Gas-jet synthesis of diamond

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Abstract. The nonequilibrium processes in flows of gas mixtures on the way to surface, where diamond structures formation takes place, are discussed. The main attention is focused on processes with thermal activation. Thermocatalitical phenomena in the collision of hydrogen and methane molecules with tungsten, nonequilibrium processes during transportation of active components in channels and on the way to the substrate, formation of gas atmosphere immediately close to the surface of diamond formation – all these processes relate to the field of modern physical mechanics. This statement can be related to the diamond synthesis from microwave plasma which is determined by generation of plasma from high frequency radiation and in most cases diffusion interaction of plasma with surface of deposition. The main content of studies in the Institute of Thermophysics belongs to a new direction of research, to synthesis of diamond from high velocity flow of gas mixtures or plasma.

1. Introduction
Diamond possesses extreme properties of hardness, thermal conductivity, frictionality, electric resistance, optical transparency, hole conductivity, chemical inertness, and biological compatibility. The possibility of gas-phase synthesis of diamond in the film form has significantly extended diamond application for surface modification, including complex-shaped surfaces. Approximately 97% of all diamonds used in industry all over the world are synthetic diamonds. Gas-phase methods of mono-, poly-, micro-, nano-, and ultrananocrystalline diamond synthesis are vigorously developed. The priority of the development of artificial diamond synthesis methods undoubtedly belongs to Russian scientists. Back in 1939, the journal “Uspekh Khimii” (Achievements in Chemistry) published a paper of O.I. Leipunskii, which contained a phase diagram of carbon that predicted a possibility of diamond synthesis at high pressures and high temperatures.

Diamond deposition from the gas (vapor) state allows synthesis of diamond films with the thickness varying from nanometers to the thickness of structural parts. The properties of the synthesized product can be widely varied depending on the gases used and specific features of technologies. This variety is caused by the difference in the methods of activation of precursor gases: activation on the surface of a hot wire, on an extended hot surface, in the plasma of a microwave discharge, in the electric arc plasma, in plasmas of various discharges, in detonation shock waves, and in the flame. Besides, carbon as atom can be delivered in different gases. The early stages of development of gas-phase methods revealed an important role of atomic hydrogen as an active agent in preparing carbon bonds to constructing the diamond structure. An example of the chain of modification of carbon bonds with participation of H and CH₃ fragments (figure 1) was published in [1] for the case of the chemical process of diamond formation on the (110) face. The formation of a
new C-C bond in six steps can be clearly seen. This scheme turned out to be popular, resulting in recognition of the leading role of the methyl group CH$_3$ as a carbon-containing fragment. In reality the channels of formation of diamond structures are versatile; one of the reasons is specific surface chemistry for each of the typical faces (100, 110, and 111). As it follows from numerous modern investigations, diamond synthesis can include C, CH$_3$, C$_2$H, C$_2$, and other ones as active fragments. Synthesis without hydrogen participation is also possible.

Figure 2 shows the relative positions of the free energy levels for graphite and diamond. Under standard conditions, graphite is in the stable state, and diamond, being stable, is a metastable material, whose free energy differs from that of graphite by 2.9 kJ/mol. Diamond growth at low pressures looks as a paradox (as violation of the second law of thermodynamics).

The question is how metastable phase formation at standard temperature and pressure arises. This can be understood by considering the phase diagram of carbon (figure 3). The domains G and D correspond to the stable equilibrium states of graphite and diamond, respectively. At low background pressures, the high internal pressure induced by surface tension provokes generation of conditions for nucleation of diamond structures in the domain D. The curve in the insert (pressure as a function of the cluster radius) shows that this pressure can reach several gigapascals. Consequently, even at low ambient pressures, a transition through the boundary of the domains G and D may occur in the cluster. The co-existence of different phases blurs the “equilibrium” boundary.

Is it possible to resolve the conflict with thermodynamic laws for various ways of diamond structure formation? Indeed, in the case of deposition from the gas phase with activation on hot surfaces, in the microwave plasma, electric arc plasma, and in the flame, conditions for diamond synthesis can be formed due to the existence of a cluster structure, which was discussed in the description of figure 3. Mechanical interpretation of chemical kinetics should have an energy-based justification. Diamond formation during detonation can be attributed to conditions of high pressure and temperature at microscales.
2. Thermal activation and interaction of C\textsubscript{2}H\textsubscript{2}, H\textsubscript{2}, and H\textsubscript{2} fragments with surfaces of forming diamond structures

The possibilities of activation of the most popular mixture H\textsubscript{2} + CH\textsubscript{4} on hot surfaces were considered in much detail in [2]. The boundary conditions responsible for the flow of atomic hydrogen from the surface to the gas have a rather complicated nature, which has not been adequately studied yet. The associated processes are dissociation of hydrogen molecules due to their collisions with the surface, hydrogen adsorption with subsequent decomposition of molecules and desorption of atomic fragments, collision of atoms with the surface and subsequent reflection after accommodation or adsorption, recombination of atoms of various origin, dissolution of hydrogen in metals, and, finally, excitation of internal energy of hydrogen molecules during their collisions with the surface. The description of hydrogen-tungsten interaction in a wide range of temperatures is complicated by a strong dependence on the surface state, in particular, on the type of the crystal face with which the particle collides and on the state of adsorbed particles, which, in turn, depends on temperature and pressure. The problem is somewhat less difficult for high temperatures (above 2000 °C) and high vacuum: in this case, the surfaces are cleaner. It should be noted that the boundaries between different surface states are rather blurred.

Apparently, the first significant contribution to studying hydrogen-tungsten interaction was made by Langmuir [3, 4]. He established the existence of a chemosorption process of hydrogen decomposition on the hot tungsten surface and derived the adsorption law in the form of an adsorption isotherm, which was named after him. The tungsten activity during interaction with H\textsubscript{2} + CH\textsubscript{4} and H\textsubscript{2} + C\textsubscript{2}H\textsubscript{2} mixtures was studied in [5]; it was shown that the tungsten surface at low pressures (within 1200 Pa) in the 1.5% C\textsubscript{2}H\textsubscript{2} + H\textsubscript{2} mixture up to temperatures of about 2600 K is carbonized to such an extent that the emissivity reaches value approximately 0.85. At temperatures above 2600 K, it decreases to 0.5, i.e., to the level of emissivity from the pure tungsten surface. Fundamental results on hydrogen interaction with the tungsten surface were obtained by molecular beam measurements in [6]. The degree of hydrogen dissociation was determined for the case of molecule collisions with the surface at temperatures from 1800 to 3000 K. The measured accommodation coefficients reported in publications are usually given for low temperatures. Therefore, their application for intensely heated and cleaned surfaces is not justified. The data on the accommodation coefficients of hydrogen molecules and atoms colliding with the tungsten surface are rather contradictory [7]. The reason is a strong dependence of accommodation coefficients on the adsorption coating.

Interaction of CH\textsubscript{4} molecules with the tungsten surface leads to formation of carbides, carbon dissolution in the volume, adsorption of atomic hydrogen, and its desorption in the atomic or molecular form. There are practically no data on the translational, rotational, and vibrational energies of reflected CH\textsubscript{4} molecules. At high temperatures (~2200 K and higher), adsorbed molecules are subjected to fragmentation into C and H with a such small lifetime on the surface that desorption can be considered as an instantaneous process. There is also little information about accommodation of reflected molecules at high temperatures. Thus, in the range of high temperatures of the activating surface, the flow of CH\textsubscript{4} molecules past an extended surface transforms to a flow of excited CH\textsubscript{4} molecules and also C and H fragments. However, the sticking coefficient of CH\textsubscript{4} to the tungsten surface is very small [2, 8]. Therefore, one has to conclude that active fragments for diamond synthesis except for diamond synthesis are formed either in the flow of molecules to the substrate or during interaction with the substrate. The low sticking coefficient of CH\textsubscript{4} to the surface almost excludes the channel of direct formation of the methyl group CH\textsubscript{3} due to CH\textsubscript{4} collision with the diamond surface.

The flow analysis of experiments with the thermal plasma definitely reveals a large set of fragments participating in diamond synthesis except for the methyl group. For example, the measured compositions of the flow in the plasma experiments [9] turned out to contain many C, C\textsubscript{2}, and CH fragments, which are active agents of diamond synthesis.

Flows of individual fragments reaching the substrate surface where diamond synthesis occurs depend not only on the composition of gases incoming from the reactor (or the source of precursor
gases), but also on the processes of particle interaction with the substrate surface. The latter are determined by the translational velocity of particles, their internal energy, the substrate temperature, blocking of carbon sites by hydrogen compounds, adsorption of particles, their accommodation, crystal face nature, and crystal lattice defects. These factors are interrelated. In estimating the atmosphere composition, one should bear in mind that the fraction of deposited atoms in the formed structure is negligibly small as compared to the initial flow. For this reason, the computational analysis of the gas composition by direct simulation Monte Carlo (DSMC) method [10] is extremely valuable, even if it involves approximate estimates for the adsorption and recombination probabilities and the accommodation coefficients.

A certain optimal precursor or an optimal set of precursor fragments corresponds to each method and, moreover, each particular combination of diamond synthesis conditions. In this aspect, data on sticking coefficients ($\gamma_w$) for molecules of various hydrocarbons to the diamond faces (100) and (111) calculated by the molecular dynamics method in [11] are very interesting. The sticking coefficients for the gas temperature of 2120 K and surface temperatures from 800 to 1100 K are listed in table 1.

It is of interest that the sticking coefficient for molecules with one and two carbon atoms increases from zero to unity as the number of hydrogen atoms decreases. The minimum value of $\gamma_w$ for methane is explained by the absence of free electrons for bonding. The same factor is responsible for the low value of $\gamma_w$ for ethylene. These results emphasize the importance of the presence of fragments interacting with diamond in the flow: C, CH, CH$_2$, CH$_3$, C$_2$, C$_2$H, C$_2$H$_2$, C$_2$H$_3$, and C$_2$H$_4$.

Von Keudell et al. [12] reported the results of a well-arranged experiment aimed at studying interaction of methyl radicals and atomic hydrogen with an amorphous hydrogenated carbon film, where they found that the presence of a sufficiently intense flow of atomic hydrogen increases the sticking coefficient of the CH$_3$ molecule approximately by two orders of magnitude (!!!) from $10^4$ to $10^6$. This occurs because atomic hydrogen opens sites on carbon atoms on the surface for deposition of CH$_3$ molecules. The synergy effect of combined injection of CH$_3$ and H, which was detected qualitatively and quantitatively, demonstrates the importance of the mutual influence of individual fragments of precursors in the mixture on deposition of carbon structures. It can be concluded that it is necessary to be cautious in forming the mixture of precursor gases transported to the substrate. In molecular dynamics calculations, the characteristic time of particle collision with the surface is taken to be of order of 1 ps. The time step is from $10^4$ down to $10^6$ ps. Heterogeneous reactions of hydrogen atoms and CH$_3$ radicals on the diamond surface were studied in [13] in the diamond temperature range from 300 to 1100 K at pressures in the interval 130 $< p < 260$ Pa. As the diamond temperature increases from 500 to 1100 K, the probability of atomic hydrogen adsorption increases from 6$x10^3$ to 4$x10^4$, and that for CH$_3$ increases from 5$x10^5$ to 5$x10^2$. In recent years, the gas-jet modification of the diamond deposition method based on thermal activation has been developed at the Institute of Thermophysics of the Siberian Branch of the Russian Academy of Sciences (IT SB RAS). The advantages of this deposition approach by activating the components of a mixture of hydrogen and methane as a result of interaction with the cylindrical surface of tungsten, as well as the problems arising from the use of this method, are described in [14–17]. A special feature of this approach is the use of heterogeneous dissociation processes that occur during multiple collisions of molecules with a hot surface [18, 19].

The research of diamond synthesis after thermal activation faced a serious problem of this activation: graphitization leading to blocking of the catalytic effect and corresponding reduction of the deposition rate. Investigations of using the microwave plasma for diamond deposition have been recently started at IT SB RAS. The idea is to generate a high-velocity flow of the active plasma.

Table 1. Sticking coefficients $\gamma_w$.

| particle | CH$_4$ | CH$_3$ | CH$_2$ | CH | C | C$_2$ | C$_2$H$_4$ | C$_2$H$_3$ | C$_2$H$_2$ | C$_2$H |
|----------|-------|-------|-------|----|---|------|-----------|-----------|-----------|-------|
| $\gamma_w$(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 |
according to the scheme similar to the existing space thrusters based on microwave energy. A jet generated by such a reactor provides the advantages of the plasmatorch jet and those of electrodeless generation of the pure plasma. Figure 4 shows a photograph of a supersonic flame of the microwave plasma.

The first successful experiments were performed. A specific feature of the developed method is the use of a high-velocity plasma jet. Popular methods of diamond deposition from the microwave plasma are based on diffusion transportation of active fragments to the deposition surface. It can be stated that the method developed at IT SB RAS occupies an intermediate position between the traditional methods with activation in the microwave plasma and activation in the electric arc plasma.

3. Numerical simulation of nonequilibrium processes in gas flows

In arranging experiments and analyzing their results, it is also important to consider the results of gas-dynamic modeling. Formation of diamond and carbon structures is determined by the composition and distribution functions of velocities and energies of fragments in the gaseous ambient medium near the substrate; these fragments are products of nonequilibrium processes in channels with cylindrical bounding surfaces and on the way from the activation channels to the substrate. Gas-dynamic, physical, and chemical processes in a high-velocity flow of the mixture were studied in [20].

An effective method of computational analysis of the flow is the DSMC method. The computations were performed for conditions used in experiments [14-17]. The estimates showed that decomposition of the initial gases (CH$_4$ and H$_2$) and further conversion to H and C components of the mixture can be considered in the one-dimensional approximation by solving chemical kinetics equations.

Figure 5 shows the computational domain geometry. The CH$_4$ + H$_2$ mixture at an initial temperature of 1500 K is injected into a cylindrical channel with a diameter $d = 0.003$ m and length $h + L$. The temperature of the hot section 2 is 2400 K. The mixture expands from the channel into a vacuum chamber (domain 3). A substrate for diamond deposition is located at a distance $L_{sub} = 0.01$ m. Its temperature is 1300 K.
Figure 6 shows the results of model calculations with ignored methane decomposition whose gas-dynamic role is insignificant. It illustrates the influence of pressure in the deposition chamber on the axial distributions of parameters of $\text{H}_2$, $\text{H}$, and $\text{CH}_4$ (densities, velocities, and translational temperatures) for the cases of expansion into vacuum and into a medium with an ambient pressure of 20 Torr. The hydrogen flow rate is 25 sccm, and the molar fraction of methane is 3%.

Three segments of flow can be clearly defined: initial ("cold") region 0.035 – 0.045 m, hot region 0.045 – 0.06 m, and region of expansion toward the substrate 0.01 m. The flows have the following typical features: in both cases (in terms of pressure), rapid dissociation of hydrogen in the cylindrical channel at the beginning of the hot region, followed by an equilibrium flow in the cylindrical channel; behind the cylindrical channel, the flow is essentially nonequilibrium in the case of expansion into vacuum and equilibrium at a pressure of 20 Torr up to a small distance from the substrate, where the influence of the processes on the boundary is intensely manifested. The particular case considered here is far from being able to characterize all specific features of various flows formed during diamond deposition, but it demonstrates the capabilities of the computational method.

Kinetic equations for 11 species were solved in modeling a one-dimensional flow with chemical processes in a mixture of $\text{H}_2$, $\text{H}$, and C$_x$H$_y$, following to [21, 22]. The computations were performed for 13 forward and backward reactions. As a result, it became possible to determine the velocity distribution functions near the deposition surface for all species and, which is particularly important, for the most probable participants of diamond structure formation: $\text{H}_2$, $\text{H}$, $\text{CH}_3$, $\text{C}$, $\text{CH}_4$, and C$_2$H$_2$.

The amount of atomic hydrogen, which is an active participant of chemical processes in the gas flow and in the synthesis of diamond structure, is characterized by the degree of dissociation $K = 0.5 n_{\text{H}}/(n_{\text{H}_2} + 0.5 n_{\text{H}})$. Here $n_{\text{H}_2}$ and $n_{\text{H}}$ are the densities of molecular and atomic hydrogen. Dissociation depends on the channel geometry and gas flow parameters.

Figure 7 illustrates the degree of dissociation for three pressure values in the expansion channel. The value of $K$ rapidly increases already in the first third of the hot channel and then rapidly decreases near the substrate. Last is determined by a superposition of the flow, radial diffusion, and diffusion of fragments from the substrate surface. The growth of pressure in the channel leads to flow deceleration in the channel, enhancement of catalytic processes, and an increase in the degree of dissociation toward the channel exit.

Important results of the flow analysis are the data on methane decomposition. The analysis of methane chemistry is one of the difficult problems. The results of evaluation of the real situation with some assumptions are shown in figure 8: axial distributions of the molar fractions of nine species ($\text{H}_2$, $\text{H}$, $\text{CH}_4$, $\text{CH}_3$, $\text{CH}_2$, $\text{C}$, $\text{CH}_4$, and C$_2$H$_2$) under the following conditions: hydrogen flow rate 25 sccm, initial mixture 3% CH$_4$/H$_2$, and expansion into vacuum. Rapid decomposition of hydrogen and methane is clearly visible. Methane decomposition has a rather complicated character along the entire hot region of the channel. The role of atomic hydrogen is significant for conversion of fragments. The chemical reactions in the region between the channel and the substrate are frozen. The dominating
fragments are C, CH₃, and C₂H₂. The maximum concentration of acetylene is smaller than the concentration of atomic carbon approximately by an order of magnitude.

The composition of gases transported to the deposition surface and their energy state at the instant of the collision with the surface determine the rate of formation and the quality of the diamond structure. Gas-dynamic modeling with the use of models of chemical transformations and DSMC simulations ensure obtaining the velocity distribution functions and internal energies of all particles participating in interaction with the diamond surface. Further intense investigations are required to study the boundary conditions on the formed surface at the atomic-molecular level.

4. Conclusion

The diamond synthesis from vapor (gas) phase is realized by complex influence of nonequilibrium processes of active fragments generation on hot surface with catalytic properties or in plasma, and further transportation in nonequilibrium conditions by diffusion or convection in channels, followed by formation specific nonequilibrium clouds in the vicinity to the surface of diamond structure formation. As concern using the thermal activation, it follows from [2],

- that the processes of formation of hydrogen atoms on the surface of tungsten (through adsorption of atoms from the gas phase or formation from the adsorbed H₂ molecules) have not been fully studied;
- there is no data on sticking coefficients of hydrogen molecules on the clean surface of tungsten crystal faces 100, 110, etc., besides 001;
- data on interaction of molecules CHₓ (x < 4) with tungsten are absent;
- data on accommodation coefficient can be used with confidence only for clean surfaces.

Nonequilibrium in the wall layer is inherent in any gas phase deposition. To date there is necessity in further investigations, uniting numerical modelling of gas flows by the DSMC simulation and molecular dynamic calculations with experiments, giving information on composition of fragments and their energetic state. The problem is complicated by manifold of conditions determining physical kinetics of diamond structure formation.

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