Translated from *Uspekhi Khimii*, 53, 753-771 (1984) U.D.C. 546.26:548.517

Synthesis of Diamond in Its Thermodynamic Metastability Region

D.V.Fedoseev, V.P.Varnin, and B.V.Deryagin

Heterogeneous and homogeneous processes in the formation of diamond at low pressures, where diamond is a metastable modification of carbon, are discussed. Data on the kinetics of the growth of diamond from hydrocarbons under conditions which give codeposition with graphite are reported, together with data on the influence of hydrogen on this process and on the resulting fractionation of the stable carbon isotopes. Chemical and plasma-chemical methods of preparing diamond and diamond-like layers are discussed, as well as methods based on the use of atomic and ionic beams. The most recent theoretical and experimental results on the homogeneous formation of diamond in the gas phase are presented.
The bibliography includes 73 references.

CONTENTS

I. Introduction 435
II. Growth kinetics of diamond powders 436
III. Preparation of diamond layers and crystals 439
IV. Homogeneous formation of diamond in the gas phase 441

I. INTRODUCTION

Before the first successful synthesis of diamond from the gas phase[1] research in this area was confined to the USSR and the USA. Most of the papers published at that time dealt with the growth of diamond on diamond seed crystals by the pyrolysis of methane. Work on the synthesis of diamond in its thermodynamic metastability region is now in progress in Poland, West Germany, Britian, Japan, and other countries. New methods of synthesis of diamond have been developed, using atomic or ionic beams, and low-temperature or high-temperature plasmas. Lastly, homogeneous nucleation of diamond directly in the gas phase has been demonstrated.

The rapid development of research on the synthesis of diamond in its metastability region was stimulated by the unique properties and great technological importance of this material. Whereas the only technical use of diamond until recently was as an abrasive, the material now has potential applications in electronics and in insulating and wear-resistant coatings. Existing methods of synthesis at low pressures can be used to prepare diamond powders and to grow diamond layers (both on diamond and on other surfaces) and diamond crystals. Work on the low-pressure synthesis of diamond is also relevant to an understanding of the origin of diamonds in nature, and to a number of problems in astrophysics.

This review deals with research on the growth of diamond, one of the family of carbon forms which includes hexagonal and rhombic graphite, cubic carbon, carbynes, diamond, and lonsdalite (though even more phases have been reported in the carbon system). The review will be concerned mainly with work published since 1975: earlier work is reviewed fully in Ref.2 and partially in Ref.3.

1. Phenomenological Survey of the Synthesis of Diamond from the Gas Phase

Metastability is not a bar to the formation of diamond (or of any other form of carbon). The process of diamond growth (or of crystal growth in general) can be divided into two main stages: the formation of seeds (or nucleation stage) and the further growth of existing, stable seeds of the new phase.

The free energy of diamond is higher than that of graphite. Therefore the equilibrium partial pressures of carbon-containing gases are higher over diamond than over graphite. The equilibrium pressure of methane over diamond at 1000 K is calculated to be double the corresponding value for graphite. Therefore, for a given partial pressure of methane, the supersaturation is always smaller over diamond than over graphite. Depending on the temperature and on the total pressure, the supersaturation difference between diamond and graphite can decrease, and thus it can influence the relative rates of nucleation of diamond and graphite. Increasing the pressure of methane decreases the supersaturation difference, thereby increasing the ratio of the nucleation rates for the metastable and the stable phase[4].

In spite of its metastability at low pressures diamond is more inert towards atomic oxygen and hydrogen than graphite. The chemical bonds in the diamond lattice show sp^3 hybridisation of the atomic orbitals, whereas in graphite the hybridisation is sp^2. Replacing two neighbours of a carbon atom in the diamond lattice by hydrogen has practically no effect on the electronic interaction between neighbouring atoms, whereas the same operation in graphite alters the nature of the electronic bonds in the whole graphite ring. The differences between the interactions of diamond and of graphite with hydrogen can be likened to the differences in hydrogenation behaviour between ethane and acetylene or between cyclohexane and benzene. The differences in kinetic activity between graphite and diamond form the basis of methods of purifying diamond.

Thus by combining two processes (deposition of carbon, which yields mainly graphite with a small amount of diamond, and gasification by atomic hydrogen, which affects mainly the graphite) we can obtain a product consisting mainly of diamond. In the deposition from atomic or ionic beams the gasification process is replaced by sputtering under the influence of atoms or ions (again, diamond is more impervious to sputtering than graphite).

Let us discuss the growth and gasification of diamond and graphite as in Ref.5, using the subscripts α and β to denote diamond and graphite respectively.

The rates of growth of diamond and graphite can be expressed approximately as

$$v_\alpha = k_\alpha c_1$$
$$v_\beta = k_\beta c_1 ,$$

where c_1 is the concentration of hydrocarbon, and k_α and k_β are the rate constants for the formation of diamond and graphite respectively.

If the surrounding medium contains atomic hydrogen at a concentration much greater than the equilibrium value for the given temperature the rates of the reverse (gasification) reactions can be expressed as

$$v_{-\alpha} = k'_{\alpha} c_2$$
$$v_{-\beta} = k'_{\beta} c_2 ,$$

where c_2 is the concentration of atomic hydrogen, and k'_{α} and k'_{β} are the rate constants of the appropriate gasification reactions. The condition for the deposition of carbon exclusively in the diamond form is

$$v_{\beta} = v_{-\beta} .$$

Hence the minimum concentration of atomic hydrogen can easily be calculated for a given pressure of hydrocarbon:

$$c_2 = \frac{k_{\beta}}{k'_{\beta}} c_1 .$$

The rate of growth of diamond is the sum of the rates of the forward and the reverse reaction:

$$v = v_{\alpha} - v_{-\alpha} .$$

Inserting the critical concentration of atomic hydrogen we find that the rate of growth of diamond not contaminated by graphite is

$$v = v_{\alpha}\left(1 - \frac{k_{\beta}}{k_{\alpha}} \cdot \frac{k'_{\alpha}}{k'_{\beta}}\right) .$$

The above calculation ignores the effect of molecular hydrogen on the crystallisation of diamond and graphite. The corrected formulae are unacceptably cumbersome, without introducing any fundamentally new considerations.

Thus the problems in the synthesis of diamond in its metastability region do not concern the formation of diamond itself: they relate to the prevention of the appearance of the stable phase (graphite), which would otherwise block the diamond nuclei.

The most specific property of carbon is its ability to form strong interatomic bonds with different types of hybridisation of the electronic orbitals, giving different crystal structures which are stable under normal conditions. The chemical potentials of these structures differ only by a small amount, and during crystallisation under high supersaturation this difference plays a negligible role. At the same time the energy barrier to be surmounted in the conversion of diamond into graphite is quite high. Therefore a carbon layer deposited by crystallisation at a high rate will (in general) contain structural fragments corresponding to sp^3, sp^2, and sp hybridisation of the atomic orbitals. This explains the difficulty in preparing perfect crystals of any allotropic modification of carbon (not only diamond).

In the growth processes at relatively high temperatures the energetically less favourable structures are partly converted into the more stable forms. Therefore the relative content of the various types of bond in carbon condensates produced at high temperatures cannot be used to characterise directly the kinetics of their formation from the gas phase.

Another important consideration concerns the two distinct aspects of the synthesis of diamond in general (not only in the metastability region). The first aspect is "purely chemical", and concerns the preparation of a carbonaceous substance in which the atoms are joined by bonds of the type found in a diamond crystal. The second aspect is crystallographic. It is not enough to prepare a carbonaceous substance with bonds of the diamond type if the aim is to produce a diamond: we must also organise the ordering of the crystal structure over regions of adequate size. The solution of this problem presents some major (and well known) difficulties even in substances with far fewer polymorphic modifications. The difficulties increase with the degree of crystalline perfection required. We consider that the main difficulty in the synthesis of diamond in its metastability region lies in identifying conditions compatible with the successful solution of both aspects of the problem.

We know that in organic chemistry the production of metastable compounds is the rule rather than the exception. In this sense the possibility of preparing a diamond-like carbon substance should not appear too remote to a chemist. Obviously, at moderately high temperatures ($\lesssim$1200 °C) the product will be obtained in the solid phase. However, unless precautions are taken to prevent the formation of graphite or carbyne carbon, one is faced with the difficult problem of isolating the diamond-like carbon in a pure form and identifying all the components of the deposited layer. The widely different properties of carbon condensates are due to differences in their content of diamond-like, carbyne-like, and graphite-like bonds.

This "mixed" state of the carbon layer is of interest because it should mirror some properties of the carbon modifications, which are determined by the nature of the interatomic bonds. For example, we know that in semiconductors the principal features of the energy spectrum are retained after transition into the amorphous state. Thus we could expect amorphous carbon to display a combination of the energy spectra of carbyne, graphite, and diamond, except for the contributions from long-range order effects. Thermodynamically such a phase must, of course, be unstable even with respect to the metastable crystalline modifications. At high temperatures solid-state reactions of the $sp^3 \rightarrow sp^2$ and $sp \rightarrow sp^2$ type are possible in the condensed layer, accompanied by annealing of the energetically less favourable types of bond, which brings the system closer to equilibrium (i.e. to the graphite phase).

It is reasonable to ask whether amorphous carbon can be produced at low pressures in a state displaying the short-range order of graphite or of diamond. Amorphous diamond is easily envisaged, by analogy with amorphous silicon and germanium, but amorphous graphite is almost impossible to conceive. Nearly all the specific properties of graphite arise from its strongly developed layer structure. The nearest atom from a neighbouring layer comes only into the fourth coordination sphere. Merely to retain the graphite properties due to the presence of hexagonal rings in the base planes of the graphite crystal requires a higher structural organisation than is usually assumed in amorphous substances (retention of the short-range order only, i.e. second coordination sphere). At best we can expect the existence of amorphous carbon with sp^2 hybridisation of the electronic orbitals of the C atoms.

Thus the problem of preparing diamond under conditions of thermodynamic metastability is found (on closer inspection) to be wider than expected. It should be formulated as a problem in the crystallisation of carbon at relatively low temperatures. We should stress that diamond is a classical three-dimensional ordered structure with a high degree of symmetry. A graphite crystal consists of two-dimensionally ordered networks. Carbyne is classified as a linearly ordered chain structure. Diamond, graphite, and carbyne can themselves exist in several modifications.

II. GROWTH KINETICS OF DIAMOND POWDERS

1. Co-crystallisation of Diamond and Graphite

The kinetics of diamond growth in the pyrolysis of hydrocarbons have been studied mainly during growth on diamond seed powders[6-8], using a gravimetric method (MacBain balance) to

determine the rate of deposition of carbon from the gas phase. The growth of diamond on the diamond seed powder is accompanied by deposition of graphite, which blocks the surfaces on which diamond can form. The rate of growth of graphite from hydrocarbons is lower than the rate of growth of diamond, and therefore the overall rate of deposition of carbon (by weight) decreases with time. From the initial linear portion of the plot of weight against time we can identify the growth rate of the diamond.

Most of the experiments (in different laboratories) were carried out with methane. It was shown that the growth of diamond is proportional to the partial pressure of methane over a wide range of pressure[2], i.e. the reaction is described by a first-order equation. At pressures of 0.01–0.5 mmHg and 1100–1300 K the activation energy of the diamond growth reaction was found[6] to be 80 kcal mole^{-1}.

The kinetic equation for the growth of diamond is

$$v_\alpha,\ \text{g cm}^{-2}\,\text{s}^{-1} = 3.5\cdot 10^{11}\cdot c_0 \exp(-80\,000/RT),$$

where c_0 is the concentration of methane (g cm^{-3}).

The growth rate of diamond and its activation energy are sensitive to the experimental details of the deposition process, the previous history of the sample, and the form of the diamond powder used as a seed. A gravimetric method was used also by Chauhan and co-workers[7], who heated the scale pan containing the diamond seed powder by radiation. In this way the methane not in contact with the diamond seed was kept cool. Pressures up to 44 mmHg were used. The rate of growth of diamond was found to be proportional to the pressure of methane, and an activation energy of 55 kcal mole^{-1} was obtained. Tesner and co-workers[8] studied the growth of diamond at pressures up to 3 atm and observed a slight change in growth rate above 0.5 atm, possibly due to the accumulation of hydrogen in the grown layers of the powder.

Defects on the surface of the diamond powder have a large effect on the rate of growth of diamond. Irradiated diamond powders have been used[9] in a study of the growth of diamond by the gravimetric method and by electrical conductivity measurements. Changes in electrical conductivity are due to the formation of a conducting layer of graphite on the surface of the particles. Diamond powders of ASM-10/7 grade (synthetic diamond powder of 7–10 μm particle size) were irradiated at room temperature by an electron beam of 1 MeV energy to a total dose of 3.6×10^{22} eV cm^{-2} or by γ rays from a cobalt source to a dose of 4.8×10^9 rad. Growth took place from a 1 : 2 mixture of methane and hydrogen at a total pressure of 0.35 mmHg and temperatures of 950 and 1000 °C. The sample was heated to the experimental temperature and cooled back to room temperature in a stream of hydrogen. The aggregate quantites of deposited diamond and graphite were measured by the increase in weight, and the relative amount of graphite by the conductance of the layer.

These experiments showed that the electrical conductivity after the growth is higher, and the increase in weight is lower, for irradiated diamond powders than for powders used without previous irradiation. This suggests a strong deposition of graphite on the irradiated powder, evidently due to an increase in the rate of nucleation of graphite in the presence of surface defects. The dependence of the conductivity on the growth time shows that irradiation of the powder increases the rate of formation of non-diamond carbon but does not cause marked graphitisation of the existing surface. Thus the imperfections in the diamond crystal lattice weaken the orienting effect of the surface forces leading to auto-epitaxial growth of the diamond crystal, and favour the formation of the stable carbon phase (graphite).

Methods used to free the grown diamond powder from graphite include gasification in hydrogen at 50 atm and 1000 °C, oxidation by atmospheric oxygen[2], and gasification by atomic hydrogen generated by a hot tungsten wire[10]. In a recently developed method the graphite is removed in the plasma of a glow discharge in air. The method relies on the difference between the activities of diamond and of graphite towards reactions with oxygen atoms and ions[11–13]. At low temperatures the difference between the specific rates of oxidation of diamond and graphite is five orders of magnitude. On raising the temperature the rate of oxidation of diamond in the air plasma is found to increase much faster than the rate of oxidation of graphite. The activation energy for the interaction of diamond with the air plasma is 46 kJ mole^{-1}, whereas that of graphite is 5.0 kJ mole^{-1}. At temperatures above 500 °C the activation energy for diamond increases because the interaction with molecular oxygen becomes appreciable. The nitrogen in the air plasma was shown (in separate experiments) to be almost inert at temperatures up to 800 °C.[11]

Exposure of the grown diamond powder to the air plasma completely removes the graphite from the surface, leaving a layer of grown diamond. The effective depth of penetration of the gasification reaction is determined mainly by the loss of active particles in the layer of already purified diamond. Similar results were obtained for the gasification of diamond and graphite in the plasma of a glow discharge in hydrogen[14]. This work has shown that atomic oxygen and atomic hydrogen are the main components of the gas mixture during its reaction with graphite.

Three growth rates can be defined in studies of the growth of diamond powders: $v_{\alpha\alpha}$ (the rate of growth of diamond on diamond), $v_{\beta\alpha}$ (the rate of growth of graphite on diamond), and $v_{\beta\beta}$ (the rate of growth of graphite on graphite). A suggested method[15] of determining these three rates is based on Kolmogorov's theory of the growth and merging of planar nuclei. According to the experimental results[15], at a methane pressure of 0.3–10.0 mmHg, 1 : 1 dilution with hydrogen, and 930 °C temperature the rates $v_{\alpha\alpha}$, $v_{\beta\alpha}$, and $v_{\beta\beta}$ are approximately in the ratio of 7 : 2 : 1. The quantity of diamond formed during the growth was determined[15] by gasification in a glow-discharge plasma.

Defect "healing" processes, and annealing of internal stresses, can take place during growth on diamond powders. A study[16] of the effect of over-growing in methane at temperatures up to 1600 °C on the crushing strength of diamond powders has shown that the thermal stability of the grown powder is increased by the treatment.

2. Mechanism of the Growth of Diamond on Seed Crystals

The kinetics of heterogeneous chemical reactions with formation of a new phase depend on the reactivity of the gas molecules and on the nature of the surface. The effect of the surface is two-fold. Firstly, the surface influences the kinetics of formation of the new phase through its molecular and valence forces. Formally this effect consists in a change in the energy of formation of the critical nucleus of the new phase (i.e. the nucleus capable of further growth). Secondly, the nature of the surface determines the collision frequency in the two-dimensional adsorption layer, and the frequency of encounters of "incident" molecules and atoms with sub-critical nuclei. This effect of the surface is expressed through the adsorption characteristics of the surface–gas system.

The diamond growth mechanism described below applies to systems without a super-equilibrium concentration of atomic hydrogen, in which the supersaturation is due exclusively

to a super-equilibrium concentration of methane. By analysing experimental results it was shown[17] that the rate of growth of diamond is the sum of two terms:

$$v_\alpha = k_{\alpha 1}(1-\theta_1-\theta_2)p_1 + k_{\alpha 2}\theta_2 p_1 \ , \qquad (1)$$

where θ_1 and θ_2 are the fractions of the surface occupied by methane and by hydrogen respectively, p_1 is the partial presssure of methane, $k_{\alpha 1}$ and $k_{\alpha 2}$ are the rate constants, b_1 and b_2 are the adsorption constants of methane and hydrogen respectively, and p_2 is the partial pressure of hydrogen. A theory of the growth of diamond was developed by using an adsorption equation of the Langmuir type in the form (for a binary mixture)

$$\theta_1 = \frac{p_1/b_1}{1+p_1/b_1+p_2/b_2}, \quad \theta_2 = \frac{p_2/b_2}{1+p_1/b_1+p_2/b_2} \ . \qquad (2)$$

The first term in the right-hand side of Eqn.(1) corresponds to the mechanism of direct addition on a part of the surface of the diamond seed crystal which is free from adsorbed molecules. The second term corresponds to the growth of diamond through the chemisorbed hydrogen.

We note that according to the physicochemical theory[18] of graphite growth the growth rate is given by the expression

$$v_\beta = k_{\beta_1}\theta_1^2 + k_{\beta_2}\theta_1 j_1 \ , \qquad (3)$$

where $k_{\beta 1}$ and $k_{\beta 2}$ are the rate constants and j is the flux of methane molecules per unit surface per unit time. Eqn.(3) satisfactorily describes the rate of growth of graphite at 800–1800 °C and methane pressures between 10^{-5} and 30 atm. The first term in Eqn.(3) describes the growth of graphite from the adsorbed two-dimensional gas, the second describes the growth by direct collisions. At low temperatures the graphite grows by the Langmuir mechanism, at high temperatures by the Rideal mechanism. Eqn.(3) was obtained by assuming that the formation of critical nuclei (nucleation step) is rate-limiting in the growth of graphite.

3. Growth of Diamond from Different Hydrocarbons and from Their Mixtures

The study of the growth of diamond from different hydrocarbons[19] is of interest for several reasons. Firstly, it had been suggested[20] that diamond can grow from the gas phase only in the presence of compounds whose decomposition produces methyl radicals. Secondly, the rate of growth of diamond in several hydrocarbons is higher than in methane. Lastly, the problem is of interest also in relation to the formation of natural diamonds outside the Earth's mantle.

In these experiments[19] the hydrocarbon pressure was varied between 10^{-2} and 1 mmHg, and helium was used as the carrier gas. Electrification effects were minimised by coating the quartz helix, the support, and the quartz pan of the MacBain balance with a thin layer of pyrolytic carbon. Diamond growth was confirmed by cleaning the seed powder in an air plasma after the growth: after removal of the non-diamond carbon the diffraction patterms of the samples showed only reflexions from the diamond lattice. Growth was at temperatures between 1000 and 1300 K. In all the hydrocarbons the rate of growth of diamond was directly proportional to the partial pressure of the hydrocarbon. Therefore the results can be described by the rate constant for a first-order reaction (g cm^{-2} $mmHg^{-1}$).

The activation energy for the growth of diamond was calculated[19] from the temperature dependence of the rate constant of the reaction. The lowest rate constant and the highest activation energy (80 kcal $mole^{-1}$) were obtained for the growth of diamond from methane, and the highest rate constant and lowest activation energy for the growth from acetylene. The straight-line kinetic plots for other hydrocarbons lie between those for methane and acetylene.

If these kinetic lines are extrapolated towards higher temperatures they all intersect at ~1400 K. This is the temperature above which diamond cannot be grown with the substrate and the gas at the same temperature[1,2,7,20] unless the gaseous medium is additionally activated (for example, by an electric discharge). At 1400 K and above only graphite grows on the diamond seed powder, completely suppressing the growth of diamond, because at these temperatures the rate constant for the growth of graphite from all the hydrocarbons becomes greater than the rate constant for the growth of diamond. We may assume that at high temperatures the orienting (auto-epitaxial) effect of the substrate on the formation of the new phase becomes weaker, allowing the carbon to crystallise in the stable form.

However, it should be possible in principle to obtain diamond at temperatures up to the spontaneous graphitisation temperature (~2000 K). An increase in temperature at constant total pressure in the system lowers the equilibrium partial pressure of methane over graphite and diamond, i.e. it increases the supersaturation. As a result the relative difference in the work of formation of the critical nucleus between diamond and graphite decreases, and the relative probability of the nucleation of diamond increases.

The growth of diamond from methane at high temperatures has been studied[21] by using laser heating. A diamond single crystal in a methane atmosphere was heated by the focussed radiation from a laser. The temperature of the crystal was measured by an optical pyrometer. After the growth the crystals were washed in boiling perchloric acid to remove graphite, and the remaining film was studied by reflection electron diffraction. The temperature range was 1300–2000 K, the pressure range of carbon-containing gases was 1–50 mmHg. The experiments with acetylene and ethylene gave only graphite layers. Growth from methane gave polycrystalline diamond films up to 3 μm thick. Structural studies showed that the films contain some highly dispersed graphite. The diamond and diamond–graphite films were prepared from methane at temperatures above 1600 K.

If the direct collision mechanism is applied to the crystallisation from a mixture of hydrocarbons, additivity of the reaction rates is always expected. The reaction rate is directly proportional to the flux of molecules to the surface of the seed crystal, which is linearly dependent on the partial pressure of the hydrocarbon (ignoring the changes in diffusion coefficient if the process is known to be activation controlled).

Additivity of the reaction rates was observed for the growth of graphite in methane–acetylene and ethane–ethylene mixtures[22,23]. However, deviations from additivity of the reaction rates were also noted[24,25] in the growth of diamond and of graphite, i.e. the growth rate of diamond and graphite from a mixture of hydrocarbons was not equal to the sum of the growth rates from the individual hydrocarbons at the same partial pressures. This is because in the growth of a new phase from adsorbed molecules the rate is proportional to the coverage of the surface, which in the case of a mixture of hydrocarbons is not (in general) equal to the sum of the coverages by the individual hydrocarbons. This interpretation is confirmed by experiments on the synthesis of diamond from methane–acetylene and ethane–ethylene mixtures[25] in which the growth rate of diamond from the mixtures was shown to be lower than the sum of the rates of growth from the separate gases. The apparent activation energy was a function of the composition of the mixture.

4. Effect of Added Hydrogen on the Growth of Diamond

The addition of hydrogen affects the growth of diamond from hydrocarbons in several ways. Firstly, the addition of hydrogen to the initial hydrocarbon lowers its rate of decomposition, and therefore also the rate of formation of the solid phase. Secondly, the dissociation of molecular hydrogen produces atomic hydrogen, which can gasify the graphite formed in the reaction. In the presence of a super-equilibrium concentration of atomic hydrogen the formation of graphite can be completely suppressed. According to the proposed mechanism, the rate of growth of diamond can be increased by diluting the hydrocarbon with hydrogen[26]. At temperatures above 1050 °C the rate of growth of diamond from methane–hydrogen mixtures is higher than from pure methane. Similar effects were found in ethane and propane. We can assume that the decrease in the growth rate of diamond from pure hydrocarbons caused by an increase in temperature is due to the preferential deposition of carbon in the graphite form. Dilution with hydrogen suppresses the formation of graphite by lowering the coverage of the surface with methane or methyl radicals. Under these conditions the rate of growth of graphite (on a graphite surface) is strongly lowered.

Experiments on diamond growth on an ASM-10/7 powder from methane–hydrogen mixtures and from pure methane at 1000 °C have been reported[26]. Growth was stopped at a prescribed value of the electrical conductivity of the powder, i.e. for a constant amount of graphite in the product. The weight of powder in all the experiments was the same (400 mg). We note from the results (Table 1) that for a fixed amount of deposited graphite the increase in weight of the diamond powder is greater when the methane is diluted with hydrogen than in the pure methane. On increasing the pressure the influence of added hydrogen on the growth rate of diamond is found to decrease.

Increase in mass (Δm) of the new phase during growth on a diamond powder from methane and its mixtures with hydrogen[26] (τ is the duration of the experiment, $\varkappa$ is the conductivity).

p_{CH_4}, mmHg	p_{H_2} mmHg	Δm, mg	τ, min	$10^{-3}\varkappa$, arbitrary units
0.03	0	0.12	45	
0.03	0.27	0.72	153	
0.30	0	0.80	60	170
0.30	0.30	1.15	120	170

The growth rate of diamond from hexane and from cyclohexane, and from their mixtures with hydrogen, has been found[19] to be independent of the degree of dilution (up to a ratio of 1:19) for a partial pressure of the hydrocarbon of 0.03 mmHg. In general the effect of dilution with hydrogen on the growth of diamond and graphite depends on the total and on the partial pressures, and on the temperature of the synthesis. However, dilution with hydrogen always lowers the rate of growth of graphite more markedly than that of diamond, owing to the difference in growth mechanism between the stable and the metastable carbon phase.

5. Fractionation of the Stable Carbon Isotopes

The forms of carbon found in nature as minerals contain a well defined ratio of the stable isotopes ^{12}C and ^{13}C. Without bringing the geochemical side of the problem into the discussion we can nevertheless note that diamonds are "heavier" than natural graphite in isotopic composition, i.e. they contain a greater proportion of the heavier ^{13}C isotope. Furthermore, in the kimberlite pipes the diamonds are isotopically "heavier" than the carbonates in the surrounding minerals. A study[27] of the fractionation of the carbon isotopes during the growth of diamond and graphite from methane has confirmed that the grown diamond is enriched in the heavier ^{13}C isotope whereas the graphite is enriched in the ^{12}C isotope.

The thermodynamic isotope effect is probably irrelevant here, since at 1000 °C (the temperature of the synthesis) its separation coefficient[28] is only 1.002 whereas the experimental value[27] is 1.025. The extent of separation of the stable carbon isotopes is strongly influenced by the rate of crystallisation. At very low or very high rates of crystallisation no separation is observed. The separation can be interpreted in terms of the mechanism of growth of diamond and graphite. The diamond surface is covered with a layer of chemisorbed hydrogen. Therefore one of the steps in the addition of a carbon atom to the diamond lattice is the formation of a $CH_4 \cdot H$ complex, whereas the growth of graphite involves mainly methyl radicals (as has been shown by extensive work[3]).

The separation coefficient can be equated (approximately) to the ratio of the reaction rates for the two isotopic forms[28]:

$$\alpha = \frac{k_1}{k_2} = \frac{s_1 s_2^{\neq}}{s_1^{\neq} s_2} \left(\frac{\mu_2}{\mu_1}\right)^{1/2},$$

where k_1 and k_2 are the rate constants of the reactions for the two isotopic forms, s_1 and s_2, $s_1^{\neq}$ and $s_2^{\neq}$ are the symmetry numbers for the isotopic forms of the compounds and of the transition complexes, and μ_1 and μ_2 are the reduced masses of the isotopic forms. Calculations by the above formula give $\alpha(CH_4 \cdot H) \approx 1.025$ and $\alpha(CH_3) \approx 0.975$, in good agreement with the largest experimentally observed[27] separation coefficients of the stable carbon isotopes.

The discussion so far has dealt exclusively with diamond and graphite. However, many other phases are present in the carbon system[29], and could be formed during the pyrolysis of hydrocarbons. Cubic carbon and alpha-carbyne have been observed[30] during the growth of diamond on powders from methane.

III. PREPARATION OF DIAMOND LAYERS AND CRYSTALS

1. Chemical and Plasma-chemical Methods of Preparing Diamond Layers and Crystals

As was shown above, the main problem in the synthesis of diamond is not organising the formation of the diamond solid phase but preventing the deposition of carbon in its stable form (graphite). Therefore all the studies of the growth of large and thick diamond films are essentially developments of methods for removing graphite and preventing its formation.

In the chemical methods this is achieved by gasifying the graphite with atomic hydrogen and with the radicals formed by activating the gaseous medium. In the first successful method of growing diamond single crystals (the pulse method[1]) the graphite nuclei formed on the surface of the seed crystals

were "re-absorbed" (gasified) in the periods between two pulses, when their diameter was still subcritical. The method gave not only monocrystalline diamond films up to 10 μm thick but also filamentary and isometric diamond crystals.

Diamonds have been grown[31,32] in a methane–hydrogen mixture activated by a glow discharge. Excitation of the electrical discharge brings the gas mixture into a strongly non-equilibrium state, with a concentration of atomic hydrogen well above the equilibrium value for the given temperature. This atomic hydrogen can interact very actively with the graphite. If a layer of graphite is previously deposited on the surface of the diamond seed crystal it is possible to remove this layer and then begin to grow a diamond layer on the clean seed surface by this method. At first only natural diamonds in the octahedral habit were used as substrates in these experiments. It was shown that a thin film of diamond grows initially in the same orientation as the substrate. This is followed by a fully mis-oriented diamond layer, and lastly by diamond layers with a rhombododecahedral texture axis. This change in orientation suggests that at high supersaturations the effect of the substrate is not very marked. Polycrystalline diamond films were deposited on silicon, molybdenum, and rhenium by the same method.

Diamond layers on a diamond substrate (and also on tungsten and gold surfaces) have been prepared by chemical transport reactions[33,34]. The method also gave separate single crystals of diamond up to 50 μm in diameter on metallic substrates[35].

The properties of diamond films prepared by chemical reactions are identical to those of natural single crystals of diamond. Unlike the diamond films deposited from ionic and atomic beams, the chemically deposited films have a high graphitisation temperature. This is obviously due to their higher crystallinity, resulting from the higher synthesis temperatures used in the chemical methods.

In the plasma-chemical methods the plasma acts both as a source of carbon and as a source of ions, which bombard the surface of the growing crystal. The ions (for example, hydrogen) and the radicals formed in the plasma can remove non-diamond forms of carbon by chemical reaction or by sputtering. The first plasma-chemical synthesis of diamond was reported in Ref. 36: a black layer of carbon, with a surprisingly high hardness, was found on the cathode when a glow discharge was struck under certain conditions in an atmosphere of gaseous hydrocarbons. A layer several μm thick was obtained from a glow discharge in acetylene. Laue diffraction patterns from separate regions of the layer, which were easily recognised, indicated a cubic structure, and the Debye diagrams clearly showed two strong diamond lines but no strong graphite lines.

The electrical conductivity and the optical absorption of films prepared by the decomposition of acetylene in a direct current glow discharge at 25–375 °C have been studied[37]. The electrical conductivity of the films covers a range of 11 orders of magnitude, depending on the growth temperature. The width of the energy gap, calculated from optical absorption data, lies between 0.9 and 2.1 eV and decreases as the deposition temperature is raised. The films become graphitic[37] at temperatures above ~425 °C.

Semiconducting films of hydrogenated amorphous carbon obtained by this method were doped with boron and phosphorus during their growth[38]. Diamond crystals of various shapes (polyhedra, platelets, needles) have been obtained[39] from a plasma excited in a low pressure of aliphatic hydrocarbons by a high-voltage d.c. or a.c. (10^7 Hz frequency) source.

The pulsed crystallisation of diamond and diamond-like carbon has been described[40], using either the gas and the cathode material or the cathode material alone as the source of material for the crystallisation. In either case the carbon is present as excited atoms or ions. Chemical reaction takes place during the expansion of the plasma, when the high-temperature components should condense. The crystallisation products are deposited on a substrate (monocrystalline silicon, glass, polycrystalline aluminium) at 300 K. Layers up to 1 μm thick had good adhesion and an electrical resistance of ~10^8 Ω in the transverse direction. Diamond, lonsdalite, and other phases were detected in the deposited layers. When the substrate temperature was raised to 723 K an amorphous layer giving diffuse diffraction lines was obtained. Applying a potential of ±800 V to the sample did not affect the stucture or the properties of the deposited layers.

A study[41] by X-ray photoemission spectroscopy of films prepared by a high-frequency plasma in butane showed that diamond-like material is obtained at moderate applied power and low rates of deposition. However, the authors stress[41] that these layers are not true diamond material and should be called diamond-like.

2. Deposition of Diamond Layers from Atomic and Ionic Beams. Physical Methods

Physical methods have been used increasingly in recent years; they consist in the deposition of carbon on various (usually cooled) substrates from beams of fast carbon ions or atoms. Depending on the deposition conditions we can distinguish the condensation from atomic beams from that from ionic beams, and from flows of carbon plasma. The condensation from atomic beams uses a stream of atoms produced by cathodic sputtering of graphite electrodes. In contrast to the stream of carbon vapour produced by thermal evaporation or in an arc, in this case there are no polyatomic groups to act as nuclei for the growth of graphite. According to calculations[42] the average energy of the atoms is greater than 100 eV. The most characteristic feature of deposition from an atomic beam is the low temperature of the substrate (usually the temperature of liquid nitrogen). This, together with the low growth rates (up to 10 Å min^{-1}) and the associated low energy flux (~3×10^{-3} W cm^{-2}), ensures that the deposited layer is amorphous and homogeneous. These features also explain the stringent purity requirements on the starting materials and the need for ultra-high vacuum conditions (better than 10^{-9} mmHg).

In deposition from atomic beams the energy of the condensing atoms is difficult to control. This problem disappears when ionic beams or streams of carbon plasma are used for the deposition. It has been suggested[43] that the techniques and procedures previously used to prepare crystals of the stable modifications could be used also in the preparation of carbon condensates with the diamond structure. The basic assumption in this method is that the energy needed for the nucleation and growth of a thin layer can be supplied as kinetic energy of the condensing material rather than by heating the substrate. It is thought[43] that by using ion beam techniques both amorphous and crystalline carbon films can be prepared, and the deposited layer should be crystalline whereas its surface layers are amorphous, since not all the surface atoms have enough energy to migrate instantly to a crystalline region. The mobility of the surface atoms can be increased by adding inert gas atoms (for example, argon) to the stream of carbon atoms. This scheme was subsequently adopted in practical applications and called the double beam method[44].

As was pointed out above, the general considerations concerning the organisation of the crystal structure are equally applicable to diamond, but only under conditions which ensure the suppression of the stable modification of carbon (graphite). Therefore the conditions of the irradiation of the growing surface with accelerated atoms of carbon or of an inert gas should be chosen primarily with the aim of preventing the formation of non-diamond forms of carbon.

The importance of suppressing the formation of non-diamond forms during the crystallisation of diamond from an ionic beam has been stressed in a paper[45] describing studies of the structural and other properties of condensates prepared by this method. The energy of the carbon and argon ions (when argon was used as a carrier) was ~50 eV. The structure of the resulting layers was determined by X-ray diffraction. The technique needed long exposure times and layers at least 2 μm thick. In many cases definite but weak diamond reflexions were observed. Much thinner (100 Å) films were studied by transmission high-energy electron diffraction, in selected areas containing relatively large crystals. In this way diffraction patterns for both monocrystalline and polycrystalline material were obtained. Bright-field photography shows many monocrystalline regions with a fourth-order symmetry axis extending over cross-sections of 1–5 μm. We note that the diffraction patterns include reflexions which are forbidden for diamond, corresponding to the interplanar spacings $d_{100} = 3.57$ Å and $d_{110} = 2.52$ Å. Some diffraction patterns show sharp reflexions from the (211) planes ($d_{211} = 1.44$ Å). The presence of forbidden reflexions is attributed[45] (by analogy with the diffraction patterns of natural diamonds) to the regular occurrence in the lattice of atoms of the inert gas used as a carrier, giving rise to superlattices. The preferred (111) orientation of the layers suggests that the growth rate of the crystallites is a maximum in this direction. This was ascribed to the greater stability towards graphitisation of the (111) plane in a diamond crystal.

These results have been confirmed by a study[46] of the dependence of the phase composition and structure of the deposited layers on the composition of the beam, the energy of the ions, and their density in the beam. By using a high-current mass spectrometer with magnetic mass separation of the ions it was possible to deposit layers from spectrally pure beams of ions of the required mass and 30–100 eV energy under ultra-high vacuum conditions (5×10^{-9} mmHg). Deposition on KCl crystals gave a preferential (≥80%) orientation of the crystallites in the (100) direction, corresponding to the orientation of the substrate, but a small number of samples showed a (110) orientation. In the whole energy range (30–100 eV) the diamond phase was formed at current densities between a few hundredths and a few units of mA cm^{-2}.

It has been pointed out[47] that in the crystallisation of diamond the situation is entirely different from the formation of stable crystals (for example, silicon) not only because diamond is metastable under the conditions of deposition of the phase but also because of the possibility of irreversible graphitisation of the diamond by radiation-induced defects. In an attempt[47] to prepare epitaxial layers on diamond it was shown that in growth from low-energy ion beams even slight surface imperfections can have a strong effect on the reproducibility of the results. The best results were obtained by deposition with ions of ~900 eV energy on carefully cleaned diamond plates heated to 700 °C. Layers a few μm thick prepared at rates of deposition of a few tenths of μm per hour invariably contained inclusions of low-density carbon. The formation of these inclusions during the epitaxial growth of diamond determines the upper limit of thickness to which a monocrystalline layer can be grown in practice.

A method of preparing diamond-like layers using two ion sources has been described[44,48]. In this case one ion source generates argon ions with an energy of up to 10 keV at current densities of 0.5–1 mA cm^{-2}, which sputter the carbon target, giving a growth rate of 5–10 Å min^{-1} of the carbon layer on the substrate. The layers have properties similar to those of ordinary thermally deposited layers unless they are simultaneously irradiated with argon ions from another source at energies between 0 and 2 keV and current densities between 0.2 and 5 mA cm^{-2}. The growth rate of the layer can be controlled between 5 and 10 Å min^{-1} (allowing for back-sputtering) by suitably choosing the current density and energy of the ions. Layers prepared in this way have properties very different from those of thermally deposited layers. In a variant of this method of deposition[49] the carbon source was a diamond powder evaporated by laser heating.

A method of preparing carbon coatings from a carbon plasma has been described[50–55]. A cooled metallic substrate is located in a plasma flow generated by an arc, and connected to a d.c. potential source negative with respect to the plasma, or to a high-frequency a.c. potential. The mechanical, electrophysical, and structural properties of the resulting condensates were studied by various methods.

To explain the formation of a diamond structure under these conditions it was suggested[53] that high temperatures and pressures (corresponding to the stability region of diamond in the carbon phase diagram) may be produced locally when the substrate is bombarded with high-energy ions and atoms. Metastable crystalline forms, including diamond, are formed by the removal of energy from the "hot" points as a result of the substrate cooling. A similar explanation[48] of the mechanism uses a dynamic concept of the synthesis of diamond and gives a rough estimate of the temperatures and pressures generated by the impact of the accelerated particles on the growth surface.

The dependence of the density of carbon condensates on the initial energy of the carbon ions has been studied[54]. For ion energies of ~50 eV the density of the condensate (4.1 g cm^{-3}) is higher than that of diamond. This large increase in density is attributed[55] to the presence of diamond and a new (C_8) carbon phase in the condensate for ion energies in the range 40 eV $\leq \varepsilon \leq$ 70 eV. The nature of the structure-formation processes under ion bombardment is discussed[54] by the following qualitative model of the dependence of the density of the condensate on the ion energy: at energies greater than 10 eV the ion can penetrate into the condensate to a depth of several interatomic distances, causing local rearrangements of the structure and the formation of point defects (mainly interstitials and vacancies). The accumulation of vacancies in the dense phases at $\varepsilon > 70$ eV and the consequent conversion into more open phases explain the decrease in density of the layers.

IV. HOMOGENEOUS FORMATION OF DIAMOND IN THE GAS PHASE

1. Theoretical Discussion of the Homogeneous Nucleation of Metastable Carbon Phases

The homogeneous nucleation of diamond in the gas phase and subsequent growth on the resulting seeds produces other forms of carbon as well as diamond. At high supersaturations the work of formation of the critical nucleus of the new phase becomes comparable to the quantity $kT = \Theta$ (a measure of the energy of the thermal motion of the atoms and molecules). However, the exact theory of nucleation is limited to low[56–58] or intermediate[59] supersaturations. At

high supersaturations some difficulties arise from the need to consider entities consisting of a small number of atoms or molecules. Therefore the analysis of the rates of nucleation at high supersaturations is only qualitative. It has been shown[60-62] that an increase in supersaturation increases the probability of nucleation of diamond as compared with graphite. A more detailed analysis is given in Ref.63.

The rate of homogeneous nucleation from the vapour is defined[56-58] as the number of critical nuclei formed in unit volume per unit time:

$$I = \frac{\alpha p^2}{\rho} \cdot \frac{(\sigma m)^{1/2}}{\Theta^2} \exp\left(-\frac{U}{\Theta}\right) , \quad (4)$$

where p is the vapour pressure, σ is the surface tension, ρ is the density of the condensed phase, m is the mass of the atom (or molecule), U is the work of formation of the critical nucleus, and α is the condensation coefficient. The rate of nucleation at constant pressure has a maximum at a value of Θ given by the condition $(\partial I/\partial\Theta)_p = 0$. Ignoring the dependence of the surface energy on the curvature of the surface and assuming a constant condensation coefficient we obtain

$$(\partial U/\partial\Theta)_p - U/\Theta + 2 = 0 . \quad (5)$$

The work of formation of the critical nucleus in the classical nucleation theory is

$$U = \frac{16}{3} \frac{\pi\sigma^3 v^2}{\Theta^2 \ln^2 (p/p_e)} , \quad (6)$$

where p_e is the pressure of the vapour in equilibrium with the condensed phase, and v is the volume occupied by each particle in the condensed state. To a first approximation we can use an expression of the type of

$$p_e = A \exp(-H/\Theta) , \quad (7)$$

where H and A are the heat of evaporation and a constant factor respectively, and have different values for the different allotropic forms. From Eqn.(6) we now obtain

$$\frac{U}{\Theta}\left[1 - \frac{^2/_3 H}{\Theta \ln p/A + H}\right] = \frac{2}{3} . \quad (8)$$

In general Eqn.(8) gives a fourth-power equation for Θ. However, because of the approximations in the analysis, the treatment has been simplified[63] by considering only the case of $p = A$, when the supersaturation is $\Theta = \infty$. This gives

$$\Theta_m = U/2 .$$

Thus different phases will have maximum rates of nucleation at different temperatures (assuming constant pressure). Each phase has a supersaturation for which its rate of nucleation is a maximum. The maximum rates of nucleation of the different phases occur at different Θ values and have different magnitudes. Increasing the surface energy lowers the maximum. The published analysis[63] is applicable to many systems as well as to the carbon system. An analysis of Eqn.(8) indicates that the probability of formation of metastable phases increases with pressure.

2. Experimental Studies of the Homogeneous Nucleation of Diamond

The homogeneous nucleation (and growth) of diamond in the gas phase has been studied by using an electrical discharge in hydrocarbon vapours[64], by explosions in carbon-containing substances[65,66], and by laser heating[62,67].

By using the energy of an explosion the synthesis of diamond is carried out (in spite of the high dynamic pressures) at a temperature higher than the equilibrium temperature of the graphite–diamond phase transition, i.e. the process takes place in the thermodynamic stability region of graphite. This method gives very small (up to 1000 Å) diamond particles, often coloured. All the diamond crystals obtained by this method are defective and stressed.

The homogeneous synthesis of diamond has been achieved under cleaner conditions by using laser heating[63]. Liquid hydrocarbons were placed in a burette with a capillary tip. The radiation of an LG-25 infrared laser was focussed on the falling drop of octane, nonane, hexane, and other hydrocarbons. By varying the drop height (from the tip of the capillary to the focus of the lens) the time of interaction of the laser beam with the drop could be varied. The diameter of the drop was determined by the bore of the capillary. The repetition frequency of the drops was controlled by the air pressure in the burette. When the drop crossed the laser beam it was violently evaporated, and radiation was absorbed by the vapour. The vapour was strongly heated, and an aerosol containing both liquid and solid particles was formed round the drop. Some of the particles were entrained by the falling drop and collected in the cell. Samples for the structural studies were taken either directly from the aerosol on suitably located substrates or from the liquid residue.

Particles up to 20 μm in diameter (usually consisting of groups of much smaller particles) were observed in the electron microscope[63]. The average size of the particles was ~0.1 μm, their shape varied from irregular to accurately spherical. Structural studies (by X-ray and electron diffraction) identified the solid particles as diamond, graphite, and carbyne. After removal of the graphite by gas etching the solid phase contained only diamond and carbyne.

The electron diffraction patterns obtained from the diamond particles suggest the presence of strong stresses and a block structure, indicated by the line broadening. Most of the spherical particles were "amorphous to electrons", though in some cases diffraction patterns from a highly distorted diamond structure, close to amorphous, were obtained. We should note that in this work[63] particles of the hypothetical forms of carbon proposed in Ref.55 were observed (for example, C_8). The exact identification of the hypothetical forms of carbon, and their place in the carbon phase diagram, are still unsolved problems. The high stresses and defect densities in diamond particles obtained by homogeneous synthesis in the gas phase are probably due to the high growth rates under these conditions. Thus in the laser method the growth time of the diamond particle is 10^{-3} s, and in the explosion method 10^{-6} s.

An important requirement for the presence of diamond among the products of the homogeneous synthesis is rapid cooling of the resulting particles[63,65]. It has also been shown[68] that rapid cooling of polycrystalline graphite from high temperatures can induce the conversion of graphite crystals into carbyne and diamond. In these experiments[68] the temperature of the graphite did not exceed 3000 K. The mechanism of the solid-phase graphite–diamond transition at atmospheric pressure is not self-evident. It may involve compression of the graphite crystallites during rapid cooling. It has been shown[69] that the bonds of the graphite lattice are broken in molten carbon. Fast cooling may "freeze" the states which exist at high temperatures.

3. Some Consequences of the Homogeneous Nucleation of Diamond

These results may help to explain the origin of the natural diamonds found in kimberlite pipes. The diamonds could have been nucleated by local explosions, with gaseous hydrocarbons as the source of carbon. Evolution of hydrocarbons

occurs (as it did at the relevant time) in practically all the pipes containing diamonds. However, calculations show[70] that the strength of the rocks is insufficient to contain the pressures corresponding to the region of thermodynamic stability of diamond.

Very interesting reports of the possible existence of very fine diamond particles in interstellar space have been published[71]. Carbon is the most probable constituent of cosmic dust, and carbon particles could be formed from matter ejected by stars. The carbon–nitrogen cycle, formulated by Bethe in 1939, is a source of thermonuclear energy in hot stars. When matter is ejected from a star and rapidly cooled the carbon vapour can condense into very small particles. At this stage various forms of solid carbon can also be formed: graphite, carbyne, diamond, and others. The nucleation of solid carbon takes place in the presence of hydrogen. We have shown[1] that hydrogen can markedly lower the growth rate of graphite, but its effect on the growth rate of diamond from hydrocarbons is much smaller. The difference in the rates of interaction with different carbon phases is even greater with atomic hydrogen. A study[14] of the interaction of atomic hydrogen generated by a glow discharge with graphite and diamond showed that up to 500 °C the gasification of diamond by atomic hydrogen is negligible, whereas the rate of gasification of graphite is substantial. This allows complete gasification by atomic hydrogen of the graphite particles formed by the condensation of carbon atoms from the plasma of stellar matter.

The diffuse luminescence of the Galaxy is said[71] to be incompatible with the hypothesis that interstellar dust consists of particles of graphite or of graphite covered with ice. It is suggested[71] that the dust probably consists of diamond particles up to 0.1 μm in diameter. The lack of direct experimental data on the homogeneous nucleation of diamond was noted with regret, and it was stated that the diamonds in the Galaxy must have a high concentration of defects (as has been found in the experiments discussed above). The phase composition of the carbon in interstellar dust could have a direct bearing on the conversion of the initially atomic hydrogen in interstellar matter almost totally into molecular hydrogen[72].

The recombination of two hydrogen atoms into a molecule requires the presence of a third particle, which could be a particle of interstellar dust. Many different organic compounds, containing hydrogen, nitrogen, oxygen, and other atoms, are found in dense interstellar clouds. When considering the evolution of such a cloud we must allow for the fact that the reactivity of graphite towards atomic hydrogen and oxygen is very high, whereas that of diamond is negligibly small. The reaction of hydrogen atoms with graphite at low pressures can produce various radicals and compounds, some of which have been observed by radio-astronomical methods in interstellar space (see Table 1 of Ref.72). Therefore the formation of organic compounds in interstellar clouds may be due (at least, partially) to the gasification of graphite particles in the interstellar dust. On the other hand the recombination of hydrogen atoms could take place on diamond particles, whose presence in interstellar space seems likely.

REFERENCES

1. B.V.Deryagin and D.V.Fedoseev, Uspekhi Khim., 1970, **39**, 1661 [Russ.Chem.Rev., 1970(9)].
2. B.V.Deryagin and D.V.Fedoseev, "Rost Almaza i Grafita iz Gazovoi Fazy" (Growth of Diamond and Graphite from the Gas Phase), Izd.Nauka, Moscow, 1977, p.115.
3. G.N.Bezrukov, V.P.Butuzov, and M.I.Samoilovich, "Sinteticheskii Almaz" (Synthetic Diamond), Izd. Nedra, Moscow, 1976, p.118.
4. B.V.Deryagin and D.V.Fedoseev, Izv.Akad.Nauk SSSR, Ser.Khim., 1979, p.1184.
5. D.V.Fedoseev, S.P.Vnukov, and B.V.Deryagin, in "Poverkhnostnye Sily v Tonkikh Plenkakh" (Surface Forces in Thin Films), Izd.Nauka, Moscow, 1979, p.206.
6. B.V.Deryagin, D.V.Fedoseev, and K.S.Uspenskaya, Zhur.Fiz.Khim., 1973, **47**, 24 [Russ.J.Phys.Chem., 1973(1)].
7. S.P.Chauhan, J.C.Angus, and N.C.Gardner, J.Appl.Phys., 1976, **47**, 4746.
8. P.A.Tesner, E.V.Denisova, M.M.Polyakova, and T.V.Tekunova, Khim.Tverdogo Topliva, 1976(4), 127.
9. D.V.Fedoseev, G.N.Pirogova, and V.P.Varnin, Dokl.Akad.Nauk SSSR, 1974, **214**, 618.
10. J.C.Angus, N.C.Gardner, D.J.Poferl, T.Dyble, and T.J.N.Pei Sung, in "Sinteticheskie Almazy v Promyshlennosti" (Synthetic Diamonds in Industry), Izd.Naukova Dumka, Kiev, 1974, p.30.
11. D.V.Fedoseev and Yu.N.Tolmachev, Izv.Akad.Nauk SSSR, Ser.Khim., 1977, 931.
12. D.V.Fedoseev, Yu.N.Tolmachev, and V.L.Bukhovets, Dokl.Akad.Nauk SSSR, 1979, **247**(6), 1427.
13. D.V.Fedoseev, Yu.N.Tolmachev, V.L.Bukhovets, and S.P.Vnukov, Zhur.Fiz.Khim., 1979, **53**, 2129 [Russ.J.Phys.Chem., 1979(8)].
14. D.V.Fedoseev and Yu.N.Tolmachev, Izv.Akad.Nauk SSSR, Ser.Khim., 1979, 1180.
15. S.P.Vnukov, B.A.Anikin, and D.V.Fedoseev, Izv. Akad.Nauk SSSR, Ser.Khim., 1980, 983.
16. B.A.Anikin, S.P.Vnukov, M.A.Voronkin, B.V.Deryagin, N.V.Novikov, and D.V.Fedoseev, Dokl.Akad.Nauk SSSR, 1980, **255**, 1362.
17. D.V.Fedoseev, S.P.Vnukov, and B.V.Deryagin, Zhur.Fiz.Khim., 1976, **50**, 2751 [Russ.J.Phys.Chem., 1976(10)].
18. D.V.Fedoseev, S.P.Vnukov, and V.P.Varnin, Dokl. Akad.Nauk SSSR, 1974, **218**, 399.
19. K.S.Uspenskaya and D.V.Fedoseev, Izv.Akad.Nauk SSSR, Ser.Khim., 1979, 2805.
20. US P.3 030 187, 3 030 188 (1962).
21. D.V.Fedoseev, I.G.Varshavskaya, A.V.Lavrent'ev, and B.V.Deryagin, Izv.Akad.Nauk SSSR, Ser.Khim., 1977, 928.
22. P.A.Tesner, "Obrazovanie Ugleroda iz Gazovoi Faze" (Formation of Carbon from the Gas Phase), Izd. Khimiya, Moscow, 1972, p.68.
23. E.V.Denisevich and P.A.Tesner, Dokl.Akad.Nauk SSSR, 1973, **212**, 660.
24. D.V.Fedoseev, R.K.Chuzhko, and A.G.Grivtsov, "Geterogennaya Kristallizatsiya iz Gazovoi Faze" (Heterogeneous Crystallisation for the Gas Phase), Izd.Nauka, Moscow, 1978, p.15.
25. D.V.Fedoseev and K.S.Uspenskaya, Zhur.Fiz.Khim., 1977, **51**, 47 [Russ.J.Phys.Chem., 1977(1)].
26. D.V.Fedoseev, K.S.Uspenskaya, V.P.Varnin, and S.P.Vnukov, Izv.Akad.Nauk SSSR, Ser.Khim., 1978, 1252.
27. D.V.Fedoseev, E.M.Galimov, V.P.Varnin, V.S.Prokhorov, and B.V.Deryagin, Dokl.Akad.Nauk SSSR, 1971, **201**, 1149.
28. E.M.Galimov, "Geokhimiya Stabil'nykh Izotopov Ugleroda" (Geochemistry of the Stable Carbon Isotopes), Izd.Nedra, Moscow, 1968, p.35.

29. D.V.Fedoseev, N.V.Novikov, A.S.Vishnevskii, and I.G.Teremetskaya, "Almaz. Spravochnik" (Diamond Handbook), Izd.Naukova Dumka, Kiev, 1981. p.78.
30. D.V.Fedoseev, B.V.Deryagin, V.P.Varnin, S.P.Vnukov, I.G.Teremetskaya and N.D.Polyanskaya, Dokl.Akad.Nauk SSSR, 1976, **228**, 371.
31. B.V.Deryagin, D.V.Fedoseev, V.P.Varnin, A.E.Gorodetskii, A.P.Zakharov, and I.G.Teremetskaya, Zhur.Eksper.Teor.Fiz., 1975, **69**, 1250.
32. V.P.Varnin, B.V.Deryagin, D.V.Fedoseev, I.G.Teremetskaya, and A.N.Khodan, Kristallografiya, 1977, **22**, 893.
33. B.V.Deryagin, B.V.Spitsyn, L.L.Builov, A.A.Klochkov, A.E.Gorodetskii, and A.B.Smol'yaninov, Dokl.Akad.Nauk SSSR, 1976, **231**, 333.
34. B.V.Deryagin, B.V.Spitsyn, L.L.Builov, G.V.Aleksandrov, G.G.Aleksandrov, V.P.Repkov, A.E.Gorodetskii, and Z.E.Sheshenina, Dokl.Akad. Nauk SSSR, 1979, **244**, 388.
35. B.V.Deryagin, B.V.Spitsyn, A.E.Aleksenko, A.E.Gorodetskii, A.P.Zakharov, and R.I.Nazarova, Dokl.Akad.Nauk SSSR, 1973, **213**, 1059.
36. H.Schmellenmeir, Z.phys.Chem., 1956, **205**, 349.
37. B.Meyerson and W.Smith, J.Non-cryst.Solids, 1980(35–36), 435.
38. B.Meyerson and F.W.Smith, Solid State Comm., 1980, **34**, 531.
39. R.Manya, R.Pampyukh, and L.Stoberski, Sverkhtverdye Materialy, 1981(3), 36.
40. M.Sokolowski, A.Sokolowska, B.Gokieli, A.Michalski, A.Rusek, and Z.Romanowski, J.Crystal Growth, 1979, **47**, 421.
41. S.Berg and L.P.Anderson, Thin Solid Films, 1979, **58**(1), 117.
42. V.M.Golyanov and V.B.Grigor'ev, Dokl.Akad.Nauk SSSR, 1974, **215**, 1985.
43. S.Aisenberg and R.Chubot, J.Appl.Phys., 1971, **42**, 2953.
44. K.Bewilogua, H.-J.Erler, H.Shearer, S.Weissmantel, and B.Winde, "Materialy Pyatoi Vsesoyuznoi Konferentsii po Vzaimodeistviyu Atomnykh Chastits s Tverdym Telom" (Proceedings of the Fifth All-Union Conference on the Interaction of Atomic Particles with Solids), Minsk, 1979, p.157.
45. E.G.Spencer, P.H.Schmidt, D.C.Joy, and F.J.Sansalone, Appl.Phys.Letters, 1976, **29**, 118.
46. E.F.Chaikovskii, V.M.Puzikov, and A.V.Semenov, Kristallografiya, 1981, **26**, 219.
47. I.H.Freeman, W.Temple, and G.A.Gard, Nature, 1978, **275**, 634.
48. C.Weissmantel, K.Bewilogua, D.Dietrich, H.-J.Erler, H.-J.Hinneberg, Klose, W.Nowick, and G.Reisse, Thin Solid Films, 1980, **72**, 19.
49. S.Fujimori and K.Nagai, Japan J.Appl.Phys., 1981, **20**(3), 194.
50. N.N.Matyushenko, V.E.Strel'nitskii, A.A.Romanov, and V.P.Tolok, Dokl.Akad.Nauk UkrSSR, Ser.A, 1976, 459.
51. V.S.Strel'nitskii, S.I.Vakula, N.N.Matyushenko, B.L.Timan, A.M.Pshisukha, and V.E.Nikolova, "Sinteticheskie Almazy" (Synthetic Diamonds), Izd.Naukova Dumka, Kiev, 1977, No.4, p.14.
52. V.E.Strel'nitskii, I.I.Aksenov, S.I.Vakula, V.G.Padalka, and V.A.Belous, Zhur.Tekh.Fiz. Pis'ma, 1978, **4**, 1355.
53. V.E.Strel'nitskii, V.G.Padalka, and S.I.Vakula, Zhur.Tekh.Fiz., 1978, **48**, 377.
54. A.S.Bakai and V.E.Strel'nitskii, Zhur.Tekh.Fiz., 1981, **51**, 2414.
55. N.N.Matyushenko, V.E.Strel'nitskii, and V.A.Gusev, Zhur.Eksper.Teor.Fiz.Pis'ma, 1979, **30**, 218.
56. Ya.I.Frenkel', "Kineticheskaya Teoriya Zhidkostei" (Kinetic Theory of Liquids), Izd.Akad.Nauk SSSR, Moscow, 1945.
57. Ya.B.Zel'dovich, Zhur.Eksper.Teor.Fiz., 1942, **12**, 525.
58. B.V.Deryagin, Zhur.Eksper.Teor.Fiz., 1973, **9**, 471.
59. B.V.Deryagin and A.V.Prokhorov, Dokl.Akad.Nauk SSSR, 1972, **207**, 1311.
60. D.B.Fedoseev and B.V.Deryagin, Zhur.Fiz.Khim., 1979, **53**, 752 [Russ.J.Phys.Chem., 1979(3)].
61. D.V.Fedoseev, B.V.Deryagin, V.P.Varnin, and G.A.Sokolina, Dokl.Akad.Nauk SSSR, 1979, **247**, 1201.
62. D.V.Fedoseev, A.V.Lavrent'ev, and B.V.Deryagin, Kolloid.Zhur., 1980, **42**, 711.
63. D.V.Fedoseev, B.V.Deryagin, I.G.Varshavskaya, A.V.Lavrent'ev, and V.V.Matveev, Zhur.Eksper. Teor.Fiz., 1981, **80**(1), 413.
64. D.V.Fedoseev, B.V.Deryagin, A.V.Lavrent'ev, I.G.Varshavskaya, V.V.Matveev, and V.K.Ershov, Sverkhtverdye Materialy, 1981(1), 5.
65. G.I.Savvakin, "Almazy i Sverkhtverdye Materialy" (Diamonds and Super-hard Materials), Izd.NIIMASh, Moscow, 1981, No.4, p.1.
66. V.I.Trefilov and G.I.Savvakin, Dokl.Akad.Nauk SSSR, 1979, **246**, 1115.
67. D.V.Fedoseev, B.V.Deryagin, I.G.Varshavskaya, and A.V.Lavrent'ev, Zhur.Eksper.Teor.Fiz.Pis'ma, 1980, **32**, 7.
68. D.V.Fedoseev, I.G.Varshavskaya, A.V.Lavrent'ev, and B.V.Deryagin, Zhur.Eksper.Teor.Fiz.Pis'ma, 1981, **33**(8), 414.
69. A.R.Ubbelohde and F.A.Lewis, "Graphite and its Crystalline Compounds" (Translated into Russian), Izd.Mir, Moscow, 1965.
70. V.G.Vasil'ev, V.V.Koval'skii, and N.V.Cherskii, "Proiskhozhdenie Almazov" (Origin of Diamonds), Izd. Nedra, Moscow, 1968, p.258.
71. W.C.Saslav and G.F.Gaustad, Nature, 1969, **221**, 160.
72. V.B.Leonas, Uspekhi Fiz.Nauk, 1981, **135**, 708.
73. P.A.Tesner, N.B.Golovina, A.E.Gorodetskii, and M.M.Polyakova, Khim.Tverdogo Topliva, 1976(1), 129.

Institute of Physical Chemistry of
the USSR Academy of Sciences,
Moscow