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Epitaxial Synthesis of Diamond in the Metastable Region

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Recent trends in the preparation of synthetic diamonds, relying on the influence of surface forces exerted by the diamond seed crystal on the carbon deposition processes, are discussed. Epitaxial synthesis can occur from carbon-containing gases or from molten metals. Foreign publications and patents are discussed as well as the work of Soviet scientists.
The preparation and properties of filamentary and of isometric diamond crystals, prepared at low pressures for the first time, are also discussed. 22 references.

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I. INTRODUCTION

Leipusnkii's theoretical work[1], published in 1939, showed that diamond can be prepared from graphite, in principle, at high temperatures and pressures. A more accurate phase diagram for carbon has since become available[2].

A team led by L. F. Vereshchagin at the USSR Academy of Sciences successfully solved the problem of the synthesis of diamonds at high temperatures and pressures in 1960. The Institute of Super-hard Materials played an important role in the development of industrial methods of production of diamonds.

The high-pressure method for the synthesis of diamond adopted in many countries, characterised by a high reaction rate, has some well-defined regions of application whose boundaries are determined by the specific crystallisation conditions. Under certain conditions the main advantage of the method—its high speed—may become a drawback by making the synthesis uncontrollable and by preventing the formation of crystals of appreciable size.

The principle of an alternative method of synthesis of diamond, briefly mentioned in Leipunskii's paper, is closely bound up with the physicochemical study of surface phenomena. In principle, if a diamond crystal is already present in the system, it can be made to grow even in the region of metastable existence of this allotropic modification (for example, under atmospheric or reduced pressure) if the flux of carbon atoms to the diamond surface is not too large.

Research on the epitaxial synthesis of diamonds began in the Surface Phenomena section of the USSR Academy of Sciences (Institute of Physical Chemistry) in 1956.

2. GENERAL THEORY OF THE NUCLEATION OF DIAMOND IN THE METASTABLE REGION

The epitaxial method for the synthesis of diamond from carbon-containing gases is based on the heterogeneous decomposition reactions

$$CH_4 \rightleftarrows \underset{\text{diamond}}{C} + 2H_2$$

$$C_2H_2 \rightleftarrows \underset{\text{diamond}}{2C} + H_2$$

The epitaxial synthesis can be explained either from the standpoint of the molecular mechanism of crystal growth or in terms of the general theory of the formation of a new phase (nucleation). If the concentration of carbon atoms (either in the form of vapour or chemically bound as methane or ethylene molecules) in the neighbourhood of a diamond crystal face is higher than the corresponding equilibrium value, the excess of carbon atoms will be deposited on the surface. These atoms will experience the force field of the crystal lattice, tending to extend the array of "building blocks" which had initially given rise to the substrate. In other words, the substrate compels new carbon atoms to take up the predetermined positions. The process by which a substrate influences the growth of a crystal modification isomorphous with or similar in structure to itself is known as epitaxy. The present example can be termed autoepitaxy (homoepitaxy). However, if the supersaturation with respect to diamond is too large, and the deposition process is too fast, the influence of surface forces may cease to control the process, and nuclei of the thermodynamically preferred modification (graphite) may be formed and grow. Initially, graphite and diamond can grow simultaneously on different parts of the surface, but if the supersaturation of carbon remains high the graphite modification will cover the entire surface and the autoepitaxial growth of diamond will stop.

The conditions under which this situation can be avoided are implied in the general theory of crystal nucleation and growth developed by Gibbs, Volmer, Kaishev, and others. It is shown that the probability of formation of a stable (critical) nucleus of a new phase decreases as the work of formation of the new phase increases. The work of formation is proportional to the surface energy of the nucleus of "critical" size: this size increases as the supersaturation decreases. Hence the probability of formation of graphite can be minimised by controlling the supersaturation at a level just sufficient to allow growth of the diamond crystal to proceed. However, if we approach too closely the boundary below which the diamond seed cannot grow, the linear velocity of crystallisation will be unacceptably low. Under these conditions, and in spite of the presence of the seed crystal, some of the stages involved in the deposition of a new layer of atoms may be rate-limited by the work of formation of a two-dimensional critical nucleus. At very low supersaturations the probability of formation of such a nucleus is low, and the growth of the diamond crystal becomes "hesitant". However, growth may be continuous on some areas of the crystal surface, either because the work of formation of the two-dimensional

nucleus is locally zero (e.g. on a (100) diamond face), or (e.g. at the outcrop of a screw dislocation) because two-dimensional nucleation is unnecessary and growth can proceed uniformly and continuously as when ascending a spiral ramp.

Thermodynamic calculations show that the equilibrium pressure of carbon-containing gas, of vapour, or of solution over diamond is approximately twice as large as over graphite. This is the basic reason for the difficulty of growing diamond epitaxially from carbon-containing gases.

The theory of the epitaxial synthesis of diamond by chemical decomposition of carbon-containing gases has not yet been developed. On the one hand, a sufficiently general theory of nucleation is not available, and on the other hand the chemical crystallisation of two competing phases (diamond and graphite) is too complex a situation. A few theoretical propositions relating to the low-pressure epitaxial synthesis of diamond have been put forward[3], and also discussed at the 22nd International Congress on Theoretical and Applied Chemistry[4].

We shall compare the rates of formation of critical nuclei of diamond and graphite on the surface of a seed crystal of diamond†. Since the (111) is both the equilibrium and the most commonly encountered face of diamond, we shall confine the discussion to this face. It consists of two layers of atoms in a puckered hexagonal configuration. The projection of the elementary edge of the hexagonal network on a (111) plane is 1.44 Å long, i.e. is not very different from the lattice constant of the graphite basal plane (1.42 Å). Hence, we shall assume that a graphite nucleus on a (111) diamond face is oriented as though the substrate were a basal plane of graphite.

The work of formation ΔG of a two-dimensional nucleus of perimeter l and thickness h can be expressed in the general form

$$\Delta G = l\varepsilon + \gamma l^2 h \Delta G_V + \gamma l^2 (\sigma_{C-X} - \sigma_{X-V} + \sigma_{C-V}) \quad (1)$$

where γl^2 is the area of the nucleus; σ_{C-X}, σ_{X-V}, and σ_{C-V} are the specific interfacial free energies at the boundaries between the nucleus (C), the crystal (X), and the medium (V); ϵ is the specific free energy of the edge. We can write

$$\Delta G_V = -\frac{kT}{\Omega} \ln \frac{p}{p_e},$$

where p is the partial pressure of carbon-containing gas, p_e is the equilibrium pressure of this gas, Ω is the volume occupied by one atom in the crystalline state, and T is the absolute temperature.

Since the distance between the graphite layers (3.35 Å) is much greater than the bond length in the diamond crystal (1.55 Å), we can equate the energy of the bond between the crystal and the graphite nucleus to the binding energy between graphite layers:

$$\sigma_{C-X} = \sigma_{X-V} - \sigma_{C-V} \quad (2)$$

In this case the last term in the right-hand side of Eqn. (1) vanishes. By maximising ΔG_V with respect to l we obtain the work of formation of the critical nucleus (ΔG^*) and the perimeter of the critical nucleus (l^*):

$$\Delta G^* = -\frac{\varepsilon^2}{4\gamma h \Delta G_V} \quad (3)$$

$$l^* = -\frac{\varepsilon}{2\gamma h \Delta G_V} = \frac{2\Delta G^*}{\varepsilon}$$

† We acknowledge V. P. Varnin's assistance in the calculation which follows.

According to the Volmer–Weber–Becker–Dering theory[5], the rate of formation of nuclei of critical size is given by

$$I = l^* a \exp\left(-\frac{\Delta G^*}{kT}\right). \quad (5)$$

The factor a depends on the molecular collision frequency and on the pressure, and is the same for diamond and graphite.

Using the subscripts α and β to denote quantities relating to diamond and graphite respectively, and introducing Eqn. (4), we obtain

$$\frac{I_\alpha}{I_\beta} = \frac{\varepsilon_\beta \Delta G_\alpha^*}{\varepsilon_\alpha \Delta G_\beta^*} \exp\left[-\frac{\Delta G_\alpha^*}{kT}\left(1 - \frac{\Delta G_\beta^*}{\Delta G_\alpha^*}\right)\right] \quad (6)$$

The equilibrium form of the two-dimensional nuclei, calculated by means of Wulff's theorem, is a regular hexagon for graphite ($\gamma_\beta = \frac{1}{\gamma\sqrt{3}}$) and a triangle with [110], [011], and [101] sides for diamond ($\gamma_\alpha = \frac{1}{\gamma\sqrt{3}}$) as shown in Fig. 1. The specific free energies of the edges are

$$\varepsilon_\alpha = \frac{\varphi_\alpha}{3d\sqrt{3}}, \quad \varepsilon_\beta = \frac{\varphi_\beta}{2d\sqrt{3}},$$

where φ_α and φ_β are the bond energies between nearest neighbours in the diamond and the graphite lattice, and d is the lattice constant of the basal graphite plane.

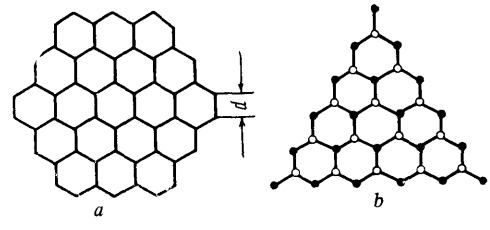


Figure 1. Nuclei of (*a*) graphite and (*b*) diamond on the (111) face of a diamond seed crystal.

The ratio of the energies of formation of the critical nuclei is

$$\frac{\Delta G_\beta^*}{\Delta G_\alpha^*} = 2.5 \frac{\ln p/p_{e\alpha}}{\ln p/p_{e\beta}}. \quad (7)$$

As stated above, thermodynamic calculations indicate that between 1000 and 2000°K (i.e. in the region of spontaneous graphitisation of diamond)

$$p_{e\alpha} = 2p_{e\beta} \quad (8)$$

Introducing the symbol

$$\frac{\ln \frac{p}{p_{e\beta}}}{\ln 2} = x,$$

we can readily show that

$$\frac{I_\alpha}{I_\beta} = 0.8 \frac{x}{x-1} \exp\left[-0.9\left(\frac{\varphi}{kT}\right)^2 \frac{1-0.6x}{x(x-1)}\right]. \quad (9)$$

The maximum of this expression corresponds to $x = 2.7$. For $x \to 0$, $I_\alpha/I_\beta \to 0$; for $x \to \infty$, $I_\alpha/I_\beta \to 0.8$. For $x = 1.67$, the exponent vanishes and $I_\alpha/I_\beta = 2.00$.

Fig. 2 shows a plot of the function (9).

In this way, classical nucleation theory can identify the most favourable region ($p/p_{e\beta}$) for the epitaxial growth of diamond. However, the present calculation, given as an example, assumes that the rates of nucleation of diamond and graphite are mutually independent, whereas under real conditions the two processes are competitive.

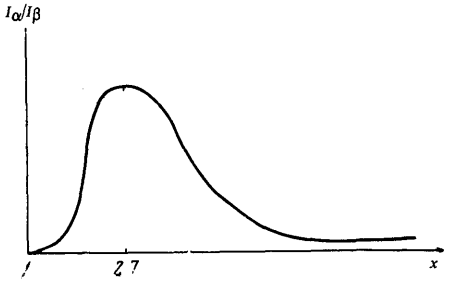


Figure 2. Variation with supersaturation of the ratio of the nucleation rates of diamond and graphite.

It should also be noted that the equilibrium pressure of methane decreases on raising the temperature, whereas that of the other carbon-containing gases (e.g. acetylene) over diamond and graphite changes in the opposite sense. Hence, the methane supersaturation (at constant total pressure) increases rapidly, whereas in an acetylene atmosphere the supersaturation changes much less rapidly with temperature.

3. MAIN METHODS OF PRODUCTION OF DIAMOND IN THE METASTABLE REGION

We shall review the most important patents and papers dealing with the epitaxial synthesis of diamond in the metastable region (between 10^{-3} mmHg and 1000 atm). In 1962 Eversole filed two patents[6]. In the first, the carbon-containing gas is passed over the diamond seed crystal held at a controlled temperature. The temperature range quoted in the patent is 600–1600°, but the best results are obtained at 900–1100°. The partial pressure of carbon-containing gases (with methyl groups) must not exceed 75 mmHg, and should preferably be in the range 0.1–1 mmHg When carbon monoxide (or a mixture of the monoxide and dioxide) is used, the pressure can be as high as 2500 atm. The preferred pressure range is 70–140 atm. Diamond grows on the seed crystal until the formation of other modifications of carbon arrests the growth. The seed can be freed from graphite, and exposed to further diamond growth. The time for the whole cycle of operations (growth and reactivation) varies from a few minutes to 100–200 h, depending on conditions. The reactant can be methane, ethane, propane, chloromethane, methanethiol, or acetone. No growth was observed with benzene, carbon disulphide, dichloromethane, and other hydrocarbons not containing methyl groups. Argon and nitrogen do not inhibit the reaction.

Most of the experiments described[6] were made with diamond powders of 0.1 μm average size, and crystals up to 0.1 carat in weight were obtained. The use of powders offers the advantage of a large specific surface area (up to 20 $m^2\ g^{-1}$).

Non-diamond carbon was removed either by boiling in a mixture of sulphuric and chromic acids, or in hydrogen at pressures up to 50 atm and temperatures between 1000 and 1100°. The latter method relies on the different kinetic activities of diamond and graphite.

The growths of diamond were identified by density measurements and by lattice parameter determinations using electron diffraction.

The maximum increase in weight of the starting powder was 59.5%. This required 85 successive cycles of growth (1.79 h) and graphite removal (4.5 h).

Eversole's second patent is an extension of the first, and essentially consists in the use of gases which can dissociate with formation of free methyl radicals. Angus and coworkers[7] repeated and checked Eversole's work in 1968. They subjected the processed diamond powders to density measurements, to spectroscopic, X-ray diffraction, and electron diffraction analysis, and they studied their microwave absorption and ESR behaviour. The starting and the grown material were identical in every respect. These workers also compared the reaction rates of diamond and of graphite with hydrogen. The activation energy of the diamond–hydrogen reaction was found to be 125 kcal $mole^{-1}$, with an approximately fifth-power pressure dependence, as compared with 85.5 kcal $mole^{-1}$ and a linear pressure dependence for graphite. However, these results were obtained over a narrow pressure range (50–70 atm).

The West German firm of Siemens und Halske filed a French patent in 1962 entitled[8] "Method of Production of Carbon in the Diamond Form at Low Pressures". The invention consists in admitting to the hot reaction zone a carbon compound whose structure is a complete or partial replica of that of the diamond lattice. One of the recommended starting materials is cyclopentane, whose five-membered ring of carbon atoms is practically unstrained (angular deformation less than 1°). In addition to cyclopentane and cyclohexane, other carbon compounds can be used if their thermal decomposition gives rise to products in which the carbon chains are a replica of the diamond lattice structure. Inert gases, hydrogen, or gaseous hydrocarbons at room temperature can be used as carrier gases for the starting material.

To assist the formation of seeds of the diamond form in the reaction zone, catalysts are used. These include substances capable of forming carbides with a cubic structure, e.g. silicon, titanium, Group V elements such as niobium and tantalum, and also a tungsten–cobalt alloy. The catalyst is introduced into the reaction zone either in the form of a solid substrate (for the preparation of crystalline layers) or as metal-containing vapours (for the preparation of carbon powders with the diamond structure). The preferred reaction temperature is between 800 and 1200°. The reaction mixture is activated by some form of electrical gas discharge.

Another patent[9] by the same firm claims every method of preparation of diamonds by means of chemical transport reactions. The pressure of carbon-containing gas must not be allowed to depart too significantly from the equilibrium value for diamond, otherwise carbon may be deposited in a non-diamond form. The theory of the transport process has been discussed by the present writers[10] from the standpoint of non-equilibrium thermodynamics.

The patent[11] "Method and Apparatus for the Replication of Crystal Structures" has interesting possibilities in microelectronics technology. The diamond seed crystal is heated by a controlled electron beam, and a carbon-containing gas is led through the reaction zone without interrupting the electron beam. According to the patent, diamond is deposited on the area where the electron beam is focussed. Gases mentioned in the patent include carbon tetrachloride, carbon tetrabromide, carbon disulphide, and some others. The diamond substrate is heated between 1000 and 3000°: the preferred temperature range is 1800–2500°. Silicon layers can be grown by the same method over the diamond layers from silicon tetrachloride, and these can in turn be overgrown with diamond layers.

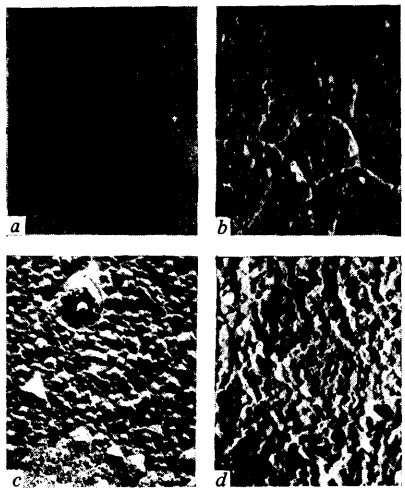


Figure 3. Successive stages in the growth of a (111) diamond face, × 10 000: *a*) initial surface, *b*) and *c*) successive growth stages, *d*) stage corresponding to the formation of a continuous crystallisation front.

In 1964, Brinkman and coworkers[12] extended their earlier work (1957) by disclosing a method for the epitaxial growth of diamond from solutions of carbon in metals. The source of carbon is a sample of graphite held at a higher temperature than the diamond seed crystal. The method can be reduced in practice to two forms: the flow method and the static method. In the flow method, liquid metal is continuously pumped through the system, and carbon atoms are transported from the graphite to the diamond. In the static method the liquid metal is saturated with carbon from the walls of a graphite crucible, the temperature is decreased by an amount corresponding to the desired supersaturation with respect to diamond, and the seed crystal is immersed in the solution. Another patent by the same workers[13] discloses a method for the production of diamond from carbon atoms emitted by a carbon source at high temperature (up to 4000°).

Litvin and Butuzov[14] published a very interesting paper on the growth kinetics of diamond from a solution of carbon in molten metal at 1150° and pressures of the order of 40 000 atm. The planar metal–graphite interface was oriented parallel to the (100) face of the diamond seed crystal. The distance between the two surfaces was of the order of 0.5 mm, and the temperature difference was not allowed to exceed 15°. The kinetic data obtained in this work are of fundamental importance for the development of a theory of crystallisation in the metastable region.

We have recently described[15] the autoepitaxial growth of diamond layers from the gas phase (methane) on natural diamond powder and also on the (111) face of a natural diamond seed crystal. Electron micrographs of successive stages of growth of the same layer are shown in Fig. 3. Fig. 3*a* shows the initial surface, Fig. 3*b* and 3*c* show intermediate stages, and Fig. 3*d* corresponds to the formation of a continuous layer.

4. FILAMENTARY DIAMOND CRYSTALS

The growth of filamentary diamond crystals is of the utmost importance. Such crystals have been obtained by the present writers in collaboration with Luk'yanovich, Ryabov, Spitsyn, Lavrent'ev, and Builov[16–19]. Filamentary crystals (or "whiskers") have a number of unique properties and have attracted a great deal of interest: they have a perfect crystal structure, they retain their elasticity and strength at high temperatures, they show complete strain recovery on subsequent heating, and they have an exceptionally high strength, close to the theoretical value. For example, whereas the tensile strength of ordinary iron is 18–23 kg mm^{-2}, iron whiskers 2 μm in diameter and ~ 2 mm long have a tensile strength of 1200–1300 kg mm^{-2}. The use of sapphire whiskers in niobium composites (50 wt. %) increases the strength of mechanical components by a factor of 4 as compared with pure niobium whilst at the same time reducing their weight: the importance of these properties in aerospace technology is evident.

Filamentary crystals had previously been grown only in the region of thermodynamic stability. Our discovery of filamentary diamond crystals has a twofold significance: on the one hand, it has demonstrated the possibility of growing whiskers under metastable conditions, and on the other hand it has shown that diamond crystals can be grown at low pressures from carbon-containing gases at appreciable linear velocities of crystallisation (at least, in principle). These velocities are many orders of magnitude higher than the linear growth rate of diamond powders (from a few to a few tens of Ångstroms per hour).

The experiments were carried out in a radiation furnace based on a super-high-pressure xenon lamp (type DKSR-6000). The apparatus has already been described in detail[20,21]. The diamond seed crystal was secured by pointed rhenium supports, and located at the focal spot of the apparatus, whose diameter was greater than the largest dimension of the seed crystal. The temperature of the crystal was measured with an optical pyrometer.

The surface of the seed crystal could be observed in a microscope during the experiment. The formation and subsequent growth of filamentary diamond crystals was established in this way. The growth rate is a function of temperature, pressure, and some other parameters. Since the parameters of the radiant flux at the focal spot are not uniform, conditions at the apex of the growing whisker are not the same as at the substrate surface. Thus, the illumination could vary by a factor of two as between the apex and the base of a whisker 400 μm long. The mean growth rate of the whiskers was 50–250 μm h^{-1}: this was genuinely a mean linear velocity, and it is reasonable to assume that much higher linear growth velocities are possible and did indeed obtain at some stage in the growth of these whiskers.

Fig. 4 shows a filamentary diamond crystal approximately 1.00 mm long, grown on the (111) face of a diamond seed crystal. The pointed rhenium seed holder is visible in the photograph.

Diamond whiskers grown on a (111) face are inclined at an angle of 50–60° to this face: their growth is probably normal to a (110) face, as in the case of silicon and germanium whiskers, which crystallise in the diamond lattice.



Figure 4. Filamentary diamond crystal, 1.0 mm long.

The cathodoluminescence of the diamond whiskers has been found to be similar to that of the substrate. After one experiment, the formations were identified unequivocally as diamond by examining the powdered whisker in an electron microscope in the electron diffraction mode. Using platinum as a standard, the interplanar spacings were calculated from the diffraction pattern and compared with tabulated values.

d_{tab}, Å	2.05	1.26	1.072	0.885	0.813	0.721
d_{calc}, Å	2.07	1.24	1.068	0.920	0.825	0.740

The electron diffraction patterns show that the whiskers are single crystals. Kikuchi lines are clearly visible in some of the patterns.

The apex of the diamond whiskers was occasionally found to be covered by a dark, spherical formation. One possible explanation is metallic contamination of the substrate surface before growth. A special series of experiments was therefore devised to study the growth of filamentary diamond crystals under droplets of molten metal by the VLS (vapour–liquid–solid) method[19]. Transparent filamentary crystals supporting a droplet of solidified metal were produced. The best results were obtained with metals in which the solubility of carbon is high and which can wet diamond (nickel, iron, manganese). No formations were observed under molten gold droplets. Evidently, the VLS method must be considered among the possible methods of growing diamond crystals. The role of the intermediate liquid metal phase in the growth of diamond has been discussed by one of us[3]. The energy of formation of a two-dimensional diamond nucleus under the layer of metal can be very much lower than the energy of formation of a three-dimensional critical nucleus of graphite. This is because surface energies at the graphite–metal interface are usually much higher than the surface energy at the graphite–air interface, and therefore the work of formation of graphite nuclei is increased and the generation of such nuclei is suppressed.

The recently observed conversion of filamentary crystals into isometric crystals is also worth noting. We were able to follow, using a microscope, the growth of a diamond whisker. When growth stopped, the crystal began to thicken until an isometric crystal of diamond with 0.1 mm average cross-section and very weakly developed facets was obtained. This crystal was examined by X-ray micro-diffraction (beam diameter 12 μm) at the top, the side, and the bottom of the crystal as grown, and it was found to be a single crystal.

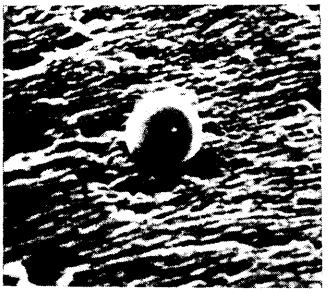


Figure 5. Isometric diamond crystal grown on a (111) face, photographed in a scanning electron microscope. Crystal diameter 20 μm.

Scanning electron microscopy is a particularly revealing technique for examining isometric crystals. A scanning electron micrograph of an isometric crystal 20 μm in diameter, taken in V. G. Spivak's laboratory at the Moscow State University, is shown in Fig. 5.

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