a larger volume chamber decreased the amount of deposition.

4.3. Modeling

We examined the literature for interactions of hydrogen with graphite. Calculations of chemical equilibrium were also performed using FLUENT [142]. Figure 2 shows that under the hydrogen

pressure and graphite temperature used in our experiments, C_2H_2 is the predominant hydrocarbon species equilibrium [115–118]. About 1/10 of the H_2 is dissociated into atomic H [119]. Although many studies have been performed to measure the reaction products between hydrogen and graphite experimentally [120–131], the definitive study was performed by Balooch and Olander [120]. They used a modulated molecular beam with pyrolytic graphite. Up to 2200 K, H_2 neither dissociated on the graphite surface nor reacted with it. (This result was confirmed recently [122].) In subsequent experiments, a beam containing atomic hydrogen was used. For surface temperatures up to 800 K, only CH_4 was produced. Between 800 and 1000 K, H recombined to H_2 but no hydrocarbons formed. From 1000 and 2200 K, C_2H_2 was the sole product.

In the traditional hot filament CVD process the gas composition at the filament is believed to be near equilibrium [44]. For hydrocarbon species, “the equilibrium composition provides a rough first approximation to the actual composition”. If the initial mixture is 0.5% methane in hydrogen at 20 Torr, the primary species between 2000 and 2500 K at equilibrium are H_2 , H, C_2H_2 , CH_4 and CH_3 [44,132]. However, since there is little homogeneous recombination of hydrogen atoms, they are present in greater than equilibrium concentration between the filament and the substrate. With such super-equilibrium H concentrations, several other low molecular weight carbon-containing species are also expected in the ppm range at 2500 K. The following species were detected above a growing diamond film by a variety of optical techniques and

by mass spectrometry: H, C₂H₂, C₂H₄, CH₃ and C₃ [65,133–139]. As noted earlier, graphite is much less effective than tungsten at catalyzing chemical reactions, so that we cannot expect these conditions to prevail in our new technique.

We used FLUENT [142] to model numerically the heat transfer and buoyancy-driven convection in our cell, neglecting chemical reactions and assuming only H₂ was present in the gas. As would be expected at these temperatures and pressures, convection had little effect on the temperature field. As shown in Fig. 3, the gas flowed upward around the heated rod and substrate, and downward near the cooled wall. The Grashof number in the chamber was on the order of 0.005, the Reynolds number 0.3 and the Peclet number for mass transfer 0.2. The flow velocities between the graphite rod and the substrate were about three orders of magnitude smaller. Simulation of the process with centrifugation yield the same convection pattern, but with velocities proportional to the total acceleration (as would be expected for such low flow rates). There was no evidence of circulation due to the Coriolis effect as observed in directional solidification [153–157].

5. CONCLUSIONS

From our experimental observations, literature review, and FLUENT modeling we have formed the following preliminary picture of the deposition process. Hydrogen atoms form in the hot gas surrounding the graphite rod. This atomic hydrogen reacts with the graphite to produce acetylene, which reacts further with the surrounding hot gas to produce other hydrocarbons. The convection serves to remove the hydrocarbons from the neighborhood of the graphite rod and gently mixes the gas in the chamber. The hydrocarbons diffuse into the gap between the rod and the substrate, where the atomic hydrogen concentration may be near equilibrium. The hydrocarbon concentration in the cell and at the substrate surface gradually increases until it is sufficient to nucleate diamond on the substrate. The subsequent growth of diamond consumes hydrocarbons, decreasing the hydrocarbon concentration at the substrate surface so that nucleation decreases and finally stops. Eventually, a steady state is reached between production of acetylene at the surface of the hot graphite and deposition of diamond. Thus, one advantage of this new technique is that the concentrations of reactants at the substrate surface tend to be self regulating — they automatically adjust to the levels required for nucleation and then growth. The traditional CVD

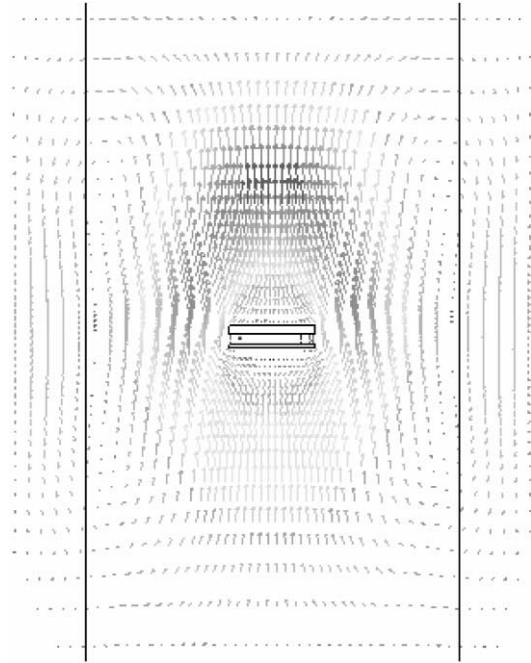


Fig. 3. Velocity field during deposition. Computed using FLUENT for hydrogen with buoyancy-driven convection. The vertical lines are an artifact of the output and should be ignored.

processes have a flowing gas of fixed composition with rapid generation of growth species that are fixed in concentration during the nucleation and growth processes. Thus, if the reactant concentration is high enough to cause massive nucleation, it will be too high to yield high-quality diamond growth. Consequently, the methane concentration is held deliberately low in the traditional processes in order to yield good diamonds, resulting in low nucleation and growth rates.

The increased nucleation and deposition caused by centrifugation is attributed to an increase in mass transfer rates due to increased convection, enhancing the removal of acetylene from the graphite rod and its transport to the substrate surface. Use of a larger chamber lowers the hydrocarbon concentration for a given acetylene generation rate during the transient phase. The preferential deposition on the copper pattern on silica occurred because once diamond nucleated on the copper, the hydrocarbon concentration dropped and was too small to nucleate on silica. On the other hand, in the absence of the copper the hydrocarbon concentration increased until it was sufficient to nucleate diamond on the silica.

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