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W. PIEKARCZYK

Institute of Physics, Polish Academy of Sciences, Poland

Crystal Growth of CVD Diamond and some of its Peculiarities

Experiments demonstrate that CVD diamond can form in gas environments that are carbon undersaturated with respect to diamond. This fact is, among others, the most serious violation of principles of chemical thermodynamics. In this paper it is shown that none of the principles is broken when CVD diamond formation is considered not a physical process consisting in growth of crystals but a chemical process consisting in accretion of macro-molecules of polycyclic saturated hydrocarbons belonging to the family of organic compounds the smallest representatives of which are adamantane, diamantane, triamantane and so forth. Since the polymantane macro-molecules are in every respect identical with diamond single crystals with hydrogen-terminated surfaces, the accretion of polymantane macro-molecules is a process completely equivalent to the growth of diamond crystals. However, the accretion of macro-molecules must be described in a way different from that used to describe the growth of crystals because some thermodynamic functions are defined in manners different for solid phases (i.e. crystals) and for molecules. The CVD diamond formation is a chemical process proceeding on surfaces of polymantane seed macro-molecules (diamond seed crystals) under conditions under which the hydrogen-terminated surfaces exist but are chemically unstable. The process consists of several cyclically recurring consecutive reactions that can be thermodynamically coupled. The present approach makes it possible to predict correlations between the growth rate as well as the phase composition of deposited films and some important process variables. The predicted dependencies are perfectly consistent with experimental results.

Keywords: diamond; chemical vapor deposition; crystal growth; growth mechanism; gas phase carbon saturation; thermodynamics

1. Introduction

The research on synthesis of diamond by chemical vapor deposition (CVD) from hydrocarbon-hydrogen mixtures under low pressure and moderately elevated temperatures in the region of thermodynamic instability of diamond started in the fifties. At the beginning the progress was slow and only in the seventies promising results were achieved when an activation of the gas phase was brought into practice. The task of the activation is to break up some components of the gas phase into constituent parts, first of all molecular hydrogen (H_2) into atomic hydrogen (H). Since that time diamond is synthesized by various CVD methods. The essential differences between these methods consist in the application of different activation techniques. The activation techniques known today range from thermal ones, utilizing high temperature of a hot filament or a direct current electrical arc, to a broad spectrum of plasma techniques utilizing electro-magnetic, e.g. microwave or radio-frequency, fields to create a plasma. The most important diamond CVD methods, already

well advanced and used to produce diamond films on an industrial scale, are:

- (a) The hot filament assisted CVD that is the simplest.
- (b) The microwave plasma assisted CVD that is most popular.
- (c) The direct current plasma jet CVD that allows one to deposit diamond films at the highest rates.

Common to all diamond CVD methods are the following indispensable requirements that must be met for diamond to form at reasonably high rates:

- (1) The temperature of the substrate surface typically ranges from around 700°C to around 1100°C. At lower substrate temperatures the deposition rates are small whereas at higher temperatures a tendency towards the formation of graphite appears.
- (2) The concentration of atomic H in the gas phase reaching the growth surface surpasses by several orders of magnitude the concentration of atomic H in the gas phase that would be at equilibrium at the substrate temperature. Such a super-equilibrium concentration of atomic H is produced during the activation of the gas phase.
- (3) The concentration of a hydrocarbon gas in hydrogen is very low; typically around 1 vol. %, close to the solubility limit of carbon in hydrogen for the given substrate temperature, T_s , and total pressure, P_{tot} .

Early reports about the successful CVD of diamond films under low pressure and moderately elevated temperatures in the region of thermodynamic instability of diamond were skeptically taken by some scientists. The experimental observation that diamond can be deposited from gas solutions that are carbon (C) undersaturated with regard to diamond is still not generally accepted although the number of experimental data which support this observation is already relatively large and is still growing. Such an attitude of some scientists is not surprising because equilibrium thermodynamic calculations show that the formation of diamond under the above mentioned conditions is indeed impossible. Hence, CVD diamond formation is a thermodynamic paradox.

The most celebrated violation of thermodynamics is the fact that CVD diamond forms under pressure-temperature conditions under which it is thermodynamically unstable. However, the violation of thermodynamics, which is most difficult to explain, is the experimentally well proved fact that diamond can form in gas environments that are C undersaturated with respect to diamond. The following experimental results provide unquestionable evidences that indeed diamond forms in such gas environments:

(a) In the so-called low pressure solid state source (LPSSS) experiments performed by ROY et al. (1993 a,b,c) as well as in experiments performed by SHAH et al., diamond was formed by acting on graphite with pure hydrogen that was activated to the state of microwave plasma. It is absolutely obvious that the gas phase was C undersaturated because it contained no carbon at all.

(b) Similarly, in the sequential diamond CVD experiments performed by the group of Stanford researchers (KELLY et al. 1992 a) graphitic carbon, deposited in the first stage by sputtering a graphite target, was converted into diamond in the second stage by acting on it with atomic hydrogen that was created in pure hydrogen gas with the aid of a hot filament.

(c) Diamond was deposited under conditions under which graphite was simultaneously etched (BADZIAN et al.; SALVADORI et al.). The graphite etching indicates that the feeding gas phase was C undersaturated with respect to graphite. Since the chemical potential of carbon in diamond is higher than that in graphite, the C undersaturation for diamond was greater than that for graphite.

From the thermodynamic point of view diamond etching, but not diamond deposition, should take place in gas environments that are C undersaturated with respect to diamond. For that reason, it seems unreasonable to consider diamond CVD a crystal growth process. This view is supported by the fact that diamond, contrary to other crystalline materials, is formed at

temperatures which are not higher, but much lower, than its Debye temperature (1860 K). It is worth mentioning that atoms in the crystal lattice do not vibrate below the Debye temperature. Such an inability to change the atom position during crystal growth process considerably increases the tendency towards crystal defect formation.

2. New approach to the problem of CVD diamond formation

Aiming at understanding the mechanism of formation of metastable diamond several theoretical diamond CVD models have been developed. None of them, however, has received a general acceptance because all these models are inconsistent with at least some experimental results. Attempts have been made in some of these models to explain the CVD diamond formation using exclusively kinetics. However, a chemical process cannot proceed if it is thermodynamically impossible, even though it is kinetically favored. Kinetics should be exercised within thermodynamics and never go against it (HWANG et al.; WANG et al.).

In this paper a new approach to the problem of CVD diamond formation which does not violate thermodynamic principles is presented. According to the present approach 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 macro-molecules of polycyclic saturated hydrocarbons belonging to the family of organic compounds called the "cage molecules". The smallest representatives of such macro-molecules are, in the growing order, adamantane (tricyclodecane, C₁₀H₁₆), diamantane (C₁₄H₂₀), triamantane (C₁₈H₂₄), and so forth (SATO). Accordingly the members of this family can be called "polymantanes".

Since polymantane macro-molecules are in every respect identical with diamond single crystals with H-terminated surfaces, that normally exist under ordinary conditions, the accretion of polymantane macro-molecules is a process completely equivalent to the growth of diamond crystals. For this reason, the phrases "the accretion of polymantane macro-molecules" and "the growth of diamond crystals" will be used exchangeably as synonyms in this paper. From the thermodynamic point of view, however, the accretion of macro-molecules is a process different from the growth of crystals, and consequently must be described in a way different from that used to describe the growth of crystals because some thermodynamic functions, e.g. activity, are defined differently for solid phases, i.e. crystals, and for molecules.

3. Properties of hydrogen-terminated diamond crystal surfaces

Since carbon-hydrogen bonds are strong, the H-terminated diamond crystal surfaces are chemically very inert under ordinary conditions. In particular, because carbon-hydrogen bonds are stronger than carbon-carbon bonds, no diamond growth can occur since depositing C atoms are not able to displace the bound H atoms on the surface (ANTHONY). It is generally accepted that for a diamond crystal to grow it is necessary to remove from the substrate surface some chemisorbed H atoms in order to create some surface growth sites (SGS) to which new C atoms from the gas phase can chemically bind. It is generally believed that SGSs can be created in large number by free H atoms in the hydrogen abstraction reaction



This belief is false because SGSs created in reaction (1) are quickly annihilated in the

hydrogen addition reaction



which is faster than reaction (1) because it, as a radical-radical reaction, has no energy barrier (BENSON). As a result, the number of SGSs produced by free H atom impact is very low, and consequently diamond crystals cannot grow fast at “low” temperatures.

It should be mentioned that all reactions considered in this paper will be exemplified by respective reactions proceeding on the diamond (011) face. It should be noted that analogous reactions proceed on other diamond crystal faces. In the above and subsequent equations $\text{H}(\text{g})$ and $\text{H}_2(\text{g})$ denote atomic and molecular hydrogen, respectively, \mathcal{C} tetrahedrally coordinated and sp^3 -hybridized C atom on the (011) face of a diamond seed crystal (polymantane seed macromolecule), $\text{H}(\mathcal{C})$ H-terminated diamond crystal surface or more precisely a H atom chemically bonded to a carbon atom \mathcal{C} , and (\mathcal{C}) univalent SGS or in other words a surface C atom with one unoccupied dangling bond.

3.1. Creation of labile hydrogen-terminated surfaces

At elevated temperatures and $p(\text{H}_2)$ occurring under typical diamond CVD conditions the chemisorbed H atoms desorb spontaneously from the diamond seed crystal surfaces (PIEKARCZYK 1992; PIEKARCZYK et al. 1993,1994). Consequently, a large number of SGSs is created. Such a situation would be advantageous because the large number of reactive SGSs would make it possible to bind to the surface a large number of new C atoms that would result in rapid growth of diamond crystals. However, the large number of SGSs is disadvantageous. A diamond crystal surface covered with a large number of such SGSs is very unstable. To attain an energetically more favorable state, such a surface undergoes a reconstruction in the course of which double sp^2 bonds are formed between the surface C 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 (PIEKARCZYK 1992; PIEKARCZYK et al. 1993,1994).

In order to avoid the sp^2 bond formation almost the entire surface must be covered with chemisorbed H atoms (OHL et al.). For this purpose it is necessary to increase the concentration of free H atoms in the gas phase reaching the growth surface in order to annihilate the SGSs according to reaction (2). As a result the H-terminated surface $\text{H}(\mathcal{C})$ is reproduced. However, it is unstable at elevated temperatures and can exist only by virtue of super-equilibrium concentration of free H atoms (PIEKARCZYK et al. 1993,1994). In other words, such a labile H-terminated surface can exist only in gas environments that are activated to a sufficiently high degree. In order to distinguish it from the stable H-terminated surface marked with $\text{H}(\mathcal{C})$ the symbol $\mathcal{H}(\mathcal{C})$ will be used hereafter to represent the unstable H-terminated surface. Since the chemisorbed H atoms are weakly bound to the unstable H-terminated surface $\mathcal{H}(\mathcal{C})$, the depositing C atoms are able to dislodge them. Due to this the polymantane seed macro-molecules (diamond seed crystals) can grow at elevated temperatures, and consequently high growth rates (GR) can be achieved. The surface fraction covered with the weakly bound surface H atoms, $X(\mathcal{H})$, can be estimated to a satisfactory accuracy using an algorithm developed by the author (PIEKARCZYK 1992), that was based upon the group additivity method (BENSON). It is obvious that GR will be proportional to the number of such weakly bound surface H atoms or in other words to $X(\mathcal{H})$.

4. Growth mechanism of the diamond lattice

According to the present approach the CVD diamond formation is a chemical process proceeding on the surfaces of polymantane seed macro-molecules (diamond seed crystals) at a constant substrate temperature, T_s , and total pressure, P_{tot} . It follows from the results of our previous investigations on processes proceeding on the surfaces of growing diamond crystals (PIEKARCZYK 1992; PIEKARCZYK et al. 1993, 1994) that the process consists of the following three cyclically recurring consecutive surface reactions:

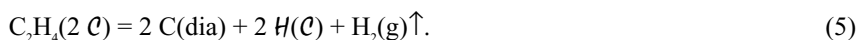
I. Formation of unsaturated (i.e. containing sp^2 bonds) carbon-hydrogen clusters on a labile H-terminated diamond seed crystal surface (polymantane seed macro-molecule):



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



III. Coalescence of the saturated clusters resulting in 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:



In the above equations C(slt) represents carbon dissolved in the gas phase with 'slt' standing for solute, and C(dia) the new carbon epitaxial layer consisting of sp^3 -hybridized and tetrahedrally coordinated carbon atoms. Since this layer is in every respect identical with diamond, we assume that its thermodynamic properties are identical with those of bulk diamond. To stress this fact we added 'dia', the abbreviation of diamond, to the symbol representing this layer. One should, however, keep in mind that this layer is a portion of a polymantane macro-molecule and not an independent unit representing the diamond solid phase. Finally, $C_2H_2(2C)$ and $C_2H_4(2C)$ denote surface-bound unsaturated ethene-like and saturated ethane-like carbon-hydrogen clusters, respectively.

It follows from our calculations that for reaction (4) to be shifted far to the right the concentration of atomic H in the gas phase reaching the growth surface must be considerably greater than the equilibrium concentration of atomic H at temperature T_s (PIEKARCZYK, 1992; PIEKARCZYK et al. 1993, 1994), i.e. the gas phase must be activated to a sufficiently high degree. It is also important to note that in the present model only these unsaturated clusters which are chemically bonded to the growth surface are converted into saturated clusters that subsequently coalesce and finally form a new diamond layer. Other possible unsaturated clusters and sp^2 -hybridized carbon structures, e.g. graphite, which can form on the growth surface but are not chemically bonded to it are not converted into diamond but are etched from the surface by free H atoms. If the deposition is faster than the etching, the remaining portion of such sp^2 -hybridized carbon structures is incorporated into the diamond film as a second phase.

Sequential deposition experiments performed by the researchers from the Stanford University (KELLY et al. 1992 a,b; OLSON et al. 1992), in which distinctly separated C and atomic H fluxes were directed alternately onto the growth surface, clearly demonstrate that the diamond CVD process not only in theory but also in practice can be divided into stages. From the sequential deposition the Stanford researchers (OLSON et al. 1994) deduced a mechanism of CVD diamond growth. According to their model the diamond growth is a

cyclic process consisting of the following surface reactions:

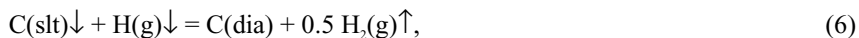
- (i) Carburization of the diamond surface.
- (ii) Deposition of highly disordered carbon on the top of the carburized surface.
- (iii) Etching of disordered carbon by atomic H.
- (iv) Conversion of the carburized diamond surface to diamond at growth sites by atomic H.

It should be noted that the above cycle deduced by the Stanford researchers from their experimental investigations (OLSON et al. 1994) is in reality identical with the cycle deduced from our theoretical investigations except for some insignificant details. As a matter of fact the formation of the unsaturated carbon-hydrogen clusters in our stage I represents the same elementary process as the carburization of 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 opinion of the Stanford researchers that only those carbon structures which are chemically bonded to the growth surface can participate in diamond formation (OLSON et al. 1994) is identical with our view. It is also consistent with the results obtained by ROY et al. (1993 a,b,c) and SHAH et al. They showed that a fine-powdered non-diamond carbon, e.g. graphite, can be converted into diamond by acting on it with atomic H created in a microwave hydrogen plasma. It should be stressed, however, that the conversion takes place only when the non-diamond carbon powder is intimately mixed with a fine diamond powder. The small diamond particles act as seed crystals (ROY et al. 1993 a,b,c). They provide surfaces on which the surface-bound clusters are formed. C atoms needed to form the surface-bound clusters are supplied to the surfaces of the seed crystals either by direct contact with the non-diamond carbon particles or possibly by a short-distance vapor transport (ROY et al. 1993 a,b,c).

5. Thermodynamic coupling of reactions (3), (4) and (5)

By adding together and then dividing by 2 reactions (3), (4) and (5) are reduced to the single reaction



which represents the overall diamond CVD process. It should be noted that reaction (6) includes only substances the thermodynamic properties of which are very well established and easily available. The H-terminated surfaces, e.g. $H(\mathcal{C})$, and carbon-hydrogen clusters, e.g. $\text{C}_2\text{H}_2(2\mathcal{C})$ and $\text{C}_2\text{H}_4(2\mathcal{C})$, 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 (6) can be performed.

If we assume that the mechanism of diamond formation in experiments of ROY et al. (1993 a,b,c) and SHAH et al. is the same as in conventional CVD experiments with the only exception that solid graphite, C(gra) , instead of gaseous carbon source, C(slt) , is used, we can describe this process by the reaction



6. Thermodynamic requirements for accretion of polymantane macro-molecules

The formation of a new carbon layer with the diamond structure, C(dia), on the diamond core of a polymantane macro-molecule according to reactions (6) or (7) is a surface process proceeding at a constant substrate temperature, T_s , and a constant total pressure, P_{tot} . The Gibbs energy change, ΔG , is a criterion for the chemical affinity of such isothermal and isobaric processes. If $\Delta G = 0$, the reaction describing the process cannot proceed because the system is in thermodynamic equilibrium. For the reaction to proceed forwards, ΔG must be less than 0, i.e. must assume negative values. The Gibbs energies of reaction (6), $\Delta G_6(T_s)$, and reaction (7), $\Delta G_7(T_s)$, at the deposition temperature T_s can be calculated from equation (8) (KARAPET'YANC)

$$\Delta G_n(T_s) = \Delta G_n^\circ(T_s) + RT_s \ln \Pi_n, \quad (8)$$

in which n , $\Delta G_n^\circ(T_s)$, R and Π_n denote the reaction number, the standard Gibbs energy of reaction n at temp. T_s , the universal gas constant, and the product of activities of reactants and products of reaction n in the activated feeding gas phase reaching the growth surface, respectively.

After substitution and expansion the following equations are obtained for $\Delta G_6(T_s)$ and $\Delta G_7(T_s)$, respectively:

$$\Delta G_6(T_s) = -RT \ln \frac{a[C(\text{slt})] \times \sqrt{p_{\text{eq}}(\text{H}_2)} \times p(\text{H})}{a[C(\text{slt})]_{\text{dia}} \times \sqrt{p(\text{H}_2)} \times p_{\text{eq}}(\text{H})} \quad (9)$$

and

$$\Delta G_7(T_s) = -RT_s \ln \frac{a[C(\text{slt})]_{\text{gra}} \times \sqrt{p_{\text{eq}}(\text{H}_2)} \times p(\text{H})}{a[C(\text{slt})]_{\text{dia}} \times \sqrt{p(\text{H}_2)} \times p_{\text{eq}}(\text{H})} \quad (10)$$

The symbols in eqs. (9) and (10) denote: $a[C(\text{slt})]$ the carbon activity in the feeding gas phase, $a[C(\text{slt})]_{\text{dia}}$ the carbon activity in the gas phase which is in thermodynamic equilibrium with the sp^3 -hybridized and tetrahedrally coordinated carbon layer C(dia) at temp. T_s , $a[C(\text{slt})]_{\text{gra}}$ the carbon activity in the gas phase which is in thermodynamic equilibrium with graphite at temp. T_s , $p(\text{H})$ and $p(\text{H}_2)$ the partial pressures of atomic and molecular hydrogen, respectively, in the activated feeding gas phase reaching the growth surface, and $p_{\text{eq}}(\text{H})$ and $p_{\text{eq}}(\text{H}_2)$ the partial pressures of atomic and molecular hydrogen, respectively, in the feeding gas phase being in thermodynamic equilibrium at temp. T_s . It should be noted that the quotient $\frac{\sqrt{p_{\text{eq}}(\text{H}_2)}}{\sqrt{p(\text{H}_2)}}$ in the above equations assumes values close to

1 under typical diamond CVD conditions.

It has been found many times (e.g., ZHU et al. 1989 a) that graphite 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:



The Gibbs energy $\Delta G_{11}(T_s)$ of reaction (11) is expressed by the equation

$$\Delta G_{11}(T_s) = -RT_s \sigma(\text{gra}) \quad (12)$$

where $\sigma(\text{gra}) = \ln \frac{a[\text{C}(\text{slt})]}{a[\text{C}(\text{slt})]_{\text{gra}}}$ denotes the thermodynamic C supersaturation of the gas phase with respect to graphite.

It is obvious that $\Delta G_{11}(T_s)$ can assume negative values only for positive values of $\sigma(\text{gra})$. This implies that graphite can be deposited only from gas solutions which are C supersaturated with respect to graphite. In addition, the supersaturation $\sigma(\text{gra})$ must be greater than (or at least equal to) the so-called critical supersaturation $\sigma_{\text{crit}}(\text{gra})$. If $\sigma(\text{gra})$ is less than $\sigma_{\text{crit}}(\text{gra})$, graphite does not deposit. Indeed, ZHU et al. (1989 a) have shown that at the low methane concentration of 0.5 %, the film consisted entirely of diamond crystals without any detectable graphite phase or other non-diamond components.

The term $\ln \frac{a[\text{C}(\text{slt})]_{\text{gra}}}{a[\text{C}(\text{slt})]_{\text{dia}}}$ in eq. (10) is negative because the activity of carbon in diamond is higher than that in graphite. This implies that $\Delta G_7(T_s)$ can assume negative values only if $p(\text{H}) \gg p_{\text{eq}}(\text{H})$. Similarly, $\Delta G_6(T_s)$ can assume large negative values even though $\ln \frac{a[\text{C}(\text{slt})]}{a[\text{C}(\text{slt})]_{\text{dia}}}$ in eq. (9) is negative, if $p(\text{H}) \gg p_{\text{eq}}(\text{H})$. This implies that diamond can be

deposited from gas solutions that are C undersaturated with respect to diamond, provided that the gas phase contains free H atoms in a sufficiently high super-equilibrium concentration, i.e. is activated to a sufficiently high degree. Indeed, it results from the reported experimental data that the deposition of diamond from activated C undersaturated gas solutions has been accomplished (PIEKARCZYK et al. 1990). Very recently, we have demonstrated that diamond deposits from C undersaturated gas solutions also in the carbon/water pseudobinary system (PIEKARCZYK 1998).

In the light of the above discussion the formation of diamond in the form of a new carbon layer with the diamond structure on the diamond core of a polymantane macromolecule in gas environments that are C undersaturated with respect to diamond is no longer a thermodynamic paradox. Also the simultaneous graphite etching and diamond deposition as well as the conversion of graphite into diamond in pure hydrogen plasma is not a thermodynamic paradox in the light of the above discussion.

7. Experimental confirmation of the present approach

The number of papers in which all process variables necessary for Gibbs energy calculations have been reported is very small. Using the reported data (HARRIS et al. 1991 a,b; HSU 1991,1992) we have computed $\Delta G_6(T_s)$, $\Delta G_7(T_s)$ and $\Delta G_{11}(T_s)$ for real experimental diamond CVD conditions. In these calculations it was assumed that the feeding gas phase behaves as an ideal gas solution. This assumption allowed us to replace activities, $a[\text{C}(\text{slt})]$, by respective atomic fractions, $X[\text{C}(\text{slt})]$, of carbon dissolved in the gas phase. The results of the computations are listed in Table 1. It is clear from the table that $\Delta G_n(T_s)$ for all listed reactions assume negative values. However, the values for reactions (6) and (7) are considerably greater than that for reaction (11). This means that diamond forming reactions (6) and (7) are much more favored than graphite forming reaction (11) under typical diamond CVD conditions.

k(CH ₄)	T _s	$\frac{p(\text{H})}{\sqrt{p(\text{H}_2)}}$	ΔG_6	ΔG_7	ΔG_{11}	r	X(H)	Ref.
(vol.%)	(K)		(kcal/mol)	(kcal/mol)	(kcal/mol)			
0.35	1073	3.59E-04	-22.13	-19.91	-2.23	8.0E-05	0.83	(1)
0.35	1073	1.95E-04	-20.85	-18.62	-2.23	1.5E-04	0.83	(2)
0.5	1200	2.12E-03	-26.02	-20.15	-5.87	1.9E-04	0.95	(3)
0.5	1200	3.02E-04	-21.39	-15.52	-5.87	1.3E-03	0.95	(4)

(1) = (HSU 1991), (2) = (HSU 1992), (3) = (HARRIS et al. 1991 a), (4) = (HARRIS et al. 1991 b)

Remarks: 1 cal = 4.184 J, 1 atm = 101325 Pa

Table 1.: Gibbs energies ΔG_6 , ΔG_7 and ΔG_{11} , factor r characterizing the contamination of deposited film with sp²-hybridized carbon, and surface fraction covered with weakly bound H atoms, X(H), (for meaning of the terms see text) calculated using reported values of methane concentrations, k(CH₄), substrate temperatures, T_s, as well as partial pressures of atomic, p(H), and molecular hydrogen, p(H₂). P_{tot} = 2.63E-02 atm.

Using eqs. (9), (10) and (12) a parameter r characterizing the contamination of deposited film with sp²-hybridized/graphitic carbon can be computed. This parameter represents the ratio of the number of C atoms which remain unchanged in the form of graphite to the number of C atoms which are converted into diamond in reaction (7) as well as the ratio of the number of C atoms in sp²-hybridization to the number of C atoms in sp³-hybridization which form in reaction (6) or coexist in quasi-equilibrium under the given stationary conditions existing at the growth surface. The parameter r is calculated from the equation

$$r = \frac{n[\text{C}(\text{gra})]}{n[\text{C}(\text{dia})]} = \frac{a[\text{C}(\text{slt})]_{\text{gra}} \times \sqrt{p(\text{H}_2)} \times p_{\text{eq}}(\text{H})}{a[\text{C}(\text{slt})]_{\text{dia}} \times \sqrt{p_{\text{eq}}(\text{H}_2)} \times p(\text{H})} \quad (13)$$

In addition, the growth rate, GR, as a function of process variables can be estimated if we assume that GR increases with increasing X(H) and decreasing $\Delta G_6(T_s)$. The correlations predicted theoretically and those determined experimentally for both the parameter r and the growth rate are graphically shown in figures 1 and 2, respectively. The ascending, descending and horizontal lines in these figures denote functions which increase, decrease and remain unchanged with the increasing variable (with other variables as constants), respectively. The dashed lines denote experimental data which deviate from the predicted dependencies or trends.

Experimental data consistent with the dependencies shown in Figs. 1 and 2 are reported by KELLY et al. (1992 a,b) for dependence 1a, KONDOH et al. (1992) and KWEON et al. for 1b, ZHU et al. (1989 b) and KONDOH et al. (1992,1994) for 1d, KELLY et al. (1992 a) and OLSON et al. (1992) for 2a, KONDOH et al. (1991,1992), KWEON et al., SPITSYN et al. and ZHU et al. (1989 b) for 2b, KWEON et al., KOMATSU et al., SASAKI et al. and ZHU et al. (1989 b) for 2c, and KONDOH et al. (1992,1994), KOMATSU et al., MATSUMOTO et al. and ZHU et al. (1989 b) for 2d. Only the observed increase in the parameter r with increasing X[C(slt)] is inconsistent with the predicted dependence 1c. This inconsistency is a consequence of the fact that the concentration of free H atoms in the gas phase reaching the growth surface decreases with increasing X[C(slt)] (HSU 1991, 1992; SCHÄFER et al.) and causes an increase in the parameter r. Hence, the effect of p(H), but not the effect of X[C(slt)], on the parameter r is observed. Other deviations shown in Figs. 1b', 1d', 2c' and 2d' can also be rationally explained.

8. Conclusions

If we assume that CVD diamond formation is a chemical process consisting in accretion of polymantane macro-molecules, we can describe it in terms of chemical thermodynamics

without violating thermodynamic principles. Such an approach allows to avoid paradoxes which appear when CVD diamond formation is considered a physical crystal growth process. In addition, the present approach makes it possible to predict dependencies between the growth rate as well as the phase composition of deposited films and important process variables. The predicted dependencies are very consistent with the available experimental data.

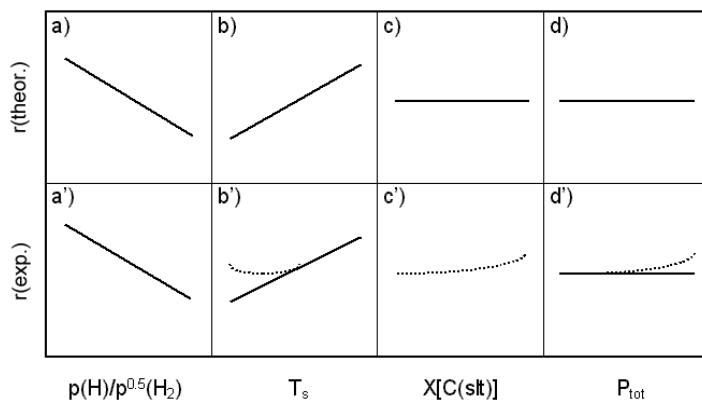


Fig. 1: Theoretically predicted and experimentally determined dependencies of factor r characterizing the contamination of deposited films with sp^2 -hybridized carbon on $p(H)/p^{0.5}(H_2)$, T_s , $X[C(slt)]$ and P_{tot} (a sketch; see text).

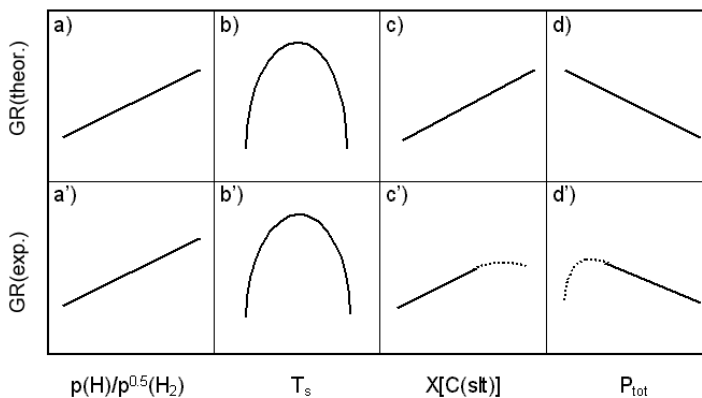


Fig. 2: Theoretically predicted and experimentally determined dependencies of growth rate, GR , on $p(H)/p^{0.5}(H_2)$, T_s , $X[C(slt)]$ and P_{tot} (a sketch; see text).

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Author's address:

Doc. dr hab. W. PIEKARCZYK
Institute of Physics, Polish Academy of Sciences
Al. Lotników 32/46, 02-668 Warszawa, Poland
Fax: +(48-22)843-0926
E-mail: piekar@ifpan.edu.pl