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How and why CVD diamond is formed: a solution of the thermodynamic paradox

W. PIEKARCZYK
Institute of Physics, Polish Academy of Sciences, Al. Lotników 32/46, 02-668 Warszawa, Poland
E-Mail: piekar@ifpan.edu.pl

Diamond chemical vapour deposition (CVD) thought of as a crystal growth process, is a thermodynamic paradox because it violates fundamental principles of thermodynamics. The most astonishing violation is the experimental observation that CVD diamond can form in gaseous environments that are carbon under-saturated with respect to diamond. A new concept of CVD diamond formation that describes the process in terms of thermodynamics, without any violation of the latter, is presented. According to the present concept the diamond formation is a chemical process consisting in accretion of polymantane macromolecules. The process proceeds on surfaces of polymantane seed macromolecules which are identical to diamond crystals which have H-terminated surfaces. Chemical thermodynamics insist that the Gibb's energy of reaction describing the process, ΔG, has a large negative value for the process to be able to proceed. However, under certain conditions, the diamond CVD may not proceed even if $\Delta G \ll 0$, because the process may be kinetically hindered. Such a situation occurs at "low" temperatures at which the abstraction of hydrogen atoms from H-terminated diamond seed crystal surfaces by free hydrogen atom impact followed by the addition of new carbon atoms to the diamond lattice, is a rate-limiting step. The kinetic parameter determining the rate of this step is correlated with thermodynamic instability, *TI*, of H-terminated diamond seed crystal surfaces. Using ΔG and *TI* functions, one can derive correlations between the film-phase composition as well as the growth-rate and process variables. The dependencies predicted by the present model are in excellent agreement with reported experimental data. © *1998 Kluwer Academic Publishers*

1. Introduction

Chemical vapour deposition (CVD) of diamond, thought of as a crystal growth process is, from the thermodynamic point of view, a paradox because it contradicts fundamental principles of chemical thermodynamics. The most astonishing and most difficult to explain violation of thermodynamics is the experimental observation that CVD diamond can form in gaseous environments that are carbon under-saturated with respect to diamond [1]. Although the number of experimental data which support this observation is already large and is still growing, this observation gains the general acceptance only with difficulty. The following experimental results provide unquestionable evidence that, indeed, diamond is formed in gaseous environments that are carbon under-saturated with respect to diamond.

(a) In the so-called low-pressure solid-state source (LPSSS) experiments performed by Roy *et al.* [2–4] diamond was formed by the reaction of graphite with pure hydrogen that was activated to the state of microwave plasma. It is absolutely obvious that the gas phase was carbon under-saturated because it contained no carbon at all.

(b) Similarly, in the sequential diamond CVD experiments performed by the group of Stanford researchers [5], graphitic carbon deposited in the first stage by sputtering a graphite target was converted into diamond in the second stage by its reaction with atomic hydrogen that was created in pure hydrogen with the aid of a hot filament.

(c) Diamond was deposited under conditions under which graphite was simultaneously etched [6, 7]. The graphite etching indicates that the feeding gas phase was carbon under-saturated with respect to graphite. Because the chemical potential of carbon in diamond is higher than that in graphite, the carbon under-saturation for diamond was even greater than that for graphite.

From the thermodynamic point of view diamond etching but not diamond deposition should take place in gaseous environments that are carbon under-saturated with respect to diamond. Because of the above inconsistency, diamond CVD cannot be considered, to be a crystal growth process. This view is supported by the fact that diamond, contrary to other crystalline materials, is deposited at temperatures (typically in the 700–1000 °C range) which are not higher but, on the contrary, much lower than its Debye temperature (~2340 K).

Aimed at understanding the mechanism of deposition of metastable diamond, several theoretical diamond CVD models have been created. None of them, however, has received a general acceptance because all these models suffer from being inconsistent with at least some experimental results. Some of these models have attempted to explain the CVD diamond formation exclusively within the aid of kinetics, ignoring thermodynamics in order to avoid thermodynamics problems. To our understanding, however, a chemical process cannot proceed if it is not possible from the thermodynamics point of view, even though it is kinetically favoured. Kinetics should be pursued within thermodynamics and never go against thermodynamics [8].

In this paper we present a new concept of CVD diamond formation which enabled us to avoid the above-mentioned thermodynamic problems. According to our present concept, diamond CVD is not a physical process consisting in growth of diamond crystals, but a chemical process resembling, to some extent, polycondensation, consisting in accretion of macromolecules of polycyclic saturated hydrocarbons belonging to the family of organic compounds called the "cage molecules", the smallest representatives of which are, in growing order, adamantane (tricyclodecane $C_{10}H_{16}$), diamantane ($C_{14}H_{20}$), triamantane ($C_{18}H_{24}$) and so on [9]. The members of this family can be generally called polymantanes.

The proposed approach is not controversial because polymantane macromolecules are, in fact, identical with diamond single crystals the surfaces of which are H-terminated. It should be noted that, under ordinary conditions, surfaces of diamond crystals are terminated with chemisorbed foreign atoms or atom groups, typically with hydrogen atoms. A polymantane macromolecule like a typical diamond single crystal, consists of a carbon core with the diamond crystal structure and a H-terminated surface. From the thermodynamics point of view, however, the accretion of macromolecules is a process different from the growth of crystals, and consequently must be described in a different way, because some thermodynamics functions are defined in a different manner for solid phases and for molecules.

With the aid of the present model, eight different correlations between the film-phase composition as well as the film growth rate and process variables have been derived. All of them are very consistent with experimental data. Such an excellent agreement for as many as eight functions cannot be fortuitous, and gives a good reason to believe that the present concept is correct.

2. Growth mechanism of the diamond lattice

According to the present concept, the CVD diamond formation is a surface process proceeding on surfaces of polymantane seed/substrate macromolecules (diamond seed/substrate crystals) at constant substrate temperature and total pressure. It follows from results of our previous investigations on processes proceeding on surfaces of growing diamond crystals [10–12] that the process consists of several cyclically recurring consecutive surface reactions. Although in real systems the reactions never occur in such an idealized form as presented in this paper, a division of process into stages is often used, especially in thermodynamic considerations, because the examination of the mechanisms of separate stages enables one to understand the features of the process as a whole.

In the above-mentioned detailed surface model [10–12], the following three consecutive surface reactions were distinguished. They will be exemplified in this paper by some reactions proceeding on diamond (0 1 1) face [12] which has been selected by way of example. It should be noted that analogous reactions proceed on other diamond crystal faces during diamond crystal growth.

I. Chemisorption of carbon dissolved in the gas phase and subsequent formation of unsaturated (i.e. containing sp^2 bonds) carbon–hydrogen clusters on a H-terminated diamond seed crystal surface (polymantane seed macromolecule)

$$2H(\#) + 2C(slt) = C_2H_2(2\#) \qquad (1)$$

II. Hydrogenation of the unsaturated clusters, i.e. conversion of the latter into saturated (i.e. containing only sp^3 bonds) clusters, by atomic hydrogen impact

$$C_2H_2(2\#) + 2H(g) = C_2H_4(2\#) \qquad (2)$$

III. Coalescence of the saturated clusters resulting in the formation of a new layer of sp^3-hybridized carbon with diamond structure, and simultaneous recreation of the original H-terminated diamond crystal surface on it

$$C_2H_4(2\#) = 2C(dia) + 2H(\#) + H_2(g) \qquad (3)$$

where C(slt) is the carbon dissolved in the gas phase, 'slt' standing for solute, C(dia) the new carbon epitaxial layer consisting of sp^3-hybridized and tetrahedrally coordinated carbon atoms. Because this layer is, in every respect, identical to diamond, we assume that its properties, including thermodynamic ones, are identical with those of bulk diamond. For the same reason, "dia", the abbreviation for diamond, is used in the symbol representing this layer;

H(g) and $H_2(g)$ are atomic and molecular hydrogen, respectively, "g" standing for gas; H(#) is the H-terminated diamond (0 1 1) face or more precisely a hydrogen atom chemisorbed on the diamond (0 1 1) face; $C_2H_2(2\#)$ and $C_2H_4(2\#)$ are surface-bound unsaturated ethene-like and saturated ethane-like carbon-hydrogen clusters which can be formed on the diamond (0 1 1) face [12], respectively; and # represents carbon atoms on the diamond (0 1 1) face, to which hydrogen atoms or carbon–hydrogen clusters are chemically bonded.

It is important to note that in the present model only these unsaturated clusters which are chemically bonded to the substrate surface are converted into saturated clusters that subsequently coalesce and finally form a new diamond layer. Other unsaturated clusters and possible sp^2-hybridized carbon structures, e.g. graphite or graphitic carbons, which can be formed on the substrate surface but are not chemically bonded to it are etched, i.e. removed from the surface, by free hydrogen atom impact, and for this reason cannot participate in diamond formation. When the deposition is faster than the etching of such sp^2-hybridized carbon structures, the remaining part is incorporated into the film as a second phase along with diamond.

Alternating/sequential experiments reported in the subject literature [5, 13–17] show that the diamond CVD process not only in theory but also in practice can be divided into stages. This is especially clearly demonstrated in the sequential experiments performed by the researchers from the Stanford University [5, 15–17], in which distinctly separated carbon and atomic hydrogen fluxes were directed alternately onto the substrate surface. By the separation of the fluxes in space and time the Stanford researchers were able to control the fluxes completely independently of each other.

From the sequential deposition, the Stanford researchers [17] deduced a mechanism of CVD diamond growth. According to their model, the diamond growth is a cyclical process consisting of the following surface reactions:

(i) the carburization of the diamond surface;
(ii) the deposition of highly disordered carbon on the top of the carburized surface;
(iii) the etching of disordered carbon by atomic hydrogen;
(iv) the conversion of the carburized diamond surface to diamond at growth sites by atomic hydrogen.

It should be noticed that the above cycle deduced by the Stanford researchers [17] from their experimental investigations is, in reality, identical to the cycle deduced from our theoretical investigations [10–12] except for some insignificant details. In fact, the formation of the unsaturated carbon–hydrogen clusters in our stage I represents the same elementary process as the carburization of the diamond surface in their stage (i). Similarly, the conversion of the unsaturated clusters into the saturated ones in our stage II, followed by the coalescence of the latter resulting in the formation of a new carbon layer with the diamond structure in our stage III, represents the same elementary process as the conversion of the carburized diamond surface to diamond in their stage (iv).

The difference between the two cycles resolves itself into the following fact. In our cycle, no reactions appear which could be the equivalents of the reactions proceeding in stages (ii) and (iii). We have not included such reactions in our model because in our opinion the highly disordered carbon does not take part in the diamond formation because it is not chemically bonded to the surface and therefore cannot be incorporated into the diamond lattice. Indeed, it can be inferred from the mechanism proposed by the Stanford researchers that the highly disordered carbon, which is deposited in stage (ii), is removed from the substrate surface in stage (iii) by atomic hydrogen etching before it could be converted into diamond in stage (iv). The Stanford researchers [17] clearly declare that "CVD diamond growth involves only the action of atomic hydrogen on surface-bound carbon".

The opinion that only these carbon structures, which are chemically bonded to the substrate surface, can participate in the diamond formation, is also consistent with results of experiments recently performed by Roy *et al.* [2–4]. They showed that a fine-powdered non-diamond carbon, e.g. graphite, carbon black or charcoal, could be converted into diamond by its reaction with atomic hydrogen created in a microwave hydrogen plasma in the so-called low-pressure solid-state source (LPSSS) process. It should be stressed, however, that the conversion took place only when the non-diamond carbon powder was intimately mixed with a fine diamond powder. The small diamond particles acted as seed crystals [2–4]. We believe that they provided surfaces on which the surface-bound clusters, necessary for diamond formation, were formed. Carbon atoms needed to form the surface-bound clusters were supplied to the surfaces of the seed crystals either by direct contact with the non-diamond carbon particles or possibly by a short-distance vapour transport [2–4].

When, instead of diamond, certain other fine-powdered crystalline materials, e.g. c-BN, SiC, Si (but not ZrO_2, Al_2O_3), were admixed to the non-diamond carbon powder, the latter was also converted into diamond by atomic hydrogen impact [2–4]. These results prove that certain crystalline materials which possess some specific structural and chemical properties can also play the role of seed crystals for diamond growth. This opinion is consistent with results of Badzian *et al.* [6] who found that silicon particles etched from the reactor walls and carburized to β-SiC on the graphite surface catalysed diamond nucleation on (0 0 0 1) graphite, which normally exhibited no nucleation. It can be conjectured that the diamond nucleation on graphite can proceed if the latter is at least locally contaminated with substances which can act as seed crystals for diamond growth.

The experiments of Roy *et al.* [2–4] prove that the diamond CVD is a surface process that cannot occur in the absence of appropriate seeds/substrates which provide necessary surfaces for formation of a new carbon layer with the diamond crystal structure. This conclusion is consistent with the well-established fact that scratching/abrading of the substrate surface with a diamond powder/paste or certain other powdered hard materials, e.g. MoB, LaB_6, TaB_2 can significantly enhance the growth of diamond film on heterogeneous (non-diamond) substrates [18, 19]. The role of abrasion is found to consist in implanting fine fragments of the abrading material into the substrate surface [18–20]. These fragments then act as growth sites for diamond deposition [18, 20].

3. Generalization of the detailed surface model

By adding together and then dividing by two, Reactions 1, 2 and 3 are reduced to the single reaction

$$\mathrm{C(slt)} + \mathrm{H(g)} = \mathrm{C(dia)} + 0.5\mathrm{H_2(g)} \tag{4}$$

which represents the overall diamond CVD process.

The representation of the overall process by only one reaction has its disadvantages and advantages. First of all, Reaction 4 does not inform us about the fact that it can proceed only on surfaces of appropriate seeds/substrates. In addition, among the disadvantages one can count the fact that all details referring to the mechanism of carbon atom addition to the substrate surface, are lost. For this reason it is impossible to gain any insight into the mechanism of structural defect formation on different substrate crystal faces or into the development of crystal morphology. On the other hand, among the advantages one can count the fact that Reaction 4 includes only substances the thermodynamic properties of which are very well established and easily available. The H-terminated surfaces, e.g. H(#), and carbon–hydrogen clusters, e.g. $C_2H_2(2\#)$ and $C_2H_4(2\#)$, the thermodynamic properties of which can only be estimated, are eliminated. Owing to this, a reliable thermodynamic analysis of the diamond CVD process according to the surface Reaction 4 can be performed.

4. Thermodynamic requirements for diamond formation

The formation of a new carbon layer with the diamond structure on the diamond core of a polymantane macromolecule according to Reaction 4 is a surface process proceeding at a constant substrate temperature, T_s and a constant total pressure, P_{tot}. The Gibb's energy change, ΔG, is a criterion for chemical affinity of such isothermal and isobaric processes. If $\Delta G = 0$, the reaction describing the process cannot proceed because the system is at thermodynamic equilibrium. If $\Delta G < 0$, the reaction can process forwards, whereas if $\Delta G > 0$, the reaction can proceed backwards. The Gibb's energy of Reaction 4, $\Delta G_4(T_s)$, can be calculated from Equation 5 [21]

$$\Delta G_4(T_s) = \Delta G_4^\circ(T_s) + RT_s \ln \Pi_4 \tag{5}$$

that after expansion turns into the equation

$$\begin{aligned}\Delta G_4(T_s) = {} & -RT_s\{\ln a[\mathrm{C(slt)}] - \ln a[\mathrm{C(slt)}]_{\mathrm{dia}} \\ & + \ln[p(\mathrm{H})/p^{0.5}(\mathrm{H_2})] \\ & - \ln[p_{\mathrm{eq}}(\mathrm{H})/p_{\mathrm{eq}}^{0.5}(\mathrm{H_2})\}\end{aligned} \tag{6}$$

where $\Delta G_4^\circ(T_s)$ is the standard Gibb's energy of Reaction 4 at temperature T_s, R is the Universal gas constant, Π_4 is the product of activities of reactants and products of Reaction 4 in the activated feeding gas phase reaching the substrate surface, $a[\mathrm{C(slt)}]$ the carbon activity in the feeding gas phase, $a[\mathrm{C(slt)}]_{\mathrm{dia}}$ the carbon activity in the gas phase which is in thermodynamic equilibrium with metastable diamond or, more precisely, with the sp^3-hybridized and tetrahedrally coordinated carbon layer C(dia) at temperature T_s, $p(\mathrm{H})$ and $p(\mathrm{H_2})$ are partial pressures of atomic and molecular hydrogen, respectively, in the activated feeding gas phase reaching the substrate surface, and $p_{\mathrm{eq}}(\mathrm{H})$ and $p_{\mathrm{eq}}(\mathrm{H_2})$ are the partial pressures of atomic and molecular hydrogen, respectively, in the feeding gas phase being in thermodynamic equilibrium at temperature T_s.

It has been ascertained many times that graphite, C(gra), and/or other forms of sp^2-hybridized carbon can be simultaneously co-deposited with diamond in the CVD process. The deposition of all graphitic carbons, including graphite, can be represented to the first approximation by the reaction

$$\mathrm{C(slt)} = \mathrm{C(gra)} \tag{7}$$

The Gibb's energy of Reaction 7, $\Delta G_7(T_s)$, is expressed by the equation

$$\Delta G_7(T_s) = -RT_s\{\ln a[\mathrm{C(slt)}] - \ln a[\mathrm{C(slt)}]_{\mathrm{gra}}\} \tag{8}$$

where $a\,[\mathrm{C(slt)}]_{\mathrm{gra}}$ denotes the activity of carbon dissolved in the gas phase which is in thermodynamic equilibrium with graphite at temperature T_s.

It should be noted that the differences $\{\ln a[\mathrm{C(slt)}] - \ln a[\mathrm{C(slt)}]_{\mathrm{dia}}\}$ and $\{\ln a[\mathrm{C(slt)}] - \ln a[\mathrm{C(slt)}]_{\mathrm{gra}}\}$ in Equations 6 and 8 are identical with the thermodynamic carbon super-saturation of the gas phase with respect to diamond, σ(dia), and graphite, σ(gra), respectively.

It is obvious that $\Delta G_7(T_s)$ can assume negative values only for positive values of σ(gra). This implies that graphite can be deposited only from such gas solutions which are carbon super-saturated with respect to graphite. In addition, the super-saturation σ(gra) must be greater than (or at least equal to) the so-called critical super-saturation σ_{crit}(gra). If σ(gra) is less than σ_{crit}(gra), graphite is not deposited. Unfortunately, σ_{crit}(gra) is not known. Hence, it is impossible to make a comparison with corresponding experimental data. Nevertheless, it has been found that graphite is not co-deposited below a certain concentration of carbon in the feeding gas phase. For instance, Zhu *et al.* [22] have ascertained that at the low methane concentration of 0.5%, the film consisted totally of diamond crystals without any detectable graphite phase or other non-diamond components.

In contrast to Reaction 7, Reaction 4 is driven not only by the carbon super-saturation σ(dia), but first of all by the super-equilibrium concentration of atomic hydrogen. Remarkably, $\Delta G_4(T_s)$ can assume large negative values even though σ(dia) is negative; however, this is only on the condition that $p(\mathrm{H})/p^{0.5}(\mathrm{H_2}) \gg p_{\mathrm{eq}}((\mathrm{H})/p_{\mathrm{eq}}^{0.5}(\mathrm{H})_2$. Such a situation occurs only when the gas phase reaching the substrate surface is in an activated/excited state. This implies that diamond can be deposited not only from gas solutions which are carbon super-saturated but also from gas solutions which are carbon under-saturated with respect to diamond; however, this is on the indispensable condition that the gas phase is activated to a sufficiently high degree. Indeed, it results from reported experimental data that the deposition of diamond from activated carbon under-saturated gas solutions has been accomplished many times [1]. Recently we have demonstrated that diamond is deposited from carbon under-saturated gas solutions also in the carbon/water pseudobinary system [23].

In the light of the above discussion, the formation of diamond in the form of the new carbon layer with the diamond structure on the diamond core of a polymantane macromolecule in gaseous environment which are carbon under-saturated with respect to diamond, is no longer a thermodynamic paradox. Also, the simultaneous graphite etching and diamond deposition [6, 7] is not a thermodynamic paradox in the light of the above discussion. Such a situation occurs when the feeding gas phase is activated to a high degree and at the same time is carbon under-saturated with respect to graphite.

If we assume that the mechanism of diamond formation in the experiments of Roy *et al.* [2–4] is the same as in conventional CVD experiments with the only exception that a solid instead of gaseous carbon source is used, we can describe this process by the reaction

$$\mathrm{C(gra)} + \mathrm{H(g)} = \mathrm{C(dia)} + 0.5\mathrm{H_2(g)} \qquad (9)$$

Reaction 9 and its Gibb's energy

$$\Delta G_9(T_s) = -RT_s\{\ln a[\mathrm{C(slt)}]_{\mathrm{gra}} - \ln a[\mathrm{C(slt)}]_{\mathrm{dia}} + \ln[p(\mathrm{H})/p^{0.5}(\mathrm{H_2})] - \ln[p_{\mathrm{eq}}(\mathrm{H})/p_{\mathrm{eq}}^{0.5}(\mathrm{H_2})]\} \qquad (10)$$

is obtained by subtraction of Reaction 7 from Reaction 4 and Equation 8 from Equation 6 respectively. Because $a[\mathrm{C(slt)}]_{\mathrm{gra}}$ is smaller than $a[\mathrm{C(slt)}]_{\mathrm{dia}}$ the difference $\{\ln a[\mathrm{C(slt)}]_{\mathrm{gra}} - \ln a[\mathrm{C(slt)}]_{\mathrm{dia}}\}$ in Equation 10 is negative. Consequently, $\Delta G_9(T_s)$ can assume sufficiently large negative values only if $p(\mathrm{H})/p^{0.5}(\mathrm{H_2}) \gg p_{\mathrm{eq}}(\mathrm{H})/p_{\mathrm{eq}}^{0.5}(\mathrm{H_2})$.

It is obvious that the gas phase (pure hydrogen) in the LPSSS experiments [2–4] is carbon under-saturated with respect to both graphite and diamond because it does not contain any carbon. Because graphite is etched, a carbon gas solution is locally formed in the proximity of graphite surface. However, the created gas solution is, at best, only carbon saturated with respect to graphite [σ(gra) = 0]. This implies that the gas phase is carbon under-saturated with respect to diamond because the chemical potential of carbon in diamond is higher than that in graphite.

Similar to Reaction 9 is the reaction

$$\mathrm{C(gra)} + \chi\mathrm{H(g)} = \mathrm{C(dia)} + \chi/2\mathrm{H_2(g)} \qquad (11)$$

which has been postulated by Wang *et al* [24, 25]. However, the derivation of Reaction 11 does not satisfy the requirement for thermodynamic coupling of chemical reactions because it has been obtained by simply adding together Reaction 12 and a portion χ, of Reaction 13

$$\mathrm{C(gra)} = \mathrm{C(dia)} \qquad (12)$$

$$\mathrm{H(g)} = 1/2\,\mathrm{H_2(g)} \qquad (13)$$

which do not have any common reactant or product [26].

4.1. Comparison with experimental data

ΔG_4, ΔG_7 and ΔG_9 are functions (of all or some) of the following process variables:

(a) partial pressures of atomic, p(H), and molecular hydrogen $p(\mathrm{H_2})$;

(b) substrate temperature T_s;

(c) carbon concentration, X[C(slt)]; and

(d) total pressure, P_{tot}.

The last variable in the above list results from the fact that both $a[\mathrm{C(slt)}]_{\mathrm{dia}}$ and $a\{\mathrm{C(slt)}]_{\mathrm{gra}}$ are functions of P_{tot} (and T_s).

To compute ΔG_4 and ΔG_9 values, it is necessary to possess the complete set of the above variables. Unfortunately, the number of experimental data which contain all the above listed variables is quite small. This results from the fact that, for the most part p(H) is not reported despite the fact that it is the most important factor in the diamond CVD process.

Using the complete sets of process variables published by Hsu [27, 28] and Harris *et al.* [29, 30] the Gibb's energy values of Reactions 4, 7 and 9 were computed for reported real experimental diamond CVD conditions. In these and subsequent calculations, it was assumed that the feeding gas phase behaved as an ideal gas solution. This assumption allowed us to replace activities, a[C(slt)], by respective atomic fractions, X[C(slt)], of carbon dissolved in the gas phase. The results of the computations are listed in Table I (together with some other quantities which will be discussed later in this paper). It is clear from the table that:

1. ΔG_4 assumes large negative values. This fact implies that the thermodynamic requirement for diamond formation is satisfied. Hence, from the thermodynamic point of view the conditions reported by Hsu

TABLE I Gibb's energies, ΔG_4, ΔG_7 and ΔG_9, film phase compositions, r, and thermodynamic instabilities, *TI* (for meaning of the terms see text), calculated using reported values of methane concentrations, $k(\mathrm{CH_4})$, substrate temperatures, T_s as well as partial pressures of atomic p(H), and molecular hydrogen, $p(H_2)$. $P_{\mathrm{tor}} = 2.63 \times 10^{-2}$ atm (1 atm = 101 325 Pa; 1 cal = 4.18 J)

$k(\mathrm{CH_4})$ (vol %)	T_8 (K)	$p(H)/p^{0.5}(H_2)$	ΔG_4 (kcal mol^{-1})	ΔG_7 (kcal mol^{-1})	ΔG_9 (kcal mol^{-1})	r	*TI*	Reference
0.35	1073	3.59×10^{-4}	− 22.13	− 2.23	− 19.91	8.0×10^{-5}	0.83	[27]
0.35	1073	1.95×10^{-4}	− 20.85	− 2.23	− 18.62	1.5×10^{-4}	0.83	[28]
0.5	1200	2.12×10^{-3}	− 26.02	− 5.87	− 20.15	1.9×10^{-4}	0.95	[29]
0.5	1200	3.02×10^{-4}	− 21.39	− 5.87	− 15.52	1.3×10^{-3}	0.95	[30]

[27, 28] and Harris *et al.* [29, 30] are favourable for CVD diamond formation.

2. ΔG_7 assumes negative yet considerably smaller values than ΔG_4. This fact implies that graphite can be formed simultaneously with diamond. However, the formation of graphite is much less probable than that of diamond under conditions reported by Hsu [27, 28] and Harris *et al.* [29, 30] ;

3. ΔG_9 assumes large negative values only slightly smaller than ΔG_4. This fact implies that the thermodynamic requirement for diamond formation is satisfied and that graphite could be converted into diamond by the LPSSS process [2–4] under conditions reported by Hsu [27, 28] and Harris *et al.* [29, 30].

5. Effect of process variables on the phase composition of deposited films

From Equations 6, 8 and 10 one can compute not only the respective Gibb's energy values for the real experimental conditions but also deduce relationships between the above listed process variables and some particular characteristics of the process, e.g. the film-phase composition or the growth rate, which then can be used for comparison with corresponding experimentally determined dependencies or trends.

Using the thermodynamic equilibrium constant of Reaction 9, K_9, one can calculate the ratio of the number of carbon atoms which remain unchanged in the form of graphite to the number of carbon atoms which can be converted into diamond according to Reaction 9, as well as the ratio of the number of carbon atoms in sp^2-hybridization to the number of carbon atoms in sp^3-hybridization which can be formed in the diamond CVD process according to Reaction 4 or to coexist in quasi-equilibrium under the given stationary conditions existing at the substrate surface. This ratio is expressed by the equation

$$r = n[\mathrm{C(gra)}]/n[\mathrm{C(dia)}] = \{a[\mathrm{C(slt)}]_{\mathrm{gra}}/a[\mathrm{C(slt)}]_{\mathrm{dia}}\}$$

$$x[p_{\mathrm{eq}}(\mathrm{H})/p(\mathrm{H})]x[p^{0.5}(\mathrm{H}_2)/p_{\mathrm{eq}}^{0.5}(\mathrm{H}_2)] \qquad (15)$$

The ratio $[p^{0.5}(\mathrm{H}_2)/p_{\mathrm{eq}}^{0.5}(\mathrm{H}_2)]$ in the above equation assumes values close to 1 and changes very little with $p(\mathrm{H})$, i.e. with the degree of the gas phase activation, and T_s. For this reason it can be ignored in general considerations without making a significant error. Also, the activity ratio $\{a[\mathrm{C(slt)}]_{\mathrm{gra}}/a[\mathrm{C(slt)}]_{\mathrm{dia}}\}$ can be considered constant because it does not change much with T_s. Note that the ratio r is independent of P_{tot} and $X[\mathrm{C(slt)}]$.

The ratio r can be directly compared with the corresponding Raman peak intensity ratio $R = I_{1550}/I_{1333}$, which is occasionally reported in the current literature (e.g. [31, 32]). I_{1550} and I_{1333} in the above ratio denote the intensities of Raman peaks for sp^2-hybridized carbon at 1550 cm^{-1} and for diamond at 1333 cm^{-1}, respectively [31, 32].

Both the r and R ratios reflect a contamination of the film with sp^2-hybridized non-diamond carbon. It is clear from Table I that r ratios in films deposited under typical diamond CVD conditions which are known to be favourable for deposition of high-quality diamond [28] are indeed very low.

5.1. Effect of partial pressure of atomic hydrogen p(H)

According to Equation 14 the ratio r decreases with increasing $p(\mathrm{H})$ (strictly speaking with increasing $p(\mathrm{H})/p^{0.5}(\mathrm{H}_2)$, at a constant T_s). This conclusion accords very well with results of the Stanford researchers [5, 16] who found that the concentration of sp^2-hybridized carbon in deposited films decreased (as demonstrated by the disappearance of bands attributed to sp^2-hybridized carbons in the Raman spectra) with increasing flux of atomic hydrogen. It is obvious that an increase in the hydrogen flux is equivalent to an increase in $p(\mathrm{H})$.

Because the number of experimental data which present the film phase composition as a function of $p(\mathrm{H})$ in scarce, it is necessary to conclude changes in $p(\mathrm{H})$ from changes in process variables which are correlated with $p(\mathrm{H})$, such as the hot-filament temperature, T_{fil}, the distance between the hot filament and the substrate surface, L_{fs} and the power supplied to the plasma, W_{p}.

It is obvious and has been confirmed experimentally [33] that $p(\mathrm{H})$ increases with increasing T_{fil}, decreasing L_{fs} and increasing W_{p}. Hence, the ratio r should decrease with increasing T_{fil}, decreasing L_{fs} and increasing W_{p}. The above predictions are very well consistent with corresponding experimentally determined dependencies, which show that indeed R decreases with increasing T_{fil} and decreasing L_{fs} [31, 32].

Also, results obtained by Kamo [34] are consistent with the prediction under discussion. He found that diamond films deposited at higher microwave (MW) power supplied to the plasma showed only a sharp line of diamond whereas films deposited at lower MW power showed a very weak diamond line and a high flourescence level in the Raman spectra.

5.2. Effect of substrate temperature T_s

According to Equation 14 the ratio r is directly proportional to $p_{\mathrm{eq}}(\mathrm{H})$ (strictly speaking to $p_{\mathrm{eq}}(\mathrm{H})/p_{\mathrm{eq}}^{0.5}(\mathrm{H}_2)$). Because $p_{\mathrm{eq}}(\mathrm{H})$ increases with temperature, the ratio r should increase with increasing T_s (at a constant $p(\mathrm{H})$; strictly speaking at a constant $p(\mathrm{H})/p_{\mathrm{eq}}^{0.5}(\mathrm{H}_2)$) as is shown in Table II.

The above prediction is very well consistent with recently obtained experimental results [31, 35]. It is, however, inconsistent with earlier experimental results which showed that the concentration of graphitic carbon inclusions in the film decreased (as indicated by Raman Spectra) with increasing T_s [22, 36, 37]. Only at high temperatures (above ~1000 °C [22]) did a deterioration of the phase purity occur because the formation of graphite was increasingly favoured [22]. It is our conviction that the above inconsistency results from the fact that, in the earlier experiments [22, 36, 37], the substrate temperature was controlled not

TABLE II Gibb's energies, ΔG_4, ΔG_7, film phase compositions, r, and thermodynamic instabilities, TI, as functions of substrate temperature, T_s. Other process variables were constant and were taken from [27]: $P_{tot} = 2.63 \times 10^{-2}$ atm, $k(CH_4) = 0.35$ vol% and $p(H)/p^{0.5}(H_2) = 3.59 \times 10^{-4}$

T_s (K)	ΔG_4 (kcal mol^{-1})	ΔG_7 (kcal mol^{-1})	r	TI
500	− 33.56	4.66	4.7×10^{-17}	0.00
600	− 29.96	5.30	2.9×10^{-13}	0.00
700	− 26.93	5.03	1.5×10^{-10}	0.01
800	− 25.01	3.52	1.7×10^{-8}	0.08
900	− 23.81	1.51	6.8×10^{-7}	0.33
1000	− 22.82	− 0.63	1.3×10^{-5}	0.67
1100	− 21.88	− 2.82	1.5×10^{-4}	0.87
1200	− 20.95	− 5.02	1.1×10^{-3}	0.95
1300	− 19.98	− 7.22	6.1×10^{-3}	0.98
1400	− 18.78	− 9.33	2.7×10^{-3}	0.99
1500	− 16.60	− 10.94	9.5×10^{-2}	0.99

by an independent auxiliary heater or cooler, but only by an energy transfer from the hot filament or the plasma. In such experiments, any increase/decrease in the hot-filament temperature or power supplied to the plasma, and consequently in $p(H)$, always caused a simultaneous increase/decrease in T_s. Consequently, the T_s effect might be overshadowed by the $p(H)$, effect or vice versa. Note that the $p(H)$ and T_s effects cause opposite results. In the earlier experiments [22], the T_s effect was observed only at temperatures above ~1000°C. At temperatures below ~1000 °C the T_s effect was overshadowed by the simultaneously occurring $p(H)$ effect.

To avoid any confusion, for verification of the above prediction, only such data should be used which were obtained in experiments, in which T_s and $p(H)$ were controlled completely independently of each other, as in experiments reported elsewhere [31, 35].

5.3. Effect of carbon concentration $X[C(slt)]$

As already mentioned, the ratio r is not a function of $X[C(slt)]$ and P_{tot}, and consequently it should be independent of both these variables. The independence of $X[C(slt)]$ seems to be inconsistent with many experimental results which showed that the content of sp^2-hybridized carbon in the film increased (as indicated by Raman spectra) with increasing carbon concentration in the feeding gas phase (e.g. [22]). We believe that the observed increase in the ratio r is caused not by an increase in $X[C(slt)]$ but by a decrease in $p(H)$.

Indeed, it has been found many times (e.g. [27, 28, 38]) that $p(H)$ decreased with increasing $X[C(slt)]$. From Table III, which lists the ratio r values computed according to Equation 14 from the experimental data reported by Hsu [27] for various values of carbon concentration represented here by the methane concentration $k(CH_4)$ it is clear that indeed $p(H)$ (strictly speaking $p(H)/p^{0.5}(H_2)$ is not constant but it decreases with increasing $k(CH_4)$.

We presume that $p(H)$ decreases with increasing $X[C(slt)]$ because the recombination of hydrogen atoms is accelerated by a higher concentration of hydrocarbon molecules which may play the role of the third body that is required for the hydrogen atom recombination to proceed readily [39]. In addition, the consumption of hydrogen atoms in chemical reactions with hydrocarbon molecules is intensified as the concentration of the latter increases.

TABLE III Gibb's energies, ΔG_4, ΔG_7, as well as film-phase compositions, r, calculated as functions of methane concentrations, $k(CH_4)$, using data from [27]: $P_{tot} = 2.63 \times 10^{-2}$ atm $T_s = 1073K$; and $TI = 0.83$

$k(CH_4)$ (vol %)	$p(H)/p^{0.5}(H_2)$	ΔG_4 (kcal mol^{-1})	ΔG_7 (kcal mol^{-1})	r
0.35	3.59×10^{-4}	− 22.13	− 2.23	8.0×10^{-5}
0.85	3.59×10^{-4}	− 24.01	− 4.10	8.0×10^{-5}
1.15	1.01×10^{-4}	− 21.95	− 4.74	2.8×10^{-4}
1.3	2.97×10^{-5}	− 19.59	− 5.00	9.6×10^{-4}
1.6	8.70×10^{-6}	− 17.40	− 5.43	3.3×10^{-3}
1.75	2.03×10^{-5}	− 19.41	− 5.61	1.4×10^{-3}

5.4. Effect of total pressure P_{tot}

As already mentioned, the ratio r is not a function of P_{tot}. Thus, P_{tot} should not have any effect on the film-phase composition. This prediction is very consistent with some experimental data. For example, Zhu *et al.* [36] found that the structure of diamond films was not sensitive to pressure (as indicated by Raman spectra). In experiments performed by Kondoh *et al.* [31, 32] the ratio r varied irregularly with P_{tot} giving no indication of a monotonic function.

Other researchers [35, 40], however, found that the content of sp^2-hybridized carbon increased (as indicated by Raman spectra) with increasing P_{tot}. In our opinion, an increase in the ratio r is a consequence of a reduction in $p(H)$ similar to the case discussed in the preceding section. For the ratio r not to change with increasing P_{tot}, $p(H)$ should increase proportionally with the square root of $p(H_2)$ or, because under typical diamond CVD conditions $p(H_2)$ is only slightly smaller than P_{tot}, with the square root of P_{tot}. However, available experimental data [40] demonstrate that at the growth surface $p(H)$ does not increase, but decreases with increasing P_{tot}. This result indicates that the deterioration of the film-phase purity is not a consequence of an increase in P_{tot} but results from a decrease in $p(H)$.

It is reasonable to presume that at higher P_{tot} the hydrogen atom recombination and destruction is faster, because the mean free path is shorter, and consequently the collisions of hydrogen with each other as well as with other molecules are more frequent. Hence, the probability of hydrogen atom recombination and consumption is greater.

6. Effect of process variables on the film growth rate

A large negative ΔG_4 value means that, from the thermodynamic point of view, the diamond CVD process is possible, i.e. can proceed under the given set of process variables. However, a thermodynamically possible process can be kinetically hindered. Under certain conditions it may proceed infinitesimally slowly. Hence, the large negative ΔG_4 value is a necessary but not a sufficient condition for a successful synthesis of diamond. For the diamond CVD process to proceed at a reasonably high rate, it is also necessary for all chemical Reactions 1, 2 and 3 to proceed rapidly. The transport of reactants, i.e. C(slt) and H(g), from the feeding gas phase across the boundary layer to the substrate surface, as well as the transport of the gaseous reaction product, i.e. $H_2(g)$, in the reverse direction, should also be fast because the rate of the overall diamond CVD process is determined by the slowest elementary process step.

From the fact that, under typical CVD conditions, diamond is deposited at reasonably high rates, it can be inferred that all elementary processes including the slowest one proceed at reasonably high rates. However, under conditions considerably deviating from the typical ones, e.g. at very low total pressures or low substrate temperatures, the rates of some elementary processes, e.g. the mass transport or the chemical reactions, repectively, can considerably decrease causing a dramatic reduction in the deposition rate independently of the large negative value of the Gibb's energy. In this paper we do not intend to examine kinetics of all elementary processes because a detailed examination would need many kinetic parameters which, for the most part, are not well established and many corresponding experimental data which are not yet available. We do, however, intend to discuss, in general, the problem of addition of new carbon atoms from the gas phase to the lattice of a diamond seed crystal. It is commonly believed that this elementary process plays a key role in diamond CVD.

6.1. The kinetics of the addition of carbon atoms to the diamond lattice

Because the carbon–hydrogen bonds are strong, the H-terminated diamond crystal surfaces are chemically very inert [41–43] under ordinary conditions. In particular, because the carbon–hydrogen bonds are stronger than carbon–carbon bonds, no diamond growth can occur because depositing carbon atoms are not able to displace the bound hydrogen atoms on the surface [44]. It is generally believed that for a diamond crystal to grow it is necessary first to remove some chemisorbed hydrogen atoms from the diamond substrate surfaces in order to create some reactive surface carbon radicals (SCR), to which new carbon atoms from the gas phase can then chemically bind. Because the mechanism of SCR formation is apparently different at "low" and "high" temperatures, the kinetics of the carbon atom addition should be discussed separately for "low" and "high" temperatures.

6.1.1. "Low" temperatures

At "low" temperatures, the chemisorbed hydrogen atoms are strongly bound to the surfaces. They can be removed from the latter only with the aid of very reactive free hydrogen atoms according to the hydrogen abstraction reaction

$$\mathrm{H}(\#) + \mathrm{H(g)} = (\#) + \mathrm{H_2(g)} \qquad (15)$$

In the above equation (#) represents a univalent SCR.

The reactive SCRs created in the above reaction are quickly annihilated by atomic hydrogen impact [10–12] according to the hydrogen addition reaction

$$(\#) + \mathrm{H(g)} = \mathrm{H}(\#) \qquad (16)$$

It should be noted that the SCR annihilation Reaction 16 is considerably faster than the SCR creation Reaction 15 because Reaction 16, as a radical–radical reaction, has no energy barrier [45], in contrast to Reaction 15. The SCRs are also annihilated by molecular hydrogen impact according to the reaction

$$(\#) + 0.5\mathrm{H_2(g)} = \mathrm{H}(\#) \qquad (17)$$

because at "low" temperatures and $p(\mathrm{H_2})$ occuring under typical diamond CVD conditions, Reaction 17 is shifted far to the right [10–12]. For the above discussed reasons, the efficacy of SCR production by hydrogen atom impact is very low. Consequently, the number of SCRs which are available for the carbon atom addition is very small at "low" temperatures. In addition, new carbon atoms from the gas phase have a very small chance to bind to the SCRs before the latter are annihilated because the number of carbon-carrying molecules is much less (typically ~100 times less) than the number of hydrogen molecules. Under such circumstances the addition of new carbon atoms to the diamond lattice cannot successfully compete with Reaction 17. Consequently, diamond crystals grow at very small rates [10] which are usually insufficient for any practical application.

6.1.2. "High" temperatures

At "high" temperatures and $p(\mathrm{H_2})$ occuring under typical diamond CVD conditions, it is not necessary to impel the chemisorbed hydrogen atoms to leave the substrate surface because they desorb spontaneously [10–12] according to the reaction

$$\mathrm{H}(\#) = (\#) + 0.5\mathrm{H_2(g)} \qquad (18)$$

Consequently, a large number of SCRs is created.

On the one hand, such a situation is advantageous because the large number of reactive SCRs would make it possible to bind to the surface a large number of new carbon atoms from the feeding gas phase, that would result in rapid growth of diamond crystals.

On the other hand, however, the large number of SCRs is disadvantageous. A diamond crystal surface covered with a large number of such radicals is very unstable [10–12]. To attain an energetically more favourable state, such a surface undergoes a reconstruction during the course of which unsaturated sp^2 bonds are formed between the surface carbon atoms. The presence of sp^2 bonds on surfaces of a growing diamond crystal is undesirable because, under conditions under which such bonds can exist, they stimulate the formation of graphite rather than diamond [10–12]. In order to avoid the sp^2 bond formation, the number of SCRs must be reduced to a relatively small admissible quantity, i.e. almost the entire surface must be covered with chemisorbed hydrogen [46]. In order to achieve this goal, it is necessary to create a super-equilibrium concentration of hydrogen atoms in the gas phase. At a sufficiently high super-equilibrium hydrogen concentration, SCRs are annihilated [10–12] according to Reaction 16. As a result, the H-terminated surface, H(#), is reproduced.

It should be stressed here that the H-terminated surfaces are thermodynamically unstable at "high" temperatures, and can exist only by virtue of super-equilibrium concentration of atomic hydrogen [10–12]. Because thermodynamically less stable species are, as a general rule, more reactive than more stable ones [45], it seems reasonable to suppose that the unstable H-terminated surfaces existing at "high" temperatures, due to the presence of super-equilibrium atomic hydrogen concentration in a labile state are more reactive than the stable H-terminated surfaces existing at "low" temperatures. Hence, one may expect that, due to the greater reactivity, the H-terminated surfaces can react not only with hydrogen atoms but also with carbon-carrying molecules, and consequently new carbon atoms can chemically bind to them. Because the number of carbon-carrying molecules is (under typical diamond CVD conditions) comparable with the number of hydrogen atoms in the activated gas phase, the addition of new carbon atoms can successfully compete with Reaction 16. Hence, the carbon atom addition to H-terminated surfaces is not a rate-limiting step at "high" temperatures. Owing to this, diamond can be deposited at high rates at "high" temperatures on the condition that other elementary processes are also fast and ΔG_4 has a large negative value.

It can be concluded from the above discussion that the chemical reactivity of H-terminated surfaces is correlated with the thermodynamic instability, TI, of the latter. Searching for a quantitative even though only approximate measure of TI we propose to express it as the fraction of the substrate surface, which would be free from the chemisorbed hydrogen atoms under equilibrium conditions, i.e. at $p(\mathrm{H}) = p_{\mathrm{eq}}(\mathrm{H})$. TI, as defined above, can assume values from 0–1. TI is a function of, and increases with, increasing T_s and decreasing P_{tot}. It depends also on the crystallographic orientation of the substrate surface. As yet, TI has not been determined experimentally. Therefore, we were obliged to estimate it using a method developed in our previous papers [10–12] and available experimental data [45]. Results of our estimations for the (1 1 1) face performed for typical P_{tot} are presented in Table II. From these results, one can draw the following conclusions.

(a) In the "high" temperature region, at $T_s \gtrsim 1200$ K, in which TI assumes values close to 1 (0.95–1), and is practically independent of T_s, the carbon atom addition is not a rate-limiting step, and consequently the growth rate, GR, is practically a function of ΔG_4 only.

(b) In the "low" temperature region, at $T_s \lesssim 1200$ K, in which TI is a very sensitive function of T_s and assumes values from 0–0.95, the C atom addition is a rate-limiting step, and consequently, GR is a function of both TI and ΔG_4.

Evidently, GR will increase with increasing TI and decreasing ΔG_4.

It is worth mentioning that the (0 1 1) face is thermodynamically less stable than the (1 1 1) face, i.e. TI for the (0 1 1) face is greater than that for the (1 1 1) face at the same T_s. For instance, TI for the (0 1 1) face attains the value of 0.95 already at $T_s = \sim 900$ K whereas TI for the (1 1 1) face equals only 0.33 at this temperature (see Table II). It can be concluded from this fact that the (0 1 1) face should grow faster than the (1 1 1) face. In fact, it has been found experimentally that the (0 1 1) face grows faster than the (1 1 1) face [47] as well as the (0 0 1) face. As the fastest growing face, the (0 1 1) face disappears during growth of diamond crystals [47] already at the early phase of diamond film deposition. Subsequently the growth is continued on slower, i.e. (1 1 1) [12] and/or (0 1 1), faces.

6.1.3. *Agents which can stimulate the desorption of hydrogen atoms*

Because at "low" temperatures, small growth rates follow as a consequence of the small number of SCRs, it is necessary to increase the latter in order to increase the growth rate. This goal cannot be achieved by a simple increase of the hydrogen atom concentration because this would intensify not only the SCR creation (according to Reaction 15) but also the SCR annihilation (according to Reaction 16). However, the above goal can be achieved by a bombardment of the substrate surface with agents which are able to stimulate the hydrogen atom desorption but are not able to annihilate the SCRs. Such ability possesses, for example, electrons with sufficiently high kinetic energy.

In fact, it has been found that positive biasing of the substrate with regard to the hot filament increased deposition rates and extended the parameter space under which diamond could be grown, with specific reference to decreased substrate temperature [48]. A diamond film can be grown at reasonable rates with positive biasing at relatively low substrate temperature of 400 °C [48]. Without the use of a d.c. bias, the lowest substrate temperature at which reasonable growth rate ($> 0.1\ \mu\mathrm{m\,h^{-1}}$) could be obtained is approximately 600 °C [48].

6.2. Effect of partial pressure of atomic hydrogen $p(\mathrm{H})$

As already mentioned, ΔG_4 is a function of all process variables listed at the beginning of section 4.1. According to Equation 6, ΔG_4 should decrease with increasing $p(\mathrm{H})$ on the assumption that T_s, $X[\mathrm{C(slt)}]$ and P_{tot} are constant. Because TI as a function of the mentioned variables is constant under such an assumption (see Section 6.1.2.), GR is a function of ΔG_4

only, and accordingly, should increase with increasing $p(\mathrm{H})$.

The results of the Stanford researchers [5, 15] and Ohl *et al.* [46] provide a direct confirmation of the above prediction. They showed that indeed *GR* was increased by increasing the hydrogen flux [5, 15] or the concentration of atomic hydrogen [46].

In addition, many other experimental data [31, 32, 49–52] indirectly confirm the prediction under discussion. It has been found that *GR* increased with increasing T_{fil} [31, 32, 49] and increasing W_{p} [50–52] as well as with decreasing L_{fs} [31, 32].

6.3. Effect of substrate temperature T_{s}

Both ΔG_4 and *TI* increase with increasing T_{s} (see Table II). For this reason, they cause the opposite effects on *GR*. At "low" temperatures at which *TI* is the principal factor determining *GR*, the latter should increase with increasing T_{s}, whereas at "high" temperatures at which *TI* is practically independent of T_{s}, and ΔG_4 is the factor determining *GR*, the latter should decrease with increasing T_{s}. As a consequence, *GR* should first increase, pass a maximum and then decrease with increasing T_{s}.

Such a behaviour of *GR* as a function of T_{s} has been indeed confirmed experimentally many times [31, 35, 36, 53, 54]. The experimentally determined maximum in *GR* is located at temperatures of around 1200 K [31, 35, 53]. This corresponds very well with data presented in Table II from which it follows that at $T_{\mathrm{s}} > 1200\,\mathrm{K}$ *TI* has value close to 1 and is practically constant. Hence, *TI* cannot influence *GR* in this "high" temperature region.

The activation energy calculated for the low-temperature branch from data collected in Table II is approximately equal to 24.5 kcal mol^{-1}. This value accords very well with reported experimentally determined activation energies [53].

6.4. Effect of carbon concentration $X[\mathrm{C(slt)}]$

ΔG_4 decrease with increasing $X[\mathrm{C(slt)}]$. Because a decrease in ΔG_4 causes an increase in *GR*, the latter should increase with increasing $X[\mathrm{C(slt)}]$ (at constant remaining process variables).

This prediction is very consistent with experimental results [35, 36, 52, 55] which indeed show that *GR* increase with increasing $X[\mathrm{C(slt)}]$. Some curves representing *GR* as a function of $X[\mathrm{C(slt)}]$ tend towards a saturation [36] while some others pass a maximum and then decrease [31]. Such a behaviour is most probably caused by a decrease in $p(\mathrm{H})$ which is known to be brought about by an increase in $X[\mathrm{C(slt)}]$ [27, 28, 38].

6.5. Effect of total pressure P_{tot}

Because $a[\mathrm{C(slt)}]_{\mathrm{dia}}$ increases with P_{tot} [1], ΔG_4 should, according to Equation 6, increase with increasing P_{tot}. On the other hand, *TI* decrease with increasing P_{tot}. Because an increase in ΔG_4 as well as a decrease in *TI* cause a decrease in *GR*, the latter should decrease with increasing P_{tot} (at constant remaining process variables). An additional decrease in *GR* can be caused by a decrease in $p(\mathrm{H})$ which is known to occur as P_{tot} is increased [40]. All in all, *GR* should decrease with increasing P_{tot}.

In fact, it has been experimentally demonstrated several times that *GR* decreased with increasing P_{tot} [31, 32, 36, 49, 52]. However, for the most part, this trend was observed only at P_{tot} greater than a certain value, at which *GR* attained a maximum [31, 32, 36, 40]. For the most part, the maximum in *GR* occured at $P_{\mathrm{tot}} = 20\text{–}30$ torr (1 torr $\simeq$ 133.322 Pa) [31, 32, 40]. Yet, a considerably greater value (~ 110 torr) was also reported [36]. At pressures below the above cited values, *GR* increase with increasing P_{tot}. We suppose that in the low-pressure region, the mass transport is a rate-limiting step.

7. Conclusion

Diamond CVD is inconsistent with the fundamental principles of chemical thermodynamics if it is considered a crystal growth process. Thus, from this point of view, the experimentally achieved deposition of diamond films is a thermodynamic paradox. Diamond CVD is, however, consistent with the fundamental principles of chemical thermodynamics if it is considered as a chemical process consisting in accretion of polymantane macromolecules. Because the latter are identical with diamond single crystals, the surfaces of which are H-terminated, the accretion of polymantane macromolecules is a process completely equivalent to the growth of diamond crystal despite the formal difference.

By regarding diamond crystals as polymantane macromolecules, we have developed a general thermochemical model of CVD diamond formation from hydrocarbon–hydrogen mixtures which is in excellent agreement with experimental data. In particular, the model correctly predicts correlations between fundamental process variables and the film-phase composition, as well as the growth rate. In addition, the present model explains very well important experimental observations which show that (i) the activation of the gas phase is necessary for diamond formation, (ii) diamond CVD is, in principle, independent of the method employed to activate the gas phase, (iii) diamond CVD is, in principle, independent of the kind of hydrocarbon source material used, (iv) graphitic carbons can be co-deposited with diamond, (v) diamond can be deposited from gas phases which are carbon under-saturated with respect to diamond, (vi) diamond can be deposited when simultaneously graphite is etched, and (vii) relatively high temperatures are necessary for diamond deposition. Moreover, from the discussion in Section 2, one may conclude that (viii) the abrading of the substrate surface with a diamond powder/paste or certain other powdered hard materials can enhance diamond formation because debris of the abrading material remaining on the surface plays the role of seed crystals for diamond growth.

The good consistency of the model with experimental data gives a reliable base to believe that the model is correct.

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