# Laser Diagnostics of CVD Diamond Film Growth

by Charles S. Feigerle and Robert W. Shaw

Snapshot:
Feigerle and Shaw describe the critical role played by laser spectroscopy in assessing diamond film growth.

Scanning electron micrograph of a diamond film grown by chemical vapor deposition

iamond has one of the most exciting combinations of properties known.[1] It is the hardest material known, has extremely high thermal conductivity, wide optical transparency, and a durability that is unmatched by other substances. The scarcity and high cost of natural diamond has precluded its use in many potential applications that would benefit from this unique combination of properties. Over the last two decades, the technique of chemical vapor deposition (CVD) of diamond at low pressure has been developed, providing the technology to produce thin and thick film coatings on a variety of materials as well as freestanding films and plates of diamond. High optical clarity diamond plates grown by the CVD method are now available in diameters that exceed that of the largest natural diamond ever found. Products spanning from diamond coated machine tooling to semiconducting diamond-based electronics have been developed using this technology. Recent estimates suggest that the global market for chemical vapor deposited diamond and diamond-like carbon films will reach $1 billion by 2000.

Laser diagnostics of diamond film growth have played an important role in the development of diamond film technology. Raman spectroscopy is widely used to verify that diamond has in fact been produced by the process and to assess the quality of the films produced.[2] Various laser-based spectroscopies have been used to probe the environment of diamond growth reactors and to characterize the chemical and physical conditions that are necessary for diamond growth.[3] Through these studies a better understanding is being developed not
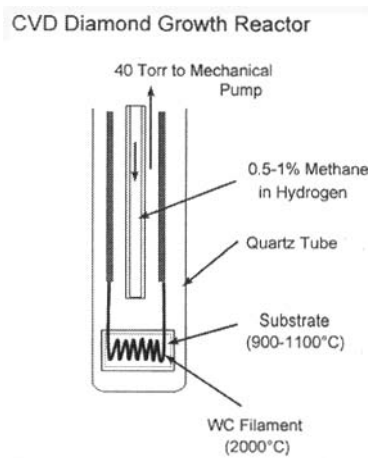
only of why certain conditions are necessary for growth but also of what the potential is for extending growth conditions to new regimes that will allow coatings to be applied to a wider range of materials.

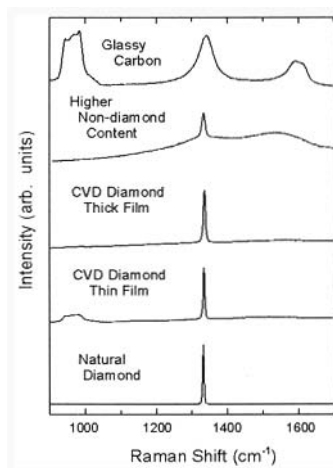CVD of diamond can be achieved by a variety of methods including hot filament, microwave plasma, plasma torch, and oxyacetylene flame deposition.[4] A key feature of all of these is that they produce reactive carbon-containing species for growth and an ability to tune the conditions to produce a selectivity for diamond growth over the more thermodynamically stable form of carbon, graphite. Diamond and graphite are fundamentally different in the way that carbon atoms are bonded together in the two materials. In diamond, each carbon atom is bonded using $sp^3$ hybrid orbitals to four surrounding carbons in a tetrahedral arrangement, forming an extremely strong three-dimensional network solid. Each carbon atom is saturated in that it is involved in four single bonds, the maximum typically possible for carbon. In graphite, the carbons are unsaturated since each carbon atom bonds via $sp^2$ hybrid orbitals to only three carbons to form planes of connected hexagonal carbon rings. During CVD diamond film growth, a delicate balance needs to be struck between maintaining saturated bonding at the surface to minimize formation of graphite and production of unsaturated active sites for carbon addition. Laser spectroscopic studies of diamond growth have provided insight into how that balance is achieved.

A hot filament reactor is one of the simplest systems for growing diamond films and for illustrating some of the principles involved. Figure 1 shows a schematic of a hot filament reactor built around a quartz tube body. Typically a tungsten filament is resistively heated to a temperature between 2000–2800 K in around 40 Torr of a dilute (~1%) gas mixture of $CH_4$ in $H_2$. The filament is typically spaced 5–10 mm from the substrate



**CVD Diamond Growth Reactor**

40 Torr to Mechanical Pump

0.5-1% Methane in Hydrogen

Quartz Tube
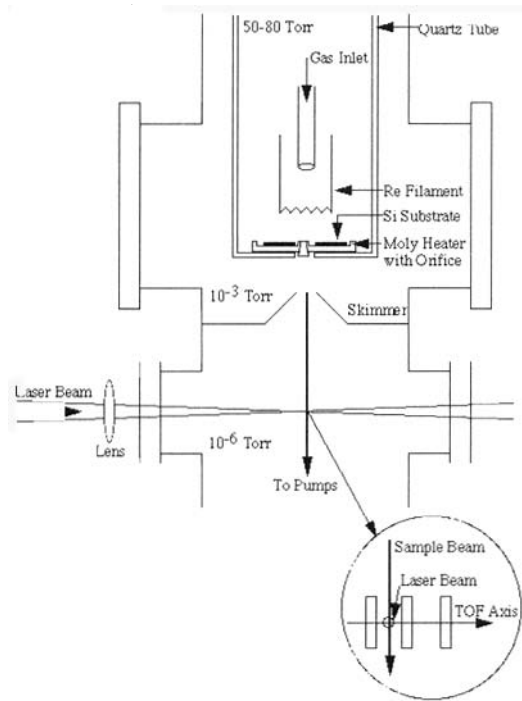
Substrate (900-1100°C)

WC Filament (2000°C)

**Figure 1.** A simple hot filament CVD diamond growth reactor base upon a quartz tube container. Here the substrate is indirectly heated by the carburized tungsten filament that also activates the gases.



Glassy Carbon

Higher Non-diamond Content

CVD Diamond Thick Film

CVD Diamond Thin Film

Natural Diamond

Intensity (arb. units)

Raman Shift (cm⁻¹)

1000    1200    1400    1600

**Figure 2.** A comparison of Raman spectra recorded from a single crystal (natural) diamond and various CVD grown samples. The thick and thin film CVD diamond samples exhibit virtually no Raman scattering intensity between 1500-1600 cm⁻¹ indicating very little graphitic contamination in these films.

that can be indirectly heated by the filament or, if the reactor is so equipped, directly heated by an independent substrate heater. The substrate is typically maintained at a temperature of 900–1200 K, though diamond growth at temperatures less than 210 °C has been reported.[5] The chemistry that takes place within the reactor has been studied by numerous laser techniques. The results of these investigations, combined with the efforts at modeling the chemical processes, have allowed some of the key chemical species typically present during diamond film growth to be identified and their roles to be determined.



**Figure 3.** Schematic of an apparatus where gases in a diamond growth reactor are sampled through an orifice in the substrate and their chemical composition analyzed using laser ionization mass spectrometry.

## Raman spectroscopy of diamond films

The Raman spectrum of diamond is dominated by the first order phonon band that appears as a strong sharp line at 1332 cm$^{-1}$. This contrasts with single crystal graphite, where the first order phonon band appears in the Raman spectrum as a sharp intense line at 1580 cm$^{-1}$. Polycrystalline graphite and other forms of non-crystalline carbon also exhibit peaks in the 1550–1590 cm$^{-1}$ region and an additional band around 1340–1360 cm$^{-1}$. The linewidth and intensity ratio of these two features vary with the type of carbon, and the linewidths become very wide for highly disordered carbons such as coke and charcoal.[2] The observation of a sharp peak near 1332 cm$^{-1}$ in the Raman spectrum is thus a good diagnostic for whether diamond is present in a CVD film. The intensity of this peak can be used as a measure of film thickness, and the linewidth and shifts of the peak relative to single crystal diamond can be used as a measure of the disorder and stress in the film.[6] The ratio of the intensity of the diamond peak to the intensity in the 1500–1600 cm$^{-1}$ region is also useful as a sensitive measure of the relative amounts of sp$^3$ (diamond) to sp$^2$ (graphitic) carbon in the film.[7] The Raman spectrum is a particularly sensitive indicator of graphitic contaminants since the cross section for Raman scattering is about 50 times that of diamond. CVD diamond films can now be grown where, in spite of the increased sensitivity for detection of graphitic carbon, the Raman spectrum exhibits a single sharp peak near 1332 cm$^{-1}$ and a flat baseline across the sp$^2$ carbon region. The use of a Raman spectrometer with a microscope attachment can allow spatial resolution to be combined with the spectral selectivity afforded by the Raman technique.

Modern micro-Raman systems frequently employ confocal imaging that can provide vertical and lateral spatial resolutions of down to 1 μm. This resolution approaches that needed to observe the microstructural detail to CVD diamond films that is evident in scanning electron micrograph images.

Figure 2 compares the Raman spectrum of natural single crystal diamond with spectra of CVD diamond films and glassy carbon grown on silicon substrates. The square shaped peak around 1000 cm$^{-1}$ is the second order phonon band of silicon, which is observed in the spectra of very thin (<10 μm) films. These spectra were obtained at 514.5 nm excitation using a micro-Raman spectrometer with the confocal aperture set to yield about 8 μm spatial resolution. As the film thickness starts to exceed this, signal

from the silicon substrate disappears when the laser is focused at the surface of the film. The broad feature that is evident in the spectrum labeled as having a higher non-diamond content is part of a more extensive photoluminescence background that grows with increased incorporation of nondiamond defects in the film.[7] Photoluminescence can also appear as well-resolved albeit broad peaks in the Raman spectrum. Photo-luminescence peaks are easily distinguished as distinct from vibrational Raman lines since the Raman shift for photoluminescence changes with excitation wavelength. Many of the diamond luminescence peaks have been identified with specific defects in the crystal.[8] For example, a luminescence peak at 2.156 eV is believed to involve a nitrogen atom in association with a vacancy and the observation of this luminescence peak can be an indication of an air leak in the growth reactor.

Raman spectroscopy is such a good analysis tool for diamond film growth that it has frequently been suggested as an *in situ* diagnostic for process control. This is a more demanding application because of interferences from photons generated by thermal or plasma emission. *In situ* Raman spectroscopy of diamond film growth has now been demonstrated for a variety of growth reactors by use of pulsed lasers and gated detection to reduce the effects of this interference.[9,10] While initially these involved the 532 nm and 355 nm harmonics of a Nd:YAG laser, improvements in sensitivity should be possible by operating further in the ultraviolet.[11]

## Laser spectroscopy of diamond reactor growth environments

Laser spectroscopy can be extremely useful for the study of diamond reactor growth environments as a result of the chemical specificity and spatial selectivity that it can provide. It can be used to directly probe concentrations of not only stable species but the reactive free radicals such as H and $CH_3$ that are key for diamond film growth. It is useful to separate the discussion of the chemistry that is involved in diamond growth into two categories, processes that have oxygen as part of the feed gases and those that do not. In normal operation of a hot filament reactor, a gas mixture of around 1% $CH_4$ in $H_2$ is used. The filament effectively dissociates hydrogen molecules into hydrogen atoms, initiating a sequence of radical abstraction and condensation reactions. Under typical growth conditions, hydrogen atoms are present at the largest concentration next to molecular hydrogen. Hydrogen atoms play many roles in the growth process,[12] including:



**Figure 4.** An energy level schematic showing the resonance enhanced multiphoton ionization scheme used to detect atomic hydrogen and a block diagaram of the laser system that generates the 243 nm light for this process.

■ as initiator of hydrogen abstraction reactions with methane and its products to produce active carbon growth species in the gas phase;
■ as surface terminator that stabilizes the diamond surface and prevents conversion to graphite;
■ as a hydrogen abstraction reactant at the surface to produce active sites for addition; and
■ as an etchant that reactants to volatilize graphitic carbon from the substrate surface.

They also play similar roles at the filament surface where the hydrogen helps clean the filament (typically tungsten) and prevent it from becoming poisoned by carbon.

Laser spectroscopic detection of ground state hydrogen atoms typically involves some sort of multiphoton excitation as a result of the large energy separation between its ground and excited electronic states. Two-photon laser-induced fluorescence detection of hydrogen atoms can be achieved using two 205 nm photons to excite the $n = 1 \rightarrow 3$ transition with detection of subsequent fluorescence to the $n = 2$ state at 656 nm.[13] The 1s $\rightarrow$ 2p excitation can be achieved using three equal 364.7 nm photons simultaneously. Absorption of an additional 364.7 nm photon ionizes the atom in a (3+1) multiphoton ionization (MPI) process to form $H^+$ and an electron, either of which can be detected by a suitably biased electrode.[14] The laser intensities that are used to produce three photon excitation are also sufficient to produce third harmonic generation (THG), where the three excitation photons are combined to form a VUV photon at a third their wavelength.[15] The phase matching condition for THG requires that the excitation occur in a region of negative dispersion in the frequency dependence of the index of refraction; this occurs to the short wavelength side of the resonant absorption. Third harmonic light can be generated over a range of wavelengths up to Lyman-α (the 1s:2p transition)and, conveniently, the shift in the peak energy of the THG distribution relative to the Lyman-α transition frequency is directly proportional to the hydrogen atom concentration. Measurements of THG using focused lasers can therefore provide a spatially resolved determination of the hydrogen atom concentration within a reactor.[15]

A great deal has been learned about the hydrogen atom chemistry that takes place within a hot filament reactor from these[15] and related studies. 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. Below 100 Torr operating pressure, the hydrogen atom concentration (*i.e.*, [H]) decays away from the filament in a diffusion-controlled manner. Direct
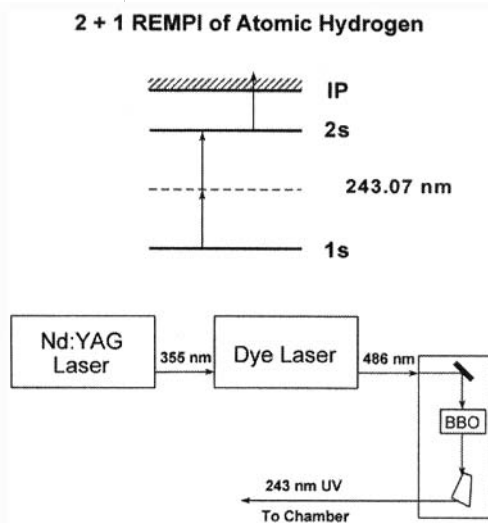
recombination of atomic hydrogen to molecular hydrogen in the gas phase does not significantly affect the [H] at these pressures. However, recombination of hydrogen at the film surface is an important process both for generating active sites for carbon addition and as a source of heat transport to the substrate. Interrogating the surface and near surface concentrations presents one of the more difficult challenges for laser spectroscopy. THG and laser-induced fluorescence have been used to measure the [H] to within about 0.25 mm from the surface before it begins to interfere with the beams. Orifice sampling (see Fig. 3, page 25) provides an alternative method for interrogating the gases even closer to the surface.[16] In orifice sampling a small aperture is inserted into the substrate allowing reactor gases from near the surface to flow through the orifice into a differentially pumped mass spectrometer. In this manner a sampling depth approximately equal to the orifice diameter is achieved. The spectral selectivity of laser spectroscopy can be added to this technique by use of resonance-enhanced multiphoton ionization (REMPI) to ionize the gases for mass analysis. A schematic apparatus for ultraviolet generation and an energy level diagram for hydrogen atom (2+1) REMPI are shown in Figure 4. Using a 200-$\mu$m orifice and 243.1 nm light to produce (2+1) REMPI through the 2s state of hydrogen, this system has been used to study the substrate temperature dependence of the [H] over a range of temperatures spanning where diamond growth occurs.[17] The [H] is seen to decrease significantly with higher temperatures, corresponding to an increase in the rate of hydrogen recombination at the surface. It is well known that the substrate temperature strongly affects growth rate and film quality, and here laser spectroscopy has implicated hydrogen with these changes.

Methyl radical has also been studied by various laser spectroscopies. It was first detected during filament-assisted growth of diamond by infrared diode laser absorption spectroscopy of the $v_2$ vibrational band.[18] The (2+1) REMPI band at 333.5 nm provided better S/N and allowed the dependence of the [CH$_3$] on the distance from the filament and on filament and substrate temperature to be studied.[19] More recently, cavity ring down spectroscopy at 213.9 nm has been used[20] to measure the radial distribution of the [CH$_3$]away from the filament. These measurements show that the [CH$_3$] initially grows with increasing distance from the filament, reaches a maximum, and then drops off at further distance. This is inconsistent with catalytic formation of CH$_3$ at the filament surface, adding support to the theory that CH$_3$ is formed by hydrogen abstraction from methane in the gas phase. Evidence continues to mount for assigning methyl radical as a key diamond growth species, though C$_2$H$_2$ may also contribute to growth.

Laser spectroscopy has shown that other carbon species such as C, CH, and $C_2$ are also present to a varying degree, depending on the reactor type and conditions. Reactors like the plasma torch that can produce significantly higher gas temperatures may involve these as growth species to a higher degree.

Oxygen is frequently added to the gas mixture in microwave plasma depositions to improve the growth rates and film quality, and to allow depositions to be performed at lower substrate temperature. Similar effects have been shown recently in filament-assisted CVD of diamond using lower oxygen concentrations, with the added benefit that low filament temperatures can also be used.[21] There have been various propositions for how oxygen modifies the chemistry of diamond growth to achieve these benefits. The hydroxyl radical is formed at high temperatures and the spatial dependance and temperature of this species has been studied using laser-induced fluorescence. The possibility that OH is important for growth continues to be debated. At lower temperatures, equilibrium calculations predict OH to be too low to be significant and indicate that the major oxygen containing species are CO and $H_2O$. It has been suggested that water may play an important role in diamond film growth at low temperatures.[22] Laser spectroscopy studies are again expected to yield important data on whether this most common of substances may be key for low temperature growth.

## The future of laser diagnostics in diamond growth

While much has been learned of the relationship between growth conditions, growth chemistry, and diamond film quality, aspects of the mechanism for diamond film growth require further clarification. It appears now that just as there are different types of growth reactors, there is more than one regime for growth parameters. Low temperature growth would appear to be influenced by different chemistry than conventional growth, and high temperature and high flux growth may involve new species as well. Laser spectroscopy can provide the spatial and chemical selectivity to help clarify these differences. Because growth additives, either as enhancements or as dopants, present new perturbations on the chemistry, laser spectroscopy will again be crucial in sorting out the details. As the new diamond technology moves inevitably forward from the discovery phase that has dominated the past 20 years to development of the myriad products that have already begun to emerge, the future would appear to be in process control. Methods like THG, laser-induced fluorescence, and coherent anti-Stokes Raman spectroscopy (CARS) hold potential as *in situ* non-intrusive probes of the chemistry taking place in the diamond growth reactor. Ideally, one would want to monitor the surface directly, but laser surface spectroscopies of diamond have been the slowest to develop and the surface chemistry involved in diamond growth continues to be one of the least understood aspects of the process. Surface sum frequency generation has successfully been performed on single crystal diamond,[23] but the laser technology needed to perform these experiments is very demanding. It is expected as the laser technology develops further, it will open up the new frontier of laser surface spectroscopy of diamond film growth.

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