

Growing Large Crystals of Diamonds

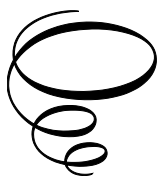
Growing Large Crystals of Diamonds:

*A Path to Gems and Other
Applications*

By

Devi Shanker Misra

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Dedicated to All CVD Diamond Researchers

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INTRODUCTION

Diamonds are not new to Indians; we have dealt with them for centuries. In '*Arthashatsra*' a classic book on politics and economics around two millenniums ago, a chapter is devoted to the '*ratna-pariksha*' meaning 'testing the gemstones'. It was common practice to train the treasurers of the kingdoms in this trait. In the current book we discuss the recent progress in the growth of single crystal diamonds by microwave plasma chemical vapor deposition (MPCVD) and their potential applications. Currently chemical vapor deposition (CVD) diamond gems are all the rage in some countries. Both the quality and size of CVD gem diamonds have grown by leaps and bounds over the last ten years. In the following chapters, we discuss the diamond growth by MPCVD and the current state of the art of their application as gems, radiation sensors, anvils and others.

In chapter one, a brief discussion of mined and CVD diamonds is presented. The basic components of MPCVD technique in chapter two; we discuss how various CVD methods require dissociating molecular hydrogen into atomic hydrogen and activating the source hydrocarbon gases, resulting in a complex mixture of hydrocarbons and reactive carbon-containing methyl [CH_3] units. Most preferred energy sources for dissociating the molecular hydrogen and hydrocarbon gases are microwave energy or a hot Tungsten filament. The Tungsten filament is kept at a temperature of about 2300 K. A high substrate temperature (in the range 800–1200°C), single crystal diamond substrates and carbon-containing gas, preferably methane in excess of hydrogen are the essential requirements of growing single crystal diamonds for various applications including gems. Among all the CVD diamond technologies, MPCVD has been widely used and is a dominant method for high-quality diamond growth today. Although, a significant amount of information about the results of the reaction kinetics of CVD growth and complex gaseous and surface processes were obtained from measurements using the hot filament CVD, low growth rates and incorporation of filament materials during diamond growth make hot filament-activated CVD methods inadequate for production of high-purity

single crystal diamonds for commercial purposes. And for this reason, chapter 2 is devoted to discussing the MPCVD method, and the role of experimental input parameters such as pressure, temperature, feed gas composition and their measurements.

After discussion on the different parts and operations of MPCVD systems, we enlist various deposition parameters such as pressure, temperature, microwave power density, plotting of substrates, design of the moly holder, and stage, etc. and the effects they have on the growth rates and quality of the grown diamonds. The applications of CVD single crystal diamonds in tools, high pressure anvils and radiation detectors, are discussed. Single crystal diamonds are natural candidates for dosimetry and radiation detectors due to their large charge carrier mobility at room temperature and the high radiation resistance. Nitrogen vacancy center (N-V center) is a prime candidate for the detection of the electron spin and magnetic field associated with it. As a result, quantum sensing of magnetic field is an application of CVD diamond becoming important recently.

We present the descriptions of special substrate holders used by various groups to increase the growth rates of single crystal CVD diamonds in chapter 3. A review of the impact of the CH_4 percentage and growth pressure on the growth rate is presented in chapter 4. The presence of nitrogen in the growth atmosphere while in general increasing the growth rate, deteriorates the quality of the diamonds significantly. Nitrogen leads to point defects as well as the nitrogen vacancy centers in the CVD diamond. The role of oxygen has been widely studied on the growth rate and the quality of the grown diamonds and it is reported that it improves the quality. In some cases, halogen and other chemistries are added. These additional gases do not alter the basic mechanism of diamond growth, but they can influence the quality of diamonds as they perturb the chemical kinetics of hydrogen and hydrocarbon and the activation of the sites for the diamond growth.

Currently, the quality of grown diamonds has improved to such an extent that it is almost impossible to differentiate them from mined diamonds through visual examination alone. This is because grown diamonds are real diamonds, having identical chemical and physical properties as mined

diamonds. However, there are spectroscopic fingerprints and features that can be used to distinguish the grown diamonds from the mined ones. These fingerprints can be easily marked by the skilled gemmologists in gemological laboratories with sophisticated equipment. In chapter 5, we will summarize the origin of color/tinge in CVD diamonds. Another category of materials called “diamond simulants” are commonplace in the gem market and these are continuously being presented as “real diamonds” to consumers. Factually, “diamond simulants” are not diamonds in any physical or chemical sense. They have different chemical bonding as well as atomic and crystallographic structures. We present a clear set of distinctions between mined and grown diamonds vs. “diamond simulants” in chapter 6 and have identified a few of these materials. It is a misconception that “grown diamonds” are bracketed with “diamond simulants”. It is, therefore, very important to inform the public and public offices in a transparent manner of the distinction between mined and grown diamonds vs. diamond simulants. While having methods of detection is important to safeguard consumers, a broader level of cooperation is needed within the mined diamond industry, diamond growing companies, traders, government and semi-government bodies, and the supply to relay technically accurate information about diamonds to consumers.

The applications of diamonds in the gem sector are obviously apparent and will be touched upon in chapters 4 and 5. Other applications of CVD diamonds are discussed in chapters 3 and 5. The CVD process is of extreme importance for diamond gem production as it is sustainable and does not have negative elements associated with mining. Also, CVD diamond gems are as scintillating and brilliant as the mined ones, with the same characteristics and longevity. The long-term implications for CVD diamonds as gems are astounding. Not only are CVD diamonds as gems important for the entire chain of trade, but there are also far-reaching implications for research and development in diamond growth for scientific applications. One important aspect of the CVD single crystal growth is the ability to grow large crystals without interruptions. The technical difficulties associated with the growth of large single crystals are discussed in chapter 4. It is of critical importance to resolve these technical issues to grow larger crystals of CVD diamond without interruptions in the growth process. This

would result in many more technological and scientific innovations and applications of CVD diamonds.

Chapter 4 describes the presence of stress in CVD diamond gems and its influence on the applications of gems. A high amount of stress present in CVD diamonds originates from structural defects such as dislocations and nitrogen impurities. The dislocations in CVD diamonds are present due to defects on substrates or seeds and can propagate into the growth. As the thickness of the CVD diamond increases, these defects fan out in an angular spread typically up to 30–40 degrees, depending on the thickness. Cross-polarized microscopy and X-ray topography are two important techniques that can be used to measure stress in a CVD diamond. A detrimental effect of the presence of stress is the cracking of the CVD diamond when laser cut. Often it is found that a feather that is already present in the grown CVD diamond can extend further or become bigger. Stress measurement is, therefore, an important aspect. The characteristics required for various applications are discussed in Chapter 5.

The appendix at the end of the book introduces the topic of diamond simulants and other diamond-like materials, which are different atomically and structurally from diamonds, yet have been created in a lab or mined to give the same brilliance as diamonds when used in a piece of jewelry. The unavailability of an alternative source of diamonds created a vacuum in which several crystals with similar optical properties as a diamond were panned out to customers as “artificial diamonds”. Zirconia (Zr_2O_3), silicon carbide, and quartz are some of the single crystals that have been offered as alternatives to diamonds in a piece of jewelry. However, these materials do not have the strength, hardness or inertness of diamonds and only imitate their brilliance. Some of the salient features of the other applications of CVD diamonds are discussed in the appendix.

I hope that the topics presented here will not only stimulate our readers but also help them to better understand CVD diamonds and their future.

CHAPTER 1

DIAMONDS

Mined Diamonds

Diamonds have been known to mankind for centuries and millenniums. Many have survived hundreds, if not thousands, of years the prime examples being the Koh-i-Noor and Darya-i-Noor diamonds which are believed to have originated in famous Golconda mines in Southern part of India. The diamonds once formed are indestructible due to their strength and inert nature. The only way a diamond can be destroyed completely is by burning it in air (read Oxygen) at a temperature greater than 600 °C. There are no liquids which can dissolve or even touch diamonds because of their inertness and bond strength. The fire and brilliance of diamonds is sourced from the unusually high refractive index and its facets which allow visible light to enter at a certain angle and the light is totally internally refracted. In addition, the purity of the diamond crystals plays a part in its brilliance.

A diamond is a transparent crystalline mineral made of pure carbon (Davies 1984). This was first shown by burning diamond in the air. The diamond crystals are 99.99% pure carbon with only some minuscule atomic impurities of other elements and minerals. Diamond is the only gem made with a single element; all others are compound of multiple elements. The carbon atoms inside a diamond crystal are bonded in strong covalent bonds in which each carbon atom is connected to four other carbon atoms. The length of the C-C bond in a diamond is 1.54 Å and each carbon atom is short of four electrons to complete its second orbit. Due to this particular electronic arrangement and bonding, a diamond has maximum cohesive energy of 7.6 eV per pair of carbon atoms, which is the highest among all solids that form a diamond structure. Such a high value of cohesive energy means that the diamond is an extremely strong solid. This gives rise to unique properties in a diamond. It is the hardest material known to mankind

and has the highest thermal conductivity (Burgemeister 1978), longevity, and inertness among other properties. The high melting temperature of a diamond makes it resistant to all kinds of harsh conditions such as acidic and alkaline environments, including high-energy ion bombardment. This makes the diamond especially useful for space applications, and several spacecrafts and space probes have diamond windows as mandatory requirements. A diamond window was used in Pioneer space probe sent from USA into space. Diamond windows are a very popular material for high power lasers. Diamonds are also excellent materials for designing anvils to achieve unprecedented levels of pressure in the laboratory. The pressures equivalent to those present at the core of the earth are achievable. The purity requirements of diamond for the application of anvils are very stringent. In addition, diamonds are perceived as the ultimate symbol of purity, indomitable brilliance, and commitment for eternal love, thus have been treasured for centuries by empires all over the world. For scientists and engineers, diamonds are an extraordinary material because of their superlative physical, mechanical, thermal, optical, and electrical properties that originate due to an extremely rigid lattice created because of strong covalent bonding between carbon atoms. These technically superior properties of a diamond can support a wide range of commercial and scientific applications,

Diamond crystals are formed when a carbon atom is bonded to four other carbon atoms in a repeating process. A carat of diamond is made of billions and billions of carbon atoms bonded together in a periodic structure. The diamonds are formed in the Earth's mantle whose depth varies from approximately 70 km below the surface to about 2900 km below the surface, respectively. The temperature and pressure in this zone of depth are suitable for diamonds to form and remain stable. Once formed the diamonds remain stable until they are exposed to lower pressure. The diamonds are rapidly brought to the surface by volcanic eruptions that eventually develop into diamond mines (called Kimberlites and Lamproites). If diamonds travel under the Earth's surface for too long or are brought to the surface too slowly, they will turn into graphite along the way, as graphite is a more stable form of carbon in an atmospheric environment.

Diamonds in stars

Diamonds can also be formed in outer space when asteroids collide (Lewis et al. 1987, Garai et al. 2006). The impact from asteroid collisions creates shock zones of high pressure and temperature that is enough to generate conducive conditions for carbon atoms to form the diamond structure into tiny diamond fragments. They are nanometer to micron sizes. The rock fragments found in a meteorite that fell into the Earth's atmosphere over the Nubian Desert in Sudan contained diamonds that were tens to a few hundreds of micrometers in size. These diamonds were too big to be created by impact from asteroid collisions. Scientific evidence indicates that these tiny diamonds were part of a larger one and existed long before the planets had settled in their orbits. Recently, scientists also discovered a White Dwarf star, composed mostly of carbon and oxygen, which is believed to have diamond cores (Boser 2008, Miyahara et al. 2015). The cores of such white dwarfs may have diamonds which are extremely pure and brilliant, but we can only speculate. Shock wave and detonation techniques of diamond powder manufacturing are based on the principle described above (Decarli 2011). Shock waves can generate high pressure and detonation high temperature required for the carbon atoms to form covalent network of *sp*³ bonded structure. The limitation of this method is that the diamond particles of only very small (mostly nanometer sizes) can be produced and have limited applications of seeding and abrasive purposes. The technique is used commonly to manufacture diamond powders with particle sizes of nanometers.

CVD diamonds

A method of growing single crystal diamonds was initiated by William G. Eversole at Union Carbide Corporation in 1952. The diamonds were grown on diamond seeds from carbon-containing gases by means of a slow and complex process using a low-pressure chemical vapor deposition (CVD) method. Further work in the CVD process was done by John C. Angus at Case Western Reserve University (USA) in the 1960s (Angus 1968, 1998). Meanwhile, a research group at Physical Chemistry Institute in Moscow, led by Boris Derjaguin (Derjaguin et al. 1968, 1976), explored diamond growth from hydrocarbons using the CVD process. The Russian group was

the first to grow small diamond crystals on non-diamond substrates in 1976 by mixing a large component of the hydrogen in the gas mix used for diamond growth. Russian group established that the large concentration of atomic hydrogen (H_2) is essential in the reaction chamber to grow diamonds.

A major achievement in the development of the CVD process for diamond growth originated from the National Institute for Research in Inorganic Materials (NIRIM), Tsukuba, Japan. The group, led by Nobuo Setaka in 1982, confirmed the activated low-pressure diamond growth from the vapor phase initiated by Derjaguin. Using the CVD process to activate methane/hydrogen gas mixtures, diamond growth rates of up to $1.0 \mu\text{m/hr}$ were successfully reported (Matsumoto et al. 1982, 1987, Setaka 1989). The critical contribution from the NIRIM group was the use of Microwave Plasma Chemical Vapor Deposition (MPCVD) process which produces atomic hydrogen much more efficiently than compared to the other techniques. With the advent of MPCVD technique, other methods such as RF assisted CVD, arc discharge and oxy-acetylene methods were relegated in the background. In MPCVD technique not only atomic hydrogen was produced efficiently, but there was also no need to use a substrate heater separately. The hydrogen and methane plasma were enough to heat the substrate holder to the required temperatures. Following this work from NIRIM group, the skepticism about the method of activated low-pressure diamond growth from the vapor phase, which was considered thermodynamically impossible at that time (Spear 1987, Wang 2011), disappeared (Bachmann et al. 1991). The clear understanding of the role of atomic hydrogen in suppressing the nucleation and growth of graphite and its role in stabilizing and preparing the diamond surface for the next growth cycle prompted numerous CVD diamond growth research programs worldwide (Bachmann and EnkeVort 1992, Goodwin et al. 1998, Thorsheim and Butler 1994).

Evolution of CVD Diamonds

Driven by the superb achievements of pioneering CVD researchers (Goodwin et al. 1998, Thorsheim and Butler 1994, Angus 2014) and the superlative properties of diamonds (Burgemeister 1978), a floodgate of research activities started in the CVD growth of diamonds in the late 1990s

(Matsui et al. 1989, Gracio et al. 2010). The research and development continued because of the belief of the scientists that it will be possible to grow single crystal diamonds of large sizes one day and more so because the diamond promises to be an excellent high temperature semiconductor and has highest thermal conductivity. It was only after decades of experimental and theoretical research that it is now possible to grow gem-grade monocrystalline CVD diamonds of the highest quality and purity with fewer defects and consistent characteristics. This was made possible due to vast improvements in the plasma-type CVD reactors, along with rigorous control and a detailed understanding of chemical kinetics in the process of growing CVD diamonds.

The most prominent of the plasma-type CVD reactors for the growth of high-quality gem-grade monocrystalline diamonds have been the Microwave Plasma CVD (MPCVD)-based reactors. They have been used by almost all the companies and research groups around the world growing diamonds, and they enable the growth of excellent-quality gem-grade diamonds. Apollo Diamond, USA was one of the first companies to announce the production of gem-grade diamonds using CVD technology (Wang et al. 2007). Their success came from growing diamonds on a polished single crystal diamond seed (i.e., natural or HPHT). Prior to this, Element Six, UK also produced gem-grade diamonds using CVD methods, but only for research purposes (Martineau et al. 2004). The commercial production of single crystalline, gem-grade CVD diamonds was achieved by Singapore-based, Ila Technologies (Wang et al. 2012). There are now several gem-grade diamond-growing companies using CVD methods in USA, China and India. The growth of single crystal diamonds in HPHT machines and MPCVD reactors resembles growth patterns of the diamonds formed in mines and outer space. These diamonds, regardless of their origin, are all made up of sp^3 -bonded carbon, having similar optical, chemical, thermal, and electronic properties as well as identical physical features.

Scientific evidence suggests that at depths where mined diamonds are created, the carbon source is likely to have come from liquid forms of carbon dioxide and water (Stachel and Harris 2009). There is also evidence to suggest that methane and hydrogen may be present at the Earth's mantle (H Scotts et al. 2004) in small amounts and possibly in liquid form. This

implies that the source of carbon is the same for the growth kinetics of mined diamonds and grown diamonds crystallizing inside the MPCVD reactors filled with methane and hydrogen. Among the techniques used for diamond growth, the CVD method has a distinct advantage over HPHT (Bundi et al. 1955) when it comes to finer control and precise placement of the impurities (i.e., boron and nitrogen) for material applications (Wang et al. 2001). The possibility of placing dopants layers such as nitrogen provides additional flexibility of creating centers at precise location in the diamond structure making novel applications possible. One such recent example is (N-V)⁻ centers with potential for quantum computing applications. Similarly, high energy radiation detectors are extremely popular made with CVD diamonds plates which are of higher purity than mined and HPHT grown diamonds.

Growing optimism to scale CVD methods to usable sizes and to the extent that they will provide an economically viable alternative to both mined and HPHT diamonds promises an entirely new range of applications. CVD diamonds also show electronic properties that are comparable to, if not better than, those of mined diamonds. The applications potential of CVD diamonds is much wider than their mined or HPHT cousins. The charge carrier mobilities of the electrons and holes of CVD diamonds are higher than their mined counter parts (Isberg et al. 2002). Most promising applications of CVD diamonds are in charge particle detectors, dosimetry (Premerger 2006). In addition, CVD diamonds can be extensively used in fabricating ultra high-pressure anvils for materials science research (Dewaele 2018), windows for high power lasers, high power diodes for battery and inverter applications (Eon and Umezawa 2018).

CVD diamonds reach market

While there is no doubt that grown diamonds are real and chemically equal to their mined counterparts, the ongoing debate within the diamond industry is over the use of the term “synthetic” to describe them. This branding disagreement mostly arises when grown diamonds are marketed for jewelry applications. The most intriguing and unsettling thing about describing grown diamonds as “synthetic” is to insinuate that they are “fake” or “artificial” or similar to cubic zirconia and Moissanite (simulants). This is

because many consumers assume that “simulants” and “synthetic diamonds” or “artificial diamonds” are the same thing, a product with similar brilliance. But diamond simulants or simulated diamonds merely imitate diamonds and have nothing in common with “real” diamonds, as far as physical and chemical properties are concerned. The Moissanites are a fancy product in their own right and should not be put in the bracket of “diamond simulants”.

Only mined and grown diamonds are made up of pure carbon (crystallized in 3D form) and their properties are distinctly dissimilar from diamond simulants that are composed of non-carbon materials. For instance, the white sapphire (Al_2O_3) is a complex compound of aluminum and oxygen. Moissanite (SiC) is made of silicon and carbon while Cubic Zirconia (ZrO_2) is an oxide of zirconium. The clear distinction is that diamonds (mined and grown) are diamonds and simulants are not diamonds at all. That’s why all grown diamond companies emphatically and unequivocally object to the use of the word “synthetic” to describe their diamonds. Diamond-growing companies have adopted terms such as “cultured” or “grown” that not only clearly establish the origin of their diamonds but also helps the retail consumer to understand a diamond grown above ground better by comparing “cultured” or “grown” diamonds with an existing jewelry product, the “cultured” pearl.

A continuing debate among jewelers and the public (consumers) rages as to whether the mined and lab-grown (read CVD) diamonds can be differentiated. Let us make one thing clear. There is no way an ordinary jeweler or a trader can differentiate between the two using an ordinary loupe. It is impossible because there is no difference in the chemical make-up and structural make-up of the two diamonds. Both types are diamonds made up of carbon atoms bonded in four-fold strong covalent bonds. Their bond-lengths are the same, have identical crystal structure, and both are 99.99% carbon atoms. They have the same refractive index, hardness, and mechanical strength, making their identification by the naked eye and by using a simple lens impossible. The only way one could identify a lab-grown CVD gem is by the following tell-tale signs:

i) Almost all CVD gems by default are type IIa, which means they do not show the nitrogen-related impurity peaks in the Fourier Transform Infrared (FTIR) Spectra in one phonon region. The one phonon region in the FTIR spectra spans from 500 – 1500 cm^{-1} . This point is related to the near absence of singly substituted nitrogen and other nitrogen defects such as N-V-N complexes and platelets in CVD diamonds (Zaitsev 2001). These defects reveal their presence in the one phonon region of the FTIR spectra. One difficulty, however, is that there are type IIa mined diamonds that too show the same characteristics. There is, therefore, obviously no difference between the type IIa mined and type IIa CVD gems. The problem is resolvable because mined type IIa diamonds are extremely small in quantities. Only 0.8% of all mined diamonds are type IIa and mostly smaller sizes. The absence of nitrogen in any form in CVD diamonds as well as type IIa-minds make them very attractive as gems because it makes them extremely brilliant and lustrous.

ii) A useful tell-tale sign of the CVD gems is the presence of a sharp peak at 738 nm (Tallaire et al. 2006, Neu et al. 2011, Wang et al. 2003), corresponding to a silicon vacancy center in the photoluminescence (PL) spectra of the CVD diamonds. Currently, all CVD gems are dominantly grown in the growth chambers of microwave plasma chemical vapor deposition machines, which deploy microwave power to generate high-temperature plasma of hydrogen and methane gases. The deposition chamber is separated from the outside environment using a quartz separator. As hydrogen present in the chamber is in an excited state of ionization, it atomically etches the quartz separator, incorporating silicon impurity into the CVD gems. The silicon impurity is very small in concentration (of the order of few tenths of ppm). However, it can be easily detected at room temperature in the PL spectra and is used as a signature of the CVD origin of a diamond. There are difficulties though with this signature as silicon vacancy impurities have been reported in mined diamonds too (Christopher and Wang 2008), and their absence is not fool-proof evidence of the CVD origin of a diamond. The situation is complicated further by evidence that certain CVD diamonds do not contain a silicon vacancy line in the PL spectra. It is possible to avoid the incorporation of silicon impurities in CVD diamond and thus it cannot be used as a foolproof signature of the CVD origin of the diamonds.

iii) CVD diamond growth occurs via a step growth process, which leads to the formation of steps that are separated by a few micron periods and each step has a height of tens of microns. When the diamonds are cut and polished, sometimes these steps are visible in fluorescence and phosphorescence microscopy (Wang et al, 2012). These tell-tale signatures are also used to determine the origin of CVD diamonds. However, these signatures are not always present and depend upon the nitrogen concentration in the gaseous environment in the chamber. If the CVD diamonds are grown in a nitrogen free environment, these steps are less prominent and sometimes even absent. The presence/absence of the steps is, therefore, no fool-proof evidence of the origin of the diamonds.

iv) The presence of $(N-V)^0$ and $(N-V)^-$ centers in Photoluminescence spectra is a signature of the CVD origin of the diamond gems (Wang et al. 2003, 2012). However, these centers are also present in type IIa mined diamonds occasionally and cannot be a sure sign of the origin. Additional signatures of the origin of the CVD diamonds arise indirectly from factors related to processing. Almost all CVD diamonds are grown with the addition of nitrogen in the gas phase currently. Nitrogen increases the growth rate and helps in stabilization of 100-oriented growth. As a result of the growth in the presence of nitrogen, a small concentration of nitrogen lands up in the diamond lattice (Loubser and Wyk 1978). This is of the order of less than 5 ppm, but it is enough to introduce a brown tinge to the grown CVD diamonds. It is not really understood what leads to this brown color/tinge. However, it is speculated that the presence of nitrogen introduces states in the band gap of the diamond, causing the brown tinge. The phenomena of the brown tinge of CVD diamonds are discussed in detail in chapter 5. The brown tinge of CVD diamonds is lightened when the CVD diamonds are annealed at a temperature greater than 2200°C in the presence of stabilizing atmosphere. CVD diamonds are generally annealed under the High-pressure and high-temperature (HPHT) conditions to lighten the tinge and to improve their optical properties. The treatment leaves an imprint on the diamonds in the form of a line in the PL spectra at 503 nm (Charles et al. 2004) and shows the color of the diamonds to be light blue/green under a phosphorescence microscope. However, the presence of this line at 503 nm in CVD diamonds annealed by the HPHT process depends on the nitrogen

content and, therefore, it is not a sure proof of the origin of a diamond. This line does not appear in HPHT treated CVD diamonds when the nitrogen concentration is low (less than 1ppm).

iv) The surest way to ensure the origin of CVD diamonds comes from the producers with a clear disclosure of the origin of the diamonds. No other test or certificate can replace this. CVD diamonds are a scientific marvel, and it would be a grave insult to the efforts of so many scientists across the world, those who have worked tirelessly to perfect the technology and science to create CVD diamonds, if these were mixed with mined diamonds and the consumer was misinformed for commercial gain. CVD diamonds look so beautiful and are in no way inferior to mined diamonds, therefore, they should be protected from being mixed with mined diamonds.

For the benefit of consumers and the larger industry, it is important to consider and apply the terminology that is perceived easily and clearly. By referring to an existing precedent of natural and cultured pearls, it becomes simpler for diamond growers to communicate to their consumers and the industry at large, what grown or cultured diamonds are, without compromising on value, quality, and authenticity. Whether grown diamonds are labeled as “cultured,” “cultivated,” “lab-grown” or “grown,” it is very important to distinguish them clearly from their mined counterparts. Both consumers and the larger industry need to be educated on the origin of diamonds to allow them to make an informed decision about the diamonds they want to buy.

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CHAPTER 2

CHEMICAL VAPOR DEPOSITION

There are several techniques to grow chemical vapor deposited (CVD) single crystals and polycrystalline diamond films of several microns in thickness (Goodwin et al. 1998). CVD gems of single crystal diamonds of carat sizes are commonly available in the market (Wang 2003). Several techniques were experimented with in the past decades, for example, hot filament chemical vapor deposition (HFCVD) (Gat and Angus 1993), oxy-acetylene flame (Jansen et al. 1992, Hirose et al. 1989), and arc discharge technique (Mitsuda et al. 1989), to name a few. The basis of all the techniques was to use a source of carbon, preferably CH_4 , diluted in copious amounts of hydrogen. Hydrogen gas is to be dissociated in its atomic constituents 'read atomic hydrogen' and that was achieved using either a thermal source of energy or an electromagnetic source. Polycrystalline diamond (PCD) films of several microns in thickness (Sikder et al 1998) were the prominent product grown by a score of Chemical vapor Deposition techniques, previously. The applications of PCD were severely limited due to the presence of grain boundaries (GB). The impurities accumulated at the GBs and deteriorated PCD properties.

The above techniques, which were initially used for polycrystalline and single crystal diamond growth by several researchers, have mostly been abandoned due to the concerns of the incorporation of the impurities in CVD single crystal diamonds, mainly the metallic impurities that gets embedded in the diamond structure due to the constituents of the reaction chamber. The constituents include metallic parts of the chamber, quartz components, and gas composition in the chamber. For HFCVD technique the metallic contaminants from the filament material are a major source of impurities. The electrode materials used in arc discharge are too a source of contaminants. In contrast, the microwave plasma chemical vapor deposition (MPCVD) technique does not suffer from the above shortcomings (Kamo

et al. 1983). The plasma size is reasonable, and the deposition region is away from the contaminating surfaces and components. The only possible serious source of contaminant in MPCVD apparatus is the Quartz separators which are essentially used to isolate the microwave antenna from the vacuum. The Quartz leads to silicon atomic impurities in diamond structure, and these can be identified as Si-V centers. For gem applications silicon impurities are not critical, however, occasionally silicon impurities in CVD diamond gems can produce bluish gray or purple tinge as discussed in chapter 5. There are ways to reduce the silicon impurities in CVD diamonds grown by MPCVD. As a result, the MPCVD technique has been exclusively used for the growth and manufacture of single crystal and polycrystalline diamonds recently for all applications, be it gems, particle detectors, or optical devices (Tarun et al. 2016). We will concentrate, therefore, wholly on the single crystal diamonds grown by the MPCVD technique in this book.

The MPCVD technique derives its name from the source of electromagnetic energy that is used to split the gases. Microwaves are electromagnetic (EM) waves in the frequency range of 0.3 GHz to 300 GHz (the wavelengths range from 1 mm to 1000 mm as specified on the website NASA.GOV Colleen Kaiser page last updated August 03, 2023). It is obvious that very high and very small wavelengths cannot be used for the deposition because the plasma size is decided by the wavelength. For a guide, the plasma size is about 50 mm for 2.45 GHz and 100 mm for 915 MHz and would be reduced to few mm for 80 GHz. The suitable frequency range for the MPCVD of single crystal diamonds is, therefore, 0.5 GHz to 5 GHz. However, one should be extra careful in using the above range of frequencies as many of them fall or overlap with the international standard frequencies used for communications purposes. In my experience as a worker in MPCVD techniques growing single crystal diamonds for many years, the best frequency is 2.45 GHz. Several workers have used 915 MHz as well. However, it must be noted that this frequency has lower energy content per photon and in many countries, it is a frequency used for mobile communication and may interfere with communication frequencies. Another frequency that could be useful for growing diamonds for gem applications and other scientific applications is 5.8 GHz. The use of this frequency, however, is not common, but needs exploring. The plasma size

may be smaller, but it would be much more efficient in atomic hydrogen generation, and the growth rate will go up. An additional issue in MPCVD technique is to explore and experiment with different types of microwave antenna as discussed in Chapter 3.

Industrial and scientific applications of diamonds

MPCVD technique has also gained prominence because it can deliver single crystal diamonds with varying characteristics ranging from gem quality to very high purity diamonds which can be used as detectors, high pressure anvils, cutting inserts and for quantum sensing. Out of the above, perhaps, easiest are to grow gem quality diamonds as the requirements of impurity controls are not so stringent. For example, the mobility of charge carriers or the strain in the diamonds plays no role in fabrication of gems. In contrast, the charge carrier mobility must be high for the fabrication of diamond detectors (Isberg et al, 2001) and diamonds be of low strain for high pressure anvil applications (Ruaff et al. 1987, Ruaff and Vohra 1989). Diamond detectors are fabricated using high purity diamond plates of thickness 0.3-0.5 mm and of the sizes 3-5 mm or larger. As the charge carrier mobility needs to be higher the impurities in the diamonds must be stringently controlled. Even a trace number of impurities can kill the charge carrier lifetimes and mobility significantly. Similarly, the undue strain present in diamonds will lead to the cracking of the diamond anvils when subject to high pressures. Strain may also affect the processing of the CVD gems however it is not such a serious problem there. Strain in CVD diamonds is a serious concern for the application of cutting inserts. The presence of dislocations and dislocations bundles which contribute to the strain introduces local high strain points which result in fracture and chipping of a diamond cutting insert.

The growth of diamonds for quantum sensing applications is a lot more challenging. (N-V)⁻ center is a prominent choice for sensing applications as it contains an electron triplet state. However, the requirement that the center must be a single (N-V)⁻ and it must be located close to the diamond surface for access makes the prospect challenging. The situation is compounded by the fact that the center is oriented along (111) crystallographic direction. An additional problem is the natural presence of ¹³C in CH₄ gas used for the

CVD of diamond and it invariably leads to the presence of ^{13}C in diamond lattice which affects the application.

Currently, there are several types of MPCVD apparatus used for CVD diamond growth. A typical system consists of four major parts: the microwave generators, flow controllers and gas valves, the chamber, and the vacuum system. All the parts are fabricated using stainless steel with an excellent finish as sharp corners or rough parts may create arcing in the system. The positive pressure in the growth chamber is maintained by using a scroll pump or a rotary pump coupled with an automated throttle valve. This valve opens or closes automatically with the requirements of the set pressure in the chamber. Inside the chamber, there are pressure and temperature measuring instruments, and viewports are provided to view the plasma inside the chamber. The parts of a MPCVD system are discussed in some details.

CVD growth chamber

The growth of CVD diamonds occurs at a substrate temperature of 800–1200°C in a well-defined and controlled environment which consists of mostly hydrogen (H_2) mixed with methane (CH_4) and some form of nitrogen (N_2). The typical values of CH_4 flow percentages are 5-10 % of the H_2 flow and N_2 concentration is of the ppm level in the gaseous environment. Nitrogen may or may not be used depending on the application. All the flow rates are calculated based on the flow of the gases in the external lines of the chamber and the actual concentrations of the gases inside the chamber are speculative in nature unless one is measuring using very sophisticated equipment. To get diamond growth, the gases in the environment must be excited to form plasma using high power in a microwave resonant cavity (read chamber). The typical power range used for the growth of CVD diamonds depends upon the frequency of the microwaves which decides the size of the plasma. The gases are passed into the chamber at a constant flow rate and a pumping system is used along with a throttle valve to create sub-atmospheric pressure in the chamber. We need to use sub-atmospheric pressure because arcing with microwave power is very common at high pressure. Arcing is dangerous for the microwave magnetron source and therefore a cutoff switch is used to protect the same. The most suitable

pressure range for the CVD diamond growth is 125 mbar to 250 mbar. The pumping system is required to continuously evacuate the gases that are being input and to create appropriate pressure in the chamber. The system must be vacuum-tight and evacuated before the start of growth to typically about 10^{-3} mbar. It requires valves, which connect gas lines to the growth chamber to insert reactive gases in a controlled manner, using mass-flow controllers. These constituent gases are removed from the chamber by a process pump system, which establishes a continuous gas flow during diamond deposition. Each system available on the market or self-built has, therefore, been theoretically optimized the size for the use of resonant microwave modes. Although some equipment manufacturers recommend using a turbo pump it is, however, not necessary for the growth of CVD single crystal diamonds for gem applications.

The gas supply of a diamond deposition system is designed to control different gas inlets with respect to, a) switching on/off gas flows, b) establishing controlled gas flows, and c) purifying the gases used for the deposition of a diamond. A typical system, therefore, controls methane (CH_4), hydrogen (H_2), nitrogen (N_2 , NH_3 , etc.), argon (or other inert gases), and possibly oxygen (O_2). The purity of gases with respect to contaminants (air, water, nitrogen, etc.) is given by gas producers, and guarantee, to a certain level, a given purity (methane for example 99.999% or to 99.9995%). The purity of the input gases is a very important control factor, which in turn controls the properties of the grown diamonds. Hydrogen cylinders can be commonly used. However, a hydrogen generator can be a much-preferred choice if one desires to grow diamonds of the highest quality. The purity of hydrogen gas produced by a hydrogen generator can be typically of higher purity than what you get from a cylinder. Some specially manufactured hydrogen generators using Palladium catalyst can provide the highest purity of 99.99999%, which implies impurity content of less than 100 ppb in the gas flow.

The calculation of ppm impurity from the percentage purity of a gas is simple. An impurity of 0.01% would mean, therefore, 100 ppm impurity in the gas. Almost all gases come with a certificate of testing from the supplier, which would specify the level of impurities in the content of the gas. For instance, a methane gas cylinder of 99.9999% (this is also called 6N or 6