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Synthesis of diamond

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Diamond is impressive because of its wide range of extreme properties. By most measures, diamond is 'the biggest and best': it is the hardest known material, has the lowest coefficient of thermal expansion, is chemically inert and wear resistant, offers low friction, has high thermal conductivity, and is electrically insulating and optically transparent from the ultraviolet to the far infrared. Diamond already finds use in many different applications including, of course, its use as a precious gem, but also as a heat sink, as an abrasive, and as inserts and/or wear-resistant coatings for cutting tools. Obviously, it is possible to envisage many other potential applications for diamond as an engineering material, but progress in implementing many such ideas has been hampered by the comparative scarcity of natural diamond. This paper reports on the progress of the long running quest for ways to synthesize diamond in the laboratory.

The high pressure, high temperature route

From a thermodynamic point of view, the conversion of graphite into diamond is characterized by a small, positive value of ΔG°:

$$C_{\text{graphite}} \rightarrow C_{\text{diamond}} \quad \Delta G^\circ = +2895 \text{ J g-atom}^{-1} \text{ at } 25\ ^\circ\text{C and 1 atm pressure}$$

This indicates that diamond is thermodynamically unstable with respect to graphite and that the reaction has thermodynamic permission to proceed in the opposite direction. Unfortunately, the thermodynamics does not give any information about the time required for a reaction to take place, and the diamond to graphite conversion is extremely slow under ordinary conditions. Increasing the temperature allows the acceleration of most reactions and this is also true for the conversion of diamond to graphite. The transformation begins to proceed at an observable rate at a temperature in the neighborhood of 1200 °C, at 1 atm, indicating that higher temperatures decrease the thermodynamic stability of diamond.

In order to allow the conversion of graphite into diamond, it is necessary to bring the reaction into a region where ΔG° is negative, *i.e.* to apply pressure, as can be seen from the graphite–diamond equilibrium curve shown in Fig. 1, where the line represents the pressure and corresponding temperature for which $\Delta G^\circ = 0$. Above the line, ΔG° is negative and diamond is the stable carbon allotrope; conversely, graphite is stable in the region below the line.

From the above analysis, it follows that the pressure required depends on the temperature: the higher the temperature, the greater must be the pressure. Unfortunately, experiments show that high pressure retards the rate of transformation of diamond to graphite and it seems reasonable to assume the transition state for the graphite to diamond conversion to be the same as for the formation of graphite from diamond. This is a very frustrating but extremely interesting situation: higher pressure leads to more favorable thermodynamics (a more negative ΔG°) for the conversion of graphite into diamond but, at the same time, leads to less favorable reaction kinetics, since the transition state could be depicted as an expanded activated complex[2] (the molar volume of diamond is 3.42 cm^3 while that of graphite is 5.34 cm^3, and the molar difference in volume $\Delta V^{\neq}$ between diamond and the activated complex is, at least, 10 cm^3).

Accordingly, the initial suggestion that graphite could be converted to diamond by 'brute force', *i.e.* by applying sufficient pressure to shorten the bonds between graphite layers to force the carbon rings to conform to the diamond lattice, must be abandoned. It would seem desirable to take the graphite lattice apart atom by atom and build the atoms one at a time into the diamond lattice; this might be accomplished by means of a solvent.

Both approaches have been applied since 1880, when J. B. Hannay claimed to have produced the first synthetic diamonds.[3] The synthesis requires a mixture of light paraffin oils and bone oil (mostly pyridine, which contains nitrogen)

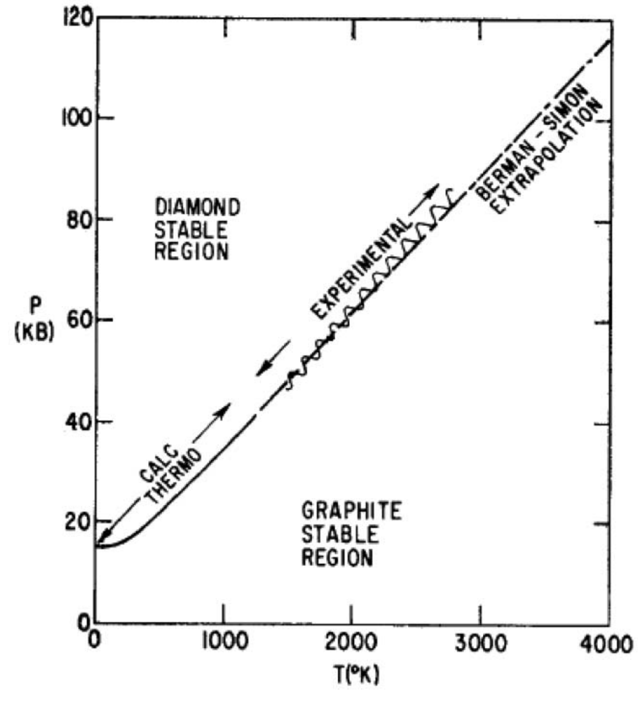

Fig. 1 The graphite-diamond equilibrium curve. Reproduced by permission from ref. 1. Copyright 1962, The American Chemical Society.

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and is catalyzed by lithium metal in a thick iron tube at red heat. The minute yield (14 mg) of type II blue diamonds exhibited all the characteristics and properties of natural diamonds. Hannay found that when carbon is liberated from a nitrogenous hydrocarbon in the presence of Li, Na, Mg or K at red heat and high pressure, the metal hydride is formed and the carbon reacts with (or is stabilized by) the nitrogen and assumes the diamond form. No diamonds were found in experiments without nitrogen.

The success of Hannay was later confirmed[4] by Londsale and Bannister in 1943 who examined twelve little crystals, applying the new technique of X-ray analysis to them. Out of the twelve, one was definitely not a diamond, a few were evidently contaminated with some impurities, but several were undoubtedly diamonds.

Later on, both published and private communications focused on the problem of Hannay's trustworthiness. In fact, at the time of Bannister and Londsale's studies, it was believed that type II diamonds were very rare and that even if only one out of the eleven 'Hannay diamonds' were of type II, that would be strong presumptive evidence that they were synthetic and not natural. On April 1943, Londsale wrote[5] to Lord Rayleigh: "*If type I diamonds are 'perfect' (in the X-ray sense) and type II diamonds are 'mosaic' in structure, then it is fairly certain that if and when a reliable laboratory method of making diamonds is discovered, it is type II diamonds that will be obtained, since no laboratory experiment can ever hope to reproduce the ideal 'annealing' conditions found in Nature's workshop in the depths of the earth.*" In his reply, Lord Rayleigh wrote: "*There is a paper by Hannay that was rejected by the Royal Society, but there is no mention in the Royal Society records of such a paper. I am informed that if submitted at all, it would have been recorded, even if rejected.*" Later skepticisms have been based on the failure of all attempts to repeat Hannay's experiments under the conditions he described. It seems, therefore, that the 'Hannay diamonds' are almost certainly natural diamonds, but whether Hannay himself knew this is uncertain, and will probably never be proved. In favor of Hannay's reputation is the letter of M. W. Travers, in which a response to the criticism of Lord Rayleigh is given;[6] nevertheless, the witness of estimation seems to be based on personal consideration, instead of on scientific evidence.

Other 'successful' syntheses were claimed after Hannay: in 1893, Henry Moissan was working with the early electric furnace when he performed the experiment involving heating up iron containing carbon to a very high temperature and suddenly cooling the molten mass, hoping to produce extremely high pressures within it, which theory predicts would aid in making diamonds. Unfortunatly, the crystals were lost and the X-ray test could not be applied to them; moreover, as reported by Lloyd, "*It has always seemed to me that if diamonds could be obtained thus, someone in carrying out the almost infinite number of heatings and quenchings of carbon-bearing iron and steel that have occurred in the course of practical ferrous metallurgy, someone else would have noticed them.*"[7] After an inquiry by Londsale in 1962, Wyart, head of the Department of Mineralogy and Crystallography at the Sorbonne, replied as follows:[5] "*Henri Le Chatelier, qui a été son successeur au Laboratoire de Chimie Générale, ne croyait pas au diamant de Moissan et dans son livre 'Science et Industrie' (Flammarion, 1925) il dit à la page 195: 'Personne ne croit plus au diamant de Moissan.' [⋯] Cette opinion de Le Chatelier était aussi celle de F. Wallerant [⋯]. Il avait vu les diamants de Moissan, et Wyrouboff [⋯] les avait soigneusement examinés au microscope polarisant. Il en avait conclu que les cristaux de Moissan n'étaient pas du diamant.*"†

In 1888, Sir Charles A. Parsons published a paper giving an account of his own experiments on diamond production;[8] Parsons' crystals, which he believed to be diamonds, were apparently not preserved, and could not be found by Londsale and Bannister, so that the X-ray technique was not applied to them.[4] However, in a letter to *Nature*,[9] Lord Rayleigh stated that Sir Charles Parsons had repeatedly conversed with him on the subject of his experiments and had told him that the crystals obtained would not burn in oxygen and therefore were not diamonds. As reported in ref. 5, on July 19 1943, H. M. Duncan (Charles Parsons' assistant) wrote "*I remember Sir Charles telling me that he had consulted the President of the Royal Society as to the best means of acknowledging that he was mistaken. [⋯] With regards to the characteristic crystals, I can tell you that these consisted of magnesia and alumina.*"

The paper by Lloyd reports other negative investigations:[7] Gunther, Geselle, and Rebentisch in 1943; P. W. Bridgman in 1947, and Slawson in 1953.

Focusing again on possible 'successful' investigations, in a letter to *Nature* of 24 August 1905, C. V. Burton claimed[10] to have synthesized diamond at ambient pressure by an unusual method, *i.e.* by dissolving carbon in a lead–calcium alloy, in which carbon is more soluble than in lead alone, then supersaturating the lead by oxidizing the calcium with steam at a very low red heat. As the calcium was converted into hydrate, without attacking the lead, a number of very small or microscopic crystals were found. With this method, the transformation temperature corresponding to atmospheric pressure is stated to be somewhere between 550 and 700 °C. Strangely, the first response to Burton's communication appeared some 80 years later, as Sebba and Sugarman repeated the experiment,[11] decomposing the alloy at 550 °C. After acidic treatment of the grey crust, a black powder with many transparent crystals was obtained; X-ray powder diffraction showed a strong peak at 0.208 nm, which is the strongest peak for diamond (but only weak for graphite). On the contrary, the strongest peak for graphite was absent. On this basis, Burton's claim cannot be unequivocally confirmed, but there is a strong presumption that diamonds were made.

Considering that Burton's experiment was repeated only in 1985, the first reproducible experiment in diamond synthesis is reported to be that of the General Electric Company[12] in 1955. The method requires the use of a catalyst material to lower the activation energy of the reaction of graphite to diamond. The direct heating of graphite, to average temperatures up to about 2800 °C and pressures up to about 80–100 kbar, was carried out over a number of experiments between 1953 and 1955, but in none of them was there any evidence of diamond, melting of graphite being the only result in a few of the tests.

As shown in Fig. 2, even conditions well up into the diamond stability region (*e.g.* a pressure of more than 400 000 atm at room temperature) result in a lack of success, since the reaction rate is negligible at the relatively low temperature at which the experiment is carried out. The intuition of the experimentalists of General Electric was to apply a relatively high pressure (at least 75 000 atm), operating at temperatures from 1200 to 2000 °C; in order to avoid the melting or chemical reaction of the wall material surrounding the graphite specimens, heating pulses, generated by discharging a large electrolytic capacitor through the graphite sample, were used. 90% of the energy was delivered in about 3 to 6 msec, thus roughly adiabatically. In a subsequent patent,[13] it is stated that the materials described as catalysts have a double function: to act as catalysts for the transformation of non-diamond carbon into diamond, and to act as a relatively good solvent for the non-diamond carbon,

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†"*Henri Le Chatelier, who succeed Moissan in the Laboratory of General Chemistry, did not have faith in Moissan's diamonds, and in his book 'Science et Industrie' (Flammarion, 1925), he wrote on page 195: 'Nobody trusts in Moissan's diamonds.' [⋯] The opinion of Le Chatelier was also that of F. Wallerant [⋯]. He had seen Moissan's diamonds and, with Wyrouboff [⋯] had carried out detailed examinations under a polarizing microscope: his conclusion was that Moissan's crystals were not diamonds.*"

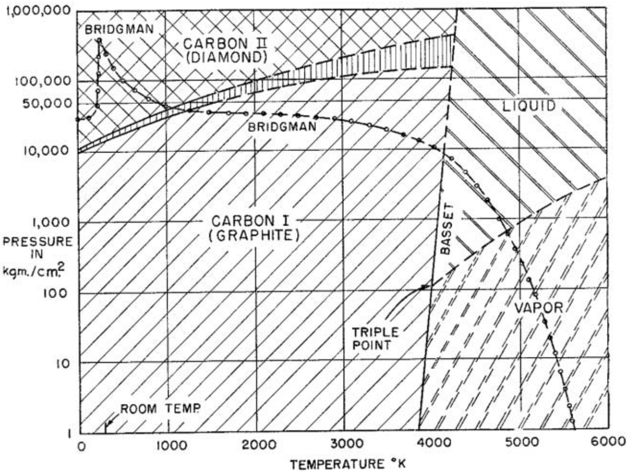

Fig. 2 Phase diagram of carbon. Reproduced by permission from ref. 12. Copyright 1955, Macmillan Publishers Ltd.

while at the same time being a relatively poor solvent for diamond. It is also believed that this solvent effect does not come into play until the catalyst is converted to a liquid metal. At the pressures and temperatures indicated above, the catalysts are metals in the liquid form. Interestingly, a paper written by Bundy[14] presents a number of experiments where different refractory materials are used to surround the graphite specimens; pyrophyllite, MgO, ThO_2, and Al_2O_3 have been used and, in all cases, the diamond synthesis was successful, although different energetic conditions were adopted, depending on the different electrical and thermal properties of the wall materials. Bundy's paper seems to be in contrast to the previous works (*i.e.* the 'joint publication' published in 1955[12] and Hall's patent in 1960[13]), as it implicitly stated that no catalysts are required for diamond synthesis.

Nowadays, the HPHT (high pressure, high temperature) synthesis is still applied for industrial purposes: unless a catalyst is used, the crystals grow only to very small sizes. Nickel and cobalt are the most frequently used catalysts and they can both be found as substitutional impurities in synthetic diamonds. With such catalysts involved, relatively large gem quality crystals can be grown: up to 4.6 carats for colorless diamonds, and up to 25 carats (5 g) for yellow ones.

On the other hand, recent papers have shown that diamond can be synthesized from graphite not only in the presence of metallic catalysts (such as group VIII metals and/or their alloys), but also using non-metallic catalysts, including carbonates,[15] oxides,[16] hydroxides, sulfates,[17] halides,[18] and some other compounds (phosphorus and sulfur,[19] for example). As a matter of fact, diamond synthesis using non-metallic catalysts generally requires higher P–T conditions, as well as a longer reaction time.

Among the reacting elements (inside the reaction cell), it seems well established that oxygen plays a significant role, affecting the growth rate and also with some effects on the morphology of the growing crystals. In this context, the paper by Wang and Kanda is a good example.[18] Some catalytic effects for CO_2 and H_2O have also been claimed by Sokol *et al.*,[16] who agree with Wang and Kanda in attributing to CO the role of "carbon transportation" inside the reacting mixture, thus allowing a higher growth rate.

As far as the growth rate of diamond crystals in oxygen-containing media is concerned, the role of water has been investigated by Wang *et al.*, who carried out the synthesis in the presence of hydrated or anhydrous magnesium sulfate.[17] Despite a difference of 600 °C in the melting points of $MgSO_4{\cdot}H_2O$ and $MgSO_4$ (at a pressure of 7.7 GPa), the diamond forming region (P–T conditions) was practically unaffected, some changes in the crystal morphology being the only consequence. In contrast, a large growth rate difference has been reported by Pal'yanov *et al.* for spontaneous diamond nucleation and growth from alkaline carbonates:[15] both the graphite to diamond transformation degree and the diamond nucleation density were clearly dependent on the cation radius. Speaking of catalytic properties, the obtained results justified the sequence $Li_2CO_3 \gg Na_2CO_3 > K_2CO_3 > Cs_2CO_3$, which may account again for a role in carbon diffusion, connected with the different stability of the chosen salts with respect to decomposition.

While HPHT research is moving toward new synthetic approaches, the 'original' metal-catalyzed route remains open to discussion: as an example, Yin *et al.* have recently focused on diamond formation from 3d transition metal carbides,[20] with the aim of suggesting a synthetic mechanism. According to these authors, diamond crystals may be synthesized from pure Fe_3C at HPHT. As a result, it seems reasonable that some carbide formation also takes place in the case of common group VIII metals catalysis, at least as a preliminary stage of the graphite to diamond transformation.

Without pretending to cover all the literature on the subject, the main scope of the above analysis is to answer the question "Who was the first to successfully synthesize diamond?" There are some doubts as to the answer, choosing among Hannay (1880), Burton (1905), and the General Electric Company (1955), and the picture is further complicated by the appearance of several claims to prior synthesis. As reported in the review article by Hall,[2] as soon as the General Electric Co. announced its success (February 15, 1955), an article entitled "*Artificial Diamonds*" appeared in the *ASEA Journal* (*Allmänna Svenska Elektriska Aktiebolaget*, Västerås, Sweden), with the statement "*ASEA produced its first diamonds on 15th February 1953*". The experimental procedures were disclosed in 1960 and were similar to those used at General Electric.[21]

The dispute just reported is quite important: leaving out the specific controversy, public opinion in the middle of the twentieth century was that nobody had made synthetic diamonds before! This conclusion implicitly deprives Hannay of his credibility (however, it must be said that General Electric itself has recently admitted[22] to have made an analogous 'gaffe' and that the successful synthesis claimed in 1955 was really only realized afterwards), raising, in contrast, the name of Burton, in spite of his work being overlooked for such a long time.

The chemical vapor deposition process

There is another perspective regarding the formation of diamond; its growth could conceptually be realized by adding one carbon atom at a time to an initial template, so that a tetrahedrally bonded carbon network (diamond) results. This could conceivably be accomplished from the gas phase at lower pressures than for the HPHT technique, an obvious advantage in terms of equipment and energy costs.

In essence, this is the logic behind the experiments of Eversole,[23] in which thermal decomposition of carbon-containing gases was used to grow diamond on natural diamond crystals heated from about 600 to about 1600 °C. The temperature range should be restricted to the range 900–1100 °C, since insufficient diamond growth takes place at lower temperatures and excessive black carbon (graphite) deposits at higher temperatures. As reported in the first of Eversole's two patents, pressures greater than about 10 atm are used when diamond is synthesized from carbon monoxide or a mixture of the oxides of carbon (reaction I), while pressures below atmospheric are suggested when the synthesis is performed starting with a methyl group-containing gas (reaction II).

$$\mathrm{I}\begin{cases}2\mathrm{CO}\rightleftharpoons \mathrm{C}_{\text{diamond}}+\mathrm{CO}_2\\ 2\mathrm{CO}\rightleftharpoons \mathrm{C}_{\text{graphite}}+\mathrm{CO}_2\end{cases}\qquad \mathrm{II}\begin{cases}\mathrm{CH}_4\rightleftharpoons \mathrm{C}_{\text{diamond}}+2\mathrm{H}_2\\ \mathrm{CH}_4\rightleftharpoons \mathrm{C}_{\text{graphite}}+2\mathrm{H}_2\end{cases}$$

The rate of growth in such early chemical vapor deposition (CVD) experiments was very low; for instance, a linear rate of approximately 10^{-4} μm h^{-1} is reported in ref. 24. Moreover, graphite was co-deposited with diamond, the growth of the latter becoming hampered by the accumulation of the former: as a consequence, the process must be stopped and the seeds cleaned to remove the black carbon, prior to the possible repetition of the growing step.

A significant growth rate improvement was achieved by Derjaguin *et al.*,[24] who reported the formation and further growth of filamentary diamond crystals, reaching a maximum linear rate of 250 μm h^{-1}. Such a result was made possible by preventing the isolation of graphite, *i.e.* by carefully controlling the temperature on the growing region. In the same year, another step forward was reported by Angus *et al.*,[25] who showed that atomic hydrogen could preferentially etch graphite rather than diamond. The etching treatment, carried out with hydrogen gas at 1033 °C and 50 atm for 7 h, has been proven to remove 99.90% of the graphite and only 0.22% of the diamond. The cleaning procedure, after the diamond deposition, is in close analogy with Eversole's process; however, the paper is original in proposing a justification for the possible difference between the densities of overgrown and virgin diamond samples. Without any uniquivocal evidence, the deposited diamond 'layer' is suggested to be highly polycrystalline, with many grain boundaries and defects. Accordingly, its decreased density may be associated with the voids, defects, and grain boundaries formed at the boundaries between the crystals.

Angus and co-workers were also able to incorporate boron into diamond during growth, giving it semiconducting properties.[26] Again, the idea was not very original, samples of boron-doped diamond with a room temperature resistivity of about 0.15 Ω cm having been already synthesized with the HPHT technique.[14] The doped diamonds obtained by Angus *et al.* had a boron concentration of approximately 10^{19} atoms per cm^3; while it was not possible to make electrical connections to the powders for resistivity measurements, the estimate of the boron content (~0.01 wt%) was based on chemical analysis. Interestingly, no evidence of doping was observed when diamond samples were annealed under a B_2H_6–H_2 gas mixture, *i.e.* in the absence of CH_4; this indicates that the boron is incorporated into the diamond as the seed crystals grow. On the other hand, the blue color observed in connection with the doping of the diamond film did not change after any of the etching tests,‡ although such etches would have removed SiO_2, most metals, metal oxides and, in particular, both B_2O_3 (soluble in acids) and elemental boron (soluble in HNO_3).

In 1981, another paper was published by the Russian school of Derjaguin and co-workers.[27] By applying a chemical transport method, they were able to synthesize diamond both on diamond seed crystals and on "foreign surfaces", like poly- and single-crystalline Cu, Si, W, and other substrates. Of particular interest was the selectivity achieved by introducing different concentrations of atomic hydrogen: its interaction with hydrocarbons, in the gas phase and on the surface, allows the growing rate to be controlled by suppression of graphite deposition. An important role was also played by the substrate temperature: diamond layers grown on diamond single crystals at 600 °C were polycrystalline, with grain sizes of 15 to 20 Å, while near-perfect single-crystalline layers were obtained on the {110} face of natural diamond at 750 °C. On carbide-forming substrates (Si, Mo, W), the diamond nucleation rate was one to two orders of magnitude higher than on substrates that do not form carbides (Cu, Au): octahedral crystals grew at ~800 °C, while regular cubo-octahedra were synthesized at ~1000 °C. Spontaneous nucleation of diamond crystals was observed mostly on defects like scratches, grain boundaries, dislocation outcrops, *etc.*, supporting the idea that nucleation takes place on the substrate and not in the gas phase.

As reported by Angus *et al.*,[26] the presence of boron may increase the rate of surface rearrangement, leading to atomically smoother surfaces. An analogous effect is reported in the Russian paper for synthesis on foreign surfaces: the constant growth rate (~5 μm h^{-1}) of the spontaneously nucleated diamond crystals, at the initial stages of growth, reduces as the substrate coverage by diamond overgrowth increases, becoming nearly that characteristic of homoepitaxial diamond film, under comparable synthesis conditions. Concerning the boron doping, Derjaguin *et al.* stated that the lattice parameter of synthetic diamond is decreased by 0.0009 Å at a B concentration of ~0.1 at%: the lattice contraction and hole conductivity of diamond indicate that, at these low doping levels, boron atoms are mostly found in lattice sites. Increasing the B concentration to ~1 at%, the lattice parameter returns to a value practically the same as that of the diamond substrate; it appears that, in this case, the film contraction due to boron incorporation in lattice sites is compensated for by lattice expansion due to interstitial boron atoms.

All the findings described above were brought together in 1982, when Japanese researchers at the National Institute for Research in Inorganic Materials (NIRIM) built a "hot filament" reactor,[28] in which good quality diamond particles and films could be grown on non-diamond substrates, from hydrocarbon–hydrogen mixtures. The system operated using 0.5–2% CH_4 in H_2, a total flow rate of 4–200 cm^3 min^{-1} (at STP), and a pressure from 0.5 to several tens of Torr. The hot tungsten filament, which was heated to about 2000 °C with a stabilized d.c. source, greatly accelerated the diamond deposition, allowing the decomposition of both the hydrogen and the hydrocarbon molecules. On the other hand, the substrate temperature was adjusted in the range from 600 to 1000 °C. Low temperatures decrease the number and size of the diamond particles formed, while, in contrast, deposition of blocky graphite particles result at high temperatures. The diamond deposition was made on silicon wafers, molybdenum plates, and silica glass plates; the different experiments independently gave products having similar morphologies and dimensions on the substrates. Significant rates (~1 μm h^{-1}) and particle dimensions up to 5 μm were obtained; the cubic or cubo-octahedral specimens showed Raman spectra very close to those reported for natural diamond (in some samples, a broad peak due to highly disordered graphite was also observed).

In 1983, the same Japanese group reported another method for achieving diamond growth, in a so-called "microwave plasma" reactor;[29,30] the synthesis conditions were quite similar to those previously reported, a microwave energy supplier being present now, instead of the hot filament. A maximum growth rate of about 3 μm h^{-1} was obtained, which significantly improves the chemical vapor deposition previously reported. Both the "HF-CVD" and the "MW-CVD" methods are shown schematically in Fig. 3.

The region of typical CVD synthesis is shown on the carbon phase diagram (Fig. 4). Note that these conditions lie well inside the region where graphite is the stable form of carbon.

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‡Hydrogen cleaning at 52 atm and 1040 °C for 7 h; treatment with aqua regia for 18 h and HF for 4 h at room temperature; treatment with aqua regia at 90 °C for 1 h; treatment with concentrated HNO_3 for 48 h at room temperature, and in fused alkali at 450 °C for 30 min.

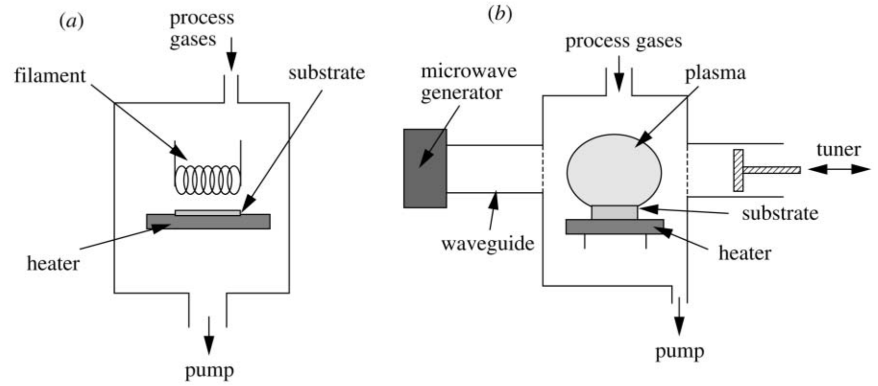

Fig. 3 Schematic representation of two types of low pressure CVD reactor: (a) hot filament, (b) 'NIRIM-type' microwave plasma reactor.

The ability to form diamond under ambient pressure is the fundamental advantage of CVD methods for low cost growth of diamond, compared with HPHT synthesis.

Following the above innovations, and starting from the mid 1980s, interest in diamond CVD research has grown in both industry and academia, and continues to the present day. A number of methods for diamond film growth have been developed, but the main difference between them is how the gas-phase carbon-containing precursor molecules are activated. The new methodologies comprise d.c. plasma,[32,33] radio frequency (RF) plasma,[34,35] d.c. plasma jet,[36,37] microwave plasma jet,[38] electron cyclotron resonance (ECR) microwave plasma,[39,40] and combustion (oxyacetylene or plasma torches) flame synthesis.[41–46] Microwave (MW) plasma and hot filament (HF) CVD growth rates are typically between 0.1 and 10 μm h^{-1}, while values in the range 50-1000 μm h^{-1} can be achieved by arc-jet and combustion flame synthesis. The other side of the question is the limitations of these methods in terms of coating areas: all techniques affect typically a few cm^2, with the exception of MW-CVD, which can coat samples in excess of 20 cm diameter. These figures are improving year by year (the 2.45 GHz microwave frequency, used by commercial microwave ovens, is the most commonly adopted in CVD reactors; but 915 MHz reactors are now becoming more attractive, as the lower frequency allows reactor size to be increased) and CVD diamond-based components are now being manufactured and sold commercially.

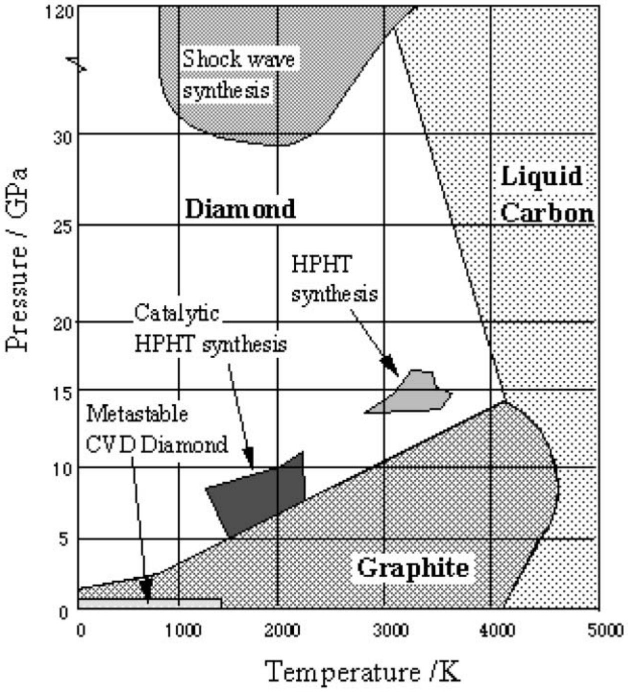

Fig. 4 The *P–T* phase and reaction diagram for elemental carbon. Reproduced by permission from ref. 31. Copyright 1980, American Geophysical Union.

"Hot filament" CVD

In order to discuss the parameters that characterize a chemical vapor deposition method, the "hot filament" process has been chosen as an example. This choice is due to the relative simplicity of the reactor (represented schematically in Fig. 5), but also from the fact that the first boron-doped diamond thin film electrodes have been synthesized with this method.

Briefly, the reactor consists of a vacuum chamber, continually pumped using a rotary pump, while process gases are fed in at carefully controlled rates (typically a total flow rate of a few hundreds of standard cubic centimeters per minute, sccm). A heater (designated 1 in the figure) is occasionally used to bring the substrate at the desired temperature (sometimes the substrate can be cooled and the heater is substituted for a cooling element); the substrate to be coated (2) sits on the heater a few millimeters beneath a filament (3), which is electrically heated to temperatures usually in excess of 2000 °C. A lot of problems and requirements must be considered to achieve a successful diamond synthesis, although synergistic effects may arise from a combination of the different factors, and each one will be examined in detail.

The filament. The HF-CVD method of synthesis is based, as its name implies, on thermal activation of the gas phase; such a role is essential in creating the gaseous species that enable and influence diamond growth. Considering the high temperature and reactive environments employed, the materials that can be used as filaments must conform to several

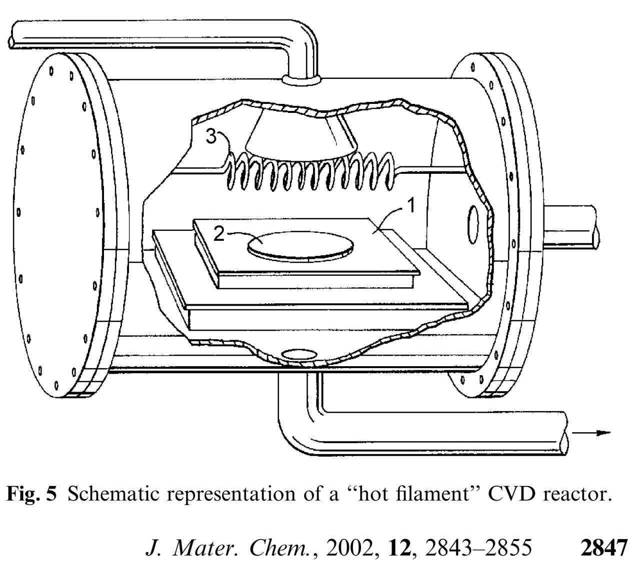

Fig. 5 Schematic representation of a "hot filament" CVD reactor.

requirements. A first, obvious, limitation concerns the melting point, which should be very high; among the elements, carbon melts at the highest temperature (3727 °C), but its reactivity and the difficulties in obtaining wires are important drawbacks. With a melting point (m.p.) of 3410 °C, tungsten is a valid alternative and, in fact, is commonly used as the filament material in this process, as well as in the production of bulbs and light sources in general; other suitable metals are rhenium (m.p. 3180 °C) and tantalum (m.p. 2996 °C). A considerable property of some of these metals is their reactivity with respect to carbon; the carburization of the filament is a consequence of gaseous species activation (*i.e.* it cannot be avoided) and significantly modifies the physical properties of the filament material. Accordingly, rhenium might be preferred because it does not suffer from distortion and embrittlement under the conditions of CVD synthesis, but tungsten is certainly preferable in terms of costs, while tantalum forms a carbide with a melting point of 3880 °C, thus allowing higher operating temperatures.

The role of the filament as a source of contamination of deposited films is possibly the main reason for the development of other CVD techniques; in fact, while some uses depend upon mechanical, thermal, or chemical properties and may tolerate a relatively high level of impurities, the requirements for electronic applications are more stringent, intentional doping levels being related to the semiconducting properties required. Furthermore, the presence of impurities has been proved to influence the quality of the films, as reported by Shaw and co-workers.[47] In their work, a number of diamond films were synthesized and neutron activation analysis was performed to define the metal content of films grown using different filament metals. Differences in the tendency to form twins and in the relative growth rates in the $<100>$ and $<111>$ directions were observed, although not obviously related to the change of filament material during the synthesis. The quantitative analysis gave the following order of contamination: $Re \gg Ta \geqslant W$; interestingly, the films with the highest metal contamination had the lowest fluorescence background, the smallest sp^2 contribution and the sharpest diamond Raman signal. While the incorporation of metal into the film could lead to defects of various sorts, a positive role seems to be the suppression of sp^2 carbon formation; such defects seem, therefore, to thermodynamically stabilize diamond, in the same way as some transition metals catalyze the HPHT diamond synthesis.

The role of the filament material cannot be easily understood if other parameters are taken into account; for example, the filament temperature can be decreased, without losses in the film quality, by addition of very small amounts ($\leqslant 0.1\%$) of oxygen or ammonia to the reactant gas mixture (as reported in ref. 47). In these cases, the good crystal quality was not due to metal incorporation in the film, but to a lower substrate temperature, thus giving evidence for the effective presence of synergistic effects. Moreover, low temperature growth with oxygen has demonstrated that the formation of volatile tungsten oxides, that might enhance metal transport to the growing film, was not a problem (instead, the lower operating temperature resulted in reduced metal incorporation). In this respect, no information about the possible reduction in service-life of the filament in the presence of oxygen in the gas phase is given in ref. 47; however, suppression of the filament evaporation rate might be expected when working in a buffer gas, as opposed to a vacuum. Concerning evaporation, it is interesting that tantalum carbide loses both Ta and C, with no resulting change in chemical composition of the filament, while tungsten carbide evaporates primarily by losing carbon, thus accounting for the lower film contamination.

In summary, film contamination is highly dependent on the temperature of the filament and the crystalline quality shows a correlation with the impurity level; the film morphology seems to be somewhat dependent on filament material. As far as the mechanical properties of the filament are concerned, rhenium does not carburize and is more durable than tungsten and tantalum; tungsten filaments carburize faster than those made of tantalum, and get deformed to a higher degree during carburization; both WC and TaC break easily, but TaC has a longer service life with respect to WC, at a given temperature.

Apart from its composition, the precise role of the filament remains a matter of some debate. At the hot filament surface, the thermal decomposition of H_2 leads to the heterogeneous production of atomic hydrogen, which rapidly diffuses into the bulk gas phase, allowing other reactions. It is not clear whether the filament acts merely as an energy supplier or as a catalyst for molecular hydrogen decomposition; it is known, however, that the addition of trace amounts of hydrocarbons causes a reduction in the H number density, measured close to the filament. A first analysis suggests, therefore, that the progressive carburization of the filament, or the eventual development of a graphitic layer on its surface, has a detrimental effect on the filament catalytic activity for H production. Without entering into the chemistry of CVD diamond growth (*i.e.* the problem of the gas-phase composition), the work of Redman *et al.*[48] supports the idea that the hot filament can provide an efficient means of heating the hydrogen molecules that adsorb onto its surface, thus promoting their dissociation. The presence of gaseous hydrocarbons further complicates the problem, as a consequence of induced modifications on the filament surface, the characteristic temperature dependence of each surface site being important in determining their own reactivity and stability. Approximately, the number density of hydrogen radicals, [H], might be exponentially related to the filament temperature, the activation energy for H_2 dissociation being estimated at 237 ± 22 kJ mol^{-1}; 0.5% CH_4 in the gas-phase mixture seems to be enough to increase the activation energy to 244 kJ mol^{-1}, thus confirming the observed changes in the filament catalytic activity.

The substrate. Whilst the filament could be considered a characteristic element of the HF-CVD method of synthesis, the nature of the substrate is an even more important factor, as it determines, directly or indirectly, the feasibility of the whole process.

Like the filament material, a first important requirement is obvious: the substrate must have a melting point (at the process pressure) higher than the temperature required for diamond growth (normally greater than 700 °C). This limitation is destined to disappear as a result of technological developments, but the possibility of coating low melting point materials (plastics, for example) will be achieved only by decreasing the deposition temperature. However, at least two other deciding factors must be taken into consideration: the thermal expansion coefficient and the chemical/metallurgical stability of the substrate material. The former is important in that it determines the adhesion between the coating and the substrate; in fact, at the high growth temperatures currently used (>700 °C), the substrate tends to expand under heating and to contract back to its room temperature size upon cooling. Since diamond has a very small expansion coefficient, *i.e.* its size is relatively unaffected by temperature changes, the coating and the substrate will experience different physical modifications, which may result in cracking or even delamination of the entire film. On the other hand, chemical/metallurgical stability is also required for diamond growth: the substrate should not 'react' with carbon or with the other gas-phase components. In the following, a more detailed analysis will be presented.

Considering the Periodic Table of the elements, four important 'groups' can be identified:

Li, B, N, O, P. These elements are (or might be) important because they act as dopants, thus conferring particular electronic properties on the diamond film.

Cu, Ag, Au, Zn, Cd, Hg, Ga, In, Tl, C(graphite), Ge, Sn, Pb. This category includes metals that do not react with carbon and in which the latter is only slightly or not at all soluble. On these elements, diamond is not expected to adhere well, since an interlayer of carbides cannot be formed at the interface between the two materials. In the case of graphite, substrate etching takes place concomitantly with diamond growth.

Fe, Ru, Os, Co, Rh, Ir, Ni, Pd, Pt. These materials act as a carbon sink, dissolving the deposited carbon and forming a solid solution. As a result, large amounts of carbon are incorporated into the bulk substrate, rather than remaining at the surface (where it can promote diamond nucleation), and important chemical and mechanical modifications of the substrate take place.

Ti, Zr, Hf, V, Nb, Ta, Cr, Mo, W. This last group of elements could be enlarged by also considering Y, Al, B, and Si; in general, they are the carbide-forming elements, *i.e.* they react with carbon, leading to the formation of a carbide layer during diamond synthesis. This 'interlayer' conveys two benefits: better adhesion of diamond to the substrate, and enhancement of the diamond nucleation rate. On the other hand, the carbide layer can severely modify the substrate mechanical properties.

The above information has been collected from ref. 49 and 50; obviously, some problems and/or limitations must be related to the methods of synthesis, which include different process temperatures, growth rates, and gas-phase compositions.

In a meeting communication, Haenni and Fryda[49] presented a detailed analysis of substrate properties in connection with their use in electrochemistry. In fact, while some materials can be suitable for diamond deposition, a more limited number of substrates possess the necessary electronic properties to be useful as electric conductors. Moreover, considering that the grown diamond film may present some imperfections and/or not all the substrate surface is coated, the number of suitable substrates becomes smaller, and is further reduced if common metallurgical requirements (*e.g.* a material that can be welded) are taken into consideration.

The thermal expansion coefficients (α_V) of some suitable substrates, including some carbides and nitrides, are reported in Table 1, while data concerning a few ceramic materials are presented in Table 2; for the sake of comparison, data referring to the boron-doped diamond (BDD), synthesized at the Centre Suisse d'Electronique et de Microtechnique, Neuchâtel, Switzerland, are also included in Table 2.

Table 1 Thermal and electronic properties of some 'metallic' substrates

Material	$\alpha_V{}^a/10^6\ \mathrm{K}^{-1}$	ρ^b/mΩ cm
Titanium	8.82	0.042
Zirconium	9.92	0.041
Niobium	8.37	0.014
Tantalum	6.3	0.014
Molybdenum	5.75	0.006
Titanium carbide	8.8	0.1
Titanium nitride	9.35	0.13
Zirconium carbide	6.5	0.06–0.1
Zirconium nitride	7.03	0.015
Niobium carbide	7.29	0.15
Tantalum carbide	6.64	0.05–0.1
Molybdenum carbide	4.4–5.67	Supra < 10 K

[a]Thermal expansion coefficient (293–1200 K). [b]Electrical resistivity.

Table 2 Thermal and electronic properties of some 'ceramic' substrates

Material	$\alpha_V{}^a/10^6\ \mathrm{K}^{-1}$	ρ^b/mΩ cm
Graphite	2.6–5.0	0.007–0.04
Glassy carbon	3.2–3.5	0.1–0.2
C-fiber/graphite	0.8–6.9	0.02–0.025
C-fiber/graphite/SiC	0.8–6.9	
p-Silicon carbide	4.6–5.12	100
p-Silicon	3.7	1–3
Molybdenum silicide	8.41	0.02
Titanium silicide		0.02
p-Diamond (BDD)	0.8–4.8	5–50

[a]Thermal expansion coefficient (293–1200 K). [b]Electrical resistivity.

Other important parameters are the substrate stability, from a metallurgical point of view, and the costs. The former factor concerns phase transformations that could take place at high temperatures: for example, α-titanium transforms into the β-form at 920 °C, while zirconium suffers from the same modification at 863 °C; these phenomena further complicate the desired match between growing film and substrate. Related to the metallurgical properties of the substrate is the availability of different geometries: metallic substrates are available in a variety of forms (plates, disks, grids, rods, cylinders, *etc.*), while ceramic substrates can only be arranged in plates, disks, large rings, or fibers. This important limitation comes together with substantial costs, as reported in Table 3.

Considering the cost of the more suitable substrate materials and the fact that most of them are devoid of the required metallurgical properties, it is justified that a great amount of work has recently been devoted to overcoming the problems related to diamond thin film synthesis on common metals. Most interest has been focused on deposition on titanium,[51–54] but other investigated materials include iron,[55] copper,[54,56,57] cobalt,[58–60] chromium,[54] aluminum,[61] zinc[61] and carbon composites,[62] as well as metals or materials mentioned above, like tungsten,[63] tungsten carbide,[63,64] molybdenum[63,65–67] and glass.[61] Evidently, the above list is intended to provide only a few examples and it is by no means complete.

Judging by the literature of the last six or seven years, a lot of work has been devoted to the rationalization of the diamond growth mechanism, and the role of the substrate has been often revisited through the effect of pre-treatments and modifications of the gas-phase mixture. Diamond nucleation itself seems to be dependent on the nature of the substrate, as well as on other parameters (*i.e.* the degree of polishing and the temperature of the substrate). Thus, it seems apposite to discuss the subject in more depth.

Nucleation. The growth of diamond begins when individual carbon atoms nucleate onto the substrate surface in a manner that allows the initiation and further construction of a tetrahedrally coordinated sp^3 network of bonds. The pioneering works of Eversole,[23] Derjaguin *et al.*[24] and Angus *et al.*[25] were all focused on diamond growth on diamond specimens. Notwithstanding the problems encountered by these researchers, it seems now that their choice was quite obvious; as stated by Haenni[49] in a workshop on the subject, "*Diamond is diamond's best friend.*", as there is really no other ideal substrate.

The problem of *how* diamond nucleates on non-diamond substrates is still a matter of discussion. The commonly accepted theory is that described, for example, by Lee *et al.*;[68] namely, a step on the substrate serves as a nucleation site for heteroepitaxial diamond growth. Although experimentally

Table 3 Costs of some 'ceramic' and 'metallic' substrates

Material	Thickness/ mm	Density/ kg dm^{-3}	Cost per kg/€	Cost per m^2/€
p-Silicon carbide	3	3.21		21 500–40 000
p-Silicon	1	2.33		2100–4300
Titanium	1	4.5	130	1000
Zirconium	1	6.44	150	1050
Niobium	1	8.4	290	2500
Tantalum	1	16.6	500	8300
Molybdenum	1	10.06	130–240	1350–2400

proved only recently, the idea that "defects" on the substrate surface could enhance the nucleation density has been pursued from the beginning, as reported in the paper by Yarbrough and Messier.[69] The simplest pretreatment involves the abrasion of the substrate surface by mechanical polishing with a diamond powder; an analogous effect has been obtained by ultrasonication of the surface in diamond powder suspensions. Both methods are believed to either (i) create appropriately shaped scratches on the substrate surface, acting as high energy sites that are preferred for nucleation or, alternatively, (ii) diamond particles, or other types of carbonaceous fragments, remain adherent to, or embedded in, the polished surface, again supplying suitable nucleation sites for diamond growth. Another approach requires the substrate to be negatively biased (a few hundred volts), allowing the ions to damage the surface, implant into the substrate lattice, or to react with the substrate, forming a carbide interlayer with appropriate sites for diamond growth. Bias enhancement nucleation (BEN) can be also applied as a pretreatment: Wang *et al.*[66] have shown that the nucleation density depends on the electron emission current (from the substrate) that occurs when the bias voltage is applied. It is interesting to observe that such experimental conditions determine the production of electrons from the substrate, allowing phenomena that are characteristic of plasma-assisted chemical vapor depositions. The magnitude of the bias seems to be directly correlated with the amount of hydrocarbons in the gas-phase mixture: at a fixed bias voltage, the nucleation density is increased by an increase in methane concentration;[67] on the other hand, at a fixed gas-phase composition, a negative bias can efficiently reduce the diamond grain size, ensuring the growth of nanocrystalline diamond films.[70] However, when an excessively high bias voltage is applied to the substrate, no films can be deposited, possibly because the ion flow, accelerated toward the diamond growing facets, possesses enough energy to destroy the diamond seeds.

As regards diamond growth on different substrates, it has been said that group VIII metals are not suitable materials, as they dissolve carbon. It is assumed, however, that once the metal is saturated with carbon, diamond nucleation can start. The carbon surface saturation takes place by C-diffusion into the substrate: such a process requires a certain amount of time, leading to a delay in the onset of diamond nucleation. The mechanism of diamond nucleation on platinum and palladium seems to be particularly interesting: Kalss and co-workers have shown that diamond crystals start growing not only on the surface, but also in the bulk material;[71,72] as a consequence, these crystals are subjected to high hydrostatic stress, as could be demonstrated by Raman spectroscopic investigations.[71]

As a curiosity, diamond film has also been reported to grow on silicon substrates modified by photochemical grafting of an adamantane derivative, capable of being covalently attached twofold to the silicon surface. The paper, by Giraud *et al.*,[73] describes how to synthesize the "chemical nucleation precursor" and reports that the nucleation density can be increased by over 5 orders of magnitude.

The composition of the gas phase. From the above considerations, it follows that this is another important factor, which plays a deciding role in the synthetic process. The early experiments on CVD diamond synthesis were performed with a gas phase supersaturated with carbon, through the thermal decomposition of methane gas. In those cases, hydrogen was used for graphite removal, after a defined deposition time (clearly, this process was discontinuous, the desired mass increase being obtained with different deposition–cleaning cycles).

The discovery that atomic hydrogen would preferentially etch the graphite *during* the deposition process undoubtedly represents a significant breakthrough in the story of CVD.[25–28] Subsequent works have shown that other gaseous species may play the same role as hydrogen, sometimes also enhancing the diamond film growth rate, as is the case, for instance, for chlorine, which can be added in the form of Cl_2 or HCl. In reality, the main reason for the introduction of chlorine-containing source gases is just the growth rate improvement (in comparison to standard C–H mixtures), as it allows the substrate temperature to be lowered. The role of chlorine atoms in the CVD process seems to be the abstraction of surface terminating hydrogen, rather than a gas-phase mechanism; in fact, kinetic calculations have shown that the rate of hydrogen abstraction by Cl atoms from a (110) diamond surface at 670 °C is some 60 times faster than abstraction by gas-phase H atoms. The other side of the coin is the degradation of the filament at high chlorine concentrations ($>3\%$ Cl_2 in the process gas mixture, as reported in ref. 74), moreover, addition of too much Cl is deleterious to diamond growth because atomic chlorine cannot adsorb on C=C to convert sp^2 carbon back to sp^3.

The role of chlorine could, alternatively, be carried out by oxygen if etching of graphitic deposits is required (it is believed that OH radicals play a role similar to that of atomic hydrogen); conversely, the diamond growth rate linearly decreases with increasing oxygen content, as a possible consequence of its reaction with carbon to form unreactive carbon monoxide. Comparing the C–H and the C–H–O system diagrams for diamond growth,[75] diamond can be deposited from an oxygen-containing gas phase, provided suitable experimental conditions are chosen (*i.e.* a higher amount of carbon in the source mixtures). In these cases, higher growth rates and better quality films are generally claimed.

Apart from the above considerations (lowering the substrate temperature), the process gaseous mixture is subject to modifications when semiconducting diamond films are required. For this reason, n- or p-doping is induced, by supplying appropriate chemical species. In both cases, Nature suggests a suitable doping substance: boron can be inserted into the diamond lattice to realize p-doping, while nitrogen leads to an n-doped semiconductor. The former is a very reproducible process, and its occurrence has been known from the first HPHT syntheses;[14] n-doping, in contrast, is still difficult to obtain. In fact, the addition of various nitrogen-containing gases, such as ammonia, methylamine, and HCN, invariably leads to the thermodynamically preferred formation of HCN, whose stability and volatility inhibit the formation of solid films containing carbon and nitrogen.[76] Moreover, lower quality diamond films are obtained with increasing amounts of nitrogen-containing gaseous species; the experimental picture reported by Atakan *et al.*[65] suggests that the qualitative influence on diamond growth is almost independent of the chemical nature of the N-containing species (N_2, N_2O, $N(CH_3)_3$, and NH_3). At low additive concentrations, the growth rate is enhanced while the film quality remains high. It has been also reported that small amounts of nitrogen are able to stabilize the $<100>$ texture of the growing film.[77] The remarkable difference between the reactivity of C- and N-containing species at the growing diamond surface has been further emphasized by Eccles *et al.*[78] who reported on the doping efficiencies of both boron and nitrogen. While a doping efficiency close to unity was found for the former, an upper estimate of as low as 10^{-3} was made for the latter. This result might seem to be somewhat surprising: nitrogen is reported to be readily incorporated into the diamond lattice, forming a deep donor level. The problem is that the donor level is so deep, with an ionization level of 1.7 eV, that N-doped films are insulating at room temperature. n-Type behavior can also be obtained by insertion of sulfur and, theoretically, oxygen; however, stable CO and CS molecules are formed, and S-doped films can only be justified by the equilibrium $^{\bullet}SH$ concentration that adsorbs onto the diamond surface and undergoes subsequent incorporation reactions.[79] Recently, successful n-doping has been achieved by using PH_3 as a gas additive; for instance, Tsang *et al.*[80] report the HFCVD of P-doped diamond films from a 1% CH_4 in H_2 gas mixture, with increasing amounts of PH_3 (from 1000 to 5000 ppm). Similarly to the case of ammonia and other N-containing gaseous precursors, where stable HCN is formed, complete phosphine decomposition is achieved at filament temperatures higher than 1700 °C, leading to HCP production. However, it seems that HCP is not stable above −124 °C and mass spectrometric investigations, like that presented in ref. 80, have been carried out indirectly, assuming HCP to be the only C-containing species responsible for any 'missing' component of the total C balance. Due to the weakness of the P–H bond (321 kJ mol^{-1}), almost all the PH_3 dissociates at a temperature at which the filament-catalyzed decomposition of H_2 is still rather inefficient; as a result, the production of methyl radicals can also be driven by these low temperature-produced H atoms, leading to a greater $^{\bullet}CH_3$ concentration and, thus, to an increase in the growth rate for the diamond film. Considering the low amounts of phosphine in the gas mixture, the above explanation cannot absolutely justify the effect of PH_3 addition on the improvement of diamond growth rate; therefore, it has been suggested that a small amount of phosphorous is deposited onto the filament, possibly catalyzing the hydrogen dissociation. At excessive PH_3 concentrations, in contrast, the adsorption of P on the filament may be the reason for the progressive inefficiency of the process; in addition, a couple of reactions may be responsible for lowering the $^{\bullet}CH_3$ and $^{\bullet}H$ concentrations:

$$CH_3 + P \rightarrow HCP + H_2 \qquad HCP \overset{2H}{\rightarrow} CH_3 + P$$

As reported in the case of n-doping with nitrogen, the presence of phosphorous in the diamond lattice leads to the formation of a donor level at about 0.46 eV below the conduction band minimum; according to Koizumi and co-workers,[81,82] a resistivity value around 10^4 Ω cm should be typical for a diamond film with a nominal P-concentration of 1000 ppm ($\sim 10^{19}$ P atoms cm^{-3}, as determined by SIMS).

In order to provide a comprehensive discussion concerning the doping of diamond films, a mention must be made of ion implantation; a short review can be found in a paper by Kalish,[83] who reports on both p- and n-doping, obtained by boron and phosphorous implantation, respectively. Interestingly, improvements in the electrical properties in the case of p-doped specimens have been reported as a result of the high thermal treatment commonly performed after the implantation (~1450 °C); in the case of n-doped samples, in contrast, the annealing was found to wash out the small amount of phosphorous-related conductivity. In another paper, Kalish *et al.*[84] suggest heating the sample prior to the ion implantation and performing the treatment at a temperature around 1100 °C, in order to avoid the graphitization of the damaged diamond surface. With this expedient, a dose implantation of about 3×10^{17} ions cm^{-2} was acheived, using 150 keV B, Li, and P ions; resistivity values below 0.01 Ω cm are reported for the boron-doped specimens, while temperature-dependent values in the ranges 1–50 and 100–10 000 Ω cm are found for lithium- and phosphorous-doped samples, respectively. Although the method allows very high conductivities to be obtained (at least in the case of p-doping), ion implantation is usually limited to depths of only a few hundreds nanometers; also notable is the possibility to achieve n-doping by lithium implantation, an option that seems to be unavailable in the case of CVD synthesis.

As previously mentioned, p-doping is a well-defined and reproducible process. In addition, and similarly to nitrogen, boron also has a role in determining the texture of the growing film; in this context, the work of Koidl *et al.*[85] provides fine examples of both structural and electrical properties induced by boron incorporation. Concerning the former effect, the presence of boron has been reported to destabilize the <100> texture[85] (in contrast to nitrogen); a decrease in growth rate was also observed, justified by an increase in the rate of surface rearrangement, to an atomically smooth surface, induced by boron itself.[26]

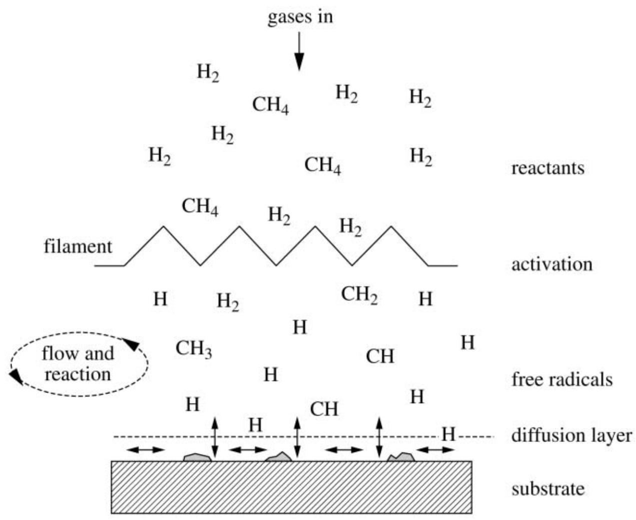

Fig. 6 Physical/chemical processes occurring during diamond CVD. Reproduced by permission from ref. 50.

Mechanism of diamond growth. Although this is possibly one of the primary aspects to be considered, it has been intentionally postponed so far. In fact, many papers have appeared in the literature concerning the gas-phase composition in the different typologies of CVD (which differ in *how* the gas is activated), as determined by spectrometric investigations, but no definite conclusions have been reached in relation to the reaction pathways that allow diamond growth. A frequently described mechanism is that presented, for example, in the previously mentioned paper by Ashfold *et al.*[50] According to that review, the precursor gases (usually methane and hydrogen) are dissociated by either electron impact (plasma methods) or thermal energy from a hot filament. Atoms and reactive species diffuse towards the substrate surface, where they absorb and coalesce to form a carbon film (Fig. 6). When the conditions of deposition are favorable, the film grows as diamond.

For example, with a CH_4–H_2 mixture, activation of the gas results in formation of hydrogen atoms, which are assumed to be responsible for H-atom abstraction from the methane molecules, and consequent formation of methyl radicals. A considerable number of papers have focused on the determination of the gas-phase composition in terms of radicals and molecules which form as a consequence of their instability. From the different spectroscopic methods, it now seems to be accepted that methyl radicals are the main species responsible for diamond growth. After being formed, they move toward the substrate surface, where they adsorb and/or coalesce, leading to film formation. As previously stated, the way the film is synthesized is another problem, with no evidence of a conclusive explanation; in one suggested mechanism, atomic hydrogen abstracts a hydrogen atom from the surface of diamond, leaving a surface radical (it should be noted that a diamond particle must be present on the substrate surface in order to allow this growing mechanism). A methyl group then adds to the 'dangling bond' and the scheme can be repeated, leading to the progressive building up of the lattice, as shown in Fig. 7.

Somewhat in agreement with this mechanism are the

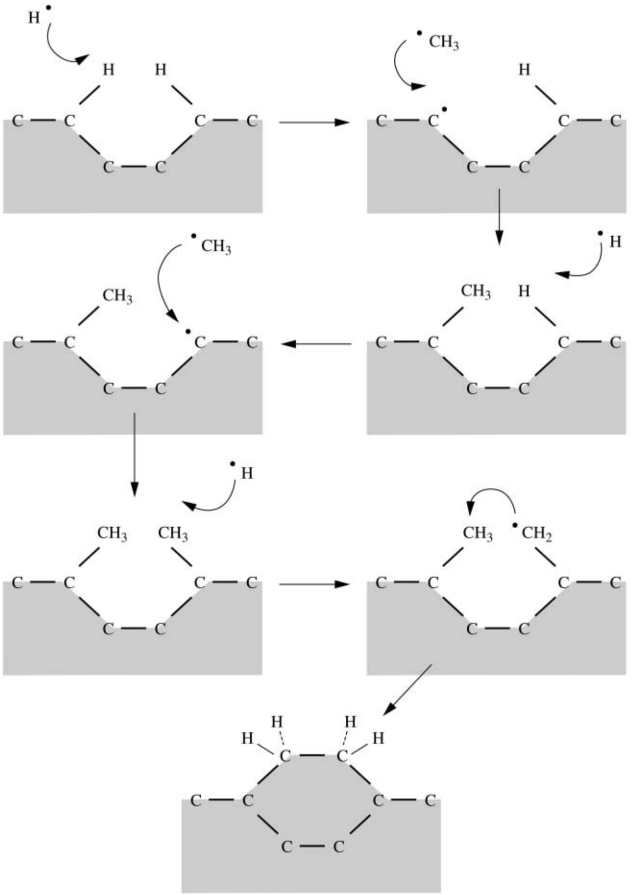

Fig. 7 Growth of diamond at a {110} trough site. Reproduced with permission from ref. 50.

molecular dynamics simulations carried out by Frauenheim and co-workers, reviewed and discussed by Busmann and Hertel:[86] referring to Fig. 7, the configuration of the fifth step would lead to interatomic H–H distances shorter than in a hydrogen molecule, yielding a high driving force for reconstruction in the presence of atomic hydrogen. The same conclusions are presented in a very recent paper by Heerwagen *et al.*,[87] who used vibrational spectroscopy to study diamond growth *in situ*; these authors have argued that the dominating species on the surface must be a tertiary carbon atom with just a single C–H bond. Moreover, they have reported that no sign of CH_3 species at the surface could be identified; recalling that the methyl radical has been considered an essential species in diamond growth, other species (such as acetylene) would be responsible. Alternatively, one could assume that methyl radicals react so quickly that their concentration is below the detection threshold: this is the opinion of the authors of ref. 87, based on the absence of any significant signal attributable to acetylene.

On the other hand, many authors have reported a relative independence of diamond growth on the nature of the hydrocarbon feed: this would imply that similar concentrations of the growth precursor(s) are present, above the growth surface, when the gas is properly activated. McMaster *et al.* studied the influence of growing diamond films with CH_4–H_2 or C_2H_2–H_2 mixtures,[88] comparing microwave plasma-assisted CVD with the HF-CVD method; in both cases, a mass spectrometric investigation led to an analogous, quantitative determination of CH_4, C_2H_2, C_2H_4, CH_3 and H. Interestingly, changes in surface temperature seem to affect the growth properties primarily by affecting the kinetics of surface processes, rather than through changes in the gas composition near the growth surface.

Zhu *et al.* were among the first to report that preferred orientation of the final film could be induced by variation in the methane concentration in the CH_4–H_2 mixture:[89] a 0.5% CH_4 concentration was reported to lead to a <100> orientation, while the <111> orientation requires the amount of CH_4 to be reduced to 0.3%. The oriented diamond films were grown on nickel substrates. Conflicting results have been reported by Busmann and Hertel:[86] they synthesized diamond films on Sb-doped (100) silicon single crystals, studying the influence of both methane concentration and substrate temperature. In general, the preferred orientation was found to move from <100> to <111> with decreasing substrate temperature and increasing methane concentration; by keeping the latter parameter constant and varying the former between 715 and 1000 °C, a complete range of growth forms was obtained, from the octahedral shape ({111} faces) to the cubic one ({100} faces). A dependence of preferred orientation on film thickness has been reported by Koidl *et al*:[90] starting from a random distribution of crystal orientations, the different vertical growth rate can be taken as the discriminating parameter, crystals with a rapid growth direction perpendicular to the substrate being the preferred candidates. As reported in ref. 90, a 2D computer simulation has been performed, showing that 11-oriented crystals (nuclei with a corner protruding in the growth direction) progressively bury the 10-oriented ones (*i.e.* crystals with faces parallel to the substrate surface). This model approach was also verified by investigating the crystal texture at different film thicknesses by X-ray diffraction.[90]

The habit of individual crystals is determined by the ratio between the growth rates of the {100} and {111} faces, usually denoted v_{100} and v_{111}, respectively; a growth parameter, α, has been defined as follows:

$$\alpha = \sqrt{3} v_{100}/v_{111}$$

With reference to Fig. 8(a), $\alpha = 1$ corresponds to cubic, $\alpha = 1.5$ to cubo-octahedral, and $\alpha = 3$ to octahedral diamond crystals; in Fig. 8(b), views of a {100} facet for $1 \leqslant \alpha \leqslant 1.5$ and of a {111} facet for $1.5 \leqslant \alpha \leqslant 3$ are shown, illustrating how it is possible to determine the habit of a crystal, by means of, *e.g.*, a scanning electron microscope (SEM).

Returning back to the topic of the diamond growth mechanism, a completely different approach has been suggested by Jeon *et al*:[91] the growth unit of synthetic diamond could be not an atom, but a much larger unit, that is to say, clusters containing hundreds to thousands of atoms. This idea was first proposed in 1990, but it was not taken under serious consideration in the diamond community. Recently, Jeon *et al.* have experimentally confirmed the existence of these hypothetical clusters in a hot filament reactor with a gas mixture of 1.5% CH_4–98.5% H_2. The cluster dimensions seem to depend on the methane content of the gas mixture: clusters of ~3000 amu were dominant for low CH_4 concentration (1% and 1.5% CH_4), while an appreciable number of large clusters, approximately 18 000 amu, existed at higher methane concentration (3% and 5% CH_4); assuming that the negatively charged clusters consisted of pure carbon, units of ~250 and ~1500 carbon atoms, respectively, can be assumed. It was also reported that diamond films deposited with 1% and 1.5% CH_4 showed good crystalline quality, while those at 3% and 5% CH_4 showed a ball-like or cauliflower-shaped structure (examples are shown in Fig. 9); in connection with the cluster dimensions previously reported, small diamond clusters would tend to land epitaxially on a growing diamond surface, leading to diamond crystals with well-defined facets, while large clusters would tend to land non-epitaxially, leading to the cauliflower shapes.

Apart from the experimental evidence for the existence of clusters, the motivation for this new mechanism originates from the consideration that there is something wrong in the previous suggestion (growing the film by addition of 'one atom

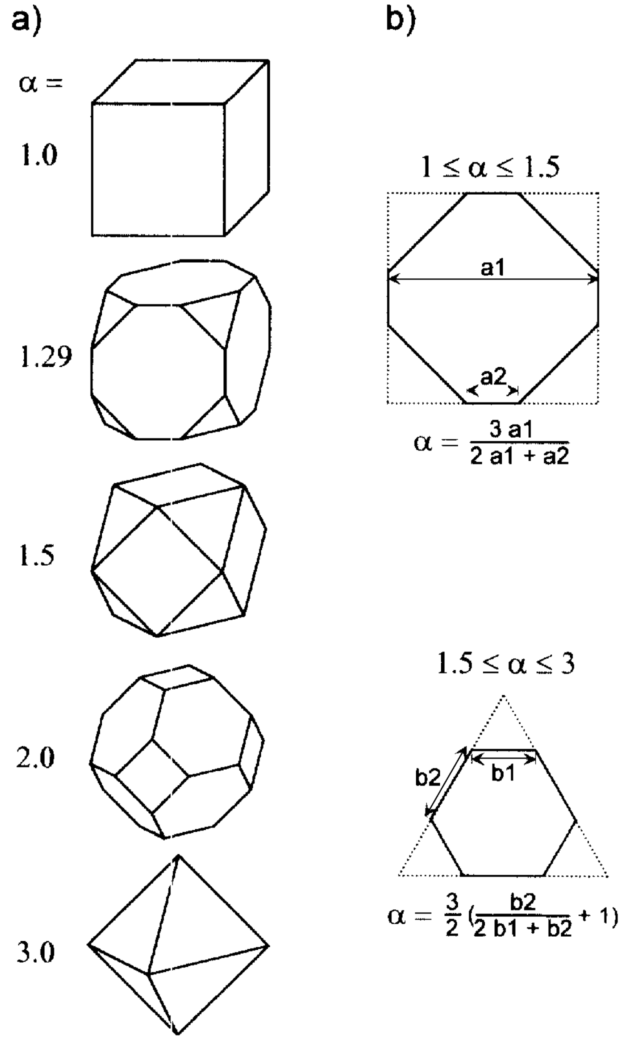

Fig. 8 (a) Growth forms of diamond crystals for different growth parameters; (b) {100} and {111} facets, which can be used to determine α. Reproduced by permission from ref. 86. Copyright 1998, Elsevier Science.

at the time'); in fact, the CVD process has been based on the deposition of the less stable diamond phase and simultaneous etching of the more stable graphite. This mechanism has been justified by assuming that hydrogen etches graphite much faster than diamond, even if this hypothesis contradicts the second law of thermodynamics. In the opinion of Jeon *et al.*, deposition and etching are opposite irreversible processes, which cannot take place simultaneously, as the driving force should be for one process or for the other, not for both. Therefore, if the CVD process is driven by the irreversible etching of graphite, the less stable diamond should be etched too. A depiction free of any paradox seems to arise assuming that diamond nucleates in the gas phase.[91] According to the cluster model, low pressure diamond synthesis would be possible in consideration of the fact that clusters are charged: this would inhibit the Brownian coagulation between them, allowing to maintain a nanometer size that, in turn, provides a high capillary pressure inside every cluster and contributes to the stabilization of diamond over graphite. Therefore, an electric charge seems to be essential, instead of hydrogen, for the low-pressure synthesis of diamond, although the etching effect of hydrogen can be beneficial in decreasing the cluster size. This hypothesis is supported by recent reports that diamond has been synthesized in a vacuum,[92] as well as in hydrogen-free environments.[93] Particularly pertinent seems to be the paper by Palnichenko *et al.*,[92] who reported that diamond particles formed in the high concentration carbon vapor phase and not on the substrate surface, as in the common CVD processes. Observing the self-assembly of aggregates, they cannot rule out the possibility that diamond particles (~10 μm in size) would be electrostatically charged.

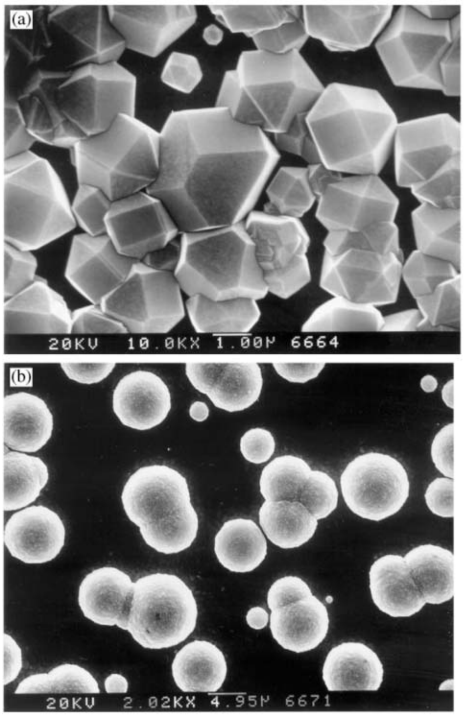

Fig. 9 SEM photographs of diamond films deposited with (a) 1% CH_4–99% H_2 and (b) 3% CH_4–97% H_2. Reproduced with permission from ref. 91. Copyright 2001, Elsevier Science.

Concluding remarks

For some, the word diamond conjures up images of brilliant gem stones, wealth, and special occasions. To the scientist, diamond is impressive because of its wide range of extreme properties. By most measures, diamond is 'the biggest and best'; it is the hardest known material, has the lowest coefficient of thermal expansion, is chemically inert and wear resistant, offers low friction, has high thermal conductivity, and is electrically insulating and optically transparent from the ultraviolet to the far infrared.

Given these many notable properties, it should come as no surprise to learn that diamond already finds many different applications including, of course, its use as a precious gem, but also as a heat sink, as an abrasive, and as inserts and/or wear-resistant coatings for cutting tools. Obviously, it is possible to envisage many other potential applications for diamond as an engineering material, but progress in implementing many such ideas has been hampered by the comparative scarcity of natural diamond. Hence the long running quest for ways to synthesize diamond in the laboratory. So-called 'industrial diamonds' have been synthesized commercially for over 30 years using high-pressure high-temperature (HPHT) techniques, in which diamonds are crystallized from metal-solvated carbon at pressures from 50 to 100 kbar and temperatures from 1800 to 2300 K.

World interest in diamond has been further increased by the much more recent discovery that it is possible to produce polycrystalline diamond films, or coatings, by a wide variety of chemical vapor deposition techniques using as process gases nothing more exotic than a hydrocarbon gas (typically methane) in an excess of hydrogen. This CVD diamond can show mechanical, tribological, and even electronic properties comparable to those of natural diamond.

Pure diamond coatings have already found important applications in the production of wear-resistant surfaces, *e.g.* for cutting tools (among the different patents on this subject, that of Grab *et al.*[94] is a good example, also referencing prior work). On the other hand, diamond layers have also been suggested as a non-irritating antimicrobial coating for medical implants.[95] Recently, Woerner *et al.* prepared CVD-diamond lenses, depositing a diamond film on a structured substrate, which was subsequently removed.[96] A variety of optical applications have thus become accessible, including lasers and tips to be used under highly abrasive conditions.

In addition, diamond films with different levels of doping have also become an interesting research subject. Low level doping has led to applications for flat field emission panels and sensor technology.[97–99] Heavily p- and n-doped diamond films are also quite actively studied for their potential industrial applications as well as in fundamental electrochemistry [both for physico-chemical studies (see ref. 100–105 and references therein) and in the field of electroanalysis[106]], because of their very high stability towards chemical and electrochemical oxidative attacks. In this context, highly boron-doped diamond thin film electrodes have been successfully applied as inert supports for the study of pure noble metal oxides,[102–104] and also for the electrosynthesis of powerful oxidants.[105,107,108] In all these potential applicative developments, the fundamentals and technology of diamond (film) production are clearly of primary importance and further research is certainly of great interest.

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