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INSTRUMENTS AND METHODS OF INVESTIGATION

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Possibilities of gas-phase synthesis of diamond structures from mixtures of hydrogen and hydrocarbons

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Contents

Abstract. To date, there is no universally recognized notion of diamond structure formation from the gas phase. The set of fragments determining this process differs for different methods of activation. Information on elementary processes of the interaction of hydrogen and hydrocarbon molecules with a surface for activation and deposition can be found in the literature, but it is scarce. Scientific problems of thermal activation relate not only to carbon structure synthesis; the description of non-equilibrium processes in channel flows with heterogeneous chemical reactions has unquestionable importance. In this review, the modern state of studies on the interaction of hydrogen and methane molecules and their fragments with high-temperature tungsten surfaces and diamond surfaces at temperatures close to 1300 K is considered, and accessible results are presented.

Keywords: gas-jet synthesis of diamond structures, atom–surface interaction

1. Introduction

The synthesis of polycrystalline and single-crystal diamond products from the gas phase has made great advances over the last 10–25 years both in experimental methods and novel technologies, even though there is no established understanding of how diamond structures form, and hence no theory is available with a predictive power sufficient to show how to design and develop new methods. Currently, it is only experimental research that can lead to new methods (such as the use of gas activation on extended surfaces).

The objective reason for the lag in theoretical understanding is the unfathomable diversity of processes by which the necessary composition of active fragments can be obtained at the molecular level for specific conditions in terms of the particle energy, density, temperature, and deposition surface structure.

This review is to a large extent concerned with using thermal activation on an extended surface and places emphasis on the use of activation products on practically clean tungsten surfaces. This made it possible to approach a new field of knowledge, where no data are available on the constants for elementary interaction reactions between molecular fragments and a solid surface. It also proved possible to elucidate the role of heterogeneous reactions in gas flows along high-temperature channels and to suggest avenues for further research into such flows under conditions intermediate between the free-molecular and continuum regimes.

The thermodynamic arguments determining the graphite–diamond phase diagram were established by Leipunskii in 1939 [1]. Thermodynamically stable diamond was first obtained under high-temperature high-pressure conditions in 1955 [2]. As the temperature and pressure are decreased, diamond preserves itself as metastable. The synthesis of diamond from the gas phase at low pressure and low temperature (i.e., in the metastable state) was achieved in the USSR and USA in the 1960s [3, 4]. One drawback of diamond synthesis at high pressure and high temperature (i.e., under close-to-natural conditions) is the limited size of the diamond single crystals produced (a few nanometers to a few millimeters). Moreover, it is impossible to fabricate extended film coatings, or coatings for complex-shaped surfaces. Deposition from the gas phase currently holds greater promise even for single-crystal synthesis. This is a rapidly developing technology, but the diamonds it produces are more costly than natural ones.

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Table 1. Comparison of CVD diamond synthesis processes.

Conditions / Method	Temperature, K	Pressure, Pa	Flux H_2, $cm^3\ min^{-1}$	Deposition rate, $\mu m\ h^{-1}$	Deposition area, cm^2
Thermal	2200 – 2500	$10^3 - 5 \times 10^3$	1 – 100	1 – 15	up to 10^4
Plasma	~ 5000	$10^{-4} - 10^5$	up to 10^3	up to 10^3	~ 1
Microwave discharge	up to 5000	$10^3 - 5 \times 10^3$	~ 1	up to 30	up to 100
Burning	up to 4000	10^5	$\sim 10^3$	up to 30	~ 1
Laser	up to 15000	10^5	$\sim 10^3$	up to 120	~ 1

This technology, which is known as chemical vapor deposition, CVD, and which we call the gas phase deposition for brevity, has been developed in several versions over the last decades, with mixtures of hydrogen and carbon-containing gases being activated (fragmentized and excited) in various ways and subjected to interaction with a relatively cold surface as they are being deposited. Without assessing the practical importance of each of these methods, we illustrate their diversity with the example of using hydrogen and methane. When thermally activated [5, 6], H_2 and CH_4 molecules partially dissociate and are excited when colliding with a heated surface. Electric activation occurs either in an arc discharge plasma [7] or in a radiofrequency or microwave discharge plasma [8–10], whereas chemical activation occurs in a burner flame [11]. Laser activation is via the interaction of laser radiation with gaseous or condensed source materials [12]. Table 1 gives an idea of the current status of CVD diamond synthesis by comparing the respective deposition rates. Many excellent general reviews are available that give a detailed discussion of diamond deposition processes under specific conditions [13–15]. Also available are area-specific reviews, as exemplified by two *Physics–Uspekhi* publications [16, 17].

Irrespective of the activation method used, the key factor controlling the gas-phase synthesis is the collision with the surface of atomic and molecular fragments existing in the atmosphere near the deposition surface. The composition and state of the atmosphere depend on the activation method and on how the resulting mixture is transported to the surface. In this review, we discuss thermal-activation-based methods, focusing to a large extent on experimental and theoretical achievements in determining the probabilities of physicochemical processes. In analyzing thermal activation, processes at the contact with extended activating surfaces (for example, in a channel flow [6]) are examined. A feature of this contact region is that heterogeneous activation and dissociation processes occur as molecules frequently collide with the hot surface. Years of research have revealed that the most important condition for the deposition of diamond is the formation of SP^3-hybridization structures due to the action of atomic hydrogen located on the C–C and C–H compounds precipitated on the diamond–carbon surface. In particular, the combination reaction of hydrogen and carbon atoms and the entrainment of hydrocarbon fragments from the deposition surface are the determining factors. It is proved that this destruction mechanism operates for both C–C and $C-H_x$, but is much faster in the latter case. There is no need to present a review of the vast literature available on the topic: this knowledge is commonly accepted and is used here.

A very convenient choice for an extended surface is a cylindrical channel along which the precursor gases move. The active gas mixture is produced both in the channel and in the region in front of the substrate. Figure 1, which is a schematic of the experiment conducted in Ref. [6], illustrates Monte Carlo results for the specific atomic hydrogen flow for activation in a cylindrical channel formed by a tungsten spiral. The optimum conditions for synthesizing diamond by the above method are unknown. There is a wide range of performance conditions and parameters that should be analyzed and investigated, including the channel surface material, the temperature of the channel activating surface, the channel size, the channel outflow geometry (a hole or a supersonic nozzle), the channel nozzle-to-substrate distance, the gas composition and flow rate, the ambient gas pressure, the substrate temperature, and the precursor gas supply method (activation during the joint supply or separate supply of activated gases). Because each of these factors can be important, the only way to solve the problem is by accumulating experimental and calculated data over a wide range of parameters. We note that the flows of interest range from free molecular to continuum, with local features characteristic of nonequilibrium processes, i.e., including flows that are dominantly influenced by heterogeneous catalytic processes, as well as transition and near-thermodynamic-equilibrium flows.

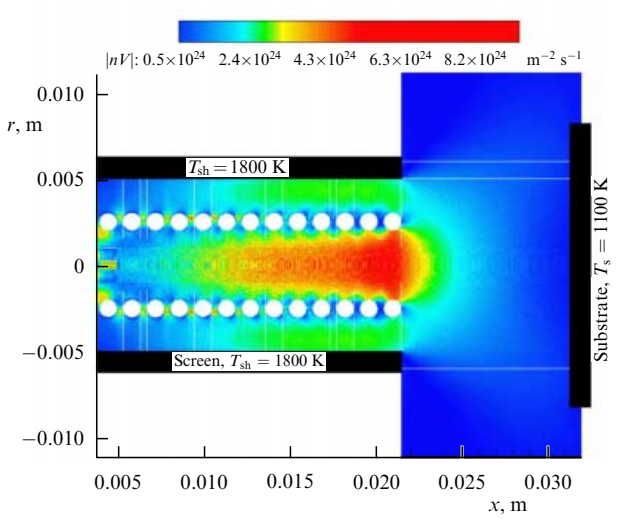

Figure 1. Experiment with an extended activation surface (schematic). Spiral temperature 2400 K, deposition chamber pressure 266 Pa, spiral exit flow rate 1300 m s^{-1}.

In what follows, only processes involving hydrogen and methane are analyzed.

2. Thermal activation of hydrogen

Thermal activation of hydrogen is part of the general carbon–surface interaction problem, which is of both fundamental

and applied significance. The most important aspects of the problem are the longevity of materials in the hydrogen atmosphere in engineering devices; the effect of atomic and molecular hydrogen on the surface of potential fusion reactors; the energetics of hydrocarbon hydrolysis and hydrogen storage problems; and, finally, the focus of the present analysis, hydrogen activation in gas-phase diamond growth devices. The boundary conditions that determine the atomic hydrogen flow from the surface into the bulk of the gas are complex and not fully understood. The processes involved include: dissociation of hydrogen molecules by collisions with the surface; hydrogen adsorption followed by molecular breakdown and desorption of atomic fragments; atom–surface collisions followed by reflection after accommodation or adsorption; recombination of dissimilar atoms; dissolution of hydrogen in metals; and, finally, inner-shell excitation of molecular hydrogen by collisions with the surface. The inclusion of these processes is important both for determining energy effects and the kinetics of elementary collisions when performing numerical simulations and in describing boundary conditions for continuous flows.

We limit the discussion to the interaction of hydrogen with tungsten. This process is difficult to describe over a wide temperature range because it greatly depends on the state of the surface with which the particles collide (in particular, on the crystal face type) and on the state of the sorbed particles (which is temperature and pressure dependent). The problem is somewhat simplified for high temperatures ($> 2000\,^{\circ}C$) and a strong vacuum, when the surfaces become cleaner. We also note that the borderlines between various surface states are very blurred.

The first and most significant contribution to understanding the hydrogen–tungsten interaction was apparently made by Langmuir [18, 19], who discovered the chemosorption decomposition of hydrogen on a hot tungsten surface and deduced the absorption law in the form of an isotherm that now bears his name. Over the last several decades, there has been much research on the subject, stimulated by the fact that a number of fundamental problems remain unsolved and by the need for detailed knowledge of the processes involved. For example, a 1975 review paper [20] noted that it was not yet clear whether hydrogen is sorbed in the form of H_2 molecules and what the role of the interaction between the adsorbate atoms is, and that there was disagreement between the calculated and experimental monolayer atomic densities (implying that the Langmuir isotherm is not unique). These questions remain open. An important factor, as noted based on the Auger spectrum, is a clean surface (that is, the absence of carbon and oxygen on it), which can be achieved by flash cleaning at a temperature of 2200 K. Zheng and Gallagher [21] in 2006 showed convincingly that the probability of hydrogen dissociation on a tungsten surface at 2200 K is independent of pressure.

We now present some published data that are useful in the remainder of this review, including in calculations. The H–H bond length is 0.74 Å, the dissociation energy is 434.6–458.8 kJ mol^{-1}, the chemosorption well depth for the H_2 molecule on the W(100) surface is 146 kJ mol^{-1} [21], the W–H bond energy is 293 kJ mol^{-1} [22], the initial adsorption heat of the H_2 molecule is 133–167 kJ mol^{-1} [22], the endothermic dissolution energy of H atoms is 135.2 kJ mol^{-1} [23], the diffusion activation energy of H atoms is 37.7 kJ mol^{-1} [23], the adsorption energy of H atoms on the W(001) surface ranges from 47.3 to 96.9 kJ mol^{-1} [23] depending on the adsorption channel, the adsorption energy of H atoms on the W(110) surface is 72.4 kJ mol^{-1} [23], and the adhesion coefficient of H atoms to W(001, 110) is less than 0.6 for atoms with an energy below 29 kJ [23]. The diffusion coefficient of H atoms in tungsten is defined by $D = D_0 \exp(-E_a/kT)$ [22]. In Table 2, we list the diffusion coefficients calculated in Ref. [23].

Table 2. Diffusion coefficients.

T, K	500	900	1450
D, m^2 s^{-1}	1.38×10^{-10}	6.81×10^{-9}	4.33×10^{-8}

Important research information on the activity of tungsten and rhenium interacting with $H_2 + CH_4$ and $H_2 + C_2H_2$ mixtures is presented in [24]. They were apparently the first to show that at low pressures (1200 Pa) in a 1.5% $C_2H_2 + H_2$ mixture, up to about 2600 K, the surface of tungsten is so much carbidized that its degree of blackness reaches a value close to 0.85. Above 2600 K, it reduces to 0.5, the level of radiation from a clean tungsten surface. A possible candidate for a heat-resistant activator material is rhenium. Unlike tungsten, a rhenium surface in an $H_2 + CH_4$ mixture retains its carbidization up to 2200 K. As the temperature is increased, the rhenium surface becomes cleaner and its blackness reduces to 0.43–0.45. The results obtained determine the operation conditions of activation surfaces, conditions when carbidization introduces virtually no uncertainty into the estimate of the state of the tungsten surface and hence into the probability of the formation of atomic hydrogen on the surface.

In [25], an experimental study of the dissociation of hydrogen molecules on tantalum and tungsten wires in a gas at rest at temperatures of 2000 K, 2300 K, and 2500 K is reported. Although there are some questions as to the data processing procedure used in Ref. [25], the following valuable conclusion appears to be well grounded: at pressures below 1330 Pa, gas-phase reactions can be ignored when assessing typical deposition technologies using hot wire activation. The authors of [26], in their summarizing work, processed the data in Ref. [24] and showed that over a wide range of temperatures allowing the generation of atomic hydrogen, the activation energy on rhenium is 100 kJ mol^{-1}, compared to 166 kJ mol^{-1} for tungsten, thus favoring rhenium as a material for activating hydrogen in gas-phase diamond synthesis.

Fundamental molecular-beam results on the hydrogen–tungsten surface interaction were obtained much earlier in [27]. Figure 2 uses the data in Ref. [27] to show the degree of hydrogen dissociation as the molecules collide with the surface in the temperature range 1800–3000 K. The energy of the incident molecules corresponds to room temperature in the source. The authors consider the state of the surface to be responsible for the observed spread in measurements. Still, it can be accepted that the dissociation probability ranges from 0.03 to 0.35 as the tungsten surface temperature increases from 2000 K to 2600 K.

Most often, literature data on measured accommodation coefficients refer to low temperatures and hence do not reasonably apply to strongly heated clean surfaces. Because the accommodation coefficients of hydrogen molecules and atoms colliding with a tungsten surface depend significantly on the sorption coating type used, much disagreement exists among their published values. In what follows, we are interested in accommodation coefficients at temperatures

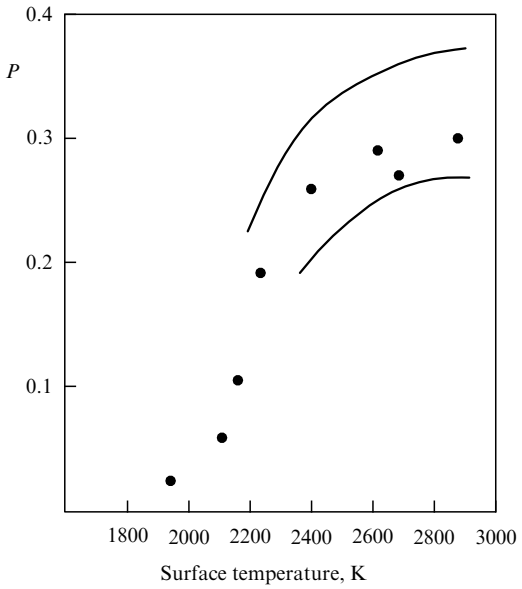

Figure 2. Degree of dissociation of hydrogen molecules in collisions with a tungsten surface at 1800–3000 K.

above 2200 K, at which the surface can be considered essentially free of a hydrogen sorbate coating and for which data on the interaction of atoms and molecules can be taken from Ref. [28].

3. Methane as a precursor of diamond component fragments

A well-developed method used in practice for the deposition of diamond structures is the thermal activation of an $H_2 + CH_4$ mixture on hot wires (HWCVD). Other hydrocarbons can also be used. It was shown experimentally in [29] that two-carbon molecules can provide a deposition rate only three times less than with methane. Plasma techniques can provide much higher deposition rates than HWCVD methods, including those using acetylene, lending further support to the idea that each diamond deposition method (or, indeed, specific diamond deposition condition) has its corresponding optimum precursor or an optimum set of precursor fragments. Illustrative in this sense are molecular dynamics data in [30] on the adhesion coefficient (γ_w) of various hydrocarbon molecules to the diamond faces (100) and (111). Table 3 provides information on adhesion coefficients at a gas temperature of 2120 K and the surface temperature of 600–1100 K.

Characteristically, the adhesion coefficient of one- or two-carbon molecules increases from zero to unity as the number of hydrogen atoms decreases. The reason why γ_w is minimum for methane is the absence of bond-forming free electrons. The same explanation applies to the very low value of γ_w for ethylene. These results show the importance of the fragments C, CH, CH_2, CH_3, C_2, C_2H, C_2H_2, C_2H_4, and C_2H_5 interacting with the diamond that are present in the flow.

4. Interaction of methane molecules with tungsten

Literature exists on the $CH_4 - W$-interaction-induced production of CH_4 fragments, interest in which is not only due to the fundamental significance of the process but also stimulated by practical problems, such as the protection of high-temperature surfaces from carbidization, tungsten carbide fabrication, large-scale catalytic production of pure hydrogen on metallized surfaces or carbon structures, and, finally, the activity and longevity of wires in HWCVD. These last problems are of special significance for this paper centered on the use of the interaction of methane with extended surfaces.

The fundamentals of the methane–hydrogen interaction were provided by Winters [31] more than 40 years ago. Drawing on the work of others, Winters presents data on the adsorption heat of CH_4 (104.8 kJ mol^{-1}) and further dissociative adsorption $CH_4(ads) \rightarrow C(ads) + 4H(ads)$ (more than 188.6 kJ mol^{-1}). This process is realized at high temperatures. In elegantly designed experiments at a high-vacuum pressure $< 10^{-3}$ Pa and temperatures from 600 K to 2600 K, it was found that the activation energy is 42.7 kJ mol^{-1} in the temperature range 1250–2600 K and 133 kJ mol^{-1} in the range 600–100 K. In fact, the nature of dissociative chemosorption was also established: this is the channel $CH_4(gas) \rightarrow C(ads) + 4H(ads)$. In [32], this channel was represented as the following cascade of reactions

$$CH_4(gas) \rightarrow CH_4(ads)\,,$$

$$CH_4(ads) \rightarrow CH_3(ads) + H(ads)\,,$$

$$CH_3(ads) \rightarrow CH_2(ads) + H(ads)\,,$$

$$CH_2(ads) \rightarrow CH(ads) + H(ads)\,,$$

$$CH(ads) \rightarrow C(ads) + H(ads)\,.$$

The fate of the adsorbed H atoms is obvious: as time goes on, they either are desorbed or recombine and are then desorbed in the form of molecules. The following fact is as important as it is indisputable: an adsorbed CH_4 molecule gives rise to atomic products whose carbon atoms, as the literature sources suggest, either form carbides and dissolve in the metal or leave the surface. Winters [31] presents evidence that the tungsten surface becomes carbon-free at 2500 K and then pushes away the C atoms that collide with it. In other words, the lifetime of C atoms on the surface is too short for this event to be regarded as an adsorption–desorption one.

As a further important result, experimental data on the adhesion probability of CH_4 molecules are provided in [31]: $\sim 3\times10^{-3}$ for 2500 K and $\sim 4\times10^{-4}$ for 1250 K. At a temperature of 2500 K and the methane pressure of 1.1×10^{-3} Pa, carbon does not deposit, and at 1400 K carbidization starts to be noticeable 6 min after contact with the gas begins. The results in Ref. [31] also suggest that the adhesion probability of molecules is independent of pressure (at least at high temperatures).

Table 3. Adhesion coefficient γ_w.

Particle	CH_4	CH_3	CH_2	CH	C	C_2	C_2H_6	C_2H_5	C_2H_4	C_2H_2	C_2H
$\gamma_w(100)$	0	0.11	0.54	0.88	0.97	1	0	0.05	0.06	0.41	0.85
$\gamma_w(111)$	0	0.11	0.5	0.85	0.97	1	0	0.08	0.41	0.35	0.9

Rettner et al. [33] were the first to apply the molecular-beam technique to the study of the methane–tungsten interaction. The pulse energy was varied from 5 to 100 kJ mol^{-1}, and the surface temperature was 800 K. High beam energies were achieved by varying the nozzle temperature and by accelerating CH_4 molecules with hydrogen or helium. The adhesion coefficient γ_w showed a very sharp increase from 4×10^{-6} to 10^{-1} in the given energy range at a surface temperature of 800 K. Varying the surface temperature leaves γ_w unchanged, which is consistent with the data in [31]. In [34], the influence of vibrational energy on the dissociative chemosorption of methane was studied and the translational and vibrational energies were shown to be equally (or comparably) responsible for the adhesion of CH_4 molecules.

Physical mechanics of the dissociative chemosorption of methane were discussed in [31, 33, 34]. The central problem was that of explaining the tunneling effect, which the small size of hydrogen atoms makes possible. This discussion was reflected both in review [32] (137 references) and in the work of those authors. It shows that despite 'in-depth' studies of methane dissociation mechanisms, serious problems arise in describing major kinetic characteristics quantitatively. Their idea was to model CH_x as a two-atomic molecule when analyzing dissociative chemosorption. Unfortunately, the examples with which the theory is illustrated are limited to the interaction of CH_4 with Ni, Pt, Zn, Ru, and Ir. An earlier review [35] (326 references) does not contain any quantitative data on methane chemosorption on tungsten.

Important information on the interaction of carbon and hydrogen atoms can be found in [36], where, in particular, data on the carbon diffusion coefficients at various tungsten temperatures is provided. The diffusion coefficient is $D[\mathrm{cm^2\ s^{-1}}] = 0.22 \exp(\sim 55{,}000/RT)$. From Fig. 3, it can be seen that at about 2200 K the diffusion coefficient is $D \approx 10^{-6}\ \mathrm{cm^2\ s^{-1}}$. This high diffusion rate ensures a virtually complete carbonization of a 0.03 mm thick foil typically used in experiments in Ref. [6].

As suggested by the data in [37–40], the interaction of CH_4 molecules with a tungsten surface at low temperatures has consequences that include the formation of carbides, the dissolution of carbon in the bulk, the adsorption of atomic carbon, and its atomic and molecular desorption. There is virtually no literature on the translational, rotational, and vibrational energy of reflected CH_4 molecules. At high temperatures ($\sim$ 2200 K and higher), the surface lifetime of the adsorbed molecules fragmenting into C and H atoms is so short that their desorption can be considered instantaneous. Thus, in the temperature range of interest here (high activation surface temperatures), the flow of CH_4 molecules along an extended surface becomes a flow of excited CH_4^* molecules and C and H fragments [according to the pattern $nCH_4 \rightarrow pCH_4^* + (n-p)C + 4(n-p)H$].

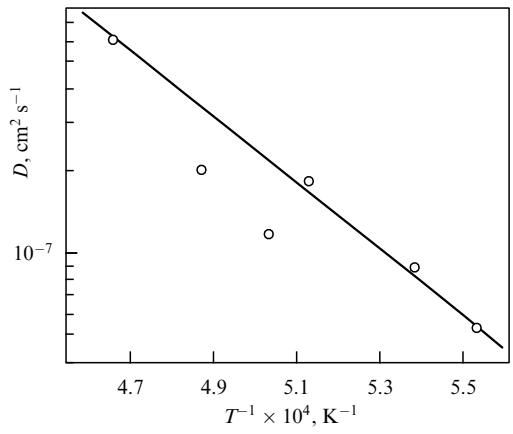

Figure 3. Temperature dependence of the carbon diffusion coefficient in tungsten.

The conclusion from the above is, inevitably, that active diamond synthesis fragments (other than atomic C) form either in the flow of molecules to the substrate or during the interaction with the substrate. A low adhesion between CH_4 and the surface virtually blocks the channel for the methyl group CH_3 being formed directly via collisions of CH_4 with the diamond surface. An alternative channel for CH_3 to appear near the surface is the hydrogenization of other surface-absorbed radicals. The gas-phase formation of the methyl group in HWCVD schemes is possible in a gas that is virtually at rest. Arc plasma flows allow this possibility if the methane molecule lifetime in the high-temperature flow is short due to the high temperature of the particles and, possibly, because the flow is partially ionized.

Clearly, information on HWCVD processes for depositing diamond structures is useful for analyzing diamond synthesis conditions near an extended surface. Reasons exist, however, why there is sometimes no unique interpretation for such information. The authors of Refs [37–40] analyzed their hot-wire experiments by assuming that the decomposition products of the $CH_4 + H_2$ mixture have an equilibrium composition in the neighborhood of the wire, which then changes due to the diffusion of fragments in the temperature field between the wire and the substrate. We note that all these analyses rely on experiments, and are not purely theoretical.

An important conclusion reached in [37] is that under typical HWCVD conditions, the main diamond growth components are the CH_3 and C_2H_2 molecules. The authors of [38] performed calculations when analyzing their experiments. Gas temperature measurements exhibited jumps of a few hundred degrees near the wire and substrate surfaces. In methane–hydrogen mixtures, increasing the wire temperature from 1400 K to 2400 K leads to a monotonic increase in the CH_3 concentration; increasing the substrate temperature from 550 K to 1000 K increases the C_2H_2 concentration, and increasing the temperature further somewhat lowers the mole fraction of C_2H_2 (all the figures are for the pressure of around 3000 Pa). The CH_3 concentration increases sharply as the substrate temperature increases from 600 K to 1000 K. Experiments with $C_2H_2 + H_2$ mixtures showed a marked conversion of C_2H_2, depending on the substrate temperature, which is inconsistent with the calculated results on the gas-phase process. The authors hypothesized that the C–C bonds break down near the diamond surface, which raises doubts as to whether the heterogeneous reactions were taken into account correctly.

Flow analysis in experiments with a thermal plasma indicates that a large number of fragments other than the methyl group participate in diamond synthesis. For example, flow composition measurements in the plasma experiments in [41] revealed a large percentage of C, C_2, and CH fragments actively involved in the synthesis of diamond structures. Other plasma flow studies [42–45] provide vast evidence on the variety of diamond structure synthesis schemes, thus

warranting the search for new diamond deposition techniques.

5. Interaction of C_xH_y, H, and H_2 fragments with the surface of an emerging diamond structure

The individual fragment flows reaching the substrate surface where the diamond structure forms depend not only on the gas composition arriving from the reactor (or from the source of precursors) but also on the interaction of particles with the surface. The factors that determine these interactions include the translation velocity and internal energy of the particles, the substrate temperature, the blocking of carbon sites by hydrogen compounds, particle adsorption, particle accommodation, the crystal face involved, and crystal lattice defects. We note that all these factors are interrelated. When estimating the composition of the atmosphere, it is to be remembered that the fraction of deposited atoms in the structure being formed is negligible compared to the original flow. This increases the value of the gas composition analysis via direct statistical simulation even when using approximate estimates for the adsorption probabilities and recombination and accommodation coefficients.

Presently, the most studied formation process for diamond structures is that using the interaction of CH_3 molecules with H atoms. In the model of the attachment of a C atom to a diamond structure (transition of C to C_d, an SP^3 hybridization atom) already presented in [46], the key role is played by CH_3:

$$C_d{-}H + H \rightarrow C_d^* + H_2\,, \tag{1}$$

$$C_d^* + H \rightarrow C_d{-}H\,, \tag{2}$$

$$C_d^* + CH_3 \rightarrow C_d{-}CH_3\,, \tag{3}$$

$$C_d{-}CH_3 + H \rightarrow C_d{-}CH_2^* + H_2\,, \tag{4}$$

$$C_d{-}CH_2^* + H \rightarrow C_d{-}C_d{-}H + H_2 \tag{5}$$

(an asterisk is used to denote unsaturated molecules or radicals).

Molecular dynamics calculations using the popular Brenner potential produced data on the adhesion coefficient γ_w on the (111) and (100) surfaces as a function of the velocity of the CH_3 molecules arriving on the surface (Fig. 4) [46]. The adhesion coefficients are significant for the particle velocities 1500 m s^{-1} [3×10^{-3} for (111) and 2×10^{-3} for (100)]. For the CH_3 velocities of the order of 2500 m s^{-1} achievable in experiments with cylindrical channels heated to 2400 K, $\gamma_w \approx 2 \times 10^{-2}$ for (111) and $\gamma_w \approx 1 \times 10^{-2}$ for (100).

In 2001, the results of an elegant experiment on the interaction of methyl radicals and atomic hydrogen with an amorphous hydrogenized carbon film were published [47], showing that if the flow of atomic hydrogen is sufficiently intense, the adhesion coefficient of CH_3 increases by about two (!!) orders of magnitude, from 10^{-4} to 10^{-2}. This is because atomic hydrogen creates sites for the deposition of CH_3 molecules on surface carbon atoms. The experiment used H and CH_3 molecular beams with the fluxes 4×10^{15} cm^{-2} s^{-1} (H_2) and 3×10^{14} cm^{-2} s^{-1} (CH_4). The authors used a resistive 2100 K source in the form of a tungsten capillary 1 mm in diameter to obtain atomic hydrogen by thermal dissociation. CH_3 molecules were produced by the dissociation of nitromethane $N_2(CH_3)_2$ in a tungsten capillary 1 mm in diameter at 1150 K. The film temperature was about 320 K. In review [48], new experimental data were presented: at a gas temperature of 300 K, $\gamma_w(CH_3) \sim 10^{-4}$, and at 600 K, $\gamma_w(CH_3) < -10^{-4}$ (the negative value indicates the erosion of hydrocarbon), and at 700 K, $\gamma_w(CH_3) > 10^{-4}$. These low adhesion coefficients were obtained without atomic hydrogen.

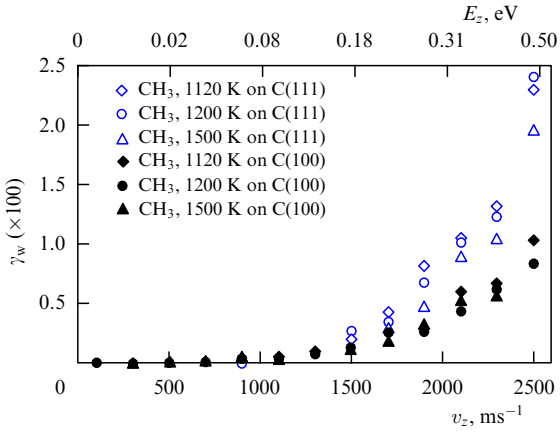

Figure 4. Adhesion coefficient of CH_3 molecules to the diamond surface as a function of the molecular velocity. E_z is the kinetic energy of CH_3.

The effect of synergy, discovered both qualitatively and quantitatively, between the simultaneous CH_3 and H supplies emphasizes the importance of the mutual influence of the individual precursor fragments in the deposition mixture for carbon structures and highlights the need to be very scrupulous in designing the composition of the precursor gases transported to the substrate.

This synergy was discovered earlier, in 1992, in work [49] on the deposition of hydrogenized solid carbon films by subjecting the mixture to activation by a radiofrequency discharge. These studies suggest that depending on the composition and thermodynamic parameters of the gas mixtures used, there is a wide diversity of mechanisms by which diamond structures can be synthesized. A theoretical justification of the synergy was proposed in [50]. That the concept of synergy did not receive its deserved attention in the literature on the justification of diamond deposition can possibly be explained by the boundless variety of combinations possible among precursor fragments.

A molecular dynamics study of hydrocarbon adsorption on a stepped diamond surface (100) in [51] showed that, while ethinyl radical C_2H is as active as CH_3 in the diamond deposition process, its concentration can be low. This is confirmed and emphasized in [52], where the deposition of diamond from a microwave CH_4 and H_2 plasma at a pressure of 100 mbar was studied. A multifold increase in the concentration of ethinyl compared to that of CH_3 caused a corresponding acceleration of diamond growth.

In [53], heterogeneous reactions of H atoms and CH_3 radicals on a diamond surface were studied in the diamond temperature range 300–1100 K at the pressure 130 Pa $< P <$ 260 Pa. The adhesion (adsorption) probability was determined from mass spectroscopic cuvette measurements. Figure 5 (from Ref. [53]), which presents the results by means of Arrhenius curves, shows that as the diamond temperature changes from 500 K to 1100 K, the adsorption probability of H increases from 6×10^{-3} to 4×10^{-1} and that

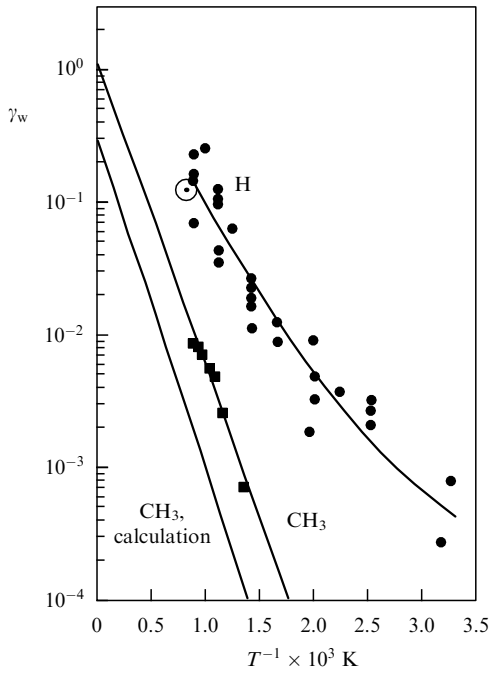

Figure 5. Adhesion coefficients of H atoms and CH_3 molecules to a diamond surface.

of CH_3 from 5×10^{-5} to 5×10^{-2}. Also presented are tabulated data on γ_w of atomic hydrogen (501 K, 9.13×10^{-3}; 702 K, 1.91×10^{-3}; 897 K, 1.06×10^{-1}; and 1119 K, 1.62×10^{-1}). Useful information on the adhesion coefficient is obtained by molecular dynamics methods. In [54], calculations of the adhesion coefficients for C_2H_x molecules as a function of the distance from an unsaturated carbon site reveal C_2 and C_2H to be the most active molecules. The C_2H_2 molecules were found to have an activity comparable to (4 to 5 times lower than) that of C_2H_3. At a distance of 2 Å from an unsaturated site, the adhesion probability approaches zero for all molecules. The calculations were performed for 300 K and 2100 K, for gases interacting with a hydrogenized (111) surface, and for molecules moving perpendicular to the surface. The particle–surface collision time was found to be 1 ps. The most thorough data on the adhesion coefficients of various hydrocarbon molecules seem to have been provided in [30, 55]. The MMC (Metropolis Monte Carlo) algorithm combined with a molecular dynamics code was used in [55]. The time increment was taken to be $10^{-4}-10^{-6}$ ps and the collision time ~ 2 ps. The incident particles had an energy of ~ 0.274 eV, close to particle energies in typical experiments with supersonic flows of hydrogen particles at a high activation temperature. The diamond temperature was 1100 K. The H atoms were removed by H – H recombination and partially via collisions with C_2 molecules [with probabilities of 0.5 on (100) and 0.87 on (111)].

In 2002, the work of Kang [56] appeared, remarkable for its description of a technology for manufacturing hexagonal diamond (possibly lonsdaleite, the highest hardness material). This work deserves special attention. Collision processes on a lonsdaleite surface have not been investigated. If the method described in the work can deposit diamond onto tool material surfaces, the development of research into lonsdaleite is of special interest.

6. Conclusion

This review of research on the interaction of hydrogen and methane molecules and their fragments with a tungsten surface and with the surface of forming diamond provides data that can already be useful today in direct statistical calculations of dilute gas channel flows with heterogeneous chemical transformations and for reasonably defining boundary conditions for continuum flows. The data from the reviewed literature that are presented here can be used in assessing conditions for the deposition of diamond structures from a high-speed gas flow activated by a heated extended surface (in particular, in a cylindrical channel). It is important to describe the level of knowledge of elementary processes in terms of interaction constants for the described processes determining the formation of diamond structures from a methane–hydrogen mixture.

(1) The dissociation probability of hydrogen on tungsten in the high-temperature range can be considered sufficiently well known.

(2) Recombination processes on a tungsten surface of hydrogen atoms sorbed from a gas phase or processes due to sorption of molecular hydrogen have not been studied.

(3) There are no data on the adhesion coefficient of hydrogen molecules to clean tungsten faces 100, 110, etc. (but not 001).

(4) The interaction of methane with a clean hot tungsten surface has been studied in the case of chemosorption.

(5) No data are available on the interaction of CH_x molecules (for $x < 4$) with tungsten.

(6) The main results on the adhesion coefficient of atoms and molecular structures to diamond were obtained by molecular dynamics.

(7) The accommodation coefficients of H, H_2, and CH_x particles belonging to light atomic structures can be estimated quite accurately for clean surfaces. For surfaces coated with a sorbate, only the results of individual studies conducted for specified conditions can be employed.

In concluding this analytical review, we note recent work [57, 58] on the influence of heterogeneous reactions on the channel flows of dilute gas mixtures.

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