

Manufacture of gem quality diamonds: a review

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Abstract

Gem quality diamonds have been grown using high temperature, high pressure processes like the solvent catalyst method and the temperature gradient method. This review with 64 references focuses on the thermodynamics, kinetics of the growth processes and the apparatus used to grow diamonds. Gem quality diamonds can be synthesized by the high pressure, high temperature process, either by the solvent catalyst method or the reconstitution technique. The Hall belt apparatus and the toroid anvil are the commonly used equipment to generate high pressures. In the high pressure, high temperature processes a catalyst is essential for synthesis. The commonly used catalysts are Fe, Co and Ni whereas recently hydroxides and carbonates have also been used to synthesize diamond. Surface chemistry plays an important role in determining the quality of the crystal. If the carbon flux to the nucleating diamond exceeds a certain limit, graphite nucleates instead of diamond. Temperature, pressure and impurities like nitrogen and boron also affect the quality and growth rates of the synthesized diamond. High growth rates have also been observed if substantial amount of paramagnetic nitrogen is dispersed in the reaction bath. Recent developments of growing diamond by chemical vapour deposition techniques like microwave plasma and hot filament technique have been reviewed. Non-destructive, optical methods to characterize diamonds have been briefly described. © 1999 Elsevier Science Ltd and Techna S.r.l. All rights reserved.

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1. Introduction

1.1. Synthetic diamonds: industrial versus gem quality

Today, 90% of the industrial diamonds produced in this world are synthetic in nature [1]. Diamonds find extensive use in industry as an abrasive, in surgery, in astronomy and in experimental physics and electronics. The consumption of diamonds in 1988 was 50 million carats of natural diamonds (1 carat=0.2 gm) and 80 million carats of synthetic grit. In 1988 the average per carat value of natural grit and stones was \$0.82 and \$9.31, respectively. Synthetic grit is priced at \$1 to \$5 per carat making it competitive to natural diamond. Most of the demand is for diamonds of 0.7 mm particle size. A few large size crystals (3–6 mm) are sold by the Sumitomo Electric Company for a few hundred dollars per carat but it forms only a small part of the market [2]. Synthetic diamonds are not to be confused with

artificial diamonds as synthetic diamonds for all purposes are the same as naturally occurring diamonds except that they are man made whereas artificial diamonds like Cubic Zirconia are imitations. Synthetic diamonds can be tailor made to suit the purpose for which they are required. In terms of dollar value the bulk of the trade is in gem quality diamonds. However due to the prohibitive costs involved hardly any gem quality crystals are manufactured except for experimental work. In the last few years a lot of techniques have been developed especially in the vapour deposition methods which have sparked a renewed interest in this field and within the next few years it may be possible to grow diamonds for ornamental purposes.

Chemical engineers, ceramics engineers and material technologists play an important role in the manufacture of synthetic diamond, especially in designing of high pressure and high temperature devices and also the process controls as it is essential to maintain exactly the same conditions over long periods of time to ensure proper growth. With the breakthroughs in metastable growth of diamonds it remains to be seen whether the equipment can be designed to reproduce on a large scale what has been done in a laboratory.

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1.2. Outline of this paper

The thermodynamics behind the conversion of graphite to diamond at high temperature and pressure is discussed next. The solvent catalyst method of growing diamonds and the various high pressure equipment used are then described. The growth processes behind producing large gem quality diamonds by the reconstitution process are looked into. Recent developments to grow metastable diamond are also looked into. In the end a brief description of the various optical methods to characterize diamond is given.

2. Modern diamond making: synthesis and thermodynamics

2.1. Introduction

In 1772, the French chemist Lavoisier discovered that diamond is made up of carbon. After that a number of attempts were made to duplicate nature's work in the laboratory, albeit unsuccessfully. Claims by pioneer workers like Hannay [3], Moissan [4], to produce diamonds turned out to be incorrect [5]. Early attempts to make diamond failed because there was little scientific knowledge and most of the work was guesswork. By the mid-twentieth century this problem was solved as the equilibrium line between diamond and graphite was established, partly by experimental work and partly by extrapolation, by Simon and Berman [6].

2.2. Modern synthesis: a historical overview

The first synthetic diamond was produced on 8 December 1954 in the General Electrical Research Laboratory, New York State, USA [7]. Since then the production of artificial diamonds has surpassed the mining of natural diamonds. The techniques to produce synthetic diamonds broadly fall into the following categories:

1. High pressure high temperature techniques

- (a) Catalyzed synthesis: In this process a mixture of carbon and catalyst metal is heated high enough for the carbon to dissolve in the molten catalyst. Pressure is applied so that the system is in a region where diamond is thermodynamically stable and diamond is formed [7].
- (b) Shock synthesis: When graphite is strongly compressed and heated by the shock produced by an explosive, diamond is formed, e.g. meteoric diamond [8].
- (c) Static pressure synthesis: Diamond can directly be formed from graphite at pressures

of about 13 Gpa and temperatures of about 3300–4000 K. Poly crystalline lumps of diamond are formed in this manner [9].

2. Metastable diamond growth.

At low pressures diamond has been grown by depositing carbon from a vapour state, onto a diamond seed crystal under conditions where diamond is thermodynamically unstable with respect to graphite. The rate of spontaneous transformation does not become significant until 1300°C. The mobility of carbon atoms on a clean diamond surface at 1000°C is high enough for them to attach themselves to the existing lattice. A competing process is the spontaneous nucleation of graphite crystals [10]. This method finds extensive use in the formation of thin films of diamond.

2.3. The stability curve

At room temperature and atmospheric pressure, graphite is the more stable form of carbon. If the pressure was to be increased, a stage would come when diamond would be the stable form. The contribution to the Gibb's free energy from the energy equivalent of pressure is reduced if the volume of carbon decreases. Diamond being denser, occupies a smaller volume than graphite and at a larger pressure the larger chemical bond energy is balanced by the smaller pressure energy. This suggests that just by compressing graphite at room temperature to a pressure over 15,000 atm, diamond would be formed. However, there is not enough thermal energy available at room temperature for the carbon atoms in graphite to break their bonds [1].

Simon and Berman [6] presented the values of changes in enthalpy (ΔH), entropy (ΔS) and Gibb's free energy (ΔG) for the transformation of graphite to diamond at zero pressure and temperatures from 0 to 1200 K. The change in volume between diamond and graphite ΔV was deduced from consideration of compressibility and thermal expansion coefficients. ΔV was assumed not to vary considerably with pressure P and temperature T so the equilibrium pressure was given by

$$P\Delta V = \Delta G \quad (1)$$

Therefore the slope of the equilibrium line of pressure versus temperature would be given by

$$dP/dT = (1/\Delta V)(\partial\Delta G/\partial T) \quad (2)$$

It was shown that $\partial\Delta G/\partial T$ is a constant if the difference of specific heat between diamond and graphite at constant pressure remains zero, an assumption which has been experimentally validated. The slope of the pressure versus temperature graph as calculated by Simon and Berman [6] is 2.73 Mpa/degree. Further experimentation

by Bundy et al. [7] showed the slope to be 3.02 Mpa/degree, thus confirming the theory.

3. Solvent catalyst synthesis

3.1. Introduction

Since very high temperature and pressures are required for the direct conversion of graphite to diamond, one can reduce the severe conditions required for the synthesis by using a solvent catalyst system. The conditions required for synthesis are reduced from a temperature of 3300 to 1600 K and pressure from 130,000 to 55,000 atm [1]. The solvent catalyst lowers the high activation energy required for transformation of graphite to diamond and also dissolves the carbon atoms present in graphite enabling the atoms to move into the appropriate positions for rebonding as diamond. Usually metallic catalysts used are iron, nickel and cobalt. Pt, Pa, Rh, Ir, Os, Ta, Mn and Cr also act as catalysts [11]. Binary alloy systems like Nb–Cu were also found effective [12]. Diamond could also be synthesized when non metallic catalysts usually hydroxides, carbonates, etc., were used [13].

3.2. Thermodynamics of solvent catalyst synthesis

If we consider a binary metal carbon system (Figs. 2 [14] and 7 [23]) in which two phases, a liquid and a solid phase, exist, the respective free energy functions G^l and G^s are described in terms of the partial free energies of the components G_c and G_m as

$$G^l = x^l G_c + (1 - x^l) G_m^l \quad (3)$$

$$G^s = x^s G_c^s + (1 - x^s) G_m^s \quad (4)$$

where x is the molar fraction of carbon in the liquid or solid phase.

$$\bar{G}_c = G + (1 - x) \partial G / \partial x \quad (5)$$

$$\bar{G}_m = G - x \partial G / \partial x \quad (6)$$

are the inverse relations. For thermodynamic equilibrium, the partial molar Gibbs free energies of each component in both phases at a pressure P and temperature T are equated. The two equations then define a point on the liquid and solid region of the system. That is, at this pressure and temperature a liquid of composition x^l is in equilibrium with a solid of composition x^s . The diamond graphite line (Fig. 1 [11]) represents the upper temperature limit for the diamond stability field.

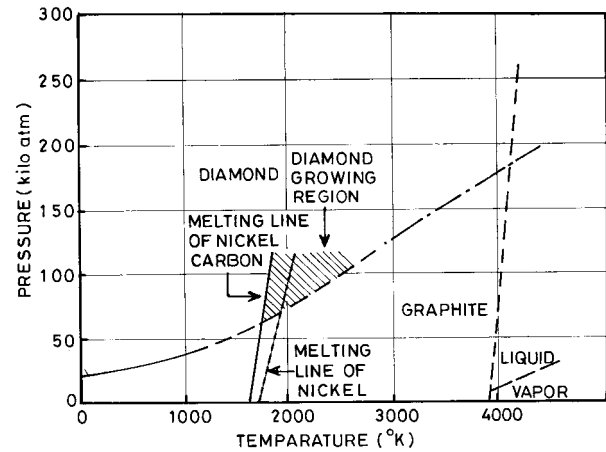


Fig. 1. Diamond equilibrium curve and diamond growing regions. Reprinted by permission from Nature 184 (1959) 1094–1098. © 1959 Macmillan Magazines Ltd [11].

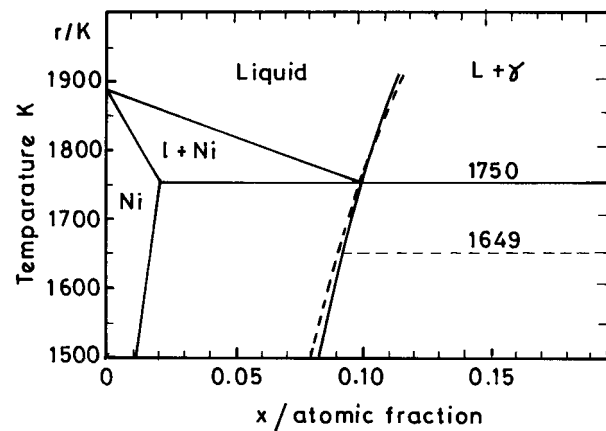


Fig. 2. Phase diagram of Ni–C system (from Ref. [14]).

The lower limit is given by the eutectic between the diamond and metallic phase or a metal carbide [14].

3.3. Equipment

The high pressure and temperature needed for the conversion requires elaborate equipment. Several types of high pressure devices such as the Bridgman flat anvil device [15], Hall belt apparatus [16], cone apparatus [17], toroid anvil [18] are used to synthesize diamond but the Hall belt and the toroid anvil are the ones commonly used.

3.3.1. Hall belt apparatus

The belt apparatus (Fig. 3 [17]) is used to generate pressure by pushing two anvils together, squeezing the sample in between. The use of slightly tapered pistons in the apparatus makes it possible for the system to avoid local high stress points and the shrinking supporting rings prevents the material from flowing out. The reaction

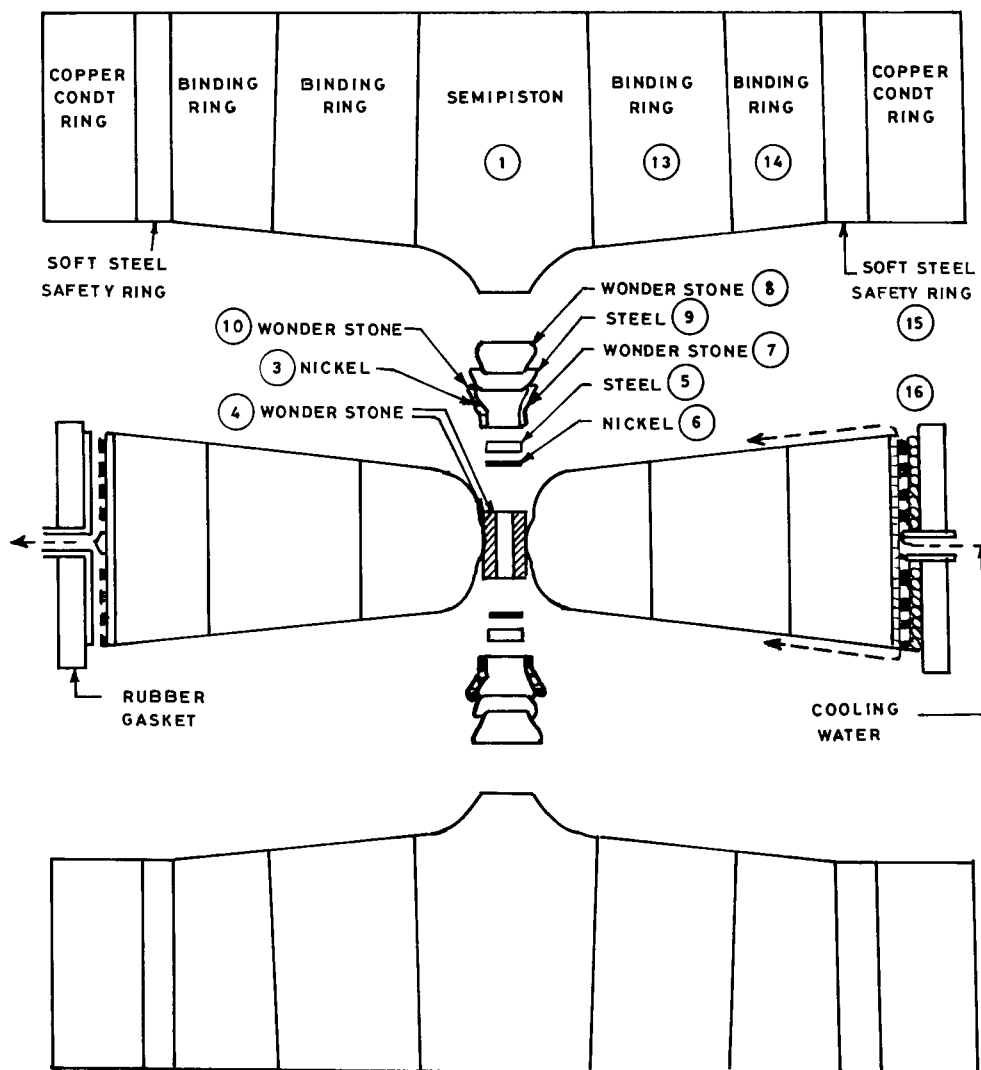


Fig. 3. The belt high pressure apparatus (from Ref. [17]).

volume is very small and a die is kept in between to increase the volume available for the synthesis as a large volume is required for large sized diamonds to be formed.

3.3.2. Toroid anvil

A modification of the Bridgman flat anvil device, the toroid anvil (Fig. 4 [18]) consists of a tungsten carbide anvil with a central cavity and a concentric toroidal groove and a set of shrunk fit alloy steel binding rings. When a pyrophyllite $[\text{Al}_2\text{Si}_4\text{O}_{10}(\text{OH})_2]$ gasket is compressed between opposed anvils, the outward flow of pyrophyllite from the central region is stopped by the inwards flow of gasket material from the toroidal region and high pressure is generated in the reaction cell.

3.3.3. Components and materials

Carboloy (tungsten carbide) is extremely stable under high pressure and can support high stresses. It is used

for making the pressurizing components. The two critical components of the high pressure apparatus are the compressible gasket and the sample holder. The gasket permits compressive movements of the conical piston and helps distribute the loading between the chamber and the piston. The sample holder provides thermal insulation between the chamber walls and the heated zone. The gasket and the sample holder are made of fine grained easily machinable stone pyrophyllite. Pyrophyllite is hydrate aluminum silicate $[\text{Al}_2\text{Si}_4\text{O}_{10}(\text{OH})_2]$.

3.3.4. Pressure and temperature calibration

High temperature is generated in the reaction volume by passing a large current from one anvil to another directly through the reaction mass if it is conducting or through a resistance heater sleeve, normally made of graphite. The temperature can be estimated using thermocouple wires. The wires run through the gasket where they experience considerable force; in some cases

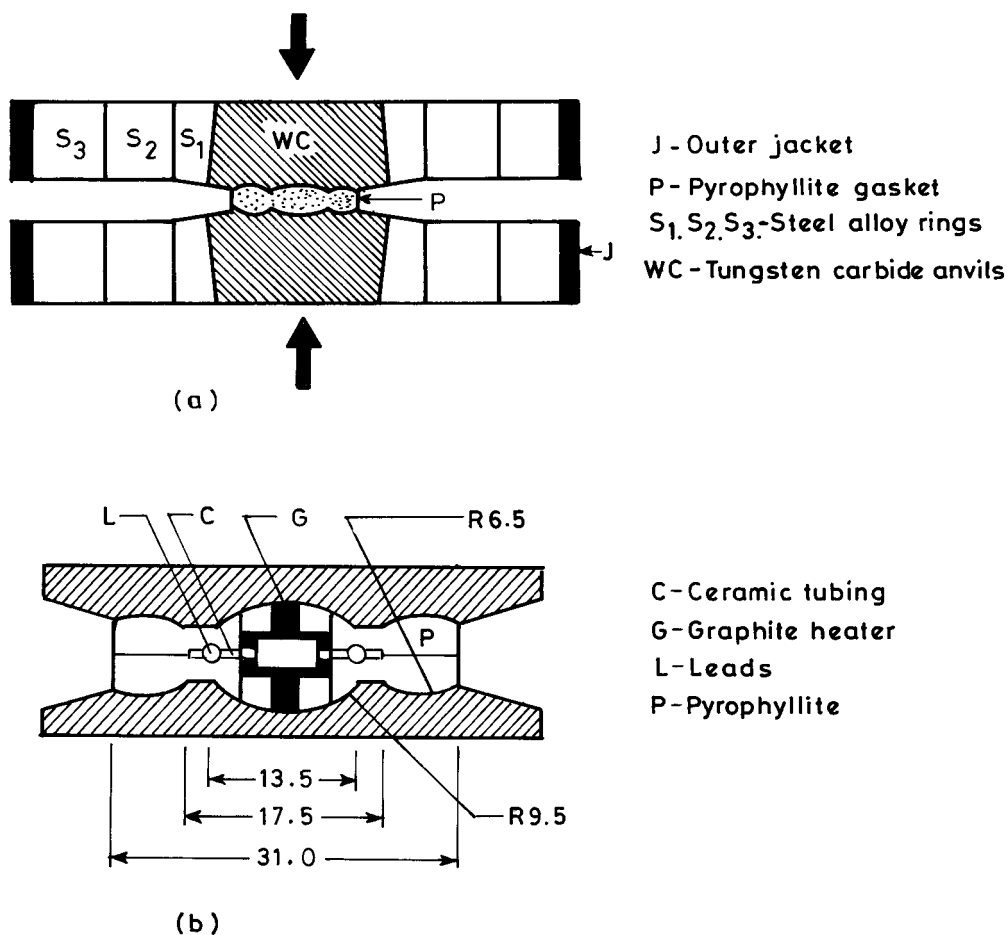


Fig. 4. Toroid opposed anvil setup (from Ref. [18]).

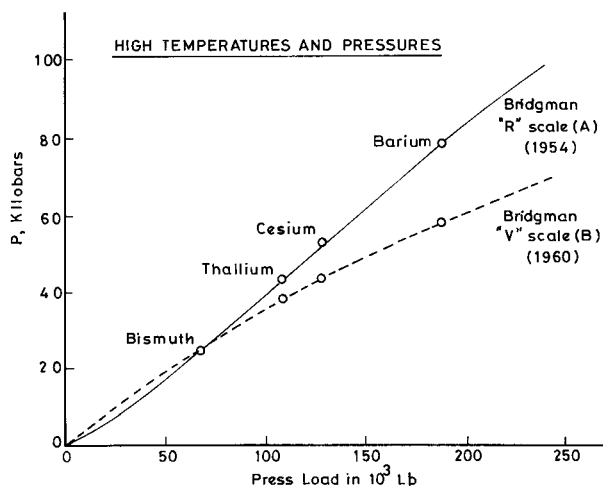


Fig. 5. Pressure calibration by measuring changes in resistance of metals like bismuth, cesium, etc. (from Ref. [17]).

they have been reduced in diameter by 20% and these deformations vary rapidly along the length of the wire [1]. Other factors which affect the readings are a combination of pressure and temperature gradients and contamination. The variation of pressure and temperature

in different high pressure cells can lead to significant differences in the relative thermocouple readings and corrections should be applied [19–21]. Usually temperature calibrations done differ from actual values by over 50 K.

Pressure calibrations are done by measuring the electrical conductivities of certain metal strips. Certain metals like bismuth, thallium, cesium and barium show sharp electrical resistance transitions at certain pressures as shown in Fig. 5 [17]. But these values have not been well established as the pressure inside the cell may vary due to volume changes which redistribute the forces. Also, the calibrations are done at room temperature and do not account the effects of high temperatures.

3.4. Reaction cells

In the solvent catalyst synthesis the following reactions cells are employed as shown in Fig. 6 [7].

1. Rod and tube cell (Fig. 6a): This cell was used for making the first rough measurements for the diamond graphite equilibrium line. Because it has very large radial and axial temperature gradients it is not used for controlled applications.

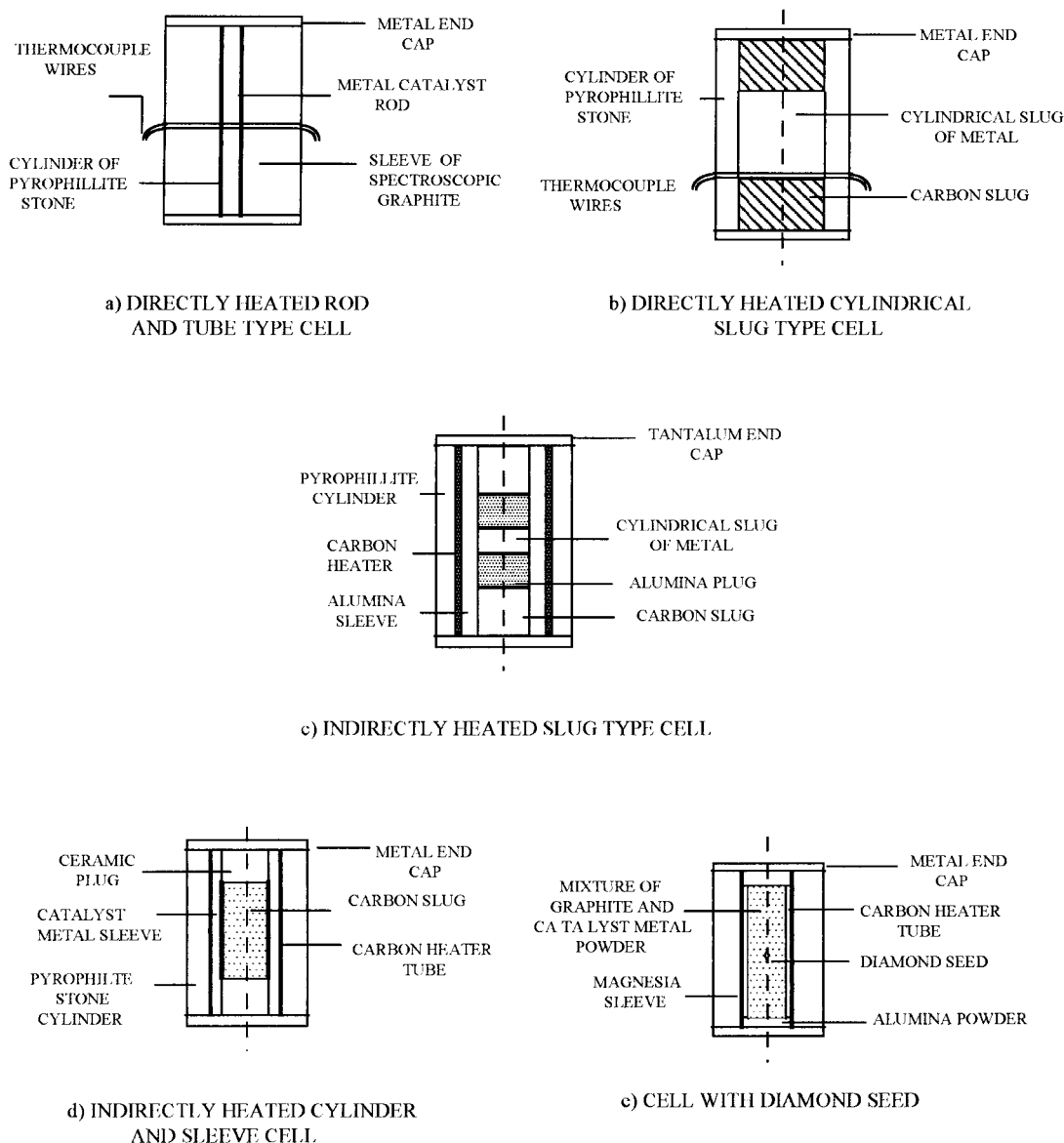


Fig. 6. Reaction cells used in high pressure diamond synthesis. Reprinted with permission from J. Chem. Phys. 35(2) (1961) 383–391. © 1961 American Institute of Physics [7].

2. Directly heated slug cell (Fig. 6b): A heating current is passed in series through a slug of catalyst metal surrounded by carbon slugs. Most of the heat is generated in the carbon slugs and the metal slug is heated primarily by thermal conduction from the carbon slugs.
3. Indirectly heated cell (Fig. 6c): An indirectly heated slug cell has a relatively large diameter carbon heater tube which is insulated from outside by a pyrophyllite cylinder. Slugs of carbon and catalyst metal are filled in the tube, with the latter being isolated from the heater tube and end caps by an inert ceramic material such as alumina or silica.
4. Indirectly heated cylinder and sleeve cell (Fig. 6d): This cell is mechanically and electrically very stable. The presence of the relatively long, thin

walled sleeve of catalyst metal minimizes irregular fracturing and leakage of the ceramic liner between the catalyst sleeve and heater winding.

5. Cells with diamond seeds (Fig. 6e): In these cells the seed diamond is placed at the interface between the metal catalyst and graphite. It is also sometimes wrapped in a foil of the catalyst metal so that it does not come in contact with the graphite phase.

3.5. Kinetics and growth

Extensive research was carried out by the General Electrical Company in the 1950s which has resulted in the following observations [11]. As the synthesis pressure and temperature is moved into the diamond stable

region away from the graphite diamond equilibrium line, the rate of nucleation and growth of the diamonds increases and their average crystal size increases but the crystal quality decreases. Too high a temperature and pressure produces such a large driving force that chaotic growth ensues. One of the ways of making large crystals is to first take the synthesis conditions far away from the Simon–Berman [6] equilibrium line into the diamond growing region so that a lot of nucleating sites are created. The reaction cell is then heated up so that the synthesis conditions are in the graphite stable region. After a short time most of the nuclei dissolve. The temperature is then lowered so that the synthesis conditions are again in the diamond growing region close to the equilibrium curve. A small number of nucleating sites ensure that the crystal growth is uniform and not chaotic.

The actual transformation from graphite to diamond occurs across a very thin film, about 0.1 mm thick which separates the carbon from the diamond [11]. The transformation is direct but the catalyst is essential. Feasible kinetics dictate that certain liquid melts or alloys be present through which carbon can diffuse. Temperature and pressure also affects the shape of the crystal. Cubes dominate at the lower temperatures; mixed cubes, cuba octahedra at the intermediate temperatures and octahedra at higher temperatures [1]. At high growth rates, foreign particles present in the mixture are often trapped by the nucleating diamond [22].

Experiments carried out by Strong and Hanneman [23] suggests a diffusional model for growth of diamond crystals. Observations reveal that the weight increase Δw in grams of the seed diamond, is given by

$$\Delta w = kt/\delta \quad (7)$$

where k is a constant that depends on the catalyst, δ is the metal film thickness and t is the growth time in seconds. If we substitute it in Fick's first law

$$J = D\nabla c \quad (8)$$

where J is the diffusive flux, then Δw is given by

$$\Delta w = D\Delta cAt/\delta \quad (9)$$

where Δc is the difference in solubility limits between the $L/L + d$ and the $L/L + g$ boundaries, D is the diffusion coefficient and A is the effective area for growth. The effective diffusion for the process is given by

$$D = k\Delta c^{-1}A^{-1} \quad (10)$$

At 1690 K and 54 kbars, k was found to be 5×10^{-9} gm cm/s, $\Delta c \approx 3 \times 10^{-3}$ gm/cm³, $A \approx 0.1$ cm² for the seeds used and hence $D \approx 2 \times 10^{-5}$ cm²/s. Similar experiments at 1840 K and 58 kbars gave a value of $D \approx 4 \times 10^{-5}$ cm²/s. This relatively small rise in the value of D for a 150 K

rise in temperature indicated that the diffusion process required an activation energy of about 30 kcal/mole. Surface rearrangement kinetics also plays an important role in the growth process. Octahedral faces dominate at high temperatures but the cubic face becomes predominant once the flux of carbon to the diamond surface exceeds a certain value. About 120 min is required to grow a crystal weighing 1/100 carat by this method. Nucleation and growth controls limit the production of good quality crystals by this method to a size of 1 mm [14]. Attempts to grow larger crystals by prolonging the cycle results in the crystals growing into each other, initiating cracking and fracture.

4. Reconstitution method

4.1. Introduction

To produce large diamonds in a relatively short time, the temperature gradient or the reconstitution process is employed in which the carbon source is diamond. In this method, diamond dissolves in a hot region and crystallize in the cooler region of the bath. The entire system is at a diamond stable pressure and the driving force for the reaction is provided by the solubility difference resulting from the temperature gradient in the cell. Fig. 7 [23] is the nickel–carbon phase diagram at 57 kbars, worked out by Strong and Hanneman [23]. The

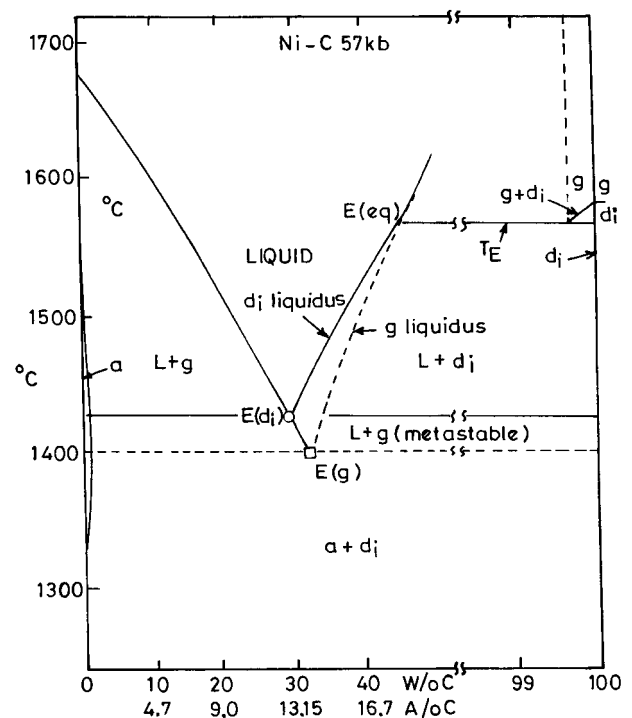


Fig. 7. Nickel carbon phase diagram at 57 kbars. Reprinted with permission from J. Chem. Phys. 46 (1967) 3668–3676. © 1967 American Institute of Physics [23].

solubilities of diamond and graphite vary with temperature. A temperature interval of 60°C is available for dissolving and crystallizing diamond in this system [24]. The growth rates can be controlled by adjusting the temperature.

4.2. Apparatus

In the reaction cell (Fig. 8 [24]), the nutrient carbon, usually a densely packed mixture of diamond and graphite, occupies the midlength. The graphite changes to diamond early in the operating period and is added to increase the average density of the starting mixture so as to minimize the pressure loss and distortion due to the change in volume. Two cooler regions near each end of the cell are available for diamond growth and diamond seeds are placed at these ends. The heat generated in the carbon tube resistance heater flows out of the cell in such a way that useful axial temperature gradients exist in the tube. The cell is compressed to operating pressures of 55–60 kbars and then the midlength is heated to around 1450°C and the seed regions to about 1420°C [24]. To obtain a greater number of diamonds Yazu et al. [25], arranged two or more independent baths in the same reaction chamber. Each bath had several seed crystals embedded at the bottom of the bath. Optimum conditions required for the synthesis were obtained by choosing different metal alloys as the solvent for different baths.

4.3. Kinetics and growth

The solubility of carbon in the nickel–carbon eutectic is higher under the operating conditions as compared to the room conditions. Hence a bath of metal saturated with carbon under atmospheric pressure will not be saturated when it melts in the reaction cell. The extra carbon is supplied from the nutrient carbon and the seeds. In the top bath the thermal convection aids diffusion and the carbon fluxes of $3 \times 10^{-4} \text{ gm s}^{-1} \text{ cm}^{-2}$ or more are observed with temperature gradients of about

$100^\circ\text{C cm}^{-1}$. In the bottom bath the temperature gradients oppose convection and the carbon fluxes are about $10^{-4} \text{ gm s}^{-1} \text{ cm}^{-2}$. A few crystals of diamond float upwards to the cool end of the top bath to become the seed crystals. The cool end of the bottom bath is more suitable for controlled growth as both the seed and impurity population is low here [24].

The seed crystals are mechanically embedded in the insulation so that they do not float up and dissolve. If the seed is too small or too exposed to the bath then it may dissolve entirely and float away and if the seed is too large, the new growth tends to be of poor quality due to prolific nucleation. If the imposed carbon flux cannot be absorbed by the nucleating diamond then graphite nucleates spontaneously despite being thermodynamically unstable under the operating conditions [24].

The diamond growth process involves the formation of a tiny patch of a new layer on the crystal edge. Then the layer starts to spread out as an advancing step to cover the face of the crystal. The thickness, number density and the frequency of formation of the layer increases with supersaturation. The base or inside corner of the step cannot advance as rapidly as the top corner. The top corner has a better supply of carbon atoms and the inside corner has a higher concentration of impurities. The diffusing away of the impurities and the absorption of the incoming flux are the limiting rate factors in growing the crystals. If carbon is supplied too rapidly then the step is roofed over and the impurities and the carbon particles get trapped within the crystal [24].

Usually a growing crystal face bears some difficult regions over which the new growth proceeds very slowly and near which the growth layer tends to pile up. If the area of the difficult regions of growth is proportional to the face size, then the time taken to traverse the face is proportional to the face area, and since the growth layers are of the same thickness, the radial growth rates are proportional to the average diameter of the crystal. Thus

$$2srb = 1 \quad (11)$$

where s is the average diameter in mm of the crystal, r is the growth rate in mm/h, b is a parameter related to the particular conditions of a bath. The time T required to grow a crystal to a size L , growing as fast as possible is

$$T(L) = \int_0^L ds/r = \int_0^L 2bsds = bL^2 \quad (12)$$

Experiments by Wentorf [24], gave the value of b to be 2.5 h mm^{-2} . Hence one may deduce that a high quality, inclusion free 3 mm crystal requires 22.5 h or a 6 mm

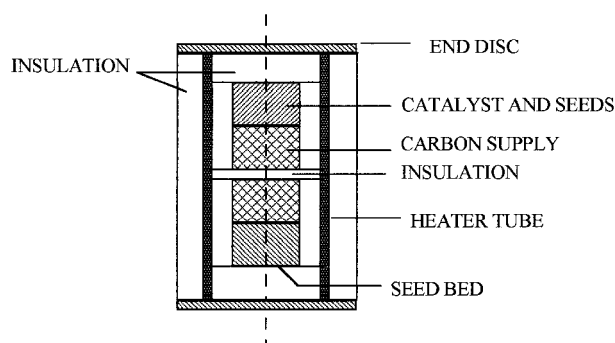


Fig. 8. Reaction cell used in manufacture of synthetic diamond using the reconstitution process. Reprinted with permission from *J. Phys. Chem.* 75(12) (1971) 1833–1837. © 1971 American Chemical Society [24].

crystal requires 90 h. However, in practice it is not possible to grow the entire crystal at a rate set by the final size and a 3 mm crystal requires about 55 hours, a 5 mm crystal 167 h. The value of parameter b changes slightly with the composition of the bath and the temperature of the bath.

Impurities affect both the growth rates and the physical properties of a diamond crystal. Nitrogen is a common impurity in diamond and it has been observed that while synthesizing large crystals free from visible flaws, growth rates of ~ 2.5 mg/h were achieved in baths having 10^{18} to 10^{19} atoms cm^{-3} of paramagnetic nitrogen dispersed in it [23]. The growth rate was restricted to ≤ 1.5 mg/h, when the nitrogen concentration was less than 10^{17} atoms/ cm^3 . The paramagnetic nitrogen also imparts a yellow colour to the crystal. White diamonds can be grown by reducing the nitrogen content in the reaction volume and adding nitrogen getters. However it is difficult to grow diamonds if nitrogen is excluded from the reaction volume [14]. Boron is another impurity which is frequently encountered in diamonds. It imparts a blue colour to the diamond and makes it semi-conducting. Some additives promote the precipitation of graphite and carbide [26]. Hydrogen gas and hydrogen compounds have an inhibitory effect on the conversion of graphite to diamond [27]. Using the reconstitution process diamonds up to 1.2 and 5 carat have been grown by the firms Sumito and De Beers, respectively [28,29].

5. Metastable diamond synthesis

5.1. Introduction

The first metastable synthesis of diamond was reported in 1968 [10]. Today, diamond is being synthesized using a variety of chemical vapour deposition (CVD) techniques such as hot filament CVD [30], microwave plasma CVD [31], DC plasma CVD [32], plasma jet CVD [33], arc discharge CVD [34], laminar oxy-acetylene flame CVD [35], turbulent oxy-acetylene combustion CVD [36]. All of these methods involve the deposition of carbon as diamond, from a mixture of a hydrocarbon and hydrogen by preferential etching of graphite over diamond by hydrogen. There have been claims of growing gem quality crystals of 1.2 mm height by homoepitaxial growth using microwave plasma CVD [37].

5.2. Thermodynamics

If the nucleation of diamond is assumed to occur via phase transition from the gas phase then according to the classical nucleation theory [38], the free energy associated with the formation of a solid particle containing n atoms from its vapour phase is expressed as

$$\Delta F = -fn + \eta\gamma n^{2/3} \quad (13)$$

where f is the bulk free energy change per atom with the transfer of an atom from the vapour phase to the solid phase, n is the number of atoms in the particle, γ is the specific surface energy and η is the shape factor which is $(4\pi)^{1/3}(3v_s)^{2/3}$ for a sphere, where v_s is the volume of the solid atom.

Let phases I and II denote the stable phase (graphite) and metastable (diamond) respectively. For ΔF_I and ΔF_{II} to be equal

$$n^* = 36\pi \left(\frac{v_I^{2/3}\gamma_I - v_{II}^{2/3}\gamma_{II}}{f_I - f_{II}} \right)^3 \quad (14)$$

If $v_I^{2/3}\gamma_I < v_{II}^{2/3}\gamma_{II}$, then phase I is always the stable phase over the entire particle range.

However, if $v_I^{2/3}\gamma_I > v_{II}^{2/3}\gamma_{II}$, then there exists a certain particle size for which phase II becomes the stable phase. For the diamond graphite system, n^* is estimated to be 270 at 1200 K [39], hence diamond nucleates even under conditions where it is thermodynamically unstable.

5.3. Equipment

Today the most commonly used methods for synthesis of diamond under metastable conditions are the Microwave Plasma Chemical Vapour Deposition (MWPCVD) and Hot Filament Chemical Vapour Deposition (HFCVD).

5.3.1. MWPCVD apparatus

In one design of the MWPCVD apparatus, as designed and fabricated in the Physics Department of IIT Bombay, a quartz tube of diameter 30–40 mm and 50 cm length is used as the reactor chamber [40]. The quartz tube is vacuum sealed from both ends and passes through a hole in the waveguide. At the end of the waveguide an applicator is used for forming standing wave pattern of electromagnetic waves (Fig. 9 [56]). Methane, hydrogen and oxygen are used for the deposition. R1, R2 and R3 are the regulators used to regulate the flow-rates and mass flow controllers M1, M2 and M3 are used to measure the flow-rates. The brass waveguide is connected to a microwave generator of 0–700 watts and 2.45 GHz frequency. The reaction chamber sits on a movable substrate assembly. A rotary pump is used to evacuate the chamber. Initially the chamber is flushed with hydrogen to remove all the impurities and then plasma treatment is carried out. After deposition the flow of methane is stopped and a plasma of hydrogen is maintained for some time.

5.3.2. HFCVD apparatus

The apparatus [40] consists of a steel chamber 28 cm in height and 15 cm in diameter (Fig. 10 [40]). The feed

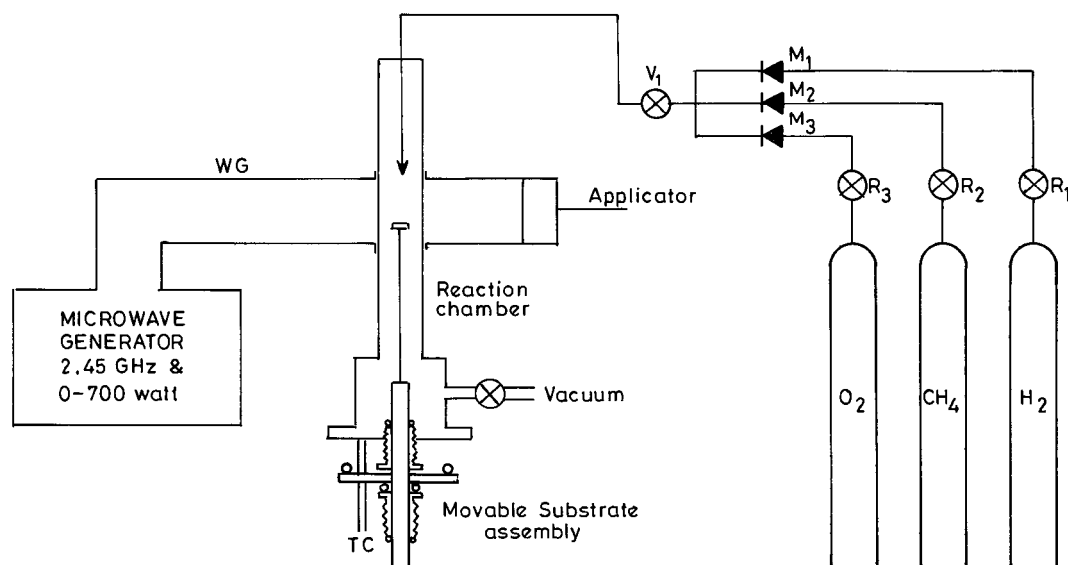


Fig. 9. A schematic diagram of the MWPCVD reactor (from Ref. [56]).

through for the electrodes are connected to the chamber by means of a flange having an aluminum gasket of diameter 35 mm. The electrodes are insulated from the chamber by using a Teflon piece attached to the flange. A view port is provided for the measurement of filament temperature using an optical pyrometer. The distance between the filament and the substrate can be changed by moving the substrate holder. The chamber can be evacuated using a rotary pump. The gas tube takes a U-turn inside the chamber so that the gas falls directly on the heated filament. The gas tube is directly connected to a mass flow controller which regulates the flow rate of the gasses. Water is used to cool the chamber and a pressure gauge is used to monitor the pressure of the system. The filament is calibrated against the current supplied. First the chamber is evacuated using the pump and hydrogen is used to flush out all the impurities. Then the filament is heated up and the distance between the substrate and the filament is adjusted. Once the desired temperature is obtained the hydrocarbon is introduced [41]. The apparatus described above has been used to grow diamond thin films only.

5.4. Kinetics and growth

The role of atomic hydrogen is to suppress the much faster formation of non diamond structures and to stabilize the diamond surface lattice which is thermodynamically unstable under the growth conditions. There is a direct proportionality between the concentration of atomic hydrogen in the gas phase and the substrate temperature [42]. The substrate temperature and hydrocarbon concentration have a significant effect on the morphology and quality of the products. The effect of substrate temperature on the growth rates is

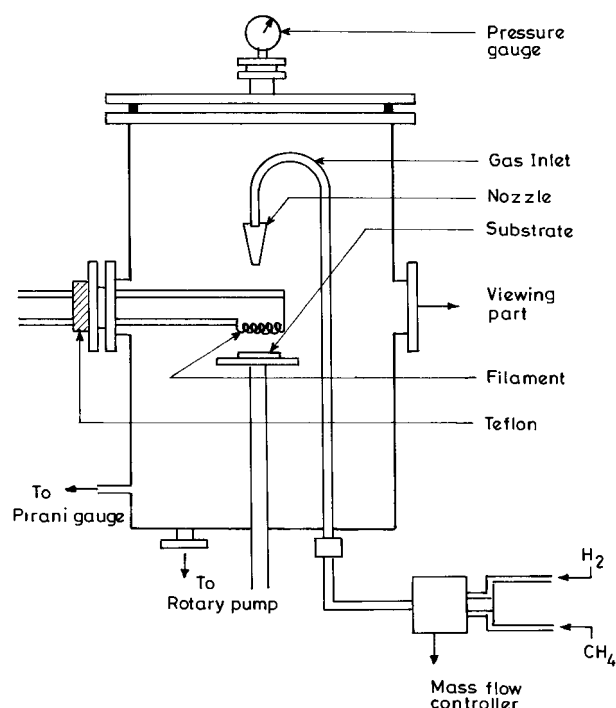


Fig. 10. A schematic diagram of the HFCVD reactor (from Ref. [40]).

not clear and contradictory results have been obtained [43–45]. A lower proportion of the carbon containing gas to large proportions of the carrier gas improves the crystalline quality of the deposits at the expense of the growth rate. If the working pressure is increased then the growth rates increase but at the same time the spatial inhomogeneities increase [46].

In order to grow single crystals, a low density of nucleation is necessary. A mild etching with a dilute mixture of hydrofluoric acid and nitric acid is some-

times used to reduce the nucleation density [47]. For a given composition of reactant gas, there exists an upper limit to the substrate temperature at which diamond nucleation is still possible. At this limit the nucleation rate is very small [48] ~ 20 atoms/cm². A high nucleation rate can be achieved if a negative voltage bias is applied to a substrate like silicon [49] or if it is scratched [50].

The crystal faces, growth rate and growth mechanisms depend on the techniques used to grow the diamond deposits and very little is known about the growth mechanisms of crystalline diamond [51]. In the HFCVD process, the distance of the filament to the substrate strongly influences the growth rates. Experiments carried out by Beckmann et al. [52] indicate that if the filament to substrate distance is ≥ 5 mm, growth rates were less than 1 $\mu\text{m/h}$ whereas the growth rate increases if the distance is between 1.25 and 2.5 mm. Also there was a possibility of depositing diamonds of high quality at higher methane concentration and higher deposition rates using low filament to substrate distance. The deposition of diamond particles can be carried out at low substrate temperatures by adding oxygen to the gas phase [53]. A lot more research needs to be done in this field before the role of the various parameters on growth and kinetics can be fully established.

6. Characterization of diamond

Many destructive and non-destructive methods used to determine the mechanical, optical, thermal and electrical properties of diamond deposits are used to characterize synthetic diamond [54,55]. Among these methods, optical characterization techniques play an important role as they are non-destructive, fast and require a minimum time for sample preparation. X-ray diffraction (XRD) is used to determine the crystal structure of the diamond present. Raman spectroscopy is a useful tool for characterizing diamond. High quality diamond shows a sharp peak at 1332.7 cm^{-1} . In addition

a broad band is observed at 1500 cm^{-1} for an impure sample [56]. In scanning electron microscopy (SEM), the secondary and the back scattered electrons are detected when a high energy beam is incident on the specimen. The morphology of the particles can be detected using this technique [57]. Fig. 11 shows a SEM of a CVD diamond film synthesized in the Physics Department, IIT Bombay. Other methods to characterize diamond include Auger electron spectroscopy [58], transmission spectroscopy [59], etc.

7. Conclusions

Gem quality crystals have been successfully synthesized by the HPHT method as well as a few CVD processes. The thermodynamic, kinetics and the growth processes of both the methods have been reviewed. For the HPHT process, the size and quality of the diamonds is limited by the volume of the high pressure reaction chamber and the duration of the synthesis process. The chemistry of the growth process has been established. For the CVD growth process the focus of the report has been on MWPCVD and HFCVD processes as they are the most commonly employed techniques to grow diamonds. The role of the various parameters in the CVD growth process is still not clear and simulation and experimentation needs to be carried out about their role. Today, gem quality diamonds are not synthesized as they are not economically feasible to grow and only a few are grown for experimental work. New ways of development may depend upon a combination of the reconstitution process and CVD processes.

7.1. Future work

In the last few years a lot of encouraging experimental work has been carried out in this field. A patent to manufacture colourless and transparent, substantially inclusion free diamonds for use as ornamental parts and in optical parts has been filed [60]. Large size diamond crystals (> 10 carat), have been grown in a relatively short time [61]. It has also been possible to grow diamonds having a low nitrogen content using the temperature gradient method [62]. In the CVD processes, there have been attempts to grow large sized diamonds using arc discharge method [48], and oxyacetylene combustion flame technique [63]. Theoretical studies have indicated that laser can be used to grow diamond crystals of over 1 cm diameter [64]. All these claims and newer ones [65–67] need to be looked into and experimental work needs to be carried out about the various growth parameters in the CVD processes, especially for larger diamonds. However, commercial success may critically depend on issues other than the technical ones reviewed here.

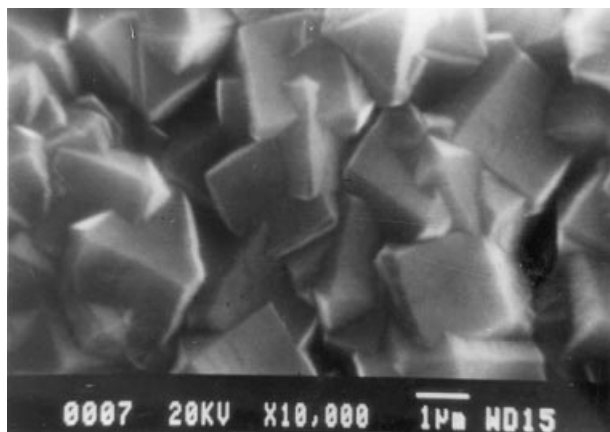


Fig. 11. Photograph of SEM of a MWPCVD film (from Ref. [56]).

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