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Thermodynamic Analysis of Processes Proceeding on (111) Faces of Diamond During Chemical Vapour Deposition

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Abstract

Chemically vapour deposited diamond is commonly synthesized from activated hydrogen-rich, carbon/hydrogen gas mixtures under conditions which should, from a thermodynamic equilibrium point of view, favour the production of graphite. Much remains to be understood about why diamond, and not graphite, forms under these conditions. However, it is well known that the presence of atomic hydrogen, is crucial to the success of diamond deposition. As part of an attempt to better understand the deposition process, we have performed a thermodynamic analysis of the processes proceeding on diamond (111) faces in hydrogen rich environments. We show for the first time that the key role of atomic hydrogen is to inhibit the reconstruction of the (111) face to an sp^2-bonded structure, which would provide a template for graphite, rather than diamond formation. The model correctly predicts experimentally determined trends in growth rate and diamond film quality as a function of methane concentration in the starting gas mixture.

Under normal atmospheric conditions the carbon-carbon bonds truncated at diamond crystal surfaces are terminated with foreign atoms; usually with hydrogen. Such hydrogen-saturated surfaces have the same structure as the bulk crystal. Hydrogen-saturated surfaces are stable at low temperatures [1]. However, in the course of heating in ultra-high vacuum, hydrogen desorbs from diamond surfaces [2], and consequently unterminated dangling bonds are created. The latter are extremaly unstable. In order to reduce the surface energy, the dangling bonds bend over and bind with each other. Ultimately, for completely dehydrogenated surfaces, double (π, sp^2) carbon-carbon bonds are formed [3]. The formation of double bonds on (111) faces must be preceded by a surface reconstruction in which the surface carbon atoms rearrange themselves into a new periodic configuration [4]. This reconstruction brings surface carbon atoms into close proximity with one another so that the double bonds may be created. Thus, at temperatures between 1200 - 1300 K [2], which are typical for diamond synthesis by chemical vapour deposition (CVD), diamond (111) faces are almost completely dehydrogenated and reconstructed, and the outermost carbon atoms are sp^2-bonded [3]. As we show below, the formation of such reconstructed surfaces favours graphite and not diamond formation.

CVD diamond is commonly synthesized from hydrogen-rich carbon/hydrogen gas solutions. The presence of hydrogen in the gas phase is expected to affect the hydrogen desorption, and consequently, the subsequent processes (such as reconstruction) proceeding on the diamond surfaces. In order to learn how much they can be affected by hydrogen, we have performed a thermodynamic analysis of these processes proceeding on the diamond surfaces in the course of heating in hydrogen gas.

In the present paper the diamond crystal is considered as a hypothetical hydrocarbon macro-molecule consisting of a large number of carbon atoms arranged in the same way as in the diamond crystal structure. Characteristic of diamond structure is a network of hexagonal carbon atom rings in the chair configuration. In the calculations it is assumed that an equilibrium is established between the gas phase and the diamond face. The latter may exist in several different forms (hydrogen-saturated, hydrogen-free, bulk-like, reconstructed, sp^2-bonded) under different conditions, (e.g., different temperatures and total pressures). These forms can simultaneously occur on a single diamond face. The mixture of the different forms of the diamond (111) face is regarded as an ideal two-dimensional surface solution. The surface fraction, occupied by a particular form, i.e. its surface coverage, SC, is a relative measure of its stability under a given set of conditions. Clearly SC for each form will change with changing conditions.

Thermodynamic properties of different forms of the diamond (111) face, or more precisely those of a diamond crystal which was covered with different forms of the (111) face, have been estimated by means of the group additivity method [5]. The calculations have been performed for temperatures ranging from 300 to 1300 K. The total pressure of hydrogen was fixed at the constant value of 0.1 atm which is typical for most diamond chemical vapour deposition experiments. It was assumed that the (111) face can reconstruct according to the Pandey π-bonded chain model [6].

The results of calculations are presented in fig. 1. As seen from this figure, in the course of heating the hydrogen-saturated, bulk-like (111) face, labelled here as C_4H_2(bulk-like), gradually releases chemisorbed hydrogen and, at the same time, is converted into the hydrogen-free, reconstructed (111) face with the outermost carbon atoms in sp^2 hybridization, labelled as C_4(reconstructed, sp^2-bonded). These two forms of the diamond (111) face were found to be dominant. Of the remaining possible forms only the hydrogen-saturated and reconstructed (111) face, labelled as C_4H_2(reconstructed), was found to exist on the diamond (111) face in any appreciable quantity (fig. 1). All other possible forms were found to be unstable under the range of equilibrium conditions considered in this study.

The results of calculations are satisafctorily consistent with those of experimental investigations on diamond surface chemistry reported in the literature. Surprisingly, the presence of 0.1 atm of hydrogen exerts only a very weak effect on the behaviour of the diamond (111) face. The calculations show that this relatively large hydrogen concentration does not, as might have been expected, inhibit the desorption of hydrogen and the reconstruction of the surface. The present calculations strongly support the Pandey [6] chain model, and especially his assumption that the carbon atoms in the surface chains are π-bonded.

According to our calculations the diamond (111) face is completely dehydrogenated and reconstructed, and its outermost carbon atoms are sp^2-bonded, at high temperatures of around 1250 K, which are considered by some authors (e.g., ref. [7]) as optimum for diamond deposition. (All calculations results cited later in this paper will be referred to this temperature). It is obvious that such a surface is not an appropriate substrate for diamond growth, not only because it is reconstructed but, most importantly, because it is densely covered with sp^2 bonds. The latter will facilitate the nucleation and growth of graphite, and thus, such a surface can act as a graphite seed [8]. In order to be able to grow diamond crystals, one should prevent the formation of sp^2 bonds on the exposed growing surfaces. In other words, one should keep the surfaces in the hydrogen-saturated state, i.e. preclude the desorption of hydrogen.

According to the Le Chatelier rule, this can be accomplished by increasing the pressure of hydrogen in the system. The required partial pressure of molecular hydrogen, $P(H_2)$, can be calculated from the equilibrium constant, $K_a(1) = 1.3\times10^{-2}$ (T = 1250 K), of the hydrogenation reaction

$$C_4(\text{reconstructed, } sp^2\text{-bonded}) + H_2(g) = C_4H_2(\text{bulk-like}) \qquad (1)$$

For instance, in order to keep 99.99 % of the surface area of the (111) face in the hydrogen-saturated and bulk-like state, $P(H_2)$ would have to be increased up to 7.5×10^5 atm. Clearly, the required $P(H_2)$ is extremely high. Thus, molecular hydrogen is ineffective in inhibiting the reconstruction.

Atomic hydrogen, H, should be much more efficacious because it is much more reactive than H_2. Indeed, it is well known that some form of activation of the hydrogen mixtures is required for successful diamond growth. The main purpose of the activation is to produce atomic hydrogen in large quantities. In what follows, the interaction of atomic hydrogen with the (111) face is explored. The equilibrium constant, $K_a(2) = 5.8\times10^{10}$ (T = 1250 K), of the hydrogenation reaction

$$C_4(\text{reconstructed, } sp^2\text{-bonded}) + 2\,H(g) = C_4H_2(\text{bulk-like}) \qquad (2)$$

is much higher than $K_a(1)$, and thus, $P(H) = 4.2\times10^{-4}$ atm should be sufficient to produce the same effect as $P(H_2) = 7.5\times10^5$ atm.

Although the above mentioned absolute value of required P(H) is low, it is 2.7×10^3 times higher than the equilibrium value at T = 1250 K and $P_{tot} = 0.1$ atm. A non-equilibrium P(H) considerably higher than $P_{eq}(H)$ can be maintained for a long period of time only in gas phases which are continuously activated or excited. Super-equilibrium atomic hydrogen (SAH) present in such activated gas phases is very unstable and thus, very reactive. Since H is present in the gas phase in a non-equilibrium concentration, the use of equilibrium thermodynamics must be treated with caution.

The basic interaction of atomic hydrogen with hydrocarbons is either abstraction or addition of hydrogen atoms from or to hydrocarbon molecules [9]. These different types of reactions lead to opposite results. Addition reactions in general destroy double bonds, whereas the abstraction create them. Thus, the resulting concentrations of reaction products depends not only on initial concentrations of reactants but also on rates of the competing reactions. Products of faster reactions are created quicker, and consequently they occur in the system in a larger quantity than those of slower reactions. When the differences in reaction rates are large, the faster reactions can play a dominant role in the process.

In order to justify the application of thermodynamics to the activated gas species, we note that generally speaking, the reaction rates are proportional to the exothermicity of the reactions [10]. If this is true, one can expect that the addition of hydrogen atoms to the diamond (111) face should be approximately 10 times faster than the abstraction of hydrogen atoms from the face because, according to our calculations, the enthalpy of the addition reaction, $\Delta H^{o}(ad) = -97.1$ kcal/mole ($T = 1250$ K), is approximately 10 times smaller than the enthalpy of the abstraction reaction, $\Delta H^{o}(ab) = -9.8$ kcal/mole ($T = 1250$ K). Indeed, it is well proved that the addition reactions are much faster [10] than the abstraction reactions, at least by one order of magnitude [9], because of the lower activation energies [10]. It can be deduced from data reported in ref. [11] and [12] that some addition reactions can be faster than the related abstraction reactions by a few orders of magnitude. We have taken advantage of this fact and relying upon the above information we have assumed that the abstraction reactions play a negligible role and can be omitted in the calculations.

Elimination of the abstraction reactions makes it possible to postulate that a pseudo-equilibrium is established between the non-equilibrium gas solution and the two-dimentional surface solution of the different forms of the diamond (111) face. The calculation results presented in fig. 2 show that the SC of the form C_4(reconstructed, sp^2-bonded) decreases whereas that of the form C_4H_2(bulk-like) increases with increasing P(H), respectively. At $P(H) > 10^{-4}$ atm the (111) face is almost completely regenerated, i.e. hydrogenated and has the bulk structure. Such a face is free from sp^2 bonds, and thus it should be an appropriate substrate for successful diamond growth. However, comparison with fig. 1 shows that at high temperatures such a face is unstable under equilibrium conditions. At high temperatures the hydrogen-saturated, bulk-like face can exist only in the presence of high concentration of super-equilibrium atomic hydrogen (SAH). Hence, the need to continuously activate the nutrient gas phase to a sufficiently high degree in order to provide sufficient quantities of SAH to ensure successful diamond growth.

The absence of sp^2 bonds on surfaces of diamond seed crystals is a necessary but not a sufficient condition for successful growth of diamond. For a diamond crystal to grow, carbon atoms from the gas phase must be added to the crystal surface. They must be added in a way leading to the extention of the preexisting diamond lattice, i.e. new hexagonal carbon atom rings in the chair configuration must be formed. Steric considerations dictate that in the case of the (111) face only those carbon-hydrogen clusters which contain 3 or more carbon atoms and are bonded to the surface with 2 or more carbon-carbon bonds can fullfil the above requirement. For convenience, the clusters which are bonded to the diamond face with more than one carbon-carbon bonds will be called, in this paper, the multiple-bonded clusters (MBCs). Simple-bonded adsorbates and multiple-bonded carbon-hydrogen clusters which can be formed on the bulk-like diamond (111) face, and have been selected for present considerations, are collected in table I. The asterisks in the parentheses, (*), represent the number of bonds with which the cluster is bonded to the diamond face.

One can expect that high growth rates can be attained only under the conditions at which a large number of MBCs can be formed on diamond crystal surfaces. To produce high quality diamond which contains only a small amount of graphitic or other sp^2 hybridized carbon inclusions, the number of double bonds formed in these MBCs should be reduced almost to zero, i.e. mainly saturated MBCs should be formed.

In order to estimate experimental parameters at which the above requirements can be met, we have carried out calculations for the following conditions: deposition temperature, $T = 1250$ K, and total pressure, $P_{tot} = 0.1$ atm. The initial methane concentration in the starting gas mixture, $C_{in}(CH_4)$, and the partial pressure of atomic hydrogen, P(H), were varied in the ranges from 1 to 10 vol.% and from 10^{-5} to 10^{-3} atm, respectively. It was assumed that, except for P(H), the composition of the activated gas phase was identical with the one of the gas mixture thermally dissociated under equilibrium conditions. Only P(H) was increased above its equilibrium value in order to show how much this affects reactions proceeding on the diamond face which is in contact with the activated gas phase.

In fig. 3 calculation results are presented for $C_{in}(CH_4) = 1$ vol.%. As seen from this figure, at P(H) $<10^{-4}$ atm "benzene-like clusters, $C_6H_3(3*)$, are most abundant. SCs of other clusters, including $CH_3(*)$, are small. Since $C_6H_3(3*)$ clusters contain a considerable number of double bonds (see table I), conditions under which such unsaturated clusters can form and exist on diamond surfaces are unfavourable for diamond growth for reasons discussed earlier. However, with increasing P(H) the surface coverage of "benzene-like" clusters, $SC[C_6H_3(3*)]$, decreases whereas that of "cyclohexane-like" clusters, $SC[C_6H_9(3*)]$, increases and eventually the latter become dominant. *Since the* $C_6H_9(3*)$ *clusters do not contain double bonds, a successful* growth of diamond can be expected in this region.

At P(H) $\sim 2.5\times10^{-4}$ atm "cyclohexane-like" clusters, $C_6H_9(3*)$, cover already ~ 50 % of the surface area. When $SC[C_6H_9(3*)]$ is high, the "cyclohexane-like" clusters coalesce and form a new continuous surface carbon layer. Coalescence reactions are spontaneous because large saturated carbon-hydrogen complexes are thermodynamically much more stable than the separate "cyclohexane-like" clusters. Standard Gibbs energies of the coalescence reactions have large negative values, implying large thermodyanamic probabilities of reactions. For instance, the standard Gibbs energy of the reaction

$$3\ C_6H_9(3*) = C_{18}H_{21}(9*) + 3\ H_2(g) \qquad (3)$$

is equal to -92.4 kcal/mol at 1250 K.

The structure of the new surface carbon layer formed by the coalescence of the saturated MBCs is identical with that of the external layer of the hydrogen-saturated, bulk-like diamond (111) face. The new surface carbon layer can be regarded as the extention of the preexisting diamond lattice. Hence, the formation of the new surface diamond layer means the growth of the diamond crystal. Formation of the new surface carbon layer with the diamond structure is expected to be possible only when $SC[C_6H_9(3*)]$ is sufficiently large. When the latter is small, the continuous surface carbon layer cannot be formed, i.e. diamond cannot grow or the growth rate is very low.

The new surface carbon layer may contain a certain amount of double bonds in form of graphitic and other sp^2 hybridized carbon inclusions. This is because the unsaturated MBCs take also part in the coalescence process. At least a part of sp^2 bonds contained in the unsaturated MBCs can be incorporated into the surface carbon layer in the course of its formation. The concentration of sp^2 bonds in the layer is expected to be proportinal to the concentration of sp^2 bonds contained in all (saturated and unsaturated) MBCs, $I = n(sp^2)/[n(sp^2) + n(sp^3)]$, before the coalescence. It follows from our calculations that the concentration I is a very strong function of P(H), i.e. changes very rapidly with the latter. It may increase by six orders of magnitude, as P(H) is decreased by only one order of magnitude. Thus, we can conclude that the concentration of double bonds in the deposited film should rapidly increase with decreasing P(H), and vice versa.

It follows from our calculations that $SC[C_6H_9(3*)]$ is a complex function of P(H) and $C_{in}(CH_4)$, and increases rapidly with both these parameters. Consequently, one can expect that the growth rate should also increase with (i) increasing P(H) and with (ii) increasing $C_{in}(CH_4)$. A high $SC[C_6H_9(3*)]$, which is needed for the spontaneous coalescence of MBCs, can be attained at various combinations of P(H) and $C_{in}(CH_4)$. This implies that it should be possible to deposit diamond, at the same or similar growth rates, from gas solutions of different chemical composition which is determined by given P(H) and $C_{in}(CH_4)$. However, the concentration of sp^2 bonds in the deposited film will not be the same because it strongly depends on P(H). Diamond films containing small amount of double bonds can only be deposited when P(H) is sufficiently high.

Conclusions discussed in the above paragraph are in good agreement with results of experimental investigations currently reported. Experimental data on the concentration of atomic hydrogen in diamond deposition systems, and especially on its influence on the deposition rate are scarce. Only very recently it was experimentally proved that the deposition rate increases with increasing P(H) [13]. Contrary to the scarcity of data related to P(H), it has been experimentally proved many times that the deposition rate increases with increasing concentration of methane in the starting gas mixture (e.g., ref. [14]). The above dependence is usually reported together with the information that the concentration of graphitic or other non-diamond carbon inclusions in deposited films also increases with increasing $C_{in}(CH_4)$ (e.g., ref. [14]). We conclude that the latter dependence is a consequence of a decrease in the concentration of atomic hydrogen which, according to recently reported data [15,16], occur as the methane concentration increases. Hsu [16] has recently reported that in a hot filament system the H-atom concentration dropped by more than an order of magnitude when the methane percentage was increased from 0.4 % to 7.2 % [16]. Such large decrease in P(H) could increase the concentration I, and consequently, the concentration of double bonds in the deposited film, by more than six orders of magnitude.

Using data published by Hsu [16] we have calculated the concentration of double bonds I and estimated the growth rate as functions of the initial methane concentration in a real experimental system. Results of our computations are presented in fig. 4. From this figure it is apparent that both the growth rate and the concentration of double bonds in the deposited layer increase with increasing methane concentration. These trends are consistent with numerous experimental data reported in the literatue. Some experimentally determined growth rates are displayed in fig. 4 for comparison. From fig. 4 is evident that the concentration of double bonds in the deposited film can increase by 4 order of magnitude when the methane concentration is increased from 0.5 to 2 %. This is consistent with many reports (e.g., ref. [14]) showing that the concentration of graphitic and other non-diamond carbon inclusions dramatically increases with increasing methane concentration in the above mentioned range.

The general conclusion resulting from our calculations and discussion presented in this paper is that super-equilibrium atomic hydrogen (SAH) plays a key role in the diamond crystal growth process. If present in a sufficiently high concentration it inhibits the desorption of hydrogen from the diamond surfaces, and consequently, the reconstruction of the latter into sp^2-bonded structures. In addition, SAH prevents the formation of unsaturated carbon-hydrogen clusters, and simultaneously advances the production of saturated carbon-hydrogen clusters on the diamond surfaces causing rapid growth of diamond crystals/films containing small amount of double bonds.

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Figure captions

Fig. 1. Surface coverages of different forms of the diamond (111) face, when the latter is heated in hydrogen gas, versus temperature. P_{tot} = 0.1 atm.

Fig. 2. Surface coverages of different forms of the diamond (111) face, when the latter is in contact with activated hydrogen gas, versus partial pressure of atomic hydrogen. P_{tot} = 0.1 atm, T = 1250 K.

Fig. 3. Surface coverages of single-bonded adsorbates and multiple-bonded carbon-hydrogen clusters formed on the bulk-like diamond (111) face, when the latter is in contact with activated carbon/hydrogen gas solutions, versus partial pressure of atomic hydrogen. $C_{in}(CH_4)$ = 1 vol.%, P_{tot} = 0.1 atm, T = 1250 K. Only clusters 1, 2, 3, 8 and 9 are shown (see table I). Other clusters have SCs lower than 10^{-5} and have thus been omitted.

Fig. 4. Growth rate of diamond crystals (solid line) and the concentration of sp^2 bonds in multiple-bonded clusters (dashed line), as estimated by using data reported by Hsu [16], versus initial methane concentration. Crosses, +, and triangles, Δ, represent the growth rates experimentally determined by Zhu et al. [14] and Tomaswick and Bruggemen [17], respectively.

Table I. Simple-bonded adsorbates and multiple-bonded carbon-hydrogen clusters formed on the bulk-like diamond (111) faces.

No	Symbol	Name	Number of double bonds
1	H(*)		
2	BD(*)	dangling bond	
3	CH_3(*)	methane-like	0
4	C_3H_4(2*)	propene-like	1
5	C_3H_6(2*)	propane-like	0
6	C_4H_5(3*)	isobutene-like	1
7	C_4H_7(3*)	isobutane-like	0
8	C_6H_3(3*)	benzene-like	3
9	C_6H_9(3*)	cyclohaxane-like	0

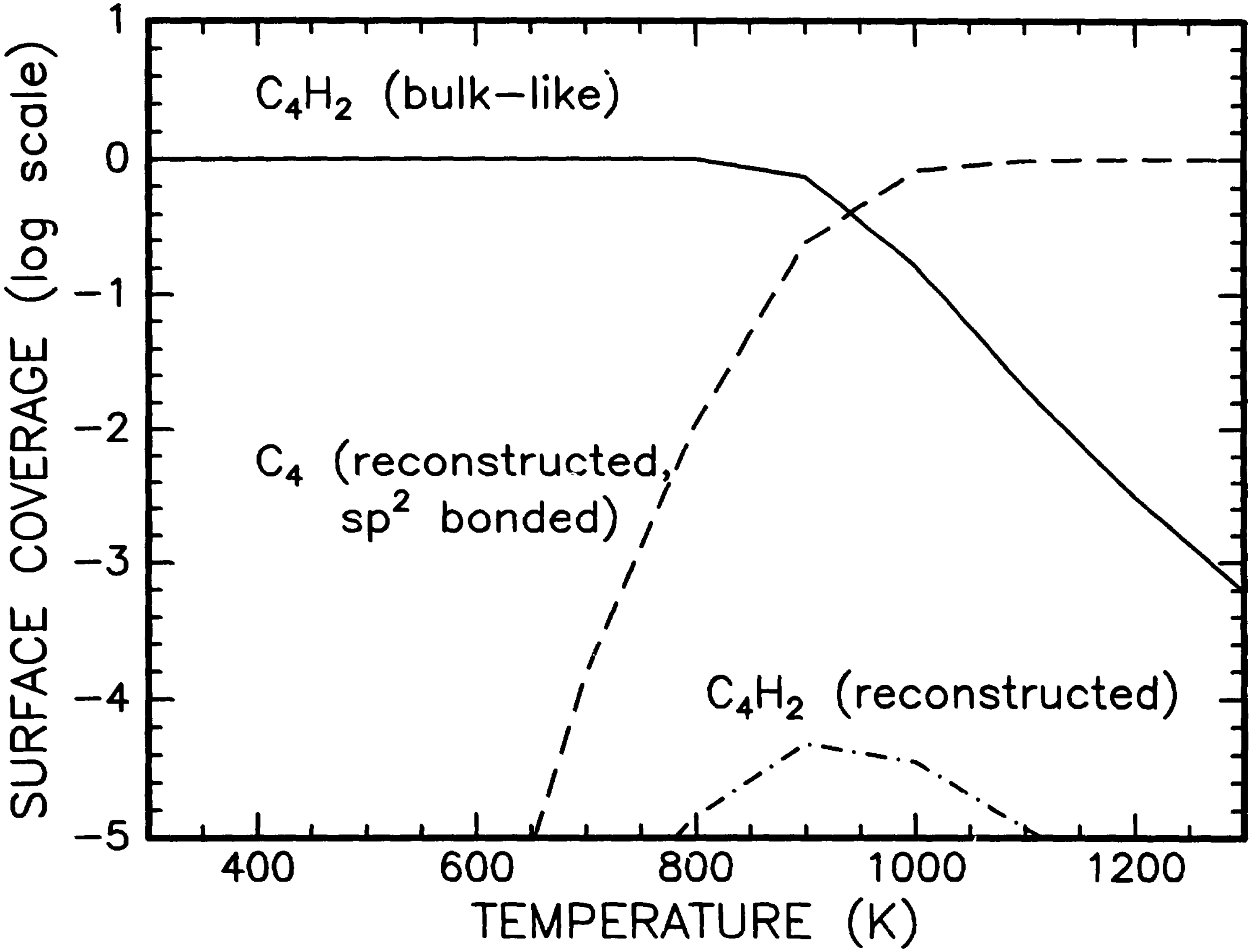

SURFACE COVERAGE (log scale)
1
0
−1
−2
−3
−4
−5
400
600
800
1000
1200
TEMPERATURE (K)
C_4H_2 (bulk−like)
C_4 (reconstructed, sp^2 bonded)
C_4H_2 (reconstructed)

Fig. 1.

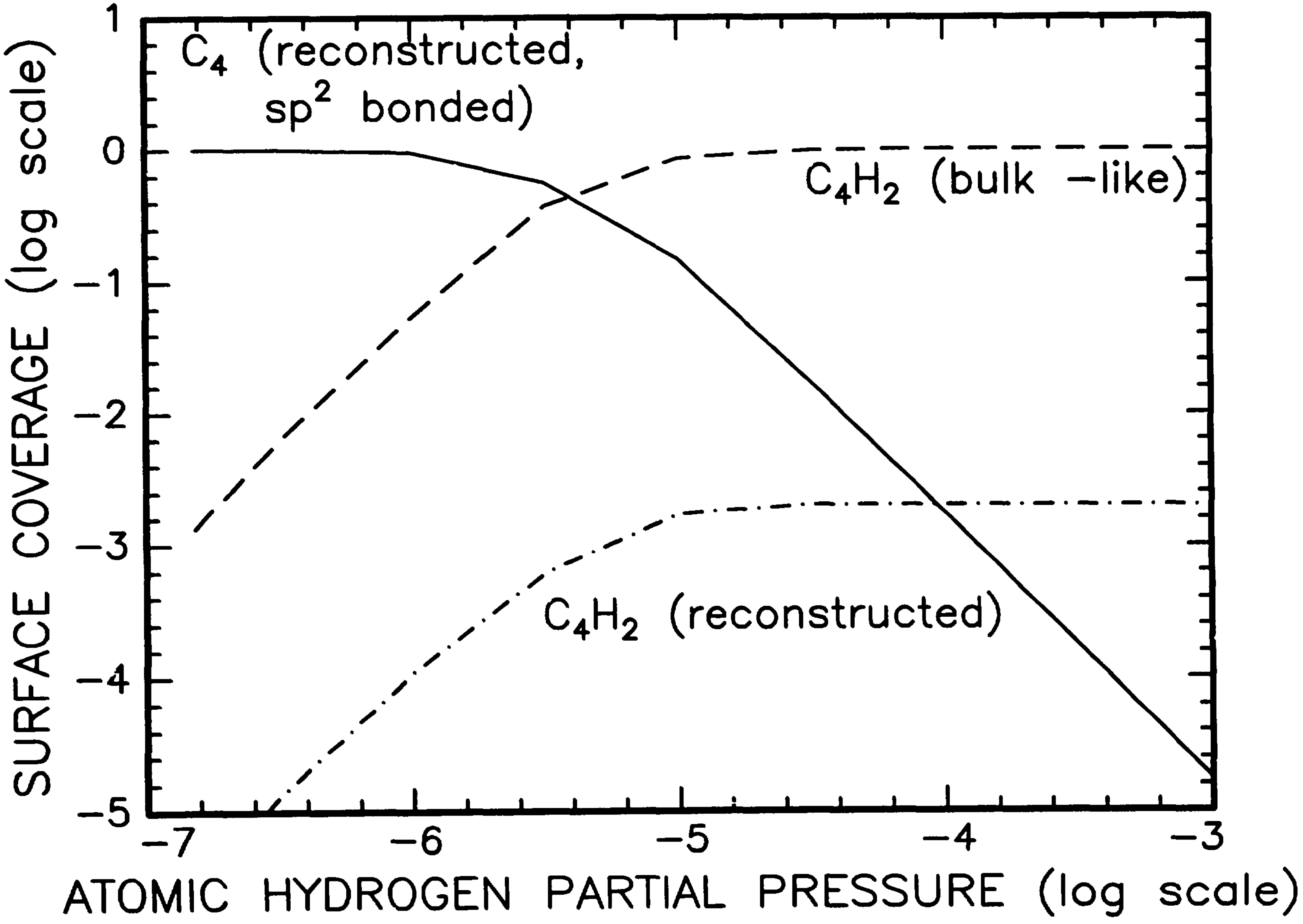
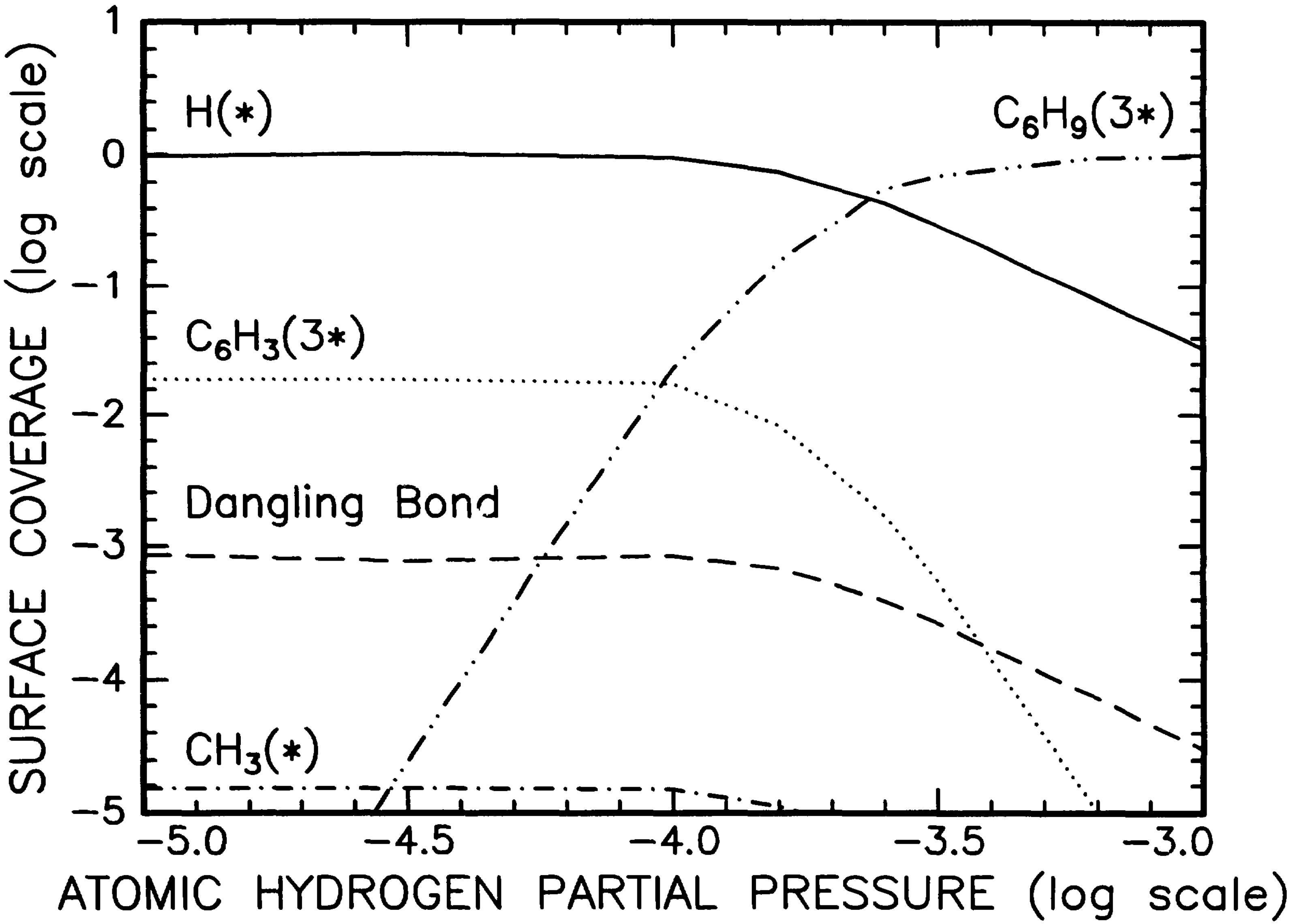
C_4 (reconstructed, sp^2 bonded)
C_4H_2 (bulk -like)
C_4H_2 (reconstructed)
SURFACE COVERAGE (log scale)
1
0
−1
−2
−3
−4
−5
−7
−6
−5
−4
−3
ATOMIC HYDROGEN PARTIAL PRESSURE (log scale)

Figure 2.



SURFACE COVERAGE (log scale)
1
0
−1
−2
−3
−4
−5
H(*)
$C_6H_9(3*)$
$C_6H_3(3*)$
Dangling Bond
$CH_3(*)$
−5.0
−4.5
−4.0
−3.5
−3.0
ATOMIC HYDROGEN PARTIAL PRESSURE (log scale)

Fig. 3

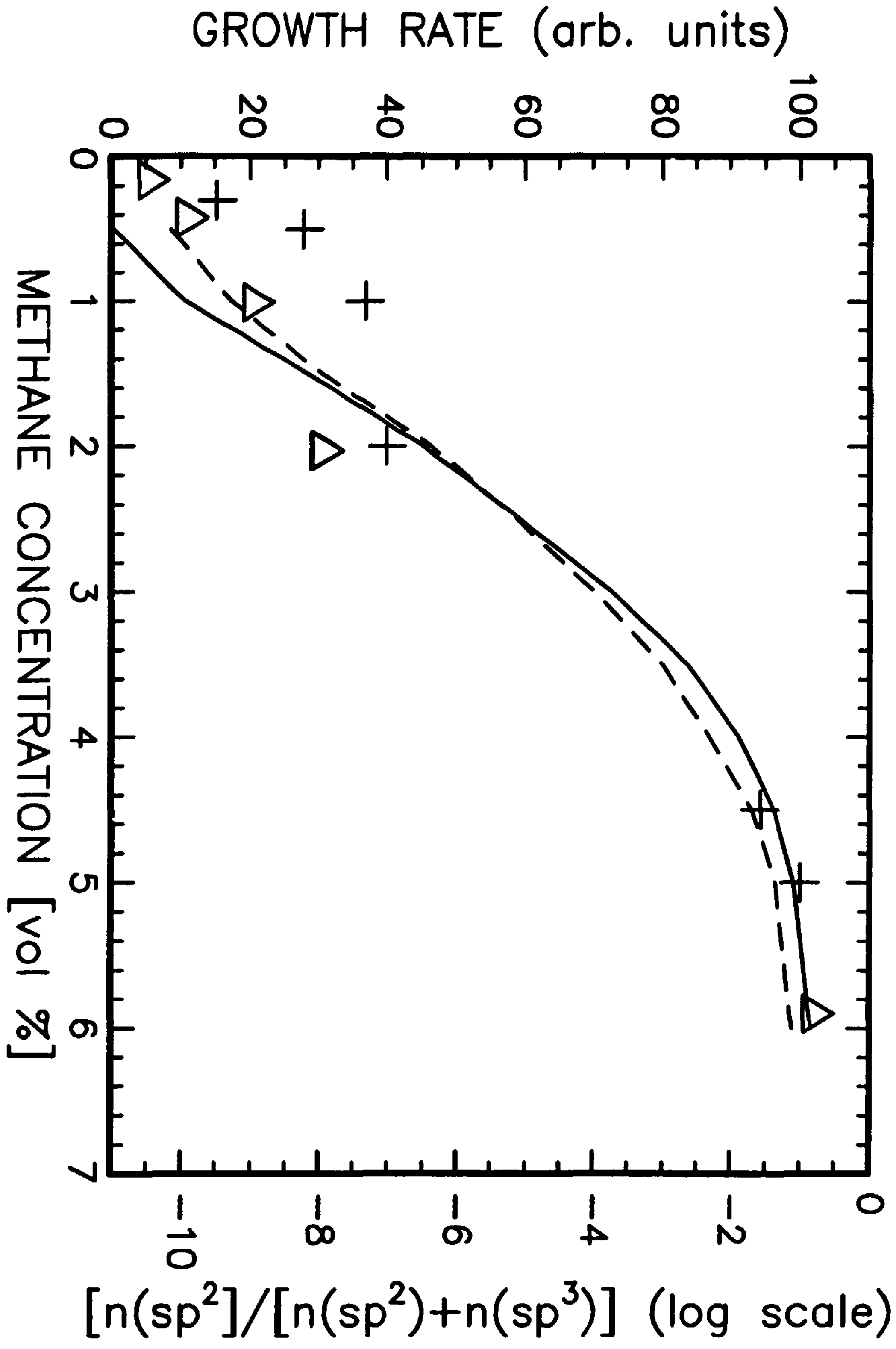

GROWTH RATE (arb. units)
0
20
40
60
80
100
METHANE CONCENTRATION [vol %]
0
1
2
3
4
5
6
7
0
-2
-4
-6
-8
-10
$[n(sp^2]/[n(sp^2)+n(sp^3)]$ (log scale)

Fig. 5.