A review of nucleation, growth and low temperature synthesis of diamond thin films

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Diamond thin films have outstanding optical, electrical, mechanical and thermal properties, which make these attractive for applications in a variety of current and future systems. In particular, the wide band gap, optical transparency and unusually high thermal conductivity of diamond thin films make them an ideal semiconductor for applications in current and future electronics. However, synthesis of diamond thin films with adequate quality remains a challenging task. Synthesis of diamond at low temperatures is even more challenging because of the difficulties in the nucleation and growth steps involved in diamond thin film deposition on a variety of substrates. Among the several deposition techniques for synthesising diamond films, plasma enhanced chemical vapour deposition is the most promising technique because of its potential for low temperature synthesis. Consequently, the first part of this paper reviews the current state of the nucleation and growth of diamond during chemical vapour deposition. A uniform and high nucleation density is a prerequisite for getting a good quality diamond film with significant growth rate. Also, since the process conditions for nucleation and growth steps are different, attempts are made in this review to identify the important parameters responsible for enhancing the nucleation and growth rates of diamond film. Describing the indispensable need for low temperature growth of diamond film, the second part of the paper reviews the research on the growth of diamond thin films at low temperatures. In spite of the slower kinetics at lower deposition temperatures, an attempt is made to identify the key processing conditions, which enhance the low temperature growth process. In addition, the mechanisms of diamond nucleation and growth are discussed based on the observations from in situ characterisation techniques such as Fourier transform infrared reflection absorption spectroscopy, real time spectroscopic ellipsometry and molecular beam mass spectroscopy.

Keywords: Low temperature growth, CVD, Nucleation and growth, Diamond film

Introduction

The diamond film research has attracted renewed interest in recent years owing to its outstanding optical, electrical, mechanical and thermal properties.[1] Among the various diamond deposition processes, developed over the past 15 years, the hot filament chemical vapour deposition (HF-CVD) process and the microwave plasma CVD (MP-CVD) method have proven to be the most used diamond deposition processes in achieving a good quality diamond film.[2] Diamond research over the years established conditions for well defined growth of the films, which included high substrate temperature (typically $>700^\circ$C) and a carbon containing precursor gas diluted in excess of H_2. However, the high substrate temperature limits the use of diamond films in many industrially important systems such as electronics substrate. Consequently, a major goal in the diamond research has been to lower the substrate temperature required for diamond growth. This will permit the use of a much wider range of substrate materials of industrial importance such as Al, Si, SiC, GaN, GaAs, Ni and steel in different mechanical, electrical, optical and electronic applications. Lowering of substrate temperature during diamond synthesis could be an important step for deposition on low melting materials as well.

Nucleation is the first and probably the most important step in achieving a good quality diamond film. A uniform nucleation throughout the substrate surface along with its density affects the subsequent growth stage. A slight change in the processing parameter such as gas composition, concentration of the precursor gases in the mixture, temperature, pressure and microwave (MW) power can alter the nucleation process. A good pretreatment of the substrate is a prerequisite for good nucleation. A uniform and dense

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nucleation leads to a better growth of the diamond film. Just like nucleation, growth of diamond film is very much dependent on the deposition parameters. The first part of this paper deals with the effect of the processing conditions on nucleation and growth of diamond film. To have a better understanding and control of the deposition process, the underlying mechanism of nucleation and growth has been discussed in view of some of the recent research findings in this area. The surface reaction and the gas phase chemistry involved in diamond film formation are explained in the light of some in situ characterisation technique such as real time spectroscopic ellipsometry (RTSE) and molecular beam mass spectroscopy (MBMS).

The second part of this paper reviews the recent results on low temperature growth of diamond film. The interest in low temperature deposition of CVD diamond films stems from its excellent mechanical, electrical, electronics, optical and thermal properties. Low coefficient of friction close to that of teflon, high hardness (hardest material), insensitivity towards moisture, highest elastic modulus and high thermal conductivity make diamond very attractive for large scale mechanical applications.[3] One of the main applications of diamond film in this area is the wear resistant coatings on cutting tools, drills and milling tools.[4] Numerous reports in the literature show the advantage of the low temperature deposition of diamond film on hard tool materials.[5–14] However, low deposition temperatures strongly reduce the growth rate and change the film morphology. Even for very thin films high roughness is frequently obtained when the film is deposited at low temperatures. Low temperature diamond deposition is also important in electronics.[15–18] Growing diamond films at low temperatures, typically <500°C, is important for many applications in electronics since substrate materials like GaAs, GaN, plastics, ZnS and MgF_2 are unstable at high temperatures[19] and also to fabricate stress free diamond film on substrate because of the difference in coefficient of thermal expansion between diamond and substrates. For optical applications, the low temperature deposition of diamond films is inevitably required because of the low melting point of the optical materials such as glass. Diamond deposition on optically transparent substrates such as sapphire, zirconia and zinc sulphide is of immense technological importance for many applications, such as infrared windows.[20–22] Single crystal diamond possesses the highest thermal conductivity (20–25 $W\ cm^{-1}\ K^{-1}$) at room temperature of any materials. This property, coupled with a low thermal expansion coefficient and a large electrical resistance, makes it the best material for heat sink application in electronic devices.[23–25] But, the use of diamond films for thermal applications requires a high crystallinity, reduced grain boundary network and very low contamination by non-carbon elements. Low temperature deposition also eliminates the risk of any Si (for Si wafer) or other substrate material diffusion into the deposited diamond layers.

A review on the growth of diamond films at low temperatures was written by Muranaka *et al.* in 1994.[26] Limitations of substrate temperature in getting good quality diamond films were discussed in the review. In general, the authors have suggested that low temperature growth promotes the formation of amorphous component at the cost of crystallinity of the film. In spite of the above difficulties, several groups have tried to deposit good quality diamond films at low substrate temperatures using different precursor gases and substrates for various mechanical, electrical, optical, electronics and thermal properties in successive years.[27–34] However, there are still some obvious problems for low temperature CVD, such as heating of the substrates by the plasma, forced cooling of the substrate stage (holder), measurement of the real substrate temperature and poor nucleation and slow growth rates. The influence of deposition parameters on low temperature growth of diamond film has been discussed and parameters that enhance the low temperature growth have been identified. Since the kinetics of diamond growth is slow at low deposition temperatures, a suitable pretreatment of the substrate, which ensures a uniform and high nucleation density, is an essential step before deposition. For further understanding of the low temperature growth process, the gas phase chemistry involved and the mechanism of the film formation at low temperature are discussed.

Nucleation of diamond

Effect of substrate

Diamond nucleation is influenced by the choice of substrates. Since the lattice parameter and structure of the substrate materials with respect to diamond are important considerations in deciding a good film growth, all substrate materials do not respond equally in getting a good adhesion of the film. Early development of the CVD diamond films has been performed on single crystal diamond substrates.[35,36] Diamond seeds have also been used in realising good diamond films.[37] The previous works are mostly confined to getting homoepitaxy of diamond. In 1982, a breakthrough in CVD diamond technology was achieved by Matsumoto *et al.* by growing diamond on to a non-diamond Si (100) substrate.[36] Hydrogen and hydrocarbon were activated by passing through a hot filament at 2000°C and the diamond film was deposited onto a non-diamond substrate located 10 mm away from the filament. Graphite was etched simultaneously by atomic hydrogen leading to a higher growth rate ($\sim 1\ \mu m\ h^{-1}$). Apart from having a very low nucleation density, a continuous film was not achieved. Diamond deposition was also carried out on a commercial purity titanium and Ti–6Al–4V alloy substrates using a hot filament (tantalum) CVD and H_2–1%CH_4 gas precursors.[38]

The nucleation and early stages of growth of diamond was studied on high performance ceramics Si_3N_4 using a gas mixture of H_2 and CH_4 by an MPCVD process.[39] The influence of the substrate on the nucleation behaviour was shown to be related to the change in microstructure during etching and to the reaction of carbon plasma species with Si_3N_4, where the incubation stage was mainly affected. An optimisation of the nucleation and growth of diamond was performed with Si_3N_4 using the same gas mixture and MPCVD where an orthogonal design of experiments was used to optimise the process parameters for achieving high nucleation density and growth.[40] The nucleation density increased considerably with decreasing reactor pressure during initial nucleation stage. Since the attack of the aggressive plasma (mainly H atoms) destroys the nuclei formed on the substrate surface at higher reactor pressure, lower gas pressure favours nucleation at early stage of growth. High pressure, on the other hand, favoured the growth rate because of the higher concentration of the reacting species in the denser plasma at higher pressure.

The quality and adhesion of diamond coatings on commercial silicon nitride (Si_3N_4) cutting tools were studied by low pressure MPCVD at various processing conditions.[41] The nucleation density decreased with increasing pressure, while it increased with increase in the CH_4 concentration. Substrate temperature and CH_4 concentration were the most important parameters in deciding overall growth rate as well as the quality of the diamond films. It was suggested that the intermediate silicon carbonitride SiC_xN_y layers can provide nucleation sites for diamond crystallite growth, enhance diamond nucleation density on non-diamond substrates and control morphology, orientation and texture of the diamond films. Several nucleation mechanisms on different intermediate layers were proposed based on an extensive review by Liu and Dandy in the literatures, which are discussed below.[42]

Nucleation on intermediate layer of diamond like amorphous carbon

It has been proposed that diamond crystallites grow from an intermediate amorphous a-C layer, which serves as nucleation sites.[43] The bonding structure of the deposited carbon clusters are changed from sp^1 to sp^2. These sp^2 bonded carbon atoms in turn are converted into a relatively stable network of sp^3 bonded carbon. The etching of the unstable phases (sp^1 and sp^2) by H plasma or OH rich plasma (for oxygen containing precursors) promotes stabilisation of the sp^3 phase. The carbon atoms try to rearrange towards {111} planes during crystallisation to minimise the energy content, which act as nucleation sites for the subsequent growth stage.

Nucleation on intermediate layer of metal carbide

Because of the better lattice matching between diamond and β-SiC (22% against 52% between diamond and Si), diamond nucleation is believed to occur on an intermediate carbide layer. Carbon from the hydrocarbon precursor gets dissolved in the substrate forming a stable carbide on top of the substrate. When the carbon concentration in the carbide layer reaches a supersaturation, diamond starts to nucleate on top of it. This effect is much more prominent on the transition metal substrate because of their strong carbide forming tendency. On Si_3N_4 substrate also diamond nucleation occurs on SiC interlayer. The thin native oxide layer (SiO_2) on Si_3N_4 is first converted to SiC during deposition in the hydrocarbon atmosphere (carburising atmosphere), which then acts as a nucleation enhancing intermediate layer.

Nucleation on intermediate layer of graphite

Diamond nucleation is also believed to occur from an underneath graphite layer. Graphite has been suggested to condense initially on the substrate surface whose {1100} prism planes are hydrogenated.[44] Diamond nuclei then grow preferentially on the prism planes of graphite, which act as interface between graphite and the diamond nuclei.

Commercial cemented WC tools of different cobalt concentrations (3, 6 and 12%Co) have also been used as substrate to deposit diamond by low pressure MPCVD to assess the role of cobalt on the quality and adhesion of the diamond coatings.[13] At lower deposition temperatures, surface Co appeared to affect the diamond growth in the early stages especially with the higher Co concentrations (6 and 12%Co). Cobalt was found to cover the growing diamond nuclei and dissolved some of the carbon (owing to its high solubility with Co) thereby extending the incubation period. This effect was more prominent at higher deposition temperature since more Co was diffused to the surface from the bulk through the grain boundaries. An improved nucleation density, adhesion and surface properties were observed in coating polycrystalline diamond onto three dimensional complex shaped cemented tungsten carbide (WC–Co) burs used for dental applications under the application of a negative bias voltage to the substrate in a modified vertical HFCVD system.[45]

Varying methane (CH_4) to hydrogen (H_2) ratios of 4 to 9% was used to coat stainless steel substrates with diamond thin film using electron cyclotron resonance (ECR) MPCVD technique.[46] Below CH_4/H_2 ratio of 4% no diamond deposition was detected. In the deposited films, graphite peak at 1600 cm^{-1} disappeared at the CH_4/H_2 ratio of 5% and then at higher ratio it reappeared, which was confirmed by Raman spectroscopy. An in situ Fourier transform infrared reflection absorption spectroscopy (FTIR-RAS) and optical emission spectroscopy (OES) were employed to study the early stages of nucleation and growth. The outward diffusion of substrate atoms to the growing surface followed by supersaturation of carbon forming metal carbon species was established. The appearance of infrared absorption peaks at 1340 and 1400 cm^{-1} were speculated to be indications of CH_3 radicals attached to the substrate as diamond precursors. The symmetric and asymmetric stretching vibration of the C–H bond of sp^3 bonded hydrocarbon occurs at 1340 and 1400 cm^{-1} in the infrared spectroscopy. The graphitic carbon phase on the substrate was believed to originate from the substrate's chemical structure rather than from species occurring in the plasma.

Chemical vapour deposition of diamond onto nitrided chromium by an oxyacetylene flame was reported.[47] Although polycrystalline diamond films were obtained at very low substrate temperatures (<400°C), extremely weak bonding or no bonding at all, between the deposited layer and the substrate was observed.

Heteroepitaxy of single crystal diamond films have recently been realised on iridium films deposited on the $SrTiO_3$ (001) substrate.[48] The resulting films showed a cube on cube orientation relationship with the substrate and a minimum mosaic spread of 0·15°. High deposition temperature (920°C) was found to produce low nucleation densities and modified the Ir surface. Nucleation at 700°C produced highly aligned diamond grains with low mosaic spread and very low fraction of randomly oriented grains. This proved the better performance of Ir films on $SrTiO_3$ for diamond nucleation as compared with pure silicon substrates. Exposure of the Ir films, grown at 950°C, to the biased enhanced nucleation (BEN) process and diamond growth conditions in the CVD reactor at 920°C (nucleation step) and 770°C (growth step) was found to yield a very low diamond nucleation density and strong modification of the Ir film surface. Since a harsh aggravated environment helps in achieving rough surface owing to ion bombardment, a high temperature was employed during nucleation. Low temperature growth environment avoids the holes formation underneath the Ir layer. Although the above-mentioned conditions such as high temperature in the nucleation step followed by low temperature growth environment modified the Ir surface to a large extent, the diamond nucleation density was very low.

A two step diamond (001) film deposition was achieved on a-plane (1120) α-Al_2O_3 (sapphire) substrate.[49] First, epitaxial (001) iridium films were grown on terraced, vicinal a-plane sapphire by ultra high vacuum electron beam evaporation at 950°C. Diamond film was then grown on the Ir layer by low pressure CVD using methane and hydrogen. The initial exposure of the epitaxial Ir to a dc biased plasma led to uniform coverage of the surface by a dense array of diamond crystallites before growth. A subsequent 60 min growth step yielded a continuous and highly homogenous (001) diamond film over areas >50 mm^2. The films were characterised by atomic force microscopy (AFM), scanning electron microscopy (SEM), transmission electron microscopy (TEM) and Raman. The initial dc biasing step was helpful in achieving high nucleation density. Because of its interfacial stability in a hydrogen plasma and high crystalline perfection, Al_2O_3 has been suggested as a valuable substrate for diamond film growth.

Nucleation and growth of diamond films on single crystal and polycrystalline tungsten substrates were studied.[50] Using a range of bias and reactor conditions, diamond films were nucleated and grown and were characterised by Raman spectroscopy and SEM. High quality and (100) textured films (Raman full width at half maximum <4 cm^{-1}) were deposited on both single and polycrystalline tungsten substrates. The substrates polished with diamond paste, resulted in high unbiased nucleation density up to $\sim 10^9$ cm^{-2}. A 60% increase in the nucleation density was observed using a -200 V bias on these substrates. However, for substrates that had been subjected to an additional polishing step with 0·5 μm Al_2O_3, a much stronger enhancement of four to five orders of magnitude from an unbiased value of $\sim 10^5$ cm^{-2} was observed. But, Raman measurements revealed that the diamond films grown on bulk tungsten exhibited considerable thermal stress ($\sim$1·1 GPa), which, together with a thin carbide layer, resulted in film delaminating on cooling owing to thermal expansion mismatch between diamond and tungsten. Careful optimisation of the reactor parameters (CH_4 4%, P = 30 torr, power = 800 W and total gas flow = 400 sccm) yielded (100) textured growth with a growth rate of 0·22 μm h^{-1}.

Beryllium metal was employed as a substrate material for the MPCVD of diamond films.[51] As long as a native oxide BeO with the hexagonal wurtzite structure was found in the temperature range of 700–800°C, no deposition was observed. The formation of the carbide (Be_2C with the cubic antifluorite structure) layer, formed above a critical substrate temperature of $\sim$750°C, triggered diamond nucleation. Without Be_2C, the diamond growth rate was low and a significant amorphous carbon component was observed. Just above the critical temperature, high growth rates were observed with high phase purity diamond. But, this Be_2C layer was found to be detrimental for thick films (>30 μm) grown above the critical temperature. Formation of diamond on beryllium required the electrophoresis seeding technique, which helped in getting a significant degree of the epitaxial growth.

Since the formation of diamond on carbon materials occurs on the edges of the grapheme planes owing to the higher reactivity than that of the basal planes and a highly disordered carbon surface gives a better diamond nucleation than a surface consisting of the basal planes, several carbon–carbon composites with tailored surface features have been used as substrates for diamond deposition. A carbon–carbon composite reinforced with vapour grown carbon fibre and another reinforced with polyacrilonitrile fibres were used as substrates to deposit diamond films using a low pressure CVD with a mixture of methane, hydrogen and oxygen as the precursors.[52] The activation energy for diamond growth was dependent on the nature of the substrate and either a higher deposition temperature or a higher oxygen concentration produced diamond films with higher crystalline qualities.

Diamond deposition was reported on polycrystalline $CoSi_2$ substrates.[53–55] The diamond film grown on $CoSi_2$/Si substrate by bias enhanced MPCVD showed high nucleation density of $\sim 10^9$ cm^{-2} with a positive biasing, which was much higher than with negative biasing.

Because of similar cubic crystal structure, excellent lattice matching (just 1·14% between diamond and copper), poor solubility of carbon in copper and no carbide formation between copper and carbon, Cu has been used as substrate to study the possibility of diamond heteroepitaxy.[56–59] Bias enhanced nucleation of diamond on polycrystalline Cu substrates was used.[60,61] The results indicated that with higher CH_4 concentration, the nucleation density was increased and saturated at 10%CH_4, but the quality of the diamond was decreased. Bias voltages played an important role in the nucleation of diamond. The nucleation density was highest at -250 V. Thin transparent films of diamond were grown onto highly polished copper substrate at a rate of $\sim$1 μm h^{-1} by CVD method using an HFCVD reactor.[62]

Nucleation and growth of diamond film was studied on c-BN crystal and microstructural characterisation was performed using high resolution SEM and micro-Raman spectroscopy.[63] c-BN crystal of 200–350 μm was grown by a high pressure high temperature process and was embedded in a Cu substrate to be used as a substrate material for diamond nucleation. The deposition experiment was carried out from 15 min to 5 h. A well shaped cuboctahedral diamond crystallites with diameter of 100 nm were realised on 111 faces of c-BN within 15 min of the experiment. As the deposition proceeded, diamond crystallites grew in size and formed clusters on c-BN faces. After 40 min, 0·5 μm diamond particle was observed with very high particle density of the order of 10^8 cm^{-2} with a pseudo fivefold symmetry owing to presence of multiple twins in it. After long deposition period some carbon tubes of $\sim$100 nm in diameter and 1 μm length were found and attributed to the plasma sputtered contamination from Cu substrate. An unusual diamond crystal with a deep, pyramidal shaped hole in the centre was observed on the Cu substrate between the c-BN crystals.

Effect of substrate pretreatment

Because of very low nucleation density, only of the order of 10^4 cm^{-2} on non-scratched substrates,[64] surface modifications of different kinds like mechanical abrasion/scratching, seeding, electrical biasing, covering/coating, ion implantation, pulsed laser irradiation and carburisation have been used to realise very high and uniform nucleation density leading to a good quality diamond film (Table 1 (Ref. 42)). For Si substrates, which is the most extensively studied substrate material for diamond growth, a nucleation density of 10^7–10^8 cm^{-2} has been obtained after scratching with diamond powder. Among different surface pretreatment techniques, biasing is found to be the most effective in achieving high nucleation density followed by scratching, seeding, covering/coating, and ion implantation. Nucleation on activated surface generally occurs on carbon rich particles or defects, like scratches, grain boundaries, particle boundaries, dislocations, electron bombardment induced damages and edges of pits or craters as discussed in Ref. 42 and references therein.

Mechanical abrasion

The effect of scratching of the substrate surface with diamond powder was first observed in 1987,[65] and since then it has been extensively studied using different abrasive materials like oxides, silicides, nitrides, carbides and borides. Scratching with SiC, cubic boron nitride, Cu or stainless steel, ZrB_2, TaC and even Fe powder has been proposed in the literature.[42,66–69] But, scratching by these materials was not as effective as by the diamond powder. The effectiveness of abrasion on the nucleation followed the order, silicides $<$ SiO_2 $<$ nitrides $<$ ZrO_2 $<$ carbides $<$ borides $<$ Al_2O_3 $<$ c-BN $<$ diamond.[70] Scratching or abrasion of the Si substrate surface with diamond grit enhanced the nucleation density by roughly three orders of magnitude compared with non-scratched Si (up to 10^7 cm^{-2}). The grit size of the diamond powder used for scratching also affected the nucleation density; a 0·25 μm grit was the most effective for scratching by hand and a 40–50 μm powder was the best for scratching by ultrasonic agitation.[64] The method used for scratching the substrate surface by diamond also influenced the nucleation density. The nucleation density decreased with increasing particle size of diamond abrasive paste used for polishing, but it increased with increasing particle size in the ultrasonic scratching treatment.[71] However, the optimum size of abrasive particle was dependent on the pretreatment methods, deposition process, growth conditions and nature of substrate materials. The nucleation density was proportional to the scratching time and the morphology of the deposited film depended on the scratching time. Large isolated crystal was found for short scratching times whereas longer scratching produced crystals of smaller size and higher density.[72]

Table 1 Typical surface nucleation densities of diamond on non-diamond substrates after various surface pretreatments[42]

Pretreatment method	Nucleation density, cm^{-2}
No pretreatment	10^3–10^5
Scratching	10^6–10^{10}
Ultrasonic scratching	10^7–10^{11}
Seeding	10^6–10^{10}
Biasing	10^8–10^{11}
Coating with Fe film	$4{\cdot}84\times10^5$
Coating with graphite film	10^6
Coating with graphite fibre	$>10^9$
Coating with a-C film (first scratched)	3×10^{10}
Coating with C_{70} cluster and applying bias	10^6–10^{10}
Coating with Y_2O_3–ZrO_2, a-BN, cSiC layer	Enhancement
C^+ ion implantation on Cu	Enhancement
As^+ ion implantation on Si	10^5–10^6
Pulsed laser irradiation + coating a-C, WC, c-BN layer	Enhancement
Carburisation	Enhancement

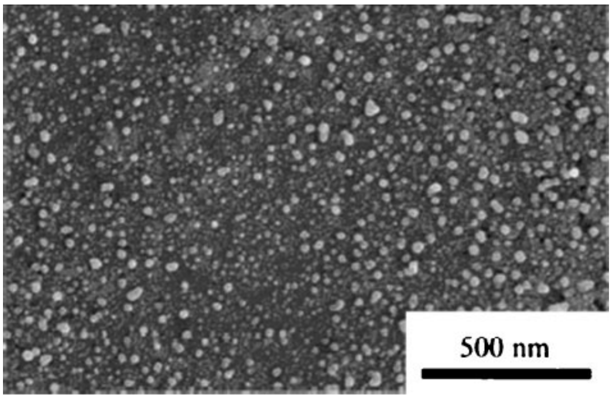
Mechanism of nucleation enhancement by mechanical abrasion

Mechanical abrasion with diamond powder, followed by cleaning the surface with acetone or alcohol, damages the surface because of the continuous bombardment of the substrate surface by diamond particles. Some diamond debris also might be left on the surface even after cleaning. Whether the surface defects caused by the abrasion is responsible or the diamond debris left behind is causing the nucleation enhancement is not clear. Abrasion with materials other than diamond has also been tried. The findings of these experiments and different opinions are discussed below.

Nucleation enhancement by scratching was attributed to seeding effects, minimisation of the interfacial energy on sharp convex surfaces, breaking up of the surface bonds or presence of the dangling bonds at sharp edges, strain field effects, rapid carbon saturation (fast carbide formation) at sharp edges and removal of surface oxides.[42] A schematic diagram of mechanisms for diamond nucleation enhancement on scratched surfaces was presented in Ref. 73.

One possible mechanism for nucleation enhancement by scratching was the production of non-volatile graphitic particles through local pyrolysis of absorbed hydrocarbons at the scratched surface of the substrate. These graphitic clusters in turn get hydrogenated in the atomic H environment under the CVD conditions to form the precursor molecules, which enhanced nucleation. Another view is that, during scratching with diamond, c-BN, or α-SiC powder, the residual powder or fragments left in the scratched groove act as seeds for the diamond growth. Although c-BN and α-SiC are not diamond, their structures are close enough to that of diamond. Thus, diamond grows easily on them. It has been observed that fragments of diamond existed in the scratched grooves of Si and diamond growth occurred on them.[74] The nucleation density was found to be linearly proportional to the diamond seed particle density and it is approximately one tenth of the seed particle density.[75]

It was also suggested that scratching with powder created a change in the surface morphology and produced defects such as edges, steps and dislocations. These defected regions were identified as chemically active sites, which preferred to adsorb diamond precursors owing to enhanced bonding at high energy



1 Nucleation density on Br passivated Si substrate with following deposition conditions: temperature, 620°C; nucleation time, 30 min; CH_4/H_2, 51%; MW power, 1000 W (reprinted with permission from Ref. 77, copyright 2000 by American Physical Society)

interfaces with a high density of unsaturated bonds and low coordination numbers.[76]

Chemical treatment

Apart from mechanical abrasion, a number of chemical etching were tried to enhance the nucleation density for different applications of the diamond films. Diamond nucleation on the ridges lithographically etched on non-scratched Si was observed by SEM studies.[69] Enhanced nucleation on Si etched by HF/HNO_3 was also observed.[76] However, attempts to enhance nucleation by creating etch pits on non-scratched Si using acids, H^+, or other reactive gases were unsuccessful.[64,68]

Surface passivation was tried to suppress the deleterious effect of Si surface oxides (like SiO_2) in order to enhance heteroepitaxial diamond nucleation.[77] X-ray photoelectron spectroscopy showed the H, Br and I passivated Si surfaces to be free from silicon oxides and carbides. A dramatic enhancement of nucleation density of the order of 10^{10} cm^{-2} was observed on Br passivated Si surface. The degree of nucleation enhancement was related to the saturation value of electron emission current from the passivated surfaces, which increased in the order of H, I and Br passivation. The same order was also observed in the adsorbate desorption temperature from the Si surface. Greater nucleation enhancement was observed when the adsorbate desorption temperature was closer to the nucleation temperature. Fairly uniform and high nucleation density for the Br passivated Si substrate is shown in Fig. 1.

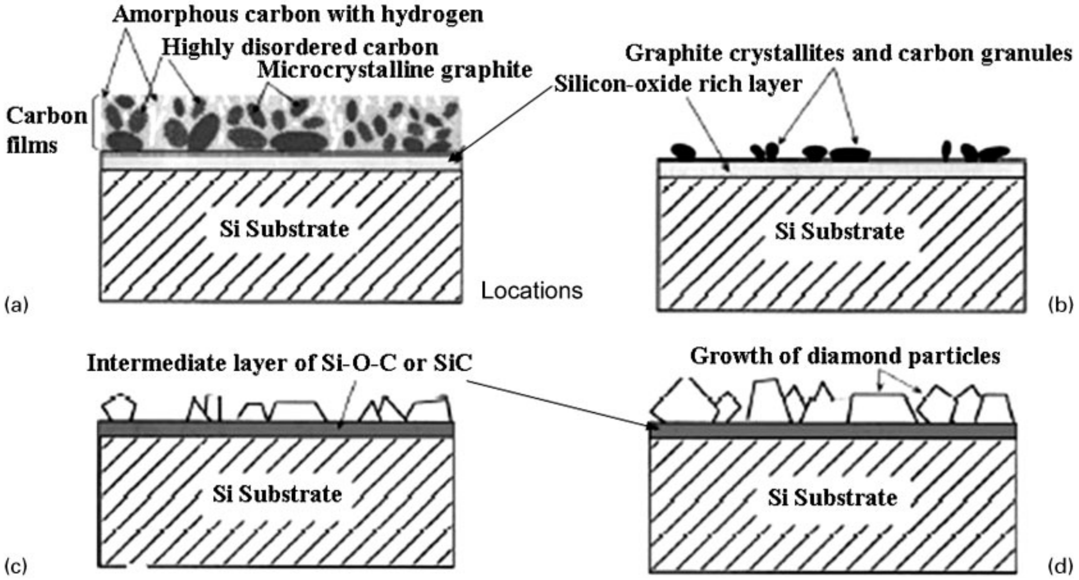
Surface coating

Nucleation enhancement was achieved by covering the substrate with thin films of metals (Fe, Cu, Ti, Nb, Mo, Ni), C-70, Y_2O_3–ZrO_2, amorphous-BN, SiC, hydrocarbon oil, graphite, amorphous-C, diamond like carbon (DLC), C-60 and even with mechanical oil.[42,78–82] The effect of these coatings in nucleation enhancement was ranked as C-70 > amorphous-C > DLC > graphite fibre > graphite film > Fe > Cu > Ti > Ni > Mo > Nb. The nucleation enhancement was attributed to the physical and chemical changes to the substrate surface (the coatings enhance carbon saturation on the surface and provide high energy sites or nucleation centres) and changes to the gas chemistry in the immediate vicinity of the substrate surface.[78] In order to avoid delamination of the diamond film from the tool materials surface because of the thermal expansion mismatch between the two and to avoid the detrimental effect of some metals like Co, Fe on the nucleation and growth of diamond, several interlayer coatings were applied on the tool materials.[8–10] The hard coatings of TiN, TiC, Si_3N_4, SiC, SiC_xN_y, (Ti, Si)N_x and pulsed arc deposited a-C (laser arc) were also investigated for their suitability as interlayers for diamond growth.[7] The nucleation density was dependent on the interlayer materials and substrate temperature. The nucleation densities were 10^5–10^8 cm^{-2} for the titanium and silicon containing interlayers. The ultrasonic pretreated amorphous-C layers had nucleation density of $\sim 10^{10}$ cm^{-2} compared with 4×10^7 to 6×10^7 cm^{-2} for the untreated samples. No dependence of the nucleation density on amorphous-C layer thickness was found. The nucleation density for different interlayer and process conditions is summarised in Table 2.

A high nucleation density was obtained on a carbon film coated Si (100) substrate over a wide region in a magneto active MPCVD method using $CH_4/CO_2/He$ gas mixtures.[83] Nucleation densities as high as 10^9 cm^{-2} was attained for small CO_2 concentrations of 1–2% during the pretreatment process, while no successful enhancement was observed for Si substrates pretreated at high CO_2 concentrations beyond 3·7%. Diamond nucleation was dependent on the structure and property of the predeposited carbon films, which influenced the etching and agglomeration in the subsequent growth process. A model was proposed for the diamond nucleation based on a two step process as shown in Fig. 2. When the carbon film consisting of a mixture of microcrystalline graphite and an amorphous-C phase is deposited (Fig. 2*a*), the initial stage the anisotropic etching creates

Table 2 Diamond nucleation densities for different interlayers and process conditions[7]

Interlayer	Interlayer thickness, μm	Substrate pretreatment with diamond powder	Substrate temperature, K	Nucleation density, cm^{-2}
TiN	5·8	Yes	920	10^8
TiN	4·6	Yes	1140	2×10^5
S_3N_4	6·8	Yes	910	10^8
S_3N_4	5·0	Yes	1080	6×10^6
SiC_xN_y	7·8	Yes	960	10^8
SiC_xN_y	5·5	Yes	1030	10^8
SiC	9·6	Yes	920	10^8
SiC	15·0	Yes	1070	10^8
a-C	0·01	No	850	4×10^7
a-C	0·1	No	860	6×10^7
a-C	0·01	Yes	860	10^{10}



a carbon film consisting of microcrystalline graphite and amorphous-C phase; *b* graphite crystallites and carbon granules are created on silicon oxide rich layer on substrate; *c* diamond precursors are nucleated from carbon clusters; *d* diamond particles grows on carbide intermediate layer

2 Schematic model of diamond nucleation and growth processes after nucleation enhancing treatment (reprinted with permission from Ref. 83, copyright 2000, American Institute of Physics)

graphite islands. Since the graphite crystallites are large enough in size to remain stable in the diamond growth plasma during the subsequent treatment process, the highly disordered and defective carbon regions around the microcrystalline graphite are etched off first by H, O and OH radicals and ions (Fig. 2*b*). This created graphite crystallites or carbon granules (such as those in carbon black or fullerenes), which remain non-volatile or aggregate to form various kinds of carbon clusters. Some of these clusters may be converted to precursors for diamond nucleation (Fig. 2*c*) and growth of diamond particles (Fig. 2*d*).

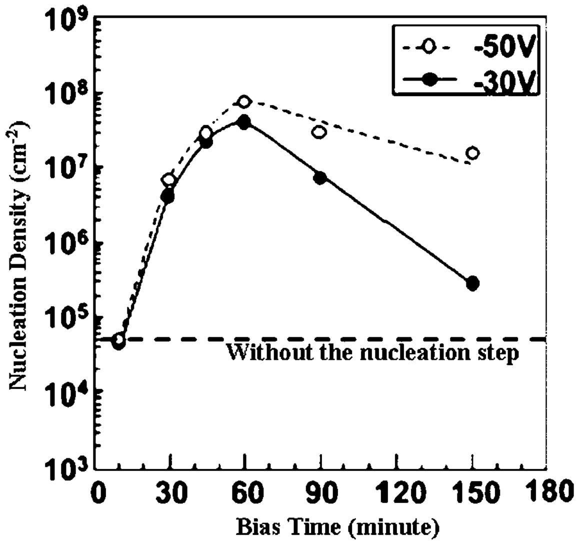
Ion implantation/ion bombardment

The ion implantation is generally employed to modify the surface energy and surface structure of the substrate in order to enhance the nucleation density. However, implantation induced reduction in nucleation is also reported in the literature. Implantation of C^+ (with a dose of 10^{18} ions cm^{-2}, 65–120 keV) on Cu substrate and As^+ (with a dose of 10^{14} ions cm^{-2}, 100 keV) on Si substrate enhanced nucleation.[42] Si^+ implantation (with a dose of 2×10^{17} cm^{-2}, 25 keV) on a mirror polished Si wafer also enhanced nucleation.[84] The surface structure was changed owing to implantation, but the Si composition of the surface remained unchanged. However, Ar^+ implantation (with a dose of 3×10^{15} ions cm^{-2}, 100 keV) on Si substrate was deleterious in enhancing the nucleation density.[85] Si^+ implantation enhanced nucleation because it created nanoscale surface defects on the Si substrate, which served as the active sites for the adsorption of hydrocarbon radicals necessary for initial diamond nucleation. A similar effect was found in the growth of diamond on porous silicon whose surface had nanoscale microstructure.[86] The lattice damages like strain, amorphous disorder and twinning created by the ion implantation were suggested for enhanced nucleation. The strain was the main reason for enhanced diamond nucleation on ion implanted substrates.

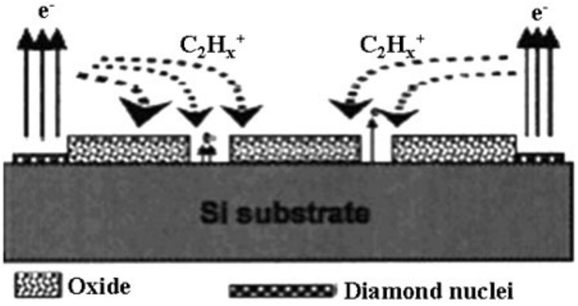
Biasing

Among the various pretreatment techniques studied in the literature, biasing the substrate has been the most effective in enhancing the nucleation density of diamond film. Since the surface free energies and lattice constants of Si/SiC are different from those of diamond, it is difficult to nucleate diamond on mirror polished Si substrate. Both the positive and negative biases have been fruitful in achieving high nucleation density for diamond growth.[42,64] An enhanced diamond nucleation density of about 10^9–10^{11} cm^{-2} on a mirror polished Si substrate was obtained by applying a negative substrate bias voltage.[87,88] Biasing a substrate helps in reducing the oxide formation on the substrate, removing the already formed oxide layer and overcome the activation energy required for the stable nuclei formation. Negative bias produced roughening of the grown surface owing to continuous bombardment by the cations, whereas positive bias led to a smooth surface. The grain size and non-diamond phase in diamond films were decreased with increasing bias current, leading to high Young's modulus and fracture strength. By applying a negative bias to the substrate, the nucleation density, adhesion and surface properties were improved while trying to coat complex shaped tools such as dental burs with polycrystalline diamond films in a modified HFCVD system.[45]

The nucleation density also increased with bias time at a bias voltage of –300 V. The highest nucleation density was $0{\cdot}9\times10^{10}$ cm^{-2} for a bias time of 30 min. The nucleation density and crystallinity of the diamond film was studied recently by applying a negative substrate bias as a function of bias time using an ECR plasma.[89] The mean ion energy onto the substrate was kept at 30 and 50 eV by controlling the bias voltage. For short bias times of 10–60 min, the nucleation density increased with time and the highest nucleation density of 10^7–10^8 cm^{-2} and crystallinity were obtained at 60 min of biasing (Fig. 3). For long bias times of 60–150 min, the



3 **Nucleation density on n-Si (100) substrate as function of time for bias voltages of −30 and −50 V: horizontal broken line represents density after growth step but without nucleation step; reprinted from Ref. 89, copyright 2004, with permission from Elsevier**



4 **Schematic diagram of electron emission enhanced diamond nucleation on partially patterned SiO_2/Si substrate (reprinted with permission from Ref. 100, copyright 2001, American Institute of Physics)**

nucleation density decreased with time. The deterioration of the film crystallinity for longer bias times was due to a reduction of the effective substrate bias voltage caused by the delamination of the deposited amorphous carbon film. The incubation period for nucleation was estimated between 10 and 30 min, which were associated with the formation of an amorphous hydrogenated carbon matrix suitable for nucleation.

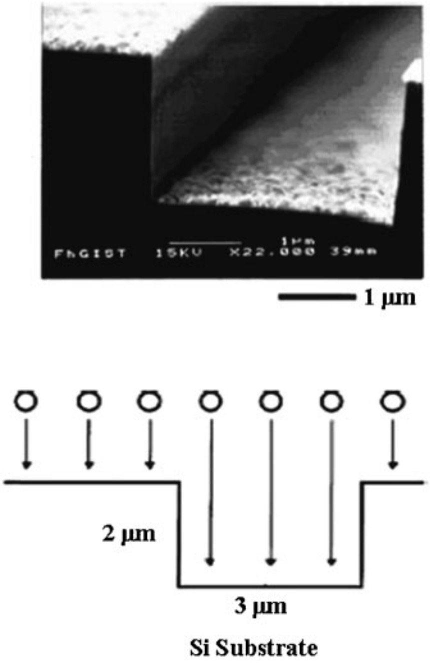
A negative bias is not found helpful in achieving nucleation enhancement for films grown by HFCVD method. Positive bias enhanced nucleation has helped in achieving the growth of textured diamond films on Si (111) and carbon face 6H–SiC (0001) in an MPCVD.[90] A bias voltage of 100 to 300 V, 3%CH_4 concentration in bias step and 0·33%CH_4 concentration in growth step were used to synthesise the films. Highly oriented diamond films were observed by SEM and X-ray diffraction (XRD). The interface between diamond and Si substrate was smooth (revealed in cross-sectional TEM), while it was normally rough between diamond and SiC without the bias. More examples of the positive bias in enhancing the nucleation density in dc plasma enhanced CVD (PECVD) and HFCVD were reported in Ref. 42.

However, if the plasma is generated by the bias voltage, an enhancement of nucleation similar to that obtained for MPCVD can also be achieved for HFCVD. Stubhan *et al.*[91] and Chen *et al.*[92,93] demonstrated that, in HFCVD system, diamond nucleation enhancement can also be realised when a negative bias is applied to the substrate. The highest nucleation density can reach 10^9–10^{10} cm^{-2} on mirror polished Si, which is similar to the results obtained using the MPCVD system.

Bias enhanced nucleation mechanism has been widely studied and different models have been proposed. Yugo *et al.*[94] and Gerber *et al.*[95] have suggested a shallow ion implantation model in which the sp^3 bonded carbon clusters, formed by low energy ion implantation, function as the nucleation precursors. The negative bias causes the positively charged ions in the growth chamber to accelerate towards the substrate surface and bombard it. This process helps in removing the surface contamination and facilitates cluster formation on the surface. These events in turn advance diamond nucleation. Stoner *et al.*[96] on the other hand, have suggested that critical process should be a change in plasma chemistry. Substrate biasing can increase the concentration of atomic hydrogen in the plasma or help in the formation of a thin carbide layer on the surface, which helps in enhancing the nucleation. Jiang *et al.* found the overall temporal evolution of the nucleation density agreed well with a surface kinetic model involving immobile active nucleation sites, germs (an intermediate species in the formation of nucleus) and nuclei.[97,98] They also suggested that, in addition to surface defects (point defects, steps and sp^3 bonded carbon clusters) serving as the nucleation sites, the enhanced surface diffusion and sticking probability of carbon on Si surface owing to ion bombardment should be the decisive factors. The enhancement of the surface diffusion of carbon species was identified by investigation of the distribution of the first nearest neighbour distances.[97] Therefore, the role of ion bombardment is crucial to enhancing the diamond nucleation.

It has also been suggested that diamond crystallites formed during the bias enhanced nucleation stage, serve as nucleation centres for the subsequent diamond growth.[99] It is concluded that the variation in the substrate temperature rather than the changes in the MW input power or plasma chemistry drive the observed structural changes and increase in nuclei density. The model for bias enhanced nucleation suggests that the ion bombardment leads to the formation of predominantly sp^3 coordinated carbon clusters, which then undergo a recrystallisation to form diamond crystallites. These diamond crystallites subsequently serve as nucleation centres for the growth of diamond films.

An electron emission enhanced nucleation mechanism has been proposed to describe the bias enhanced nucleation of diamond on a Si substrate, using a SiO_2 mask (Fig. 4).[100] The variation of nucleation density on the partially patterned SiO_2/Si substrate also reveals that the BEN of diamonds in the MPECVD process follows the proposed mechanism. The results suggest that the diamonds cannot be formed on sample which is covered by the completely insulated (patterned) SiO_2. Other workers also have claimed that diamond nucleation always begins in areas covered by bias plasma (or secondary plasma) during the BEN step in MPECVD.



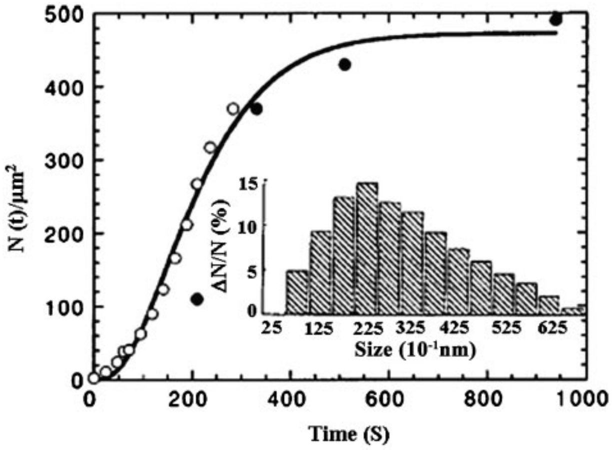
5 **Selective growth of diamond crystals on grooved silicon wafer containing both faces perpendicular and parallel to substrate: difference in nucleation densities on different faces is noticeable; reprinted with permission from Ref. 102, copyright 1998 by American Physical Society**

Electron emission has been found to enhance the nucleation of diamonds on the edge of the insulated substrates by initially forming diamond nuclei on neighbouring Si substrates that are not electrically insulated. The emitted electrons come from the diamonds on the Si surface of the patterns. Reactive gases are generated and the concentration has been found to increase with the pattern size since more electrons generated more reactive gases over a larger Si area. This assumption is supported by the fact that the nucleation density can reach 5×10^{10} cm^{-2} on the most exposed Si on the two sides. This observation supports that the BEN behaviour of diamonds in the MPECVD process is generated by electron emission enhanced nucleation.

In general, the nucleation of a particular phase demands formation of a nucleus exceeding a critical size and to become thermodynamically stable. According to the kinetic theory, the nucleation proceeds via the following steps:[101]

(i) vapour species such as atoms, molecules and/or radicals arrive on the substrate surface and get adsorbed
(ii) the species then diffuse over the substrate surface and part of the adatoms get desorbed from the surface into the vacuum
(iii) the adatoms get combined with each other and form clusters owing to fluctuations of the local species concentration
(iv) nuclei then grow by capturing the adatoms or by direct impingement of the atoms from vapour phase.

The critical size of the nuclei is dependent on the total free enthalpy of formation, which is related to the surface free energies of the nuclei and the substrate. The above sequence has been pictorially depicted in the reference mentioned above. The author has suggested that because of an energetic advantage, the nuclei are formed on the surface defects, like steps, dislocations or surface impurities, which are often called active sites for nucleation. Roles of factors contributing to bias enhanced nucleation of diamond are described below.



6 **Nucleation density (islands per μm^2) *v.* deposition time: solid curve is obtained by computer modelling using three step kinetic models; open and full circles in plots represent data calculated from crystal size distribution (inset) and obtained by direct particle counting respectively; reprinted with permission from Ref. 102, copyright 1998 by American Physical Society**

Role of ion bombardment

The directional flux of the energetic species on the substrate surface is essential to achieve a bias enhanced nucleation. This has been shown by performing BEN on topographically structured Si wafers containing grooves with vertical side walls as shown in Fig. 5.[102] This was created either by reactive ion etching or by SiO_2 masked Si substrates. The mean free path of ions in the flux is ~5 μm at gas pressure ~19 torr. Consequently, the ions flying towards the substrate cannot feel the groove surface structure and hence the parallel faces (with the substrate surface) will get bombarded with the high energy ion flux, while the side walls will not. Diamond nucleation on the parallel surface of the wafer justifies the role of ion bombardment in BEN.

Role of kinetics

Since a surface kinetic model[103] involving immobile active sites, germs (intermediate species in the formation of nucleus) and nuclei, is insufficient in describing the temporal evolution of overall nucleation density on Si wafers, a three step kinetic model was proposed.[104] Since in the BEN unscratched Si wafer is used as the substrate, the nucleation centres are only formed during the BEN stage. Therefore, an extra step for the generation of the nucleation sites has to be incorporated into the kinetic scheme. With this extra step, the kinetic scheme becomes

$$R\rightarrow N^{+}\rightarrow m\rightarrow N \qquad (1)$$

where R, N^{+}, m and N are densities of the surface centres that can be transformed into a nucleation site, the nucleation sites, the unstable clusters and the stable nuclei (nucleation density) respectively. The excellent agreement (as is shown in Fig. 6) between the theoretical curve obtained from the computer modelling using the three step kinetic scheme, as proposed by Tomellini and Polini,[104] and the experimental data calculated from crystal size distribution (open circles) (inset) and those obtained by direct particle counting (solid circles) justifies the role of kinetics in BEN.

Role of surface diffusion

The role of surface diffusion of the growth species in BEN was demonstrated by measuring the first nearest neighbour distance distribution of the nuclei. If surface diffusion of the mobile species (adatoms) towards immobile nuclei is involved in the nucleation process then the presence of nuclei (act as sink to the mobile species) should reduce the probability of formation of new nuclei in their immediate vicinity. The first nearest neighbour distance distribution of the nuclei should therefore deviate from a random distribution.[102] This has really been observed in SEM and AFM investigations. The measured distributions were found to shift to larger distances compared with the random distribution for a fixed nucleation density of the order of 10^{10} cm^{-2} for different samples. A depletion zone of the nuclei is found to increase from 12 nm for $V_b = -150$ V to 35 nm for $V_b = -250$ V. The increased depletion as a function of bias voltage confirms the contribution of surface diffusion towards BEN.

Based on the above observations the nucleation sequence under BEN condition is thought to proceed as:

(i) formation of nucleation sites
(ii) formation of carbon clusters owing to enhanced surface diffusion
(iii) formation of stable diamond nuclei.

Pulsed laser irradiation

Pulsed laser irradiation of a thin layer of a-C or WC or c-BN deposited on various substrates enhanced diamond nucleation as well as the adhesion of the film to the substrate.[42] It was speculated that the irradiation converted a part of the a-C on the substrate surface into diamond.

Carburisation

Carburisation of the substrate surface also helps in achieving high nucleation density because of its ability to cover the substrate surface with a thin coating of carbide or to make the surface layer saturated with carbon, both of which help in diamond nucleation.[42]

Most of the pretreatment techniques used to enhance nucleation also lead to damage of the surface by introducing different kinds of defects on it. Moreover, all the surface treatment procedures (like scratching, seeding) can not be applied equally well to substrate with complicated geometry and shape. Also, some applications demand very smooth and clean surfaces, like those used in electronics device applications, optical windows and smooth wear resistant coatings. There are some alternative ways to improve the nucleation without damaging the substrate surface. These include changes in process parameters, such as substrate temperature, gas pressure, precursor composition or the effect of different additives into the precursor gases for enhancing nucleation as described below.

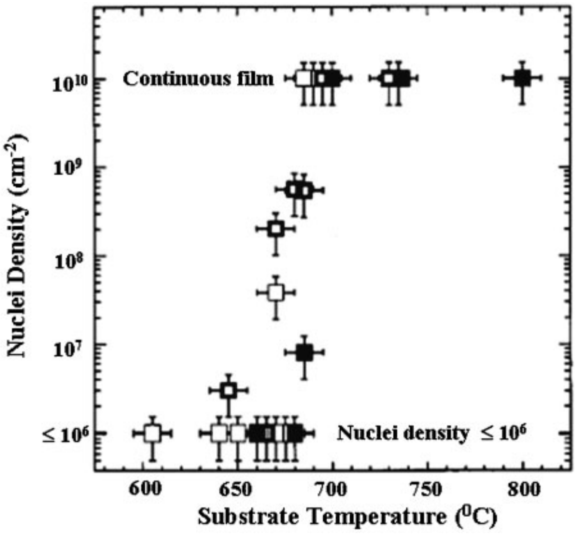
Seeding

Seeding the substrate by diamond particle of different dimensions (nanometre to micrometre range) has long been known to enhance the nucleation density. Seeding is achieved either by dip coating or by electrophoresis. In dip coating, the substrate is immersed in a purified diamond suspension of ultrafine particle size. In electrophoresis, diamond particle in suspension being negatively charged gets deposited at the positive electrode (the substrate to be seeded) under the application of an electric field between two electrodes dipped in the suspension.

Dip coating used a methyl alcohol based ultra pure and unltrafine (5 nm) diamond suspension in water and achieved a very high nucleation density of the order of 10^{11} cm^{-2} in 10 min on single crystal Si (100) wafer in a magneto active MW plasma process.[105,106] An acetone based diamond suspension of particle size 3–6 nm is used for seeding the single crystal Si wafer by dip coating process to achieve high nucleation density in a low temperature CVD diamond growth process.[107] A very high nucleation density of the same order (10^{11} cm^{-2}) led to diamond growth at 200°C.[106]

Electrophoresis technique is used to seed the substrate with micrometre size diamond particle to achieve (111) oriented diamond film synthesis[108] or to coat WC–Co cutting tool by CVD diamond.[109] Electrophoretic seeding in acetone medium produced a more uniform seeding at 500 V with high nucleation density leading to highest diamond growth in an HFCVD process.[108] Seeding with smaller grains (0·25 μm) produced randomly oriented non-faceted diamond growth whereas seeding with 5 μm grain size led to (111) oriented growth. For coating the WC–Co cutting tool by CVD diamond film, insufficient nucleation density of the scratched substrate led to no film formation when the substrate Co was not removed by acid. But, electrophoretic seeding of the substrate produced film type deposit under similar conditions. Although the nucleation density was not high, it increased with applied voltage. An increase in voltage from 10 to 1000 V led to an increase in nucleation density from 20×10^{-6} to 350×10^{-6} cm^{-2} after 600 s of the electrophoresis. Although most of the work on electrophoresis describe diamond particle as negatively charged in the suspension and hence deposited at positive electrode, positively charged diamond particle in electrophoretic suspension is also reported.[110] The origin of the surface positive charge of the diamond particle was attributed to the adsorption of the H^+ ion in the suspension. In acetone medium H^+ ions are generated as a result of keto enol tautomerism catalysed by H_2O and I_2, which gets adsorbed on diamond surface. The author has suggested isopropyl alcohol solvent to provide more stable suspension when I_2–H_2O–acetone is used for electrophoresis. It was observed that for smaller particle dimension (0·5–1 μm) low applied voltage (50 V) is preferable to generate uniform coating and to prevent particle agglomeration.[110]

Beside the electrophoresis and dip coating in nanodiamond suspension another important technique includes imparting a positive surface charge to the substrate surface followed by dip coating in a diamond suspension.[111] A high and uniform nucleation density is reported on a variety of substrate material such as, single crystal silicon wafer, a commercial glass capillary tube (Fisher Scientific), soda lime silicate commercial glass slide (Fisher Scientific), fused quartz commercial



7 Nuclei density (after complete deposition cycle) as function of substrate temperature: open symbols – substrate temperature adjusted by external heating (MW input power 280 W (open square), 320 W (bold open square)); closed symbols – substrate temperature adjusted by variation of the MW input power; reprinted with permission from Ref. 99, copyright 1996, American Institute of Physics

slide (SPI). Using polyethyleneimine as cationic polymer to impart a surface positive charge to the negatively charged substrate surface followed by dip coating in diamond suspension of different grain sizes (3/4 μm) very high and uniform nucleation density was obtained over a wide area.[111]

All these seeding techniques are important particularly when dealing with very large and wide substrate area pretreatment. Since seeding of the diamond particle over wider substrate area produce uniform and dense nucleation in a shorter time and at lower substrate temperature, this technique is particularly suitable for low temperature growth of CVD diamond film.

Effect of temperature

Nucleation density N_d generally increased with temperature for a fixed set of other deposition parameters such as pressure, MW power, gas composition and particular gas flow rate. An enhancement of nucleation density from $\leqslant 1\times10^{6}$ cm^{-2} to 1×10^{10} cm^{-2} in a narrow temperature range between 670 and 700°C was obtained during deposition of a polycrystalline diamond film using bias enhanced nucleation, while the other deposition parameters such as the MW input power were kept constant.[99] The enhancement of nucleation density with temperature is shown in Fig. 7. The intensity of the diamond plasmon in the electron energy loss spectroscopy increased with the substrate temperature, which was the signature of enhanced diamond crystallites concentration embedded in the amorphous carbon matrix. It was suggested that diamond crystallites formed during the pretreatment served as nucleation centres. The variation in the substrate temperature rather than the changes in the MW input power or plasma chemistry was proposed to drive the observed structural changes and enhanced nucleation density.

The nucleation density increased with increasing filament temperature, reached the maximum at 2100°C and then decreased thereafter in HFCVD.[112] The decreased nucleation beyond 2100°C was attributed to the enhanced etching of the nucleation sites. A number of examples of enhanced nucleation with temperature are found in for different deposition methods and an optimum temperature has been found to exist ~860°C where the nucleation density becomes maximum.[42] The enhanced nucleation with increasing temperature is suggested to be caused by the change in the adsorption state and surface diffusion length of growth species. The reactive species or molecules get adsorbed on the substrate surface physically <900°C and chemically beyond this temperature. This results in an abrupt change in diffusion length at ~900°C. The sticking probability of the reactive species on the substrate surface increases as the temperature approaches 860°C.

Effect of pressure

The pressure dependence of nucleation density is a result of competition between β-SiC formation (which enhances the diamond nucleation density) and the atomic H etching (which decreases the nucleation sites). Recently, a high density of diamond nucleation (10^{9}–10^{11} cm^{-2}) was achieved on mirror polished Si substrates using HFCVD under very low pressures (0·1–1 torr) without applying surface scratching or a substrate bias.[113] Using this method, diamond grains with a density $>10^{10}$ cm^{-2} can be achieved, which is more than two orders of magnitude higher than the highest density (10^{7}–10^{8} cm^{-2}) that can be obtained on scratched substrates under conventional pressure (10–50 torr). High nucleation density of diamond is achieved on a 4 in Si (100) wafer in a low pressure (0·2 torr) process, but the quality of the film was not good.[114]

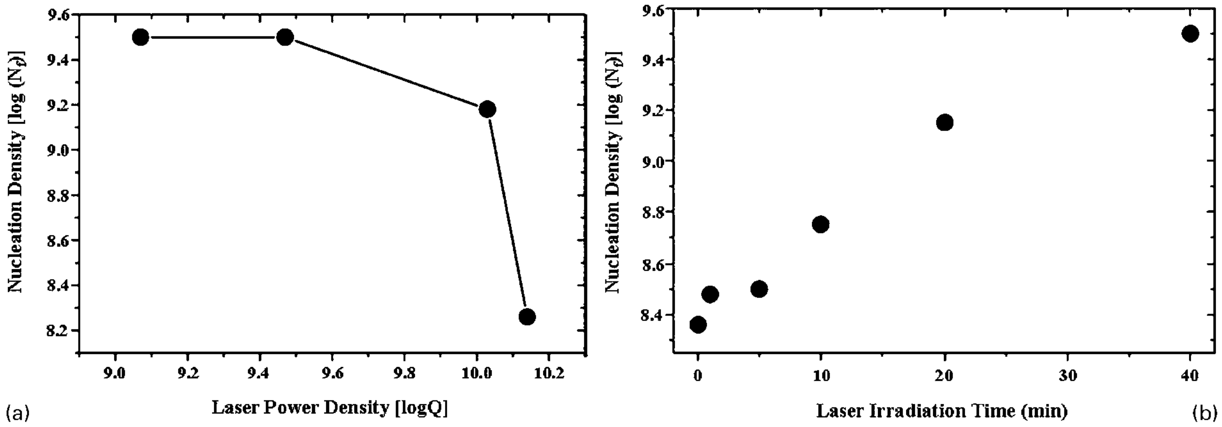
Effect of precursor gases

The precursor gas also affects the nucleation density either by stabilising the diamond nucleus precursor[115] or by enhancing the carbon saturation of the substrate surface, which triggers nucleation.[83,116] The enhanced methyl radical (CH_3) density produced by the precursor gases is also responsible for enhanced nucleation density as reported in most of the literatures.[117]

An increase in overall growth rate by 7, 16 and 39% at substrate temperatures of 850, 750 and 650°C respectively, using chloromethane instead of methane as precursor in an MWCVD was attributed to the higher nucleation density induced by chloromethane precursor.[115] Chloromethane was found to reduce the time required for film formation and increased the nucleation density significantly, particularly at low growth temperatures (Table 3). In Table 3, time period for film forming stages is defined by the end of the temperature rise programme to the moment of first reflection intensity minimum. The time periods of film forming

Table 3 Time period for film forming stages and nucleation densities at first reflection intensity minimum for 1·5% of CH_4 and $CHCl_3$ (Ref. 115)

Temperature, °C	Time, min		Nucleation density, $\times10^{8}$ cm^{-2}	
	$CHCl_3$	CH_4	$CHCl_3$	CH_4
850	39·2	57·1	18	9·2
750	30·8	63·8	18	3·1
650	30·7	100·6	36	13



8 Diamond nucleation density as function of *a* laser power density and *b* irradiation time: nucleation density in ordinate (of *a* and *b*) was expressed in unit of cm^{-2} and laser power density in abscissa (of *b*) in unit of W cm^{-2}; reprinted from Ref. 118, copyright 2001, with permission from Elsevier

stages were measured by laser reflective interferometry. Nucleation densities were counted from SEM micrograph. The reason that chloromethane enhances the total growth rates was attributed mainly to its ability to stabilise diamond nucleus precursor, particularly at low temperatures, to enhance diamond nucleation.

Diamond film with high nucleation density was obtained using a $CH_4/CO_2/H_2$ gas mixture.[83] Nucleation densities as high as ~10^9 cm^{-2} was obtained for small CO_2 concentrations of 1–2% during the pretreatment process, while no successful enhancement was observed for pretreatment at high CO_2 concentrations beyond 3·7%. The curved sheet like structure of the predeposited carbon films and its porous nature influenced diamond nucleation. The nature of reacting species present in the plasma and their emission intensities with increasing CO_2 in the precursor gases were monitored by in situ OES and quadrupole mass spectroscopy. These informations were used to support the enhanced nucleation for 1·9%CO_2 concentration in the gas mixture. The morphology and composition of the specimens also supported the observed effect.

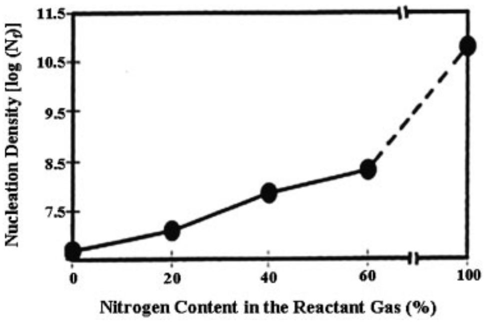
A high CH_3 radical density, leading to enhanced nucleation, was observed from a CH_4/He gas mixture in a bias enhanced large area diamond nucleation on Si (001) using ECR MPCVD.[117] With a CH_4/H_2 gas mixture the nucleation density of the order of 10^7 cm^{-2} was obtained using high CH_4 concentration. However, CH_4/He produced a nucleation density as high as 10^9 cm^{-2} even at low concentration of CH_4 gas with a bias voltage of +30 V. The main difference between the two plasmas was the difference in H concentration rather than CH_3 concentration and plasma density. It was suggested that the proper balance between the carbon related radicals and H radical density on the substrate surface could make the nucleation density high.

Effect of variation in process or additives in precursor gases

Variation in the synthesis process or addition of any special gases with the precursors affects the nucleation process greatly.

A rapid increase in nucleation density was obtained on mirror polished Si substrate by a pulsed Nd:YAG laser beam.[118] The laser beam was used to excite and decompose the reactive gases and to enhance the etching of the non-diamond phases. An enhanced nucleation density from 10^8 to 10^{10} cm^{-2} was observed with decreasing laser power density from $1{\cdot}38\times10^{10}$ to $1{\cdot}17\times10^9$ W cm^{-2} and deposition pressure from 760 to 3 torr, which is one to two orders of magnitude higher than that obtained on a similarly treated substrate using hot filament activation with a pulsed laser power density range $4{\cdot}6\times10^4$ to $2{\cdot}65\times10^5$ W cm^{-2}. At lower substrate temperature (as low as 650°C), however, the pulsed laser beam could not help in enhancing nucleation. The variation of nucleation density at the centre of the laser irradiation spot with laser power density is shown in Fig. 8*a* for nucleation at the substrate temperature of 700°C, CH_4 concentration of 2%, pressure of 30 torr and irradiation time of 40 min. The enhanced nucleation and growth of diamond crystallites was attributed to the effective excitation of reactive gases and etching of the non-diamond carbon phases by pulsed laser beam. The highest nucleation density obtained was up to 10^9–10^{10} cm^{-2} at $1{\cdot}17\times10^9$ to $10{\cdot}7\times10^9$ W cm^{-2} laser power density range and then decreased with further increase in the laser powder density. Since high laser powder density was not beneficial to the adsorption and reconstruction of the nucleating species on the substrate surface, high laser power reduced the diamond nucleation. The nucleation density also increased with irradiation time at a constant laser power density as shown in Fig. 8*b*. The nucleation density increased steadily from $2{\cdot}3\times10^8$ to $3{\cdot}2\times10^9$ cm^{-2} during an irradiation time from about 2 s up to 40 min.

N_2 addition in the precursor gases has sometimes been found beneficial for enhancing the nucleation density.[119] An increase in the nucleation density was obtained in synthesising diamond films by an HFCVD using a $CH_4/N_2/H_2$ gas mixture. With increasing nitrogen concentration in the gas mixture, the nucleation density increased and the crystal size decreased. The increase in nucleation density with increasing N_2 content is shown in Fig. 9. The observed result agreed well with those reported by Zhou *et al.*, where nanocrystalline diamond (NCD) was synthesised by MPECVD using N_2/CH_4 as the reactant gases without any additional H_2.[120] But, an adverse effect was found in the work of Yang *et al.* where increasing N/C ratio in the feed gases ($CH_4/Ar/H_2$) decreased the nucleation density as shown in Fig. 10,[121]

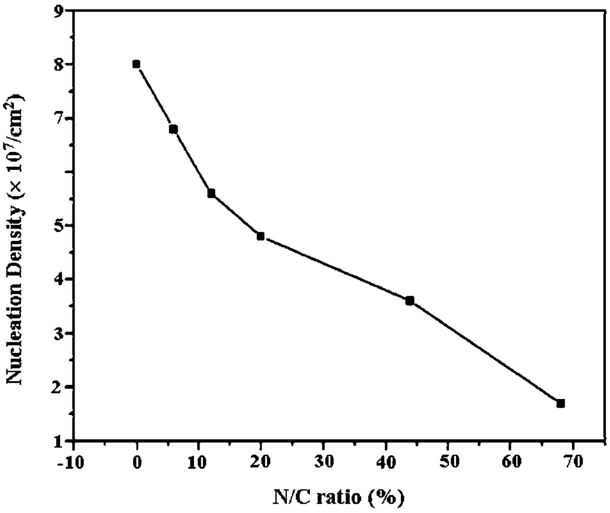


9 Dependence of nucleation density on N_2 additions in reactant gases, $N_2/H_2/CH_4$: nucleation density in ordinate was expressed in unit of cm^{-2}; deposition experiments were carried out at 35 torr pressure and at substrate temperature of 650–750°C on (100) Si wafer; reprinted from Ref. 119, copyright 1999, with permission from Elsevier

and these authors have suggested a lower covering ratio of the diamond grains on the substrate with increasing N/C ratio in the nucleation stage.

Diamond is a metastable phase under CVD condition and its formation needs high activation energy compared with more stable phase of graphite. So the nucleation of diamond from carbon containing precursors under CVD conditions does not follow the conventional route where the adatoms get agglomerated to form a critical nucleus of a stable size. The process parametric window is narrow for diamond nucleation on non-diamond substrates. On an atomistic scale diamond nucleation can be thought of proceeding via the following steps. The atoms or ions from the gas phase impinge the deposition surface and get adsorbed on high energy sites. The adatoms may either desorbs or diffuse over the surface. In course of time, the surface concentrations of the adatoms increase and get combined to form clusters. These clusters may grow or decay depending on the statistical fluctuations of the local adatom concentrations.[97]

Beyond a critical size (3–5 nm) the probability of growth is more than the decay. So the cluster, which qualifies the critical size during concentration fluctuations becomes stable. The stable cluster eventually grow either from the continued migration of the adatoms or from the impingement of ions or atoms from the gas phase. For deposition, surfaces which already have diamond grains on it provide better nucleation by shortening the incubation period (time to start nucleation). All the pretreatments contribute to one or more of the above stages to occur more efficiently thereby enhancing nucleation keeping in view the same mechanism. Since diamond being known as the material of highest surface energy (5·3 J m^{-2} for (111) surface), a majority of the pretreatment procedures for diamond deposition on non-diamond surface are mainly aimed at creating a high energy surfaces by generating defects or sharp edges or by creating unsatisfied bonds on the surface. Mechanical abrasion, ion bombardment/ion implantation, chemical treatments all provide a defected surface with high energy sites on it, which accelerates the adsorption of the atoms or ions from the gas phase. Seeding the substrate helps in lowering the incubation period for nucleation. Pretreatments like coating or carburisation is targeted for providing carbon rich areas on the surface, which are potential sites for cluster to form and trigger nucleation. Substrate materials, in many cases (like transition metals such as Ti, Mo, Ni, Fe), have been chosen which are either susceptible to carbide formation or carbide itself, such as WC, SiC, Be_2C, TiC. Lattice match and crystal structure of the substrate plays an important role in enhancing nucleation on non-diamond substrate. Ir and c-BN for example have very good lattice match with diamond (diamond 3·57 Å versus c-BN 3·62 Å and Ir 3·84 Å), which helps in achieving heteroepitaxial nucleation on these substrates. Biasing the substrate is aimed at accelerating the ionic flux towards the deposition surface thereby enhancing the growth of the stable cluster whose sizes are bigger than the critical size.



10 Effect of N/C ratio on nucleation density of diamond films deposited on molybdenum substrate by dc arc plasma jet (reprinted from Ref. 121, copyright 2004, with permission from Elsevier)

Besides the pretreatment procedures, process parameters like temperature, pressure, gas compositions, also help in nucleation in view of the general mechanism discussed before. Temperature helps in adatom diffusion/migration on the surface to form a stable cluster. Pressures and gas composition are critical in promoting the cluster to achieve the critical size otherwise they will reevaporate/desorbs from the surface rendering nucleation to occur.

Growth of diamond

The nucleation is followed by the growth stage. A successful nucleation is required in order to have a good quality diamond film, since nucleation affects the growth process in terms of growth rate, texture, roughness and the overall quality of the film. Diamond films are often classified as microcrystalline diamond (MCD), NCD, ultrananocrystalline diamond (UNCD) and ballas diamond based on the morphology (especially grain size) and the hybridisation of the carbon atoms present in that phase. Microcrystalline diamond consists of micron size grains, which range from one to hundreds of micrometres and sp^3 bonded carbon atom in the crystal structure. Whereas in NCD the grain sizes are normally <100 nm. The UNCD consists of equiaxed grains of dimension 3–5 nm. Both the NCD and UNCD contain a significant fraction of sp^2 bonded carbon atom along with sp^3 bonded carbon in the diamond structure. Amorphous carbon film with NCD normally consists of sp^2 clusters connected by sp^3 network. Ballas diamond is roughly ball shaped, the pieces are very tough and impact resistant. They do not show the cleavage characteristics of single crystal diamond.

Many investigations have been carried out in order to study the effect of nucleation on the growth of diamond films. Diamond films were grown on silicon substrates with low (10^4–10^5 cm^{-2}) and high nucleation densities ($>10^{10}$ cm^{-2}). From the same growth run, a highly $\langle 110 \rangle$ textured 300 μm thick white diamond film with a growth rate of 2·4 μm h^{-1} was obtained from high nucleation densities ($>10^{10}$ cm^{-2}) and a white diamond film of 370 μm in thickness with a higher growth rate of 3 μm h^{-1} was obtained from low nucleation densities (5×10^4 to 10^5 cm^{-2}).[122] The best quality film obtained in this experiment was found to have very smooth crystalline facets free of secondary nucleation and the full width at half maximum of the diamond Raman peak was 2·2 cm^{-1}, which was as narrow as that of IIa natural diamond. The results suggested that under suitable growth conditions, nucleation density had little effect on the film quality and low nucleation density resulted in higher growth rate than the high nucleation density owing to less intense grain growth competition. Since the grains in a polycrystalline film with the highest vertical growth velocity with respect to the substrate surface has the highest probability of survival, grains that grew normal to the Si surface propagated and survived. But, the growth of the grains that grew off normal to the substrate surface was terminated.

Sometimes the nucleation rate affects the subsequent growth of diamond film. The nucleation rate had a significant effect on the heteroepitaxial growth of diamond films on silicon surface. Highly oriented epitaxial growth of diamond was achieved on mirror polished silicon substrate.[123] Low and high nucleation rates led to some discrete big diamond crystals and polycrystalline diamond films respectively. A high nucleation rate resulted in a simultaneous and rapid growth of multi-oriented nuclei, facilitating the formation of polycrystalline grains.

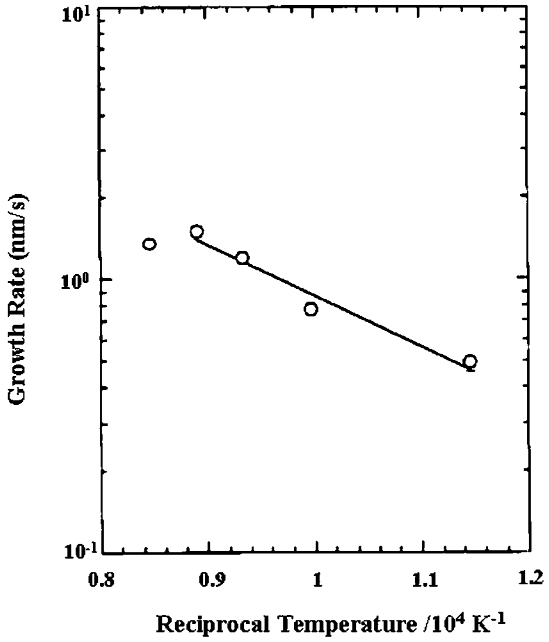
The relative quality of the diamond film, grown at low pressures (<2 torr) using an ECR PECVD system, was found to be dependent on the initial nucleation density and amount of the grain boundary fractions present in the film.[124]

Nucleation density also affected the surface roughness of the deposited film in the early stages of deposition. A nucleation density in the range of 10^8–10^{11} cm^{-2} (obtained by applying a coating of the diamond powder (diameter 0·038 μm) in a fluid on Si substrate) was used to study the effect of nucleation density on the film quality, surface roughness and growth rate.[125] Samples pretreated and processed under similar conditions to minimise the effect of different deposition conditions on film morphology showed similar surface texture and morphology. Samples with the highest primary nucleation density had the smoothest film surfaces at all deposition conditions.

Besides the quality, the morphology of the diamond film is related to the nucleation and growth rate. It has been found in several studies that high secondary nucleation with low growth rate generally favours the NCD, whereas low secondary nucleation with very high growth rate produces MCD. The processing parameters also affect the morphology of the produced film. A high bias voltage, substrate temperature, CH_4 concentration and low total gas pressure enhance the frequency of secondary nucleation and hence favour an NCD. A high gas pressure and MW power gives MCD. The effect of an additive gas in the precursor sometimes changes the morphology of the film. Addition of noble gases such as Ar, He and Xe to the conventional CH_4/H_2 mixture produces NCD films. Presence of N_2 gas in the precursor favours NCD film formation. Recently an Ar rich plasma (CH_4/Ar) has been very effective in producing UNCD film.[37]

The growth and quality of diamond film is strongly dependent on the processing conditions. The substrate, pretreatment, precursor gases, any additive gas in the precursor and process parameters such as temperature, pressure and MW power equally influence the growth rate and the quality of the film. A lot of research has been conducted in the past 25 years to study the effect of different processing parameters on the growth of diamond film on different substrates.[126–134] Besides the conventional CH_4/H_2 mixture, graphite/H_2 has also been used to form the film.[126] But, instead of continuous film only blocks of films and particles were obtained. Among the catalytic effect of various metal particles, those containing Co and Ni were found to enhance the growth rate and the growth mechanism in the presence of metal particle was found similar to that of low pressure CVD. Since the growth of the diamond phase occurred as a result of gas phase reaction either from methane conversion or from hydrogen radicals generated from hydrogen reacted with graphite on the sample surface, growth mechanisms for diamond synthesis methods either from gas precursor or solid precursor were similar to that of low pressure CVD diamond. The RTSE study was conducted to monitor the effect of different processing conditions during the course of deposition.[133] In addition to the accurate surface temperature measurement and close monitoring of the nucleation and early growth stage, this study also provided information on bulk layer thickness, mass thickness of the sp^2 C in the bulk layer and void volume fraction in the bulk layer. An attempt was made to optimise the different process variable such as reactor pressure, substrate temperature, gas flow rate and CH_4 concentration upon diamond film growth on Si_3N_4 and SiC substrates.[40,134] It was shown that the conditions for initial nucleation and film growth were different in two cases. For SiC substrate, nucleation density was strongly dependent on the CH_4 concentration and on pressure but growth rate mainly was influenced by CH_4 percentage at the deposition temperature range of 780–885°C. For the Si_3N_4 substrate on the other hand, nucleation was favoured by low process pressure and CH_4 concentrations (1·2–1·6%), while the growth rate was enhanced mainly by increasing the reactor pressure. The deposition experiments were carried out at 800–900°C.

Since the conditions for growth related to a specific substrate–precursor combination are different from the other substrate–precursor combination, we briefly discuss the effect of the different process parameters on the growth of diamond films for a particular substrate–precursor combination below.



11 Temperature dependence of diamond growth rate (reprinted with permission from Ref. 128, copyright 1999, American Institute of Physics)

Effect of temperature

The homoepitaxial diamond film deposition on (111) face of high pressure and high temperature synthesised diamond, in a cylindrically coupled MW plasma reactor with a radio frequency (RF) induction heating system using CH_4/H_2 gas mixture, showed an increased hydrogen incorporation and enhanced growth rate with increasing substrate temperature.[128] The increased growth rate with temperature (600–920°C) is shown in Fig. 11. The growth rate was found to follow an Arrhenius behaviour and was expressed as

$$G = A\exp\left(\frac{-E}{RT}\right) \qquad (2)$$

where A, E, R and T are the pre-exponential factor, the activation energy for growth, the universal gas constant and the absolute temperature respectively. A similar behaviour of growth rate with temperature was reported in the literature.[129–131] However, the activation energy for growth (36 ± 6 kJ mol^{-1}), calculated from the least square fitting of the Arrhenius plot is different from those reported earlier for growth on (100) and (111) faces. The observed difference in activation energy was suggested to be due to the difference in heating method employed for the deposition experiment. It might also be due to uncertainty in measuring the actual surface temperature during deposition.

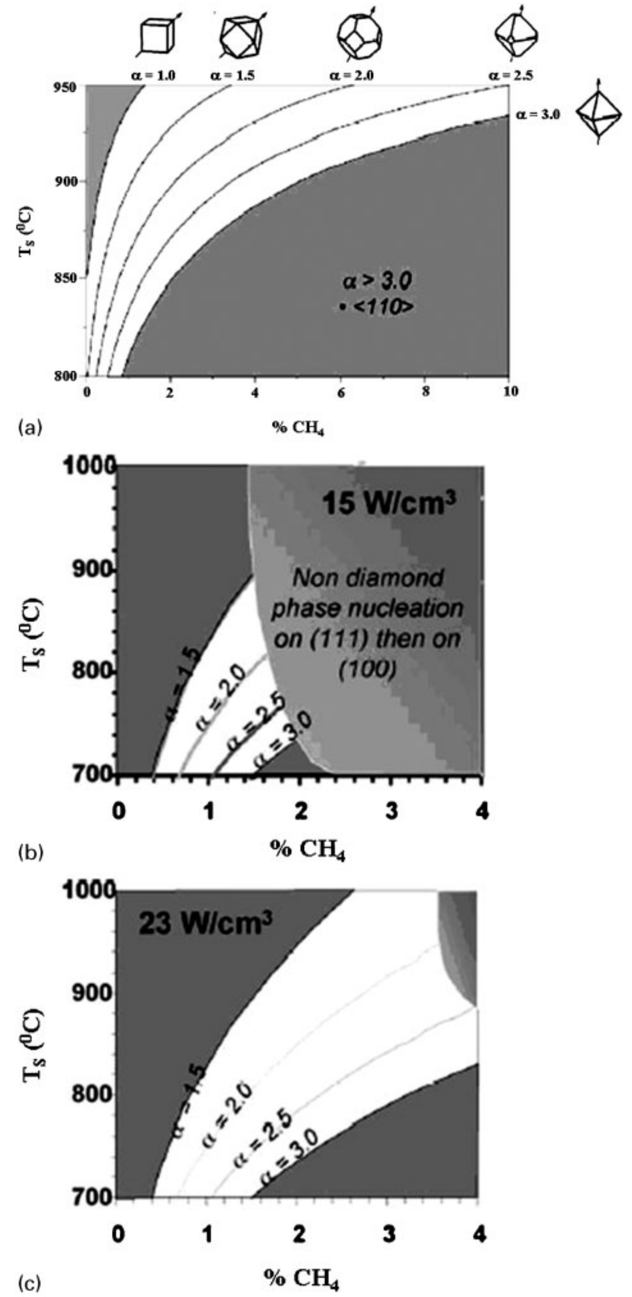
The effect of decreasing filament temperature on growth of diamond films using HFCVD has been reported.[135] Well faceted diamond crystals were obtained at a low filament temperature in the range 1500–1700°C using a CH_4–H_2 gas mixture. The deposition rate decreased with decreasing filament temperature. Although at lower filament temperature (1300°C) the morphology of the grains looked ball like, the diamond characteristics was still there as confirmed by XRD and Raman spectroscopy. However, the growth rate and quality of the film improved to a certain extent by introducing an inert gas.

The influence of substrate temperature and CH_4 percentage on diamond film quality, texture, morphology and growth rate was already reported in the literature.[136–138] Besides CH_4 concentration, textured growth of diamond film is a function of the growth temperature. The competitive growth between (100) and (111) planes decides the texture of diamond film. Displacement of these planes from the nucleation centre is a function of CH_4 concentration as well as deposition temperature. For textured growth, the 'α' parameter (which is defined as $\alpha = 3^{1/2}V_{100}/V_{111}$, where V_{100} and V_{111} represents the displacement rates of the (100) and (111) planes respectively) is dependent on the substrate temperature. When $\alpha = 1$, cubic crystallites are formed with (111) texture, but when $\alpha = 3$, pure octahedron diamond crystallites are obtained with distinct (100) morphology. The variation of 'α' with $\%CH_4$ and T_S (substrate temperature) is shown in Fig. 12*a*. It shows that decreasing CH_4 concentration and increasing substrate temperature gradually favours cubic crystallites with (111) morphology than the octahedron crystallites with (100) texture. Therefore, the $\langle 100 \rangle$ texture associated with (111) morphology is favoured by high CH_4 percentage and low substrate temperatures (conditions which provide high hydrocarbon supersaturation). But, the $\langle 110 \rangle$ texture associated with (100)(111) morphology is favoured by low CH_4 percentage and high substrate temperature (low supersaturation). The combined effect of $\%CH_4$ and substrate temperature on diamond film characteristics were discussed for two different MW power densities and the combined effect of $\%CH_4$, substrate temperature and MW power density is shown in Fig. 12*b* and *c*.[17] It is interesting to note that a (100) texture with an α value of 2·5 was obtained either at 1·7%CH_4, 780°C and 15 W cm^{-3}, or at 4%CH_4, 875°C and 23 W cm^{-3}. However, $\langle 110 \rangle$ texture associated with (111)(100) morphology was obtained at high temperature and low methane concentration irrespective of the MW power density.

Effect of pressure

High pressure normally increases the growth rate. Recently some reports showed very high growth rate using high gas pressures.[139,140] High growth rates, up to 4·5 μm h^{-1}, were obtained at high pressure (188 torr) and low CH_4 concentration for diamond deposition by MPCVD process using ellipsoidal reactor. H_2 desorption from the diamond surface under atomic hydrogen flux was found to limit diamond deposition rate. A nearly linear increase of the diamond deposition rate with the total pressure was observed at a CH_4 concentration of 0·5%. The deposition rate increased from 0·7 μm h^{-1} at low pressure (94 torr) to 4·5 μm h^{-1} at 188 torr. The observed variation of the growth rate from 0·7 to 4·5 μm h^{-1} was correlated to the deposition temperature from 727 to 1060°C respectively. A similar trend of growth rate was obtained at high power, high CH_4 concentration, high temperature and at high pressure up to 150 torr by Chein *et al.*[141]

Homoepitaxial growth of diamond film with growth rate as high as 50 μm h^{-1} was achieved[140] by an MPCVD process with 170 torr pressure, 2·52 kW MW power and 7%CH_4 as the precursor. A cooled stage was used for the experiment. The variation of the process parameters produced films with lower growth rates



12 *a* variations of α-parameter as function of CH_4 concentration and substrate temperature T_S at MW power density of 23 W cm^{-3}, and combined effect of CH_4 concentration (%CH_4) and substrate temperature T_S on diamond film characteristics at MW power density of *b* 15 W cm^{-3} and *c* 23 W cm^{-3}: grey zone indicates domains where nucleation of non-diamond phases first occurs on (111) faces and then on both (111) and (100) faces (as %CH_4 or T_S increases); reprinted from Ref. 17, copyright 2001, with permission from Elsevier

(10–20 μm h^{-1}). However, the surface conductive electrical properties of the film with highest growth rate were inferior to those deposited at lower growth rates owing to their increased surface roughness. Since the surface roughness affects the carrier transport, surface conductive properties are greatly deteriorated by the increased surface roughness of the film. The film deposited at such high growth rates was found comparable with those obtained by other methods such as dc arcjet.[142]

Effect of MW power

A high MW power coupled with high gas pressure and temperature has sometimes been found to affect the growth rate and morphology of the deposited film. The texture of the film is related to the input MW power during the deposition. Pulsing of the MW helps in achieving the low substrate temperature as well as the good growth rate.

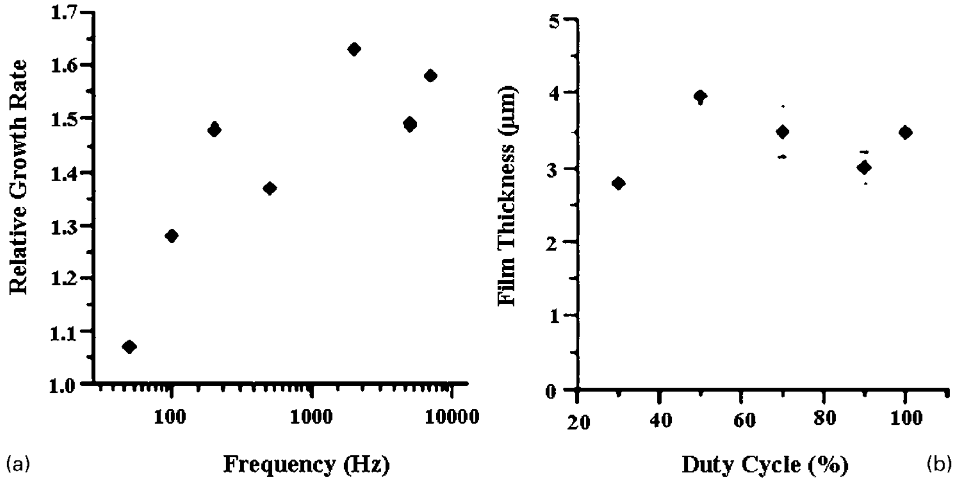
A growth rate of 9·3 μm h^{-1} was obtained for diamond films deposited at CH_4 concentration of 2–4% in H_2, an input power of 4·5 kW and gas pressure of 120 torr using a 5 kW MPCVD reactor.[143] The films were found to be either ⟨100⟩ or ⟨111⟩ textured, which was determined from the peak height ratio of the (111) and (400) reflections in the XRD pattern. The dependence of film texture on CH_4 concentration and substrate temperature for the 5 kW CVD reactor was, however, significantly different from that of 1·5 kW CVD reactors. Addition of small amount of oxygen ($O_2/CH_4 = 0{\cdot}06$) in the precursor gases increased the growth rate by 50% from that without the oxygen, while the addition of larger amount (O_2/CH_4 = 0·06 to 0·5) suppressed the growth rate to 3·8–2·8 μm h^{-1}.

An increased deposition rate of polycrystalline diamond film was obtained by varying the MW pulse repetition rate and duty cycle.[144] An increase in growth rate was found with pulsing frequency for the same average power. Changing the duty cycle for a fixed total plasma on time resulted in the same film thickness for all duty cycles, which suggested that growth took place only when pulse was on. The dependence of growth rate on pulse frequency and film thickness on duty cycle is shown in Fig. 13.

Effect of precursor gases

The precursor gas composition also affects the growth of diamond film. Despite the most commonly used CH_4/H_2 mixture, CH_4/N_2, CO/H_2 or $CO/H_2/O_2$ or halogenated precursor like chloro- and fluoro-carbon have also been used to enhance the growth rate.[145–152] Sometimes different gas mixtures have been used to deposit highly oriented diamond film.[153] Effect of CH_4/H_2 ratios have been used to study the effect of CH_4 concentration on the quality of the film.[46] The presence of a small amount of N_2 in the precursor gases proved beneficial to getting NCD films. Presence of O_2 in the precursor gases either as a pure O_2 or in the form of some oxides like CO_2 or CO helps in achieving low temperature growth. Halogenated precursors are also suitable for the low temperature growth of diamond.

Varying proportion of diamond and graphite was obtained in Raman spectroscopy during deposition of diamond on stainless steel substrate at low pressure and temperature with different CH_4/H_2 ratios from 4 to 9%.[46] The early stage of film growth revealed that the adsorbed amount of sp^3 and sp^2 C on the substrate was related to the ratio of CH_4 to H_2 in the precursor gases, which was identified from an in situ FTIR, employing reflection–absorption geometry (FTIRRAS) and OES. The sample grown with 5%CH_4 in H_2 showed no contribution from graphitic carbon but, it reappeared at ~1650 cm^{-1} in Raman spectra for CH_4 concentration $\geqslant$6%. However, the presence of a graphitic carbon phase on the substrates was believed to occur owing to factors related predominantly to the substrate chemical

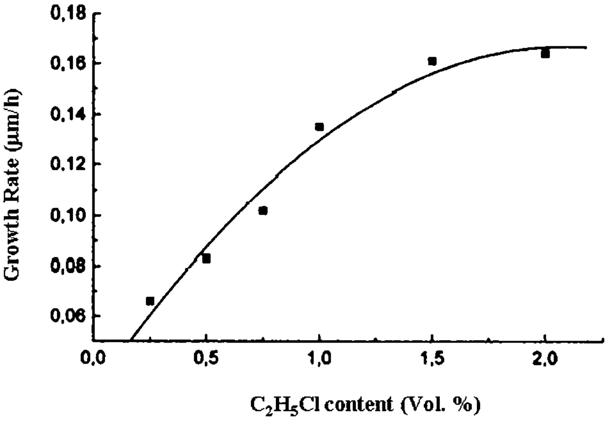


13 **Dependence of *a* growth rate on MW pulse frequency and *b* film thickness on duty cycle for total plasma on time of 4 h: reprinted with permission from Ref. 144, copyright 1999, American Institute of Physics**

structure rather than to factors associated with species occurring in the plasma. No diamond growth was observed for $<4\%CH_4$ in H_2 owing to high etching of the film by atomic H in the CH_4/H_2 plasma. For intermediate CH_4/H_2 ratios about 4 to 9%, sp^3 carbon was present in the form of diamond.

Presence of N_2 in CH_4/N_2 mixtures strongly influenced the growth rate and morphology of the NCD films prepared by MPCVD process.[145] The bonding, however, was almost unaffected. Raman spectra showed the presence of sp^2 bonded carbon in the matrix, although according to electron energy loss spectroscopy and X-ray photoelectron spectroscopy investigations, the sp^2 content was very small. Infrared spectra showed the hydrogen atom to be bonded primarily to the sp^3 CH_x groups.

Different types of growth behaviour of diamond film were seen on Si, Zn, Al and glass substrates at substrate temperatures between 650 and 1073 K with 0·5–2·0%C_2H_5Cl + H_2 precursor gas using HFCVD and MPCVD processes.[149] C_2H_5Cl helped in reducing the substrate temperature for diamond deposition <700 K. Increased halogen content in the feed gas increased the growth rate, as shown in Fig 14, at the cost of decreased phase purity. This was suggested to be due to a lack of etching of the carbon phases by halogens (Cl and F). On Si substrate, the adhesion of diamond films deposited at low temperature was poor, probably owing to the lack of an intermediate SiC layer. On Al substrates good adhesion was observed, even at a very low substrate temperature of 643 K. Deposition onto glass and Zn substrates was difficult. On glass, the formation of diamond films was observed only at low temperature. However, the adhesion of these films was poor. The deposit on Zn was mainly consisted of an amorphous graphitic phase, with some sporadic diamond crystallites.



14 **Growth rate for diamond films deposited from C_2H_5Cl/H_2 gas mixtures at *T*=1073 K as function of C_2H_5Cl content (reprinted from Ref. 149, copyright 2001, with permission from Elsevier)**

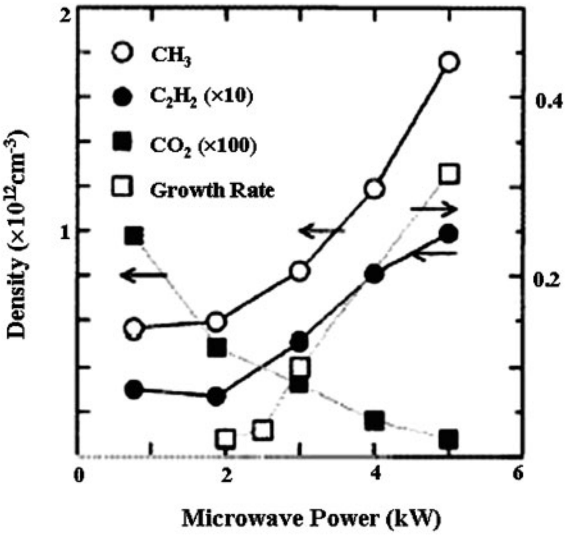
Diamond deposition domain is very much dependent on the feed gas composition, which was predicted by Bachmann in 1991. Recent research shows that the diamond growth domain is also dependent on the radical species present inside the reactor.[154,155] The new C–H–O ternary diagram based on the radical species clearly distinguishes three different regions, non-diamond carbon growth region, diamond growth region and no growth region. The analysis of the computational results explains the contradicting experimental results based on the non-typical gases (H_2/CH_4 gas mixture is considered as the typical precursor for diamond growth). Although the CO containing precursors such as CO/H_2 or $CO/H_2/O_2$ have been used quite extensively to grow diamond at relatively low deposition temperatures with high growth rate and adequate quality, the simulation results predicted CO as a non-participatory species in the growth process. The effect of pressure, temperature and MW power on the growth of diamond phase is also predicted based on the participating species on the growth process. Although at lower pressure the diamond deposition domain widens, it is very difficult to distinguish the non-diamond carbon growth region, diamond growth region and no growth region at higher pressure, which suggests that non-diamond deposition at higher pressure is obvious. The simulation results also suggest that for the processes operating at MW power of 500–1500 W, the participating species decrease with increasing pressure. The main effect of increase in power and pressure is to affect the bulk gas phase temperature and composition. With increase in power and pressure the proportion of the radical species increases near the vicinity of the growth surface thereby widening the diamond deposition domain. Temperature also affects the participating species composition in the growth process. For constant feed gas composition, the participating species composition migrates from diamond growth domain to the non-diamond carbon growth domain for temperature beyond 1400 K. So the higher deposition temperature will end up with higher non-diamond fraction in the deposited diamond phase. Even though the new C–H–O ternary diagram based on the radical species inside the reactor chamber nicely explains many experimental data points in the Bachmann diagram, the computational results do not apply when the bulk gas phase temperature is >1150 K. The assumption that the bulk gas phase temperature is equal to the growth surface temperature of ~1150 K restricts the analysis of diamond growth behaviour based on the radical species involving Ar rich plasma where the bulk gas phase temperature is much higher than 1150 K.

Effect of variation in processing conditions and additives in precursor gases

Sometimes the variation in the processing conditions such as local laser assisted heating of the selected substrate area, pulse modulation of the ECR plasma, early CH_4 introduction in the reaction chamber and combination of a RF plasma with HFCVD influences the diamond growth.[156–159] The presence of an additive such as H_2, N_2, F_2, Ar, Xe, H_2S and PH_3 in the precursor gas also affected the diamond growth.[160–169]

The enhanced nucleation and growth of diamond film was achieved by introducing CH_4 right from the beginning instead of introducing it after 5 min, at substrate temperature T_S>700°C using the RF and HFCVD methods.[159] The film obtained was very smooth and the contamination from W filament was reduced to a large extent by preheating the filament in CH_4 and H_2 atmosphere and placing it close to the upper electrode. Although, graphite formation could not be avoided in the initial phase of the growth, it stopped after some time.

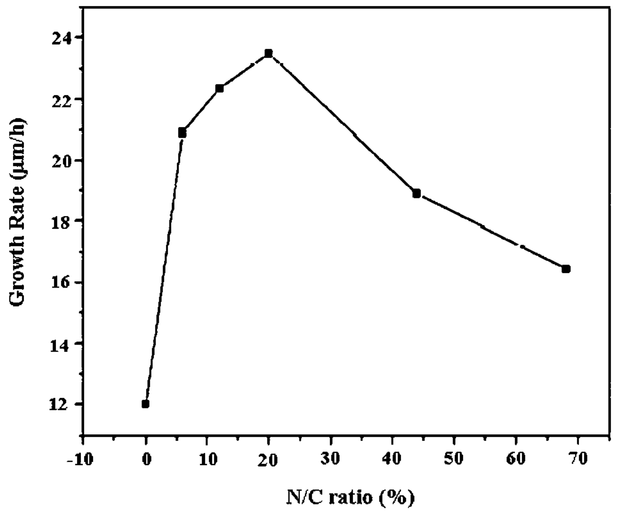
A factor of three increases in growth rate of diamond film was obtained by using an ECR MW plasma discharged in pulse modulation mode compared with that obtained in a continuous plasma of time averaged power near the threshold value required to trigger diamond growth.[157] The time averaged CH_3 radical density, measured by infrared laser absorption spectroscopy, was also enhanced by pulse modulation and was up to 1·3 times larger than that in the continuous plasma. The number of carbon atoms supplied as CH_3 radicals (measured by infrared laser absorption spectroscopy) was found larger than the actual growth rate by almost two orders of magnitude. The enhancement of growth rate and CH_3/C_2H_2 radical density with MW power is shown in Fig. 15. The enhancement of CH_3 and C_2H_2 radical density showed a similar trend with MW power. The radical density did not change much up to 2 kW but beyond that it increased monotonically with power up to 5 kW. The density of CO_2, on the other hand, decreased continuously with increasing MW power. The growth rate did not show any significant change initially, but, beyond 2·5 kW it suddenly increased from 0·05 μm h^{-1} (at 2·5 kW) to 0·35 μm h^{-1} (at 5 kW).



15 **Growth rate and densities of CH_3, C_2H_2 and CO_2 versus MW power in continuous wave discharge plasma (reprinted with permission from Ref. 157, copyright 1996, IOP Publishing Limited)**

The effect of N_2 addition in the precursor feed gas ($CH_4/H_2/Ar$) was found beneficial to diamond synthesis. In small quantities (<100 ppm) it improved the diamond quality and favoured growth of {100} texture. However, in higher quantity it led to black diamond films owing to the presence of a large amount of graphitic or amorphous carbon in the film. Nitrogen doped diamond film, grown at 30 torr pressure, 800°C and at varying (N/C) ratio from 0·06 to 0·68 using $CH_4/H_2/Ar$ mixtures by a 100 KW dc arc plasma jet CVD, showed significantly improved film morphology, growth rate, crystalline orientation, nucleation density and fracture strength for freestanding diamond films.[121] Although the grain size decreased with small addition of nitrogen (N/C=0·06) and increased further with increasing nitrogen content from N/C=0·12 to 0·22 resulting in grain size of hundreds on nanometres for an MCD films. It was not mentioned whether the nitrogen was incorporated in the diamond structure or was at the grain boundary. The variation of growth rate with increasing N/C ratio is shown in Fig. 16. The growth rate of this diamond film, grown by dc arc plasma jet system, increased rapidly from 12 μm h^{-1} for N/C=0 to 23·5 μmh^{-1} for N/C=20%. But, for larger nitrogen fraction in the gas mixture the growth rate decreased to 16·5 μm h^{-1} for N/C=68%. The deleterious effect of N_2 addition in the precursor gas (CH_4/H_2) on the mechanical properties was displayed by a continuous decrease in measured fracture strength with increasing N/C ratio. An enhanced secondary nucleation and the {100} facet development was observed in nitrogen doped diamond films at CH_4 concentrations 0·5–3% and N_2 concentrations from 0 to 3000 ppm in the feed gas with averaged power density of 15 W cm^{-3}.[162] Along with enhanced growth rate and chemical purity of the film, surface electrical resistance and surface morphology was also affected. The presence of nitrogen in the feed gas affected the quality of the film *R*, which was defined as

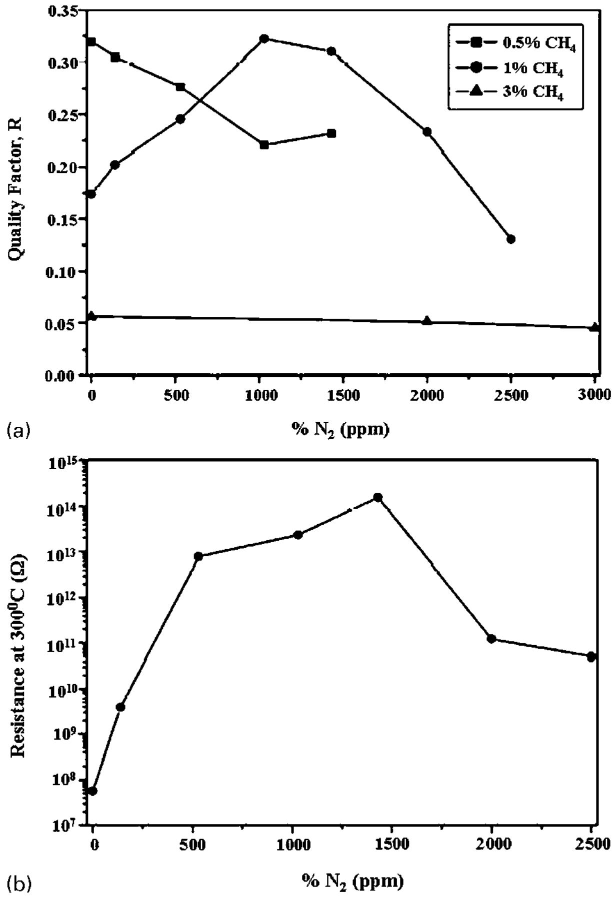
$$R=\frac{I_{sp^3}}{I_{fl}+I_{sp^3}+\sum_{k} I_k} \quad (3)$$



16 Growth rates of diamond film as function of nitrogen to carbon ratio (reprinted from Ref. 121, copyright 2004, with permission from Elsevier)

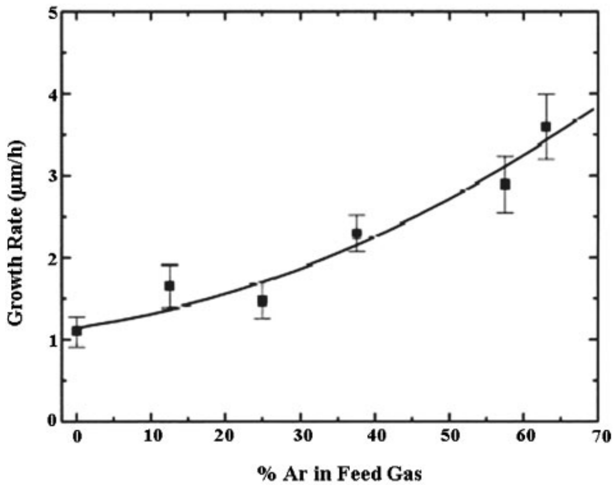
where I_{sp^3} was the intensity of the diamond line, I_{fl} the intensity of the fluorescence background and I_k was the intensities of the non-diamond contributions originating from adjacent Raman bands (especially graphite D and G bands). The variation of the quality factor and the surface resistance at 300°C are shown with varying N_2 concentration in Fig. 17*a* and *b* respectively. The incorporation of N_2 in the feed gas affected the diamond film quality in different ways for a range of CH_4 concentration in the gas mixture. An optimal value of 0·32 for *R* was obtained for the N_2 concentrations from 1030 to 1430 ppm. Thereafter, it continuously decreased to 0·12 for 2500 ppm N_2 in the film. For 0·5%CH_4, on the contrary, the quality *R* monotonously decreased from 0·32 to 0·23 for N_2 content varying from 0 to 1430 ppm. But, for higher CH_4 concentration (namely 3%), the N_2 concentration dependence of quality factor was very weak and the *R* value remained constant ~0·5. At low CH_4 concentration nitrogen degrades the film crystallinity and structural properties of the film, but at higher CH_4 level nitrogen improves the (100) texture formation causing secondary nucleation on the (111) faces, resulting in MCD films. The surface resistance also increased by six orders of magnitude (from 10^8 to 10^{14} Ω) with N_2 in the film. The resistance gradually increased with increasing N_2 concentration and reached a maximum at 10^{14} Ω corresponding to N_2 concentration of 1430 ppm. It decreased thereafter up to 2500 ppm N_2. This unusual behaviour was explained on the basis of the compensation of the doping state of the diamond. Diamond film grown in the absence of N_2 behaved as a p-type doping material, but in the presence of N_2 it behaved as an n-type doping material. When N_2 is incorporated in small amount in the film, the p-type doping may become compensated, which progressively increased the resistance. For further increase in N_2 concentration, the film resistance reached a maximum for ~1430 ppm N_2, a situation where p-type doping was totally compensated by the n-type doping. A further increase in N_2 concentration induced the n-type doping behaviour and the resistance decreased.

These results showed that nitrogen was incorporated in the diamond structure and contributed to the electrical conduction of the film. The deleterious effect of N_2 is also reported in the literature.[161,163] These studies were conducted with conventional H_2/CH_4 gas mixture. Although no discussions were made whether nitrogen was incorporated into the diamond structure or was at the grain boundary region. Increasing nitrogen content changed the faceted morphology to cauliflower structure and for nitrogen content >1000 ppm in the gas mixture NCD structure was observed.[161] The effect of nitrogen addition in the conventional H_2/CH_4 gas mixture in an HFCVD process resulted in reduced grain size with increasing nitrogen content and finally ended up with ball like morphology.[163] Nitrogen was found to be chemically bonded to diamond structure to a maximum content of 3·3 at.-%, which was confirmed by X-ray photoelectron spectroscopy studies.

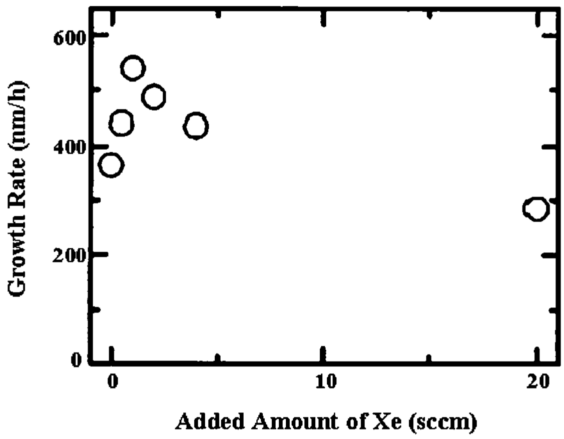


17 Variation of *a* diamond film quality factor *R* as function of N_2 concentration for various CH_4 concentrations and *b* surface resistance (measured at 300°C) as function of N_2 concentration for 1%CH_4: reprinted from Ref. 162, copyright 2002, with permission from Elsevier

An enhanced growth rate of diamond film was observed in presence of Ar gas (0–85 vol.-%) in the feed mixture of ethanol and hydrogen gas, which was associated with an increase in carbon free radicals, C_2 (up to ~40 vol.-%Ar) or to the increase in the filament temperature in an HFCVD process.[165] The increased growth rate with Ar addition is shown in Fig. 18. Analysis of SEM showed an increase in the diamond grain size and increased defects in the deposited films, which was also confirmed from room temperature photoluminescence spectroscopic studies. However, well



18 Diamond growth rate as function of argon concentration in gas feed (reprinted from Ref. 165, copyright 2000, with permission from Elsevier)



19 Variation of diamond growth rate with Xe addition at 790–830°C (reprinted with permission from Ref. 167, copyright 1998, American Institute of Physics)

faceted diamond films of good quality were obtained only at lower Ar concentration up to 65 vol.-%. Higher concentrations (85 vol.-%Ar) led to diamond like carbon or other complex carbon structures.

Ar addition to the precursor gases was found to increase the growth rate and decrease the grain size of polycrystalline diamond film synthesised by an MPCVD method in our laboratory. Using ultrasonically activated Si substrate in a 20–40 μm diamond slurry, deposition temperature of 800°C, pressure of 95 torr and 900 W MW power polycrystalline diamond film was fabricated using 1%CH_4, 4–99%H_2 and 95–0%Ar. The growth rate increased from 0·49 μm h^{-1} for no Ar addition to 1·37 μm h^{-1} for 80%Ar addition in the CH_4/H_2 mixture. However, at higher Ar concentration (95%Ar), the rate decreased to 0·76 μm h^{-1}. The biggest grain size (2·24 μm) was obtained for a gas mixture composition of 39%H_2, 60%Ar and 1%CH_4 using the above deposition parameters.[166]

A positive driving force for diamond growth was observed in presence of F_2 in the precursor gas.[164] The driving force was taken as the difference in chemical potential of carbon in the solid (diamond) and gas phases. A positive driving force indicated a decrease in the chemical potential of carbon in diamond phase or in other words only a positive driving force dictated diamond formation from the gas phase. The experiment showed that the driving force for diamond growth was positive at a particular temperature range (980–1240 K) and within that temperature range, the growth of diamond under low pressures was possible. The driving force for graphite was negative in the temperature range of 980–1240 K. The effect of F_2 addition in the reaction system on the driving force for diamond and graphite formation was divided into two parts. For λ (the molar ratio of fluorine to the mixture of fluorine and hydrogen $F/(F+H)$) = 0 to 0·12, the driving force for diamond growth was positive whereas that for graphite was negative, which meant that only diamond could be grown in that region (free of any graphite contamination). But, for higher F_2 content (λ>0·12), diamond quality deteriorated owing to the presence of graphite in the deposited film.

A decreased growth rate, at higher temperature, owing to a reduction in the concentration of CH_x species in the plasma (in the presence of H_2S gas in the precursor) was observed in a CVD diamond film deposition experiment.[168] At lower substrate temperatures (560–690°C), the authors speculated that an increasing adsorption of atomic sulphur in the growing diamond surfaces influenced the growth mechanism. The deposited diamond films preserved their excellent quality even for the highest H_2S concentrations (nearly 1%), which was evident from micro-Raman measurements. The electrical properties were unchanged by the S incorporation. As per the author, sufficient S incorporation is required to make the S doped diamond film electrically active. The S doped diamond film which showed n-type conductivity also contained B as the contamination and the presence of B accelerated the S incorporation in the film. Since these S doped diamond films were devoid of any B contamination, no change in electrical properties was observed.

Diamond growth conditions are strongly influenced by the presence of phosphine (PH_3) in the precursor gases. At a methane to hydrogen ratio of 0·15% and substrate temperature of 950°C, a smooth (111) oriented homoepitaxial diamond thin film was obtained in an MPCVD process in the presence of PH_3 gas up to 1000 ppm.[169] The (111) surface was found to be the best surface for the growth of phosphorous doped diamond. The film showed n-type conductivity over a wide range of temperature, which was confirmed by Hall effect measurement. For the best sample (PH_3 concentration 600 ppm), the Hall mobility was 28 cm^2 Vs^{-1} measured over a temperature range of 400–600 K.

About 50% increase in growth rate was observed in the presence of 1%Xe in the CH_4 and H_2 precursors using an MPCVD process.[167] A morphological change from the cubic to platelet grain structure was observed without degradation of the crystallinity. The favourable effects of Xe addition were attributed to its low dissociation and excitation energies (8·28 eV for Xe radicals), which were sufficient for the formation of CH_3 but not CH_2 radicals. The addition of Xe led to a higher density plasma and lower temperature. The enhanced growth rate and good quality of the film was due to the presence of a large amount of the atomic H and CH_3 radical (precursors for diamond formation) and a small amount of the CH_2 in the plasma. The increased growth rate with Xe addition is shown in Fig. 19.

The growth of chemical vapour deposited diamond film is influenced by the deposition process conditions such as substrate, nucleation, temperature, pressure, gas compositions and presence of additive gases in the precursor gases. The quality and the morphology of the deposited film are dependent on these parameters. Smaller grain sizes and smoother surface finish is obtained at high nucleation density for a particular temperature, pressure and MW power. Lower nucleation density, on the other hand, produces diamond films of bigger grain sizes and rougher surface texture. Gas compositions and the presence of additive gases in the precursor affect mainly the quality and texture of the film. Presence of N_2 in the precursor gases reduces the grain sizes leading to NCD film. O_2 and O_2 containing precursors or the presence of small amount of halogen gas in the precursor help in achieving low temperature growth of diamond film. Small amount of inert gas additives such as He, Ar, Xe in the precursor gases reduce the grain size of the diamond film owing to enhanced secondary nucleation in the deposition process. Temperature or pressure affects the growth rate of diamond film irrespective of the deposition process such as MPECVD or HFCVD. An increase in substrate temperature and gas pressure increases the growth rate owing to enhanced diffusion of the growth species on the substrate surface and increased concentration of the growth species respectively. But the success in achieving high growth rate of vapour deposited diamond film in the recent research results has mostly come through increased power density irrespective of the deposition system employed. Four orders of magnitude increase in linear growth rate was observed with increasing power density per unit area for major types of the deposition processes such as MW, hot filament, RF, oxyacetylene torch, atmospheric plasma jets and ion beam.[170] Although the rate depends mainly on the type of CVD process used, the source gas composition and pressure also affects the growth rate. The increased growth rate with increased power density is associated with the creation of hydrogen free radical or atomic hydrogen in the reaction environment. The strong endothermic conversion of atomic hydrogen from molecular hydrogen is strongly favoured by the increased energy input in the system. The generation of hydrocarbon species in the gas phase with increased power density also affects the growth rate significantly. Since atomic hydrogen and the hydrocarbon species do contribute to the diamond growth mechanism, the enhanced growth rate with increasing power density is expected.

Growth mechanisms in plasma environment

Since diamond is a metastable phase compared with graphite, the conversion of diamond C_d from the more stable graphite C_g seems to be a thermodynamic paradox. This should be impossible at the subatmospheric pressure owing to an overall increase in the Gibbs free energy

$$C_g \rightarrow C_d, \Delta G^0_{298} = 2{\cdot}9\ \text{kJ mol}^{-1} \quad (4)$$

A careful look at the CVD diamond process suggested that the conversion of diamond from stable graphite under the typical CVD conditions did not violate the thermodynamic laws, which require a negative change in Gibbs free energy for a chemical reaction to occur spontaneously. The diamond formation from graphite proceeds through the following steps,[3] molecular H_2 dissociation by hot filament, plasma, or electric gas discharge

$$H_2 \rightarrow 2H,\ \Delta G^0_{2500} = 75\ \text{kJ mol}^{-1} \quad (5)$$

$$C_g + 4H \rightarrow CH_4 \text{(gasification of graphite)},$$
$$\Delta G^0_{1500} = -470\ \text{kJ mol}^{-1} \quad (6)$$

formation of CH_x radicals (x=3)

$$CH_4 + H \rightarrow CH_3 + H_2,\ \Delta G^0_{1500} = -42\ \text{kJ mol}^{-1} \quad (7)$$

$$CH_3 + H \rightarrow CH_2 + H_2,\ \Delta G^0_{1500} = 17\ \text{kJ mol}^{-1} \quad (8)$$

$$CH_2 + H \rightarrow CH + H_2,\ \Delta G^0_{1500} = -38\ \text{kJ mol}^{-1} \quad (9)$$

$$CH + H \rightarrow C + H_2,\ \Delta G^0_{1500} = -84\ \text{kJ mol}^{-1} \quad (10)$$

The generated carbon atoms are then added to the diamond lattice (C_d represents a C atom in diamond lattice)

$$C + C_d \rightarrow 2C_d,\ \Delta G^0_{1500} = -480\ \text{kJ mol}^{-1} \quad (11)$$

Although it is seen that all the reactions shown above are not thermodynamically favourable owing to positive change in Gibbs free energy, addition of all the thermochemical reactions from equations (5) to (11) gives a thermodynamically favoured net reaction for the graphite to diamond transformation driven by the input of atomic H

$$C_g + 8H \rightarrow C_d + 2H_2,\ \Delta G^0_{1500} = -1097\ \text{kJ mol}^{-1} \quad (12)$$

Hydrocarbon species (ions or radicals) are generated during the interaction of the precursor gases with plasma and hot filament. These species are then either attracted with applied bias or without applied bias to the substrate surface. They then tend to migrate towards each other and get combined to form the diamond film. The energy required for migration in the neighbouring site is different for different species. Surface migration of CH_2 on diamond (111) surface requires less energy than that of CH_3.[171] The chemisorption and desorption of these reactive species followed by surface reaction constitute diamond growth. Although a lot of work has been carried out to study the growth mechanism and ample evidences are there to support each and every step, the exact nature of nucleation and growth is still a matter of controversy. Though the basic mechanism is same for all the systems, little variation is observed from system to system depending on the precursor gases, substrate used, diluent gas used, deposition temperature and gas pressure.

Although the above approach was only applied to growth on (100) facets, the key role of CH_3 radicals and H atoms in diamond growth was verified by another mechanism, which tried to depict the correct qualitative behaviour[172,173]

$$C_dH + H \rightarrow C_d^* + H_2 \quad (13)$$

$$C_d^* + H \rightarrow C_dH \quad (14)$$

$$C_d^* + CH_3 \rightarrow C_dM \quad (15)$$

$$C_dM \rightarrow C_d^* + CH_3 \tag{16}$$

$$C_dM + H \rightarrow C_dM^* + H_2 \tag{17}$$

$$C_dM^* + H \rightarrow C_dH + C_d + H_2 \tag{18}$$

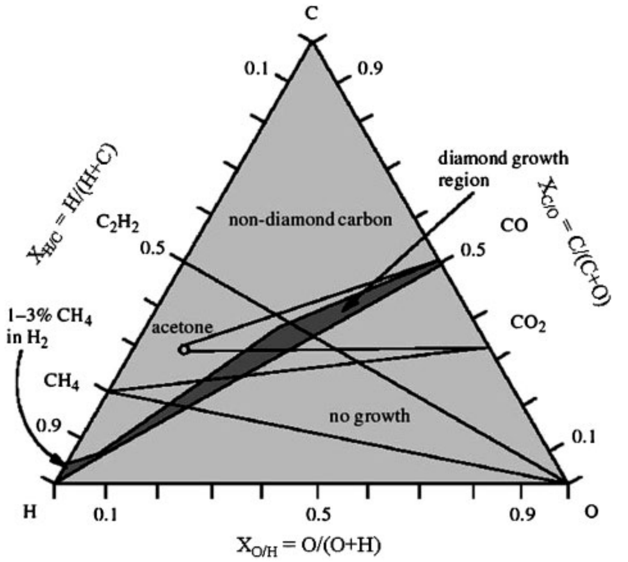
where C_dH stands for a generic hydrogenated surface site and C_d* the site with hydrogen removed, i.e. a radical site. C_dM represents an adsorbate methyl group, C_dM* with a hydrogen atom removed and C_d an atom of bulk diamond. Without considering each step in details the model considered the following steps in explaining the diamond growth mechanism:

(i) establishment of a steady state surface radical site coverage via reactions (13) and (14)
(ii) attachment of reactive hydrocarbon species (unsaturated molecules or radicals) to the surface at these sites via reaction (15)
(iii) removal back of the surface adsorbates to the gas phase either by thermal desorption (via reaction (16)) or attack by atomic hydrogen (etching, via reaction (17)) and finally incorporation of the adsorbate into the diamond lattice (with abstraction of adsorbate hydrogens by H) via reaction (18)

The role of CH_3 radical and atomic H in diamond growth is also evident from the observed reduction of growth rate with depleting H and CH_3 radical for diamond synthesis in an HFCVD process using $CH_4/H_2/N_2$ and $CH_4/H_2/NH_3$ gas mixtures.[174] With NH_3, contrary to N_2, clear depletion of both H atom and CH_3 radical number densities were observed, which were also confirmed from a modelling of the gas phase chemistry including C/H/N. Calculations for C/H/N gas mixtures showed significant N atom production owing to successive 'H shifting' reactions $NH_x + H \Leftrightarrow NH_{x-1} + H_2$ (=1 to 3), which accounted for the observed H depletion in the system. Irreversible reaction of these atomic N with CH_3 radical produced HCN thereby reducing the hydrocarbon species available for diamond growth. Molecular nitrogen, N_2, in the prevailing CVD environment was found unreactive.

For bias enhanced growth of diamond, the mechanism was said to be a combination of the surface process, which is typical of CVD diamond growth and subplantation process, typical for growth by energetic species.[175] Since CVD conditions help in etching out the graphitic carbon from the surfaces and the biasing conditions used in the experiment was the same as the energy required for subplantation process, the high concentration of smooth NCD films consisting of mainly sp^3 carbon was thought to form by the proposed mechanism.

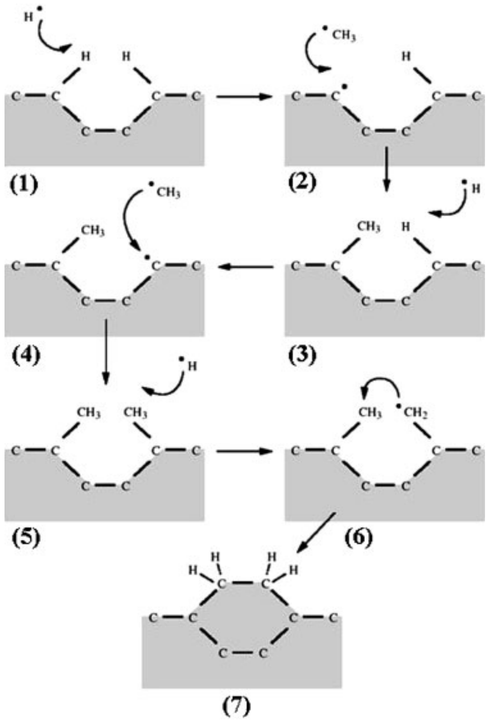
But, the diamond formation looked different in case of the laser ablation of the graphite target in an oxygen atmosphere. The presence of C_2, CO or ionised carbon species was observed near the substrate surface, which was identified in the optical emission spectra.[176] CO molecules were formed by the reaction of the emitted carbon species with O_2 gas. It was suggested that the ionised carbon species with a high kinetic energy react with each other or with ambient oxygen gas to form C_2 or CO. The formation of diamond crystals were proposed to be related to the existence and reaction of these highly excited molecules near the substrate surface.



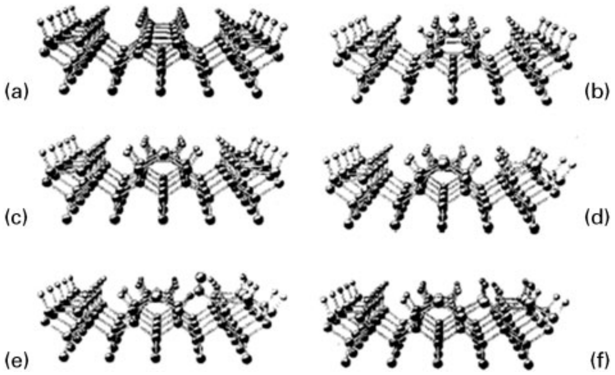
20 Simplified form of Bachmann triangle C–H–O composition diagram: numbers in axes represent atomic fractions; 'acetone' in non-diamond carbon region represents undiluted compound; reprinted with permission from Ref. 1, copyright 2000, the Royal Society

Current understanding on growth of chemical vapour deposited diamond films

The chemical and physical processes that take place during the CVD of diamond films in the MW plasma are complex. The gases after mixing in the deposition chamber face an activation region (hot filament in case of HFCVD or MW plasma in case of MPCVD) whereby they form ions, radicals, neutral atoms and electrons. These reactive species undergo complex reactions before they get adsorbed onto the substrate. Surface diffusion of these adsorbed species followed by addition or subtraction reaction with the neighbouring species (ions or radicals or neutral atoms) leads to the formation of stable diamond nuclei. After 70 deposition experiments with different reactors and process gases, Bachmann concluded that diamond film will only grow when the gas composition is close to just above the CO tie line in Fig. 20. Below the tie line no deposition is found to occur. Above the tie line non-diamond carbon is the major phase except for a narrow window where polycrystalline diamond film grows. He also found that the diamond growth is independent of the nature of gas phase precursor. Since the gas phase chemistry is rapid, the precursor gases essentially brake down to smaller reactive components to form the diamond film. Although the presence of many atomic, molecular or ionic species such as C, CH, C_2, C_2H, CH_3, C_2H_2, CH_3^+ is detected in the plasma, CH_3, C_2 and H have been identified as the principal growth species for diamond synthesis. In the H_2 rich plasma, like in conventional H_2/CH_4 plasma, CH_3 radical was found to be responsible diamond growth species. But in H_2 poor plasma, like in $Ar/H_2/CH_4$ plasma, C_2 was considered as the primary diamond growth species. But, some authors have also suggested C_2 radical as the responsible growth species for growth of MCD at high rates by high pressure and high power density MW plasmas in gas mixtures of CH_4 and H_2 without the Ar gas.[177,178]



21 Schematic of reaction process occurring at diamond surface leading to stepwise addition of CH_3 species and diamond growth (reprinted with permission from Ref. 1, copyright 2000, the Royal Society)



a [(100)–(2×1)]/H reconstructed diamond surface; *b* C_2 molecule inserts into C–C surface dimer bond; *c* C_2 molecule inserts into adjacent C–C surface dimer bond, forming new surface dimer perpendicular to previous dimer row; *d* second C_2 molecule forms new surface dimer in adjacent dimer row; *e* third C_2 molecule inserts into trough between two previously incorporated C_2 molecules; *f* third C_2 molecule completes insertion into trough, forming dimer row perpendicular to previous surface row

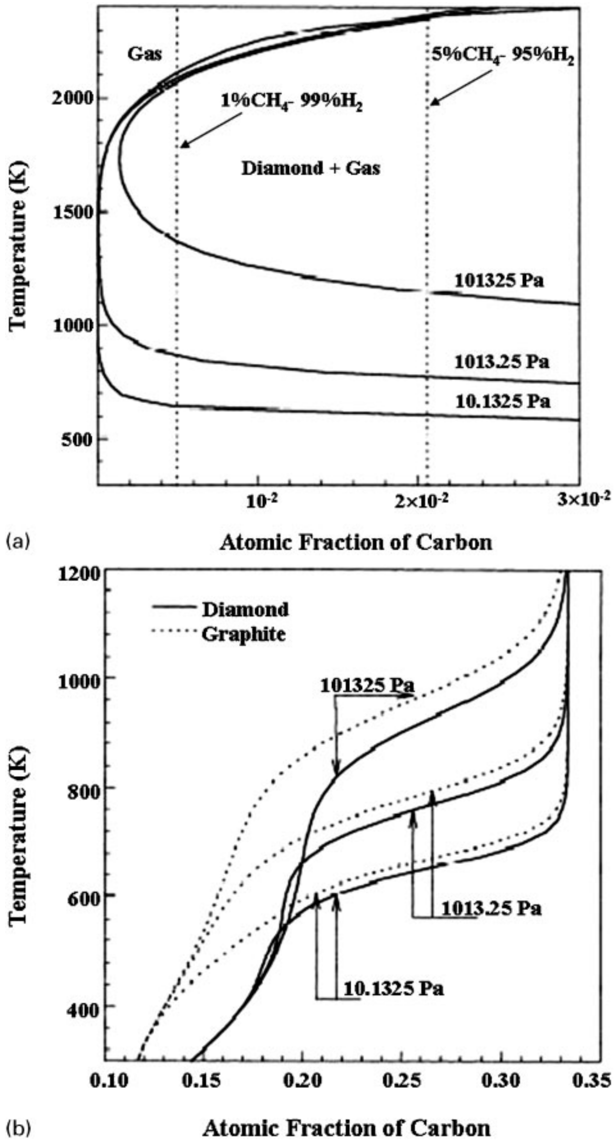
22 C_2 diamond growth model (reprinted with permission from Ref. 181, copyright 1995, American Institute of Physics)

Atomic H plays an important role and considered to be the most critical component driving the deposition chemistry. Therefore, a high concentration of atomic H is crucial to the diamond growth process. Termination of the surface dangling bonds to prevent the cross-linkage and surface graphitisation is performed by the atomic H. Atomic H is also responsible for etching of graphitic sp^2 carbon. In addition, it breaks the long chain hydrocarbon into smaller pieces to reduce the chances of sticking those hydrocarbons onto the growing diamond surface. Creation of the reactive radicals such as CH_3 by reacting with the neutral species CH_4 is also performed by atomic H. The growing diamond surface is fully saturated with atomic H, which limits the number of sites available for hydrocarbon species, namely CH_3 to get adsorbed and block the surface diffusion of the adsorbed species. The sequence of diamond growth is schematically shown in Fig. 21. Atomic H abstracts a surface H to form molecular H_2 and leaves behind a reactive site on the surface (step 1). This reactive site either may get engaged by a neighbouring H to go back to the original stable configuration or may react with a CH_3 radical, effectively adding one C atom in the diamond lattice (steps 2 and 3). This process of H subtraction and consequent CH_3 addition may occur on a neighbouring site to the attached CH_3 group (step 4). A further H reduction from any one of the attached methyl group leaves behind a radical (steps 5 and 6), which then combines with the neighbouring CH_3 group to form the ring structure (step 7), making two C atom incorporated into the diamond lattice. Therefore, diamond growth can be considered as a stepwise addition of carbon atom to the existing diamond lattice catalysed by atomic H. For oxygen containing precursor, OH plays the role of H and also since OH is more effective in etching the graphitic carbon from the growing diamond surface, the growth rate and quality of the film is improved.

The growth of UNCD involves C_2 dimer radical as the principal growth species.[179,180] Since the chemisorption of C_2 to diamond (110) and (100) surfaces is highly exothermic and involves lower activation energy, diamond growth may proceed on these surfaces without the need of atomic H. The growth mechanism involving C_2 dimer does not require any hydrogen abstraction reactions from the surface as proposed by Gruen *et al.*[181] The proposed mechanism involves the successive addition of the C_2 molecule onto the surface C–C dimer bond as follows: the growing diamond surface was considered as $[(100)-(2\times1)]$/H reconstructed surface, which is shown in Fig. 22*a*, where big atoms are C and smaller atoms are H terminating the surface. A reacting C_2 molecules hit the surface and insert into the surface C–C dimer bond (Fig. 22*b*). Another C_2 molecule gets inserted into the adjacent C–C bond to form a new surface carbon dimer (Fig. 22*c*). In the same way C_2 molecule forms a new surface dimer on an adjacent row (Fig. 22*d*). In the next step, a new C_2 molecule gets inserted into the trough between the two new surface dimer formed (Fig. 22*e* and *f*). This new surface dimer row formed by the C_2 molecules is perpendicular to the previous dimer row. In this way C_2 molecules get incorporated into the surface C–C dimer bond of the growing diamond surface and form the new surface dimer C–C and the growth process continues.

Low temperature diamond synthesis

From different investigations, diamond nucleation and growth have been found to be a surface phenomena and thermally activated process. So lowering of the substrate temperature leads to a very slow growth rate, which makes the process economically unviable. Numerous investigations have been conducted concerning the



23 Metastable CVD phase diagram for *a* C–H system and *b* C–H–O system for diamond (continuous lines) and graphite (broken lines) deposition: in left of curves only gas phase is stable, but in right of curves two phases (gas and diamond) are stable; reprinted from Ref. 182, copyright 2000, with permission from Elsevier

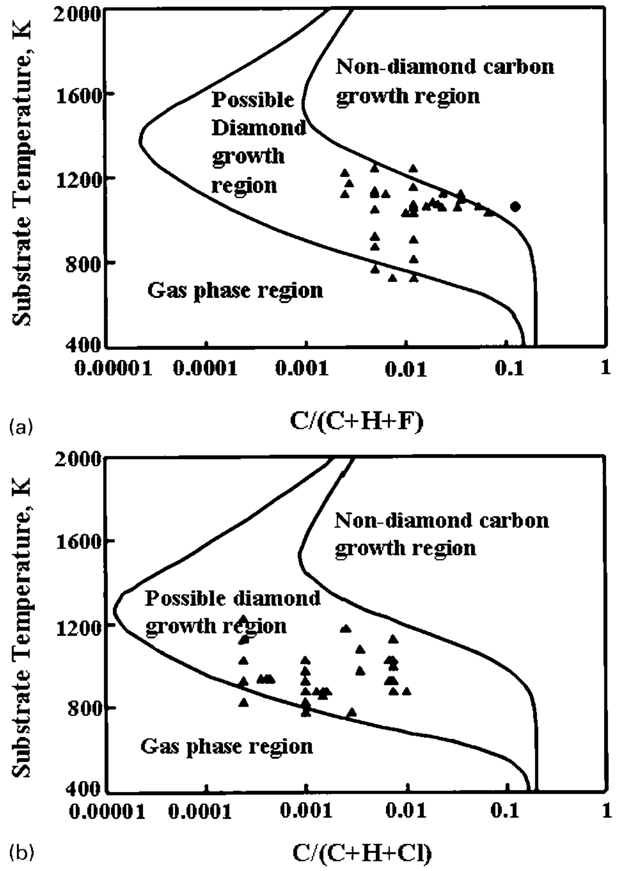
thermodynamics of the processes involving either a C–H/C–H–O precursor systems or a halogen containing gas phase.[182–184]

The deposition of diamond or graphite from the gas phase is a problem of kinetics or a kinetic barrier. But, thermodynamically the conditions can be predicted under which diamond or graphite is not stable with respect to the gas phase. The thermodynamic limit of the substrate temperature for which diamond can be deposited at a particular pressure was evaluated in the C–H and C–H–O systems.[182] The conditions for the lower limit of substrate temperature were different for the C–H and C–H–O systems. In the C–H system, the pressure of the CVD reactor was an important parameter for the lower limit of the substrate temperature, which is shown in Fig. 23*a*. For a gas mixture of 1%CH_4–99%H_2, which is shown by the left vertical dashed line in the figure, the lower limits were 1400, 900 and 600 K under 101 325 Pa (760 torr), 1013·25 Pa (7·6 torr) and 10·1325 Pa (76 mtorr) respectively. At atmospheric pressure (760 torr) diamond was deposited inside the C shape domain at temperatures >1400 K. But <1400 K, only the gas phase was stable. With increasing CH_4 concentration to 5% (indicated by the right vertical broken line in the figure), the deposition domain was extended and the lower limit was 1100 K. But increasing the CH_4 concentration degraded the quality of diamond by producing the non-diamond phase. It was suggested that reducing reactor pressure was more effective in achieving low temperature deposition than increasing the CH_4 concentration in the C–H system.

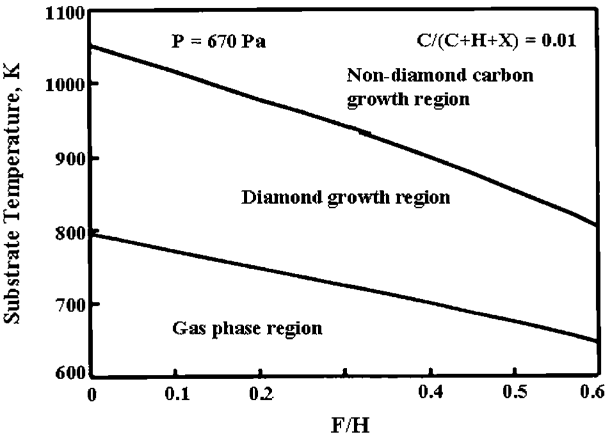
In the C–H–O system however, the thermodynamic lower limit of the substrate temperature was found as low as room temperature. Unlike the C–H system, the carbon solubility continuously decreased with decreasing temperature, which is shown in Fig. 23*b* at the fixed ratio of O/H=1 for three different pressures. But, according to Bachmann's diagram, the diamond deposition is possible along the narrow composition band close to the ratio of O/C=1.[185] Since the data in Fig. 23*b* were based on O/H =1, an overall composition ratio of C/O/H=1 : 1 : 1 was proposed in Fig. 23*b* for diamond deposition. This ratio corresponded to the gas mixture of 50% C_2H_2/O_2 for which the atomic fraction of carbon became 0·33. This carbon fraction is close to the solubility line at 1200 K for 101 325 Pa, at 900 K for 1013·25 Pa and at 700 K for 10·1325 Pa. The carbon solubility decreased below these temperatures.

Thermodynamics of diamond film deposition at low pressure in the C–H–*X* (*X*=F, Cl) system was studied[183] according to a non-equilibrium thermodynamic coupling model proposed by Wang,[186] which is not discussed in this article. The projective and sectional temperature–gas composition phase diagrams for the C–H–F system in the pressure range of 100–6670 Pa and for the C–H–Cl system between 100–5000 Pa are shown in Fig. 24*a* and *b* respectively. The projective phase diagrams were drawn to cover a wide range of pressures studied in the literature. Each phase diagram consisted of three regions: a gas phase region, a possible diamond growth region and a non-diamond carbon growth region. The possible diamond growth region signified a diamond deposition probability for the constraint of substrate temperature and C/(C + H + *X*) ratio within the region. The coincidence of the experimental data (solid triangles for diamond growth experimental points and solid circle for non-diamond carbon growth experimental point) with the probable diamond growth region predicted by the theory (model) showed the validity of the proposed model. Thermodynamic analyses also showed a lower temperature range of deposition with increasing *X* in the precursor, which became narrower with further increase in *X*, as shown in Fig. 25. A continuously decreasing trend of substrate temperature is observed with increasing F/H ratio at 6700 Pa pressure and carbon content of C/(C + H + X) = 0·01.

Although low temperature is a hindrance to the growth of diamond films with good growth rate, several researchers have tried to deposit diamond at low substrate temperatures using various experimental conditions as discussed below.



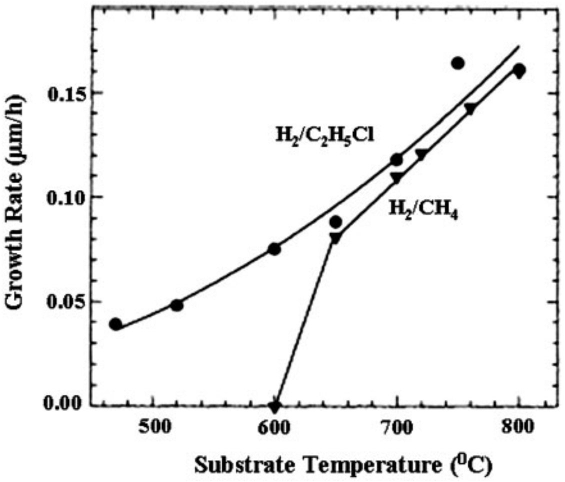
24 Comparison of temperature–gas composition phase diagram of carbon deposition with reported experimental results from *a* C–H–F systems over pressure range from 100 to 6670 Pa and *b* C–H–Cl systems over pressure range from 100 to 5000 Pa: reprinted from Ref. 183, copyright 1999, with permission from Elsevier



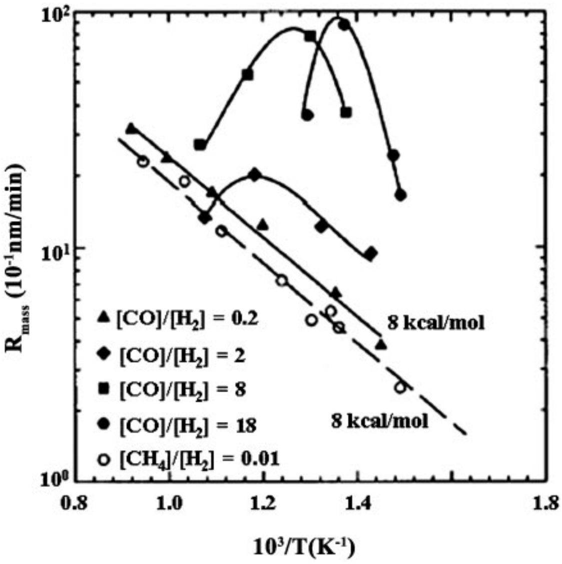
25 Dependence of substrate temperature range suitable for diamond deposition on F/H ratio at 670 Pa pressure (C/(C + H + X) = 0·01): reprinted from Ref. 183, copyright 1999, with permission from Elsevier

A thorough review of the low temperature diamond growth was conducted by Muranaka *et al.* in 1994.[26] The low temperature studies were divided into two categories, experiments which achieved the low temperature deposition without heating the substrate at all and which achieved the low temperature by controlling the substrate temperature itself by varying the experimental conditions. The non-substrate heating driven low temperature deposition was achieved by varying the process itself like sputtering, RF plasma and laser excitation. The substrate heating process, on the other hand, was achieved by using different precursor gas systems like CO–H_2, CO–H_2–O_2 or halogenated hydrocarbons. Source gases capable of generating atomic O and an excess of H was beneficial for low temperature growth since these species were capable of removing the amorphous and non-diamond component from the film. The lowest substrate temperature suggested was ~400°C for the diamond growth with crystallinity close to that of natural diamond. Growth rates of 0·01–0·2 μm h^{-1} near 400°C and 0·035–0·3 μm h^{-1} at 130°C were suggested. Ar or He addition to source gases were beneficial for higher growth rate but at the cost of lowered film quality.

Halogen containing hydrocarbons such as different chloromethane (CCl_4, $CHCl_3$, CH_2Cl_2) and fluromethane (CF_4, CHF_3) has long been known as diamond precursors. In early days diamond has been grown at much higher growth rate and with better quality using these halogenated precursors compared with the conventional CH_4/H_2 precursor. Most of the early experiments involving halogenated precursors were carried out at typical diamond growth temperatures of 700–900°C. In 1991, polycrystalline diamond film was grown on Si (100) substrate from an 8% CF_4/H_2 mixture without any surface pretreatment in a low pressure RF plasma assisted CVD process at 850°C.[187] Very high nucleation density followed by high growth rate was obtained without any pretreatment of the substrate. First report of diamond growth in an MW plasma assisted CVD using CF_4/H_2 precursor came in 1992.[188] CF_4 (2·5–40%) in H_2 precursor was used to grow polycrystalline diamond film at 750–820°C temperature, 40 torr pressure and low MW power of 300–400 W. Although at 40%CF_4 carbon soot was formed, the diamond quality was good at lower concentration of CF_4. The difference in diamond growth rate was studied using CH_4 versus chloromethane reactants, CCl_4, $CHCl_3$ and CH_2Cl_2 at 10 torr pressure, 700–900°C temperature in an HFCVD process in 1993.[189] Whereas the growth rate decreased drastically with decreasing temperature for CH_4 precursor, the effect was insignificant for the chloromethane reactants. In the same year, diamond growth at lower temperatures of 380–700°C was reported by the same group using the chloromethane precursors in HFCVD process.[190] Although the growth rate of diamond was only 0·05 μm h^{-1} at 380°C using CCl_4, it was almost impossible to grow diamond <600°C using CH_4 precursor. Better adhesion and higher growth rate of diamond film on WC–Co tool material was obtained at 900°C using CF_4 as the reactant in an MWCVD process in 1993.[191] Three times increase in adhesion and four times increase in growth rate was observed using CF_4 instead of CH_4 reactant. A difference in growth behaviour <850°C was noticed owing to termination of the active sites on the diamond surface by fluorine compounds in an MWCVD process performed using fluorocarbon species, CF_4, CHF_3 as against one using CH_4 in 1994.[192] The growth rate as well as quality of the film improved >850°C owing to rapid removal of non-diamond phase by fluorination reaction. Although in most of the diamond growth experiments enhanced



26 **Comparison of growth rates of diamond films deposited using H_2/CH_4 and H_2/C_2H_5Cl (reprinted from Ref. 150, copyright 1999, with permission from Elsevier)**



27 **Growth rate of MPECVD diamond on diamond film substrates as function of inverse temperature using different CO/H_2 and CH_4/H_2 gas mixtures (reprinted with permission from Ref. 147, copyright 1997, American Institute of Physics)**

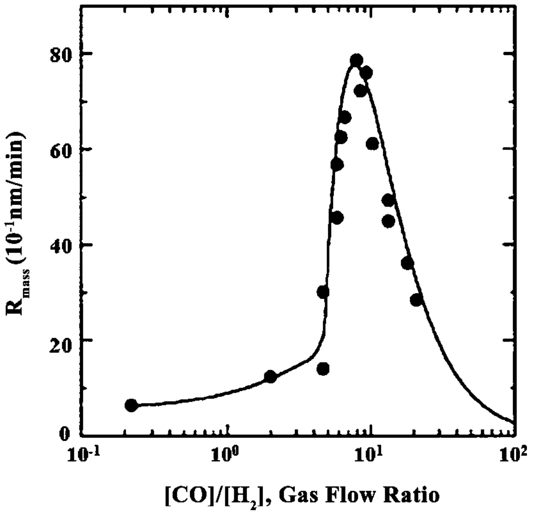
growth rate is observed using halogenated precursor, decreased growth rate at higher chloromethane concentration owing to faster etching rate is also reported.[193] The enhanced growth rate in these diamond growth experiments in the halogenated precursor environment attributed mainly to:

(i) increased halogenated carbon radical generation in the gas phase owing to the lower C–X (X = Cl, F) bond energy compared with C–H bond energy
(ii) faster surface dehydrochlorination or dehydrofluorination compared with dehydrogenation reaction.

Since hydrogen abstraction or dehydrogenation from the growing diamond surface has been found to be the rate determining step in the diamond growth process, enhanced growth rate is observed for the halogenated hydrocarbon precursors. Low temperature diamond growth research using halogenated precursors became intense in the successive years. The deposition temperatures were obtained typically <550°C. Some interesting results on the low temperature diamond growth experiments using halogenated precursors in the recent years are discussed below.

Recently, different halogenated precursors like C_2H_5Cl, CHF_3 and CF_4 with an abundance of H_2 gas were used to achieve low temperature diamond growth. A substrate temperature of 370°C was reported for diamond films grown by an HFCVD process using CHF_3, C_2H_5Cl and H_2 gas as the precursor.[150] The role of halogen was suggested in creating active surface sites for diamond nucleation and growth. The role of halogen containing precursor on the growth rate is shown in Fig. 26 where growth rate is plotted against substrate temperature for two precursors, H_2/C_2H_5Cl and H_2/CH_4. A significant (although low) growth rate was observed even at 370°C for H_2/C_2H_5Cl gas system, whereas no growth at all was observed for H_2/CH_4 gas system below 600°C. The growth rate suddenly increased from zero to 0·08 μm h^{-1} upon changing the substrate temperature from 600 to 650°C and then increased monotonically with temperature for H_2/CH_4 system but for H_2/C_2H_5Cl, a gradual increase of growth rate was observed with temperature in the range of 370 to 850°C. To confirm the low deposition temperature, diamond film was also grown onto low melting substrate like Al, Zn and glass using 0·5–2·0% C_2H_5Cl/H_2 by HFCVD and MPCVD processes in the temperature range between 650 and 1073 K.[149] In another experiment, a significant decrease in T_{sub} down to 370°C was achieved during processing of the diamond films by an HFCVD process using CHF_3 and C_2H_5Cl in the precursor gas.[151] However, at lower temperature only graphitic deposition was observed and the lowest substrate temperature for diamond growth was suggested to be dependent on the deposition parameters. A decrease in temperature was observed with decreasing C content in the precursor gas in the case of MPCVD process or decreasing filament to substrate distance in the case of HFCVD process.

Different oxygen containing precursors have also been used to deposit diamond film. A high growth rate of up to 2·5 μm h^{-1} at relatively low plasma powers (0·5 kW) was observed at low substrate temperature range $350°C<T<500°C$ for fabricating NCD film by MPCVD process using CO/H_2 gas mixtures.[147] A CO rich mixture of CO and H_2 was found to exhibit an increase and sharp maximum in growth rate as the temperature was reduced. The conventional H_2 rich mixtures of CH_4 or CO and H_2 exhibited monotonic decrease in the diamond growth rate with temperature between 800 and 400°C. The low temperature growth behaviour of diamond as function of the CO/H_2 and CH_4/H_2 ratios was studied by an RTSE and the results are shown in Fig. 27. The growth rate measured by RTSE was expressed in terms of the mass thickness given by $d_{mass} = f_d d_b + 0{\cdot}5 d_s$, where f_d was the volume fraction of diamond in the bulk layer of thickness d_b, and d_s was the thickness of the surface roughness layer. This figure also shows that when CO or CH_4 is highly diluted with H_2, the rate decreases with decreasing temperature with an activation energy of 8 kcal mol^{-}. In another experiment using the same precursor system,



28 Growth rate of MPECVD diamond on diamond film substrates as function of CO/H_2 gas flow ratio (reprinted with permission from Ref. 146, copyright 1997, American Institute of Physics)

a CO/H_2 gas flow ratio of 18 produced a growth rate peak near 450°C, which was ~20 times higher than that obtained with the standard H_2 rich mixtures of CH_4/H_2 and CO/H_2 as shown in Fig. 28.[146] The growth parameters in this study were a substrate temperature of 480°C, an MW power of 500 W, a pressure of 10 torr and a CO flow rate of 9 sccm. The growth rate was measured by RTSE and was expressed in terms of the diamond mass per area.

CH_3OH/H_2, CH_4/H_2, and CH_4/CO_2 have also been employed to fabricate diamond films at low temperatures. Adherent diamond thin films was obtained on sapphire substrates using 1%CH_3OH and 99%H_2 gas mixture at substrate temperature of 500–550°C and low pressure (1 torr) in an ECR MPCVD process.[34] The shifting of the diamond peak by ~6 cm^{-1} in Raman spectroscopy suggested the presence of very large compressive stresses (3·2 GPa) in the film. However, the film showed excellent transmission characteristics with >80% optical transmission at wavelengths >2 μm.

Using CH_4–CO_2 gas mixture polycrystalline diamond film was deposited at 250°C by an MPCVD method.[22] The low temperature deposited films showed electrical resistivity three orders of magnitude less than that obtained in case of conventionally deposited diamond films. The trapped H atom in the film was found to dominate the conduction mechanism. The films were found to exhibit a rectifying behaviour using Pt as the upper electrode.

Conventional CH_4/H_2 gas mixture was also used to achieve low temperature ($\leqslant$600°C) deposition of diamond on single crystal Si substrate by cooling the substrate holder with nitrogen gas,[194] on WC–Co based cutting tools[15] to improve the adhesion and the mechanical properties and on Ti–6Al–4V alloy[30] using MPCVD method. A decrease in the diamond grain size and growth rate and an increased surface smoothness were observed with decreasing Si substrate temperature.

The limits for low temperature growth of diamond films depend substantially on the gases employed as well as on the carbon concentration in the particular system.[195] With decreasing substrate temperature, the non-diamond fraction normally increases in the deposited film. The addition of oxygen improves the film quality and also helps in getting low temperature deposition. The lowest temperature has been realised in CO rich systems.

The intentional addition of small amounts of N_2 to different C/H/O gas systems was studied in getting low temperature diamond deposition.[161] The effect of N_2 on growth was found different for different gas mixtures, with or without oxygen. Whereas adding N_2 to C/H mixtures resulted in a significant change in film morphology, growth rate, defect formation and incorporation of H_2, its effect on growth from CO rich C/H/O systems was much less pronounced. The film quality seriously deteriorated with increasing N_2 concentration in the C/H gas mixture. However, the quality did not change with increasing N_2 concentration in the CO rich C/H/O gas mixtures. The presence of oxygen in these gas mixtures somehow removed the deleterious effect of nitrogen in the formation of defects.

Low temperature growth through changes in processing conditions

Low temperature diamond growth has also been achieved by alteration of the processing conditions like coating the substrate with another material, pulse modulation of the MW plasma, cyclic modulation of the CH_4 flow rate and changing the substrate state.

Polycrystalline diamond film with very smooth surface was obtained at <600°C by controlling the secondary nucleation and growth process at low temperature.[14] Since <700°C secondary nucleation was difficult on diamond (111) surface, a thin gold layer was deposited on top of the diamond film grown initially, which enhanced the renucleation process. Application of gold layer on diamond film helped in getting low roughness film as well at low temperature.

Low temperature (<500 °C) deposition of diamond films was achieved by placing the substrate away from the plasma source, otherwise under the normal deposition condition (4%CH_4, 40 torr, 1100 W).[196] Both the untreated and pretreated (by 30 μm diamond powder) substrates were used for the experiment. Among various substrates studied (untreated Si, pretreated Si, pretreated quartz, untreated glass and pretreated glass), pretreated quartz and pretreated glass enhanced the diamond formation at low temperature, while untreated glass gave only graphite formation under the same deposition conditions. Diamond films were also deposited on pretreated glass at various CH_4 concentrations and produced the largest grain size with 3% of CH_4 concentration. The growth rate of the film increased with increasing CH_4 concentration.

Using magnetic field discharge activation and by pulse modulation of the input MW power polycrystalline diamond films were synthesised at backside substrate temperatures down to 300°C in a low pressure CH_4–H_2–O_2 MW plasma.[197] Diamond films grown at backside substrate temperatures of 300–500°C exhibited characteristic 1333 cm^{-1} Raman phonon peaks with line widths of 5·7–3·1 cm^{-1} and clearly defined crystallites in SEM images. The non-diamond carbon content of the films was low for temperatures down to 350°C, as estimated from the broad peak of the Raman spectra ~1550 cm^{-1}. The non-diamond carbon content was estimated by considering the area under the Raman peak at ~1550 cm^{-1}.

An oxyacetylene flame was used to deposit polycrystalline diamond films onto nitrided chromium using very low substrate temperatures (<400°C).[47] But, at these low temperatures, extremely weak bonding, or no bonding at all, was observed between the deposited layer and the substrate. To obtain stronger bonding, although higher substrate temperatures (700–1000°C) were used initially but, it was lowered down step by step to 250°C at the later stages of the growth. However, lowering the substrate temperature below ~500°C from the initial temperature led to delamination owing to generation of thermal stresses in the film.

Using a combination of diamond–nanoseeding on the substrate and magnetoactive plasma CVD, diamond growth was obtained at 200°C.[19] The lowering of the substrate temperature was achieved by forced cooling of the substrate holder by a circulating fluid containing water and ethylene glycol. A colloidal solution of 3–5 nm diamond powder was used for the diamond–nanoseeding on the Si substrate. The deposited film, however, was inferior to those fabricated at conventional temperature owing to the presence of non-diamond carbon phase in the film.

A cyclic modulation of CH_4 flow rate was used to enhance deposition of diamond film with high nucleation density on pretreated glass substrate at relatively low temperature of ~450°C.[18] The cyclic modulation was carried out through the on/off control of the CH_4 flow, which was started from H_2 and CH_4 plasma (CH_4 flow on) and ended in H_2 plasma (CH_4 flow off). Longer cyclic modulation time interval was suggested beneficial for growth enhancement owing to the increased amount of the atomic H concentration in the reaction system. Since atomic H concentration gradually increases during CH_4 flow off time and decreases when CH_4 flow is on, a larger modulation time (like 90 s : 90 s) produced larger concentration of the atomic H than smaller modulation time (like 30 s : 30 s).

The study of the low temperature growth of diamond film reveals that since the low temperature growth of diamond is limited by slow kinetics, a good pretreatment is necessary in order to achieve an appreciable growth rate at lower deposition temperatures. Seeding the substrate by nano-diamond particle has been an effective way to improve the nucleation density by reducing the incubation period. Low temperature diamond growth from conventional H_2/CH_4 precursor ends up with very poor quality film with high content of graphitic sp^2 phase. Extremely low growth rate and poor quality of the film at lower temperature is associated with the reduced surface diffusion of the growth species on the substrate surface. The faster and efficient etching of the graphitic phase by hydroxyl radical (OH) compared with that by atomic H helps in achieving better quality diamond film with significant growth rate at lower deposition temperatures using oxygen or oxygen containing precursors. The lower bond energies of the C–X (X=Cl, F) bond in the halogen containing hydrocarbons compared with C–H bond energy in the hydrocarbon itself provides lots of hydrocarbon ions or atoms in the plasma containing halogenated precursors. The increased growth rate from the halogenated precursors at lower deposition temperature is due to the availability of the excess growth species in the gas phase.

Low temperature growth mechanism

The enhanced low temperature growth rate using the halogenated precursors like CHF_3 and $CHCl_3$ compared with that using the common CH_4 precursor was explained by considering both the thermodynamic equilibrium states and reaction kinetics.[152] Based on the observation that CHF_3/H_2 helped in reducing the deposition temperature whereas no deposition was obtained with CF_4/H_2 precursor suggested that the bond energies alone could not explain the positive effect of the CHF_3 towards growth at low temperature. But for $CHCl_3$, the low temperature growth could be explained based on the bond energy data. Since C–Cl bond energies in $CHCl_3$ are much smaller (331 kJ mol^{-1}) than the C–H bond energies in CH_4 (426 kJ mol^{-1}) and C–F bond energies in CHF_3 (527 kJ mol^{-1}), the generation of CH_3 radical is much easier and thermodynamically favourable for $CHCl_3$.

For $CHCl_3$ both bond energies C–H (402 kJ mol^{-1}) and C–Cl (331 kJ mol^{-1}) are lower than for methane, C–H (427 kJ–mol^{-1}). But for CHF_3 both bond energies C–H (431 kJ mol^{-1}) and C–F (527 kJ mol^{-1}) are higher than for methane. Since radical formation also involves a chemical reaction, both the thermodynamic equilibrium and reaction kinetics have been suggested as factors. The formation of HF from any fluorine containing molecule in the gas phase is thermodynamically favourable. The activation energies for the radical (CH_3 and CF_3) formation from the precursor gases used are

$$H+CH_4 \rightarrow H_2+CH_3,\ E_a=20 \text{ to } 63 \text{ kJ mol}^{-1} \qquad (19)$$

$$H+CF_4 \rightarrow HF+CF_3,\ E_a=83 \text{ to } 160 \text{ kJ mol}^{-1} \qquad (20)$$

$$H+CHF_3 \rightarrow H_2+CF_3,\ E_a=40 \text{ kJ mol}^{-1} \qquad (21)$$

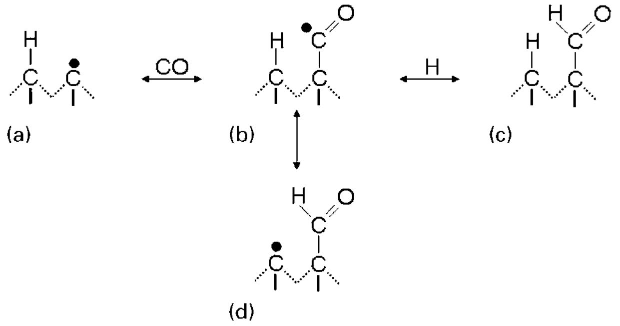
Since CF_4 is a non-polar and very stable compound, formation of CF_3 from CF_4 requires very high activation energy and was suggested to be the main obstacle to diamond formation from CF_4. Because of the similar activation energies, CHF_3 or CH_4 could not be distinguished as a better option for a precursor as per the kinetic data. However, surface chemistry was found different for the two precursors. Considering CH_3 as the main diamond growth species, the H_2 abstraction from two neighbouring CH_3 groups on the surface was found to be an endothermic process

$$H_3C+CH_3 \rightarrow H_2C-CH_2+H_2,\ \Delta H=68 \text{ kJ mol}^{-1} \qquad (22)$$

This would require higher temperature in order to shift the equilibrium in the direction of the products. But for the fluorinated system, the process requires the abstraction of HF instead of H_2, which is an exothermic process and thermodynamically favourable.

$$HFCF+HCHF \rightarrow HFC-CHF+HF,\ \Delta H<0 \qquad (23)$$

Therefore, to shift the thermodynamic equilibrium to the product side, low temperature is required (Le Chatelier's principle). The above mechanism justifies the faster growth rate using CH_4/H_2 at higher temperatures and CHF_3/H_2 at lower temperatures.



29 Model for growth of diamond film in gases containing CO on diamond surface (reprinted with permission from Ref. 199, copyright 2001, American Institute of Physics)

In another low temperature growth studies using CHF_3, C_2H_5Cl and Cl_2 precursors at 350°C by HFCVD and MPCVD method, the role of halogens were suggested in the surface reaction leading to the formation of active surface sites at which diamond growth species could be adsorbed.[198]

But, the mechanism involved in the C–H–O system for the low temperature diamond growth is different. The lower value of the activation energy for the diamond growth in C–H–O system than for the CH_4/H_2 systems suggested a different gas surface chemistry for CH_4/CO_2 plasmas.[199,200] Using MBMS, the dominant gas phase species present during growth over a wide range of plasma gas mixtures (0–80%CH_4, balance CO_2) was measured and the experimental results were simulated using CHEMKIN computer package. The calculated trends for all species agreed well with the experimental observations. Using the experimental and simulated data, the overall gas phase chemistry was reduced to only four overall reactions as

$$CO_2+CH_4 \rightarrow 2CO+2H_2 \qquad (24)$$

$$CH_4 \rightarrow C_2H_2+3H_2 \qquad (25)$$

$$CO_2+H_2 \rightarrow CO+H_2O \qquad (26)$$

$$H_2O+C_2H_2 \rightarrow CH_4+CO \qquad (27)$$

The simulated result showed that the gas phase concentration of CO within the CO_2/CH_4 plasma was ~100 times that of atomic H and CO was considered as an alternative species that could terminate the growing diamond surface. The surface chemistry of diamond growth involving CO is shown in Fig 29. The Fig. 29*a* represents a reactive site on the growing diamond surface with an unpaired electron (indicated by dot) on the C atom. This unpaired electron reacts with a gas phase CO molecule to form an unstable carbonyl radical adduct as shown in Fig. 29*b*. Since CO contains an unpaired electron, this CO terminated structure is unstable and prone to desorbs back to stage in Fig. 29*a* in subsequent stages. This unstable carbonyl adduct might react either with a H atom from the gas phase and form an aldehyde as shown in Fig. 29*c* or with a terminating H atom from the neighbouring surface site (Fig. 29*d*). In this process a 'dangling bond' can migrate across the growing diamond surface (e.g. to a step edge). A CH_3 radical in the CH_4/CO_2 plasma react with dangling bonds on the surface adding a carbon to the lattice. Since in the mixtures, the observed concentration of CH_3 both in experiment and simulation coincided very precisely with the narrow window for optimum diamond deposition (50%CO_2/50%CH_4) and the similar maxima in the concentration of CO or any other species around this narrow concentration window was absent, CH_3 was considered to be the main species responsible for diamond growth rather than the CO or C_2H_2.

Growth of polycrystalline diamond thin film has recently been demonstrated on single crystal Si (100) and SiC (6H) substrates at low surface temperatures of 370–530°C from an Ar rich $Ar/H_2/CH_4$ plasma using high MW power and gas pressures in an MPECVD system by our group.[201] The phase pure diamond samples with very high growth rate (1·3 μm h^{-1} on SiC) and grain sizes of 2–7 μm show very high thermal conductivity of 6·5 W cm^{-1} K at room temperature.[202] Different low temperature diamond deposition reports based on different processes used, precursors, substrates, pretreatments, process parameters like temperature, pressure and power used are summarised in Table 4. The growth rates obtained for different experiments are also included in the table.

Conclusions

The need for synthesis of diamond film at temperatures <500°C is described because of the requirements in many applications in electronics. An understanding of the nucleation and growth phenomena during processing of diamond films is essential to achieve a successful lowest temperature growth possible. Since at low temperatures the kinetics itself is slow, a good surface pretreatment is required for enhanced nucleation.

Consequently, the first part of the review covered nucleation and growth of the diamond films. The influence of processing parameters such as temperature, pressure, MW power and pretreatment of the substrates on the nucleation and growth is discussed. Different pretreatment techniques such as scratching/abrasion with hard powder materials, surface passivation with H^+, Br^-, I^- ions, surface coating with different carbon containing materials or metals, ion implantation, biasing, pulsed laser irradiation and carburisation have been found beneficial for enhancing nucleation density. Forty to fifty micrometres diamond slurry activation is most effective nucleation promoting mechanical abrasion process. Br passivated Si surface produced a dramatic increase in nucleation density of 10^{10} cm^{-2}. Among the various nucleation enhancement approaches, the application of a bias potential to the substrate is quite effective in achieving high nucleation density. Bias enhanced nucleation produced nucleation density on the order of 10^9–10^{11} cm^{-2}.

In general, substrate pretreatments produce defects such as scratches, grain boundaries, particle boundaries, dislocations, electron bombardment induced damages, edges of pits or craters, or coating of a thin layer of carbide or amorphous carbon, which are identified as potential sites for nucleation either because of the high energy interface with a high density of unsaturated bonds and low coordination number or carbon supersaturation regions on the surface.

Table 4 Summary of LTDG studies reported in literature*

Process	Precursor	Substrate	Pretreatment	Subs Temp T_S, °C	P/power, torr/W	Growth rate, μm h^{-1}	Ref.	Remarks
ArF excimer laser (193 nm)	99·3%H_2/0·7%CO	Single crystal Si (111)	Mechanical abrasion with 4–8/0·5–1 μm dia. particle	RT	8/NA	5–10	203	Growth is observed within 1 h
HFCVD	1%CH_4/H_2 (total gas flow=300 sccm)	Single crystal Si (111)	Mechanical abrasion with diamond powder	135	50/NA	1 (700°C) 0·36 (250°C) 0·28 (135°C) 0 (70°C)	204	Growth temp. can be lowered down by lowering CH_4 conc.
RF PECVD	100%CH_4 and 98%CH_4/2%Ar (V_T=50 sccm)	Si	RF (13·56 MHz) biasing between −50 and −500 V	−23 27 147	0·1/NA	–	205	a-C/H film is obtained
35 kHz RF plasma	CH_4/Ar (80 and 95%)	Single crystal Si (100)	Ultrasonication in a bath of acetone and ethanol + Ar plasma preheated for 5 min	15 and 200	0·1 and 0·3/NA	0·1 (15) and 0·2 (200)	206	Surface roughness 0·2 nm, nanodiamond fraction is very less, hardness 15 GPa
MWCVD	CH_4/H_2 and CH_4/CO_2	Si (100)	–	340–740 (IR pyrometer)	60/800	–	207	Defects/impurities are increased with N_2 contamination and lower T_S
MWCVD	CH_4/CO_2 (29/31 sccm)	Si (100)	–	275–560 (IR pyrometer)	60/600	–	208	Very low N_2 contamination level is required for good quality film
HFCVD	CHF_3/H_2 and CF_4/H_2 (V_T=200 sccm)	Si	Abrasion with diamond powder	350–850 (NiCr/Ni thermocouple)	15/NA	0·35 (for 1·5–2·0%CHF_3) and 0 for CF_4	152	Shows poor adhesion with the substrate surface.
HFCVD/MWCVD	CHF_3/C_2H_5Cl/ Cl_2	Si (100)	Abrasion with diamond powder (0·25 μm)	350 (NiCr/Ni thermocouple)	15/480	–	198	Halogen lowers the deposition temperature by surface reaction.
MWCVD	CO_2/CH_4(0–80%) (V_T=80 sccm)	Single crystal Si (100)	Abrasion with 1–3 μm diam. grit	435 (calibrated K type thermocouple)	40/1000	–	200	Conc. of CO in plasma is controlling factor in LTDG
MWCVD	CH_4/CO_2 (1 : 1, 80 sccm)	Single crystal Si (100)	Abrasion with 1–3 μm diam. grit	435–845 (calibrated K type thermocouple)	40/1000	0·1 (500°C)	199	CH_3 is the key growth species for CO_2/CH_4 plasma
HFCVD	H_2/CH_4, H_2/CHF_3, H_2/C_2H_5Cl	Si/Mo plates	Scratching with diam. powder	370 (NiCr/Ni thermocouple)	15/NA	–	151	Decrease in C content in precursor shifts T_S to lower Temp.
HFCVD and MWCVD	0·5–2% C_2H_5Cl + H_2	Si, Zn, Al and glass	Mechanical abrasion with 0·25 μm diam. powder	377–800 (IR pyrometer and NiCr/Ni thermocouple)	15/NA	–	149	Growth rate increases with increasing halogen in precursor
MWCVD	CH_4/H_2, CH_4/CO_2(O_2)/H_2, CH_4/CO_2 in varying proportions	Si (100)	–	270–540 (IR pyrometer)	60/800 (CH_4/H_2) 60/600 (CH_4/CO_2)	–	195	LTDG is influenced by O_2 and O_2 containing species
HFCVD and MWCVD	H_2/CH_4/Cl_2, H_2/C_2H_5Cl H_2/CHF_3	Si (100) Glass Al	Mechanical abrasion with 0·25 μm diam. powder	370 (Si) 490 (glass, Al)	15/480	–	150	Halogen promotes LTDG

Table 4 (Continued)

Process	Precursor	Substrate	Pretreatment	Subs Temp T_S, °C	P/power, torr/W	Growth rate, μm h^{-1}	Ref.	Remarks
PECVD	$17 \cdot 5CH_4$–$30CO_2$ $16 \cdot 1CH_4$–$30CO_2$ $17 \cdot 5CH_4$–$30CO_2$ $16 \cdot 1CH_4$–$30CO_2$	p-Si (100)	Mechanical scratching with 1–2 μm diam. powder	550–250	25–6/NA	–	19	Three orders of magnitude less in resistivity than that of conventional film
ECR CVD	1%CH_3OH–99%H_2	Sapphire (Al_2O_3)	Ultrasonication in a slurry of 0·25 μm diamond + acetone	500–550	1/NA	0·2	31	Show 80% optical transmission at λ>2 μm
Low output power MWCVD	CO(7%)/H_2 CO(7%)/O_2(2·2%)/H_2	Single crystal Si	Ultrasonication in a slurry of diamond + methanol + cleaning in organic solvent	130–750 (Thermocouple)	–	0·19–0·73 (403–750) 0·035–0·2 (411–750)	148	C–H–O is a better system for LTDG
MWCVD	CO/H_2 (CO, 9 sccm)	Si and NCD film (800°C) on seeded Si	Abraded with <0·25 μm diamond powder	350–500	10/500	2·5	146 147	NCD coating is to avoid properties variation
MWCVD	CH_4, 6 sccm H_2, 194 sccm	WC–6%CO	Ultrasonication in HNO_3/H_2O= 1 : 2 (vol.) 5 min then scratching with diamond powder in a CH_3OH bath	400	9·75/300	–	12	Cutting performance improved
MPCVD	200 sccm H_2/4 sccm CH_4	Patterned glass	H_2 plasma cleaning for few minutes	450	13/400	–	15	Cyclic modulation of CH_4 and keeping the substrate 3 cm remote from plasma enhanced LTDG
Magneto active MWCVD	CH_3OH, 15 sccm H_2, 85 sccm	p-Si (100)	Ultrasonic agitated, +30 V bias	200–600	0·075/1300	–	16	Nanodiamond phase found
MPCVD	4% CH_4/H_2	n-Si (100), glass quartz	Untreated or ultrasonication in 30 μm diamond/acetone slurry for 5 h	460 (optical pyrometer)	40/1100	–	196	LTDG achieved by putting the substrate 3 cm remote from plasma
MWCVD	H_2/CH_4 (0·25–7%) V_T=200 sccm	Si (100)	Coating of a 20 Å Au/Pd interlayer by sputtering.	400–700 (bichromatic optical pyrometer)	37·5/1000	0·001–0·01	11	Produced low roughness film owing to enhanced secondary nucleation
MWCVD	CH_4/H_2–O_2 H_2=100 sccm CH_4=17 sccm O_2=16 sccm	n-Si	Abrasion with alcohol solution of 5 μm diamond powder	300–500 (backside T_S with K type thermocouple)	3/(average 300, peak 3 kW)	0·08–0·2	197	Pulsing of MW Growth rate increased to 20–50 times than in CW mode

*T_S: substrate temperature; V_T: total volume of gas flow; RF: radio frequency; IR: infrared; LTDG: low temperature diamond growth; NCD: nanocrystalline diamond; MW: microwave; CW: continuous wave.

The process conditions for achieving good nucleation and growth are different. In general, high temperature favours both nucleation and growth processes. Using bias enhanced nucleation, an increase in temperature from 670 to 700°C led to an increase in nucleation density from 10^6 to 10^{10} cm^{-2}. A low pressure of 0·1–1 torr produced a high nucleation density of 10^9–10^{11} cm^{-2} on mirror polished Si wafer without the application of bias in an HFCVD method. Doubling the pressure from 94 to 188 torr increased the growth rate from 0·7 to 4·5 μm h^{-1} with 0·5%CH_4 concentration. The conditions of nucleation and growth are also different on different substrates. On SiC substrate nucleation is favoured by the CH_4 concentration and process pressure, whereas growth is favoured only by the CH_4 concentration and is not affected by the temperature and gas flow in the temperature range of 780–885°C. On Si_3N_4 substrate, nucleation increased with decreasing pressure but, growth increased with increasing pressure in the temperature range of 800–900°C.

CH_3 radical is considered as the main species responsible for diamond growth in CH_4–H_2 plasmas. However, recent low temperature studies based on Ar based plasma suggested C_2 as the main species responsible for growth.

The second part of the paper dealt with the LTDG and influence of the processing parameters. Most of the low temperature diamond growth work in the literature mentioned the substrate backside temperature as the surface temperature was not measured directly. But, the real surface temperature of the growing film is significantly different from the substrate backside temperature. In spite of the slower growth rate at lower deposition temperatures, factors responsible for improved growth rate are identified. The lowest temperature to grow diamond is different for different precursors as predicted by the thermodynamic calculations. In C–H system, the lowest temperature is pressure dependent. It is 1127°C at 760 torr, 627°C at 7·6 torr and 327°C at 76 mtorr based on thermodynamics. But, in C–H–O system the lower limit is all the way to room temperature. In the C–H–O system, the carbon solubility decreased with decreasing temperature.

Using a seeding of the Si wafer with 3–5 nm diamond grains, a good adherent diamond film is obtained at 200°C. The halogenated precursor gas (fluorides and chlorides) and oxygen containing precursors also helped in getting diamond film with good growth rate at low temperatures. A growth rate of 0·04 μm h^{-1} is obtained with H_2/C_2H_5Cl gas mixture at 370°C, which increased gradually from 0·04 μm h^{-1} at 370°C to almost 0·2 μm h^{-1} at 850°C. A growth rate of 2·5 μm h^{-1} is obtained using CO/H_2 gas mixtures in an MPECVD process in the temperature range of $350°C<T<500°C$ and at 500 W MW power. A 20 times increase in growth rate is observed at 450°C in an experiment using CO/H_2 ratio of 18, pressure of 10 torr, power of 500 W and CO gas flow rate of 9 sccm.

Since nucleation and growth of diamond film are affected by surface phenomena and these are thermally activated processes, a thorough and better understanding of the surface characterisation is needed to have a superior control of the final diamond film. In addition, in situ techniques for monitoring the growth chemistry and parameters are very useful tools to further understand and control the diamond synthesis. In situ Raman, FTIR, RTSE and MBMS are powerful methods to analyse and control the growth process.

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