Probe supply of methane in gas-jet synthesis of diamond structures

A A Emelyanov, M Yu Plotnikov and I B Yudin*
Kutateladze Institute of Thermophysics SB RAS 630090, Novosibirsk, Russia

*E-mail: yudinib@gmail.com

Abstract. The present work is devoted to a numerical and experimental investigation of the probe supply of “cold” methane on the growth of diamond structures during gas-jet deposition. The analysis of results of experiments on the diamond gas-jet synthesis from methane and hydrogen mixture flows are presented. The direct simulation Monte Carlo method for numerical analysis of gas-dynamic aspect of these experiments was applied. A one-dimensional approach based on the solution of equilibrium chemical kinetics equations was used to analyze gas-phase methane decomposition. The obtained results can be useful for investigation of gas-jet deposition of diamond structures.

1. Introduction

The method of gas-phase deposition of diamond structures using thermal activation (Hot Wire Chemical Vapor Deposition (HWCVD)) of precursor gases is widely used [1-4]. This method is based on the using of mixtures of hydrogen with hydrocarbons activated on hot metal surfaces and interacting with a relatively cold substrate. The deposition rate of diamond structures on the substrate is determined by the ratio of atomic hydrogen and carbon-containing decomposition fragments of the gas precursor (in our case, methane). Atomic hydrogen is obtained by dissociation on a heated surface. The principal mode of methane defragmentation is gas-phase reactions [2, 4]. Methyl is considered as the main fragment for diamond synthesis [2-4]. The contribution of heterogeneous reactions to the formation of methyl is relatively small [4, 5]. For the rapid synthesis of diamond structures, it is necessary to ensure the delivery of a large amount of atomic hydrogen and methyl to the substrate.

Gas-jet modification of the HWCVD method has been actively developed in IT SB RAS since 2012 [6]. This method has two advantages over the classic implementation of HWCVD. First, due to multiple collisions with a heated surface as gas flows through the channel, a higher degree of hydrogen dissociation is obtained [7, 8]. Secondly, the high-speed flow allows delivering of the necessary components to the substrate more efficiently. Two types of reactors were developed for gas heating and activation: using a tungsten wire helix [9] and using tungsten foil cylindrical channels [10]. In both cases, there is a problem of carbidization of heated tungsten surfaces, which led to a decrease of hydrogen dissociation. To reduce the carbidization of the heating elements, a two-channel gas supply was developed [10, 11]. An important parameter of this methodology is the rate of methane defragmentation. In [12], it was shown that the growth rate of diamond structures during gas-jet deposition correlates with the amount of methyl on the substrate.

The rate and depth of methane decomposition depend on the amount of atomic hydrogen, the gas temperature and the residence time of methane in the decomposition zone. Calculations have shown that changing the channel length can significantly regulate the composition of the gas mixture when
approaching the substrate [12–15]. In [11], a scheme for methane and hydrogen supplying through a lateral tube is used. The absence of high-temperature decomposition of methane in the tube (the temperature of the tube at a distance of 5 mm from the tube’s cut was 1300 K) allowed obtaining diamonds with facets sizes up to 60 µm [11]. The size of the facets of the synthesized diamonds using the central supply of gas-mixture did not exceed 30 µm [9-12, 15]. The disadvantage of lateral supply is the difficulty of repeating the experiments and obtaining a uniform film. In [15], the effect of channel length on the size of deposited crystals is shown.

In the present work, the probe supply of a H2+CH4 mixture is realized. It allows delivery to control the mixture to a selected point of an axisymmetric reactor. A numerical-experimental study was carried out on the effect of methane decomposition on the growth of diamond structures. Section 2 describes the experimental setup and experimental conditions. Section 3 describes the numerical methods used. Section 4 presents the results of experiments and calculations, as well as their discussion.

2. Experimental technique

![Figure 1](image.png)

**Figure 1.** The scheme of activator with the probe (a); the scheme of probe for methane supply (b).

1 – hydrogen channel, 2 – tungsten spiral, 3 – molybdenum substrate, 4 – water cooling probe for H2+CH4 supply, 5 – probe channel (probe protection tube), 6 – heat shield, 7 – probe cooling.

Hydrogen channel 1 with a diameter of 13 mm and probe channel 5 with a diameter of 4 mm are made of tungsten foil with a thickness of 30 µm. A cylindrical spiral 2, made of tungsten wire with 1 mm in diameter, is coaxially located inside the hydrogen channel. The diameter of the heat shield 6 is 17 mm. The hot part of the activator L in the experiments had a length of 22 mm, the Lsub distance is 10 mm. The diameter of the molybdenum substrate 3 is 30 mm. In the probe channel 5 there is a water-cooled copper cylindrical probe 4 with a diameter of 3.5 mm. Cooling water is supplied through channel 7. A nickel tube with a diameter of 1 mm passes through the center of the probe, through which the H2 + CH4 mixture was fed into the decomposition chamber, and only hydrogen was fed to the hydrogen channel. The length of the decomposition chamber Xz (between the cut of the probe 4 and the cut of the channel 5) varied from 2 to 22 mm. The temperature in channel 5 was measured by a tungsten-rhenium thermocouple at a distance of 5 mm from the tube’s cut. It was set at 2400 K by matching it to the power required to heat the spiral. The temperature of probe 4 was about 300 K. Through the probe channel 5 through the annular gap between the probe 4 and the probe channel 5, a co-current flow of hydrogen was supplied with a flow rate of 500 sccm. The experiments were performed under the following conditions: the synthesis time of 3 hours, the pressure in the deposition chamber of 20 torr, the flow rate of hydrogen through the probe, which varies from 0 to 1500 sccm, the total flow rate of hydrogen through the hydrogen channel and co-current flow of 1500 sccm, methane flow rate of 10 and 15 sccm.
An important measured characteristic is the resistance of the spiral. Its increase in the course of the experiment indicates an increase in the carbidization of the spiral. Increased carbidization of the spiral leads to a decrease in the dissociation of hydrogen.

3. Computation methods

The algorithm of the direct simulation Monte Carlo (DSMC) method [16] is adapted for calculating flows in cylindrical channels and behind them. The majorant frequency scheme [17] is used in the computations. The calculations were performed for the mixture of the H₂, H and CH₄. Interparticle collisions are considered with the use of the variable soft sphere (VSS) model [16]. A more detailed description of the DSMC algorithm parameters used is given in [15].

At the first stage, the calculations were performed with the inclusion in the simulation of the area with a spiral (fig. 1). These calculations show that the effect of the flux from the probe channel on the flow in the hydrogen channel is small in the considered range. At the same time, most of the computer time was spent on modeling particles in the hydrogen channel. Therefore, to speed up the calculations, it was decided to use a stream of particles from the plane (Fig. 2 – indicated by an arrow) instead of modeling the flow in the hydrogen channel. Data on the composition of the mixture, velocity and density of the flow at the outlet of the hydrogen channel were obtained on the basis of preliminary calculations. Fig. 2 shows the spatial distribution of methane flux obtained in the framework of this approach.

Obtaining more detailed information about the concentrations of particles approaching the substrate requires data on the degree of methane decomposition into fragments. In this case, it is possible to use a one-dimensional approach [13] for calculating the changes in the mixture composition along the flow axis by means of solving a system of chemical kinetics equations. A mixture of 11 components is considered when solving the equations of equilibrium chemical kinetics: H₂, H, CH₄, CH₃, CH₂, CH₂(S), CH, C, C₂H₂, C₃, and C₂H.

4. Results and discussion

Reducing the outlet at a fixed flow rate leads to an increase of the velocity of the outgoing gas. Thus, the question arises about the effect of the probe feed of mixture, the position of the probe and the flow rate of hydrogen on the processes in the probe channel. A series of numerical experiments was conducted to assess the influence of these factors on the flow velocity of the mixture and the dissociation of hydrogen. In fig. 3a there is the distribution of the flow velocity of hydrogen along the axis of the channel.
Vx for three probe positions: at the channel entrance (Xz=0.022 m), at the center of the channel (Xz=0.011 m) and at the channel’s exit (Xz=0.002 m). It also shows the same velocity for the four options for the flow rate of hydrogen supplied through a probe located in the center of the channel. Note that the calculated data are obtained by averaging over ring cells, the size of which coincides with the size of the channel. It can be seen that the position of the probe and the flow rate of supplied hydrogen affect the flow velocity. Note that a decrease in the flow velocity also leads to a better heating of the mixture flowing from the probe. The location of the probe at the exit of the channel leads to a significant decrease in the heating of methane. The equalization of the temperature and velocity of the mixture flowing out of the probe and the co-current flow occurs at a distance of 0.002 – 0.004 m from the cutoff of the probe. Fig. 3b presents the data on the dissociation of hydrogen for the same 6 variants of calculation. It can be seen that half of the channel length also provides a fairly high degree of hydrogen dissociation at the channel exit. The location of the probe near the exit from the channel leads to a significant decrease in the degree of dissociation. Reducing the flow rate of hydrogen leads to a decrease in the flow velocity, which allows dissociating hydrogen on the walls more effectively. The flow velocity affects the residence time of methane in the region of the heated flow, and the presence of atomic hydrogen affects the gas-phase decomposition rate of methane. All this affects the depth of methane defragmentation.

Figure 3. Molecular hydrogen flow velocity (a) and hydrogen dissociation degree (b) for three probe positions (Xz=0, 0.011 and 0.002 m) and for mass flow rates of molecular hydrogen: 0 sccm, 500 sccm, 750 sccm and 1500 sccm.

Figure 4 shows the flow nVx of the gas mixture near the substrate (x = 0.031) for the considered 6 variants of calculation. The approach of the probe to the substrate leads to a decrease in the flow of atomic hydrogen, to an increase in the flow of methane and methyl and to a decrease in the flow of C and C2H2. With an increase in flow rate, the flow of atomic hydrogen and methyl flow increases. A decrease in the flow rate leads to a decrease in the flow velocity and, as a result, the flow of methane decreases and the depth of methane defragmentation increases (the flow of C and C2H2 increases). More than 30 experiments were carried out to study the features of the probe supply. Both methodological issues and the search for conditions providing the highest diamond deposition rate were considered. Note a significant increase in the carbidization of the spiral compared with experiments without a probe. One of the possible reasons is the presence of a spiral cooling zone due to the probe. Attempts to reduce the cooling of the spiral through the establishment of an additional screen led to noticeable changes neither in the deposition rate of diamond structures nor in the resistance of the spiral. Therefore, the main experiments were performed without an additional screen.
Three probe positions (probe cutoff) were considered: at the entrance to the channel, at a distance of 0.011 m and at a distance of 0.002 m from the entrance to the channel. The flow rate of methane (10 sccm and 15 sccm) and hydrogen supplied through the probe (0, 150, 500, 1500 sccm) also varied. In [15], the highest rate of diamond synthesis was obtained for a channel length of 0.022 m. The channel diameter was 0.003 m [15]. In our case, the diameter of the channel for feeding the methane mixture increased to 0.004 m, which led to a slower flow velocity and an increase in the residence time of methane in the decomposition zone. Therefore, based on the results of [15], it was expected that in order to increase the growth rate, the probe should approach the substrate. The co-current flow contributed to accelerating the flow in the probe channel and the production of atomic hydrogen. Experiments with the probe at the entrance have confirmed the non-optimality of such an arrangement of the probe: diamonds turned out to be small and rare. Therefore, the main experiments were performed for the probe in the center and at the exit.

1.1. Probe in the center.

The use of a large flow rate of hydrogen through a probe (1500 sccm H$_2$ + 10 sccm CH$_4$) led to the formation of a large amount of soot and rare diamonds (up to 15-18 µm) (apparently, excessive defragmentation of methane or lack of atomic hydrogen for such a flux of carbon-containing fragments). Reducing the flow rate of hydrogen to 500 sccm led to a decrease in the formation of soot on the substrates. This allowed obtaining diamonds up to 25 microns in size (500 sccm H$_2$ + 10 sccm CH$_4$). With an increase in methane flow rate, the largest diamonds were obtained with size up to 40 microns (500 sccm H$_2$ + 15 sccm CH$_4$). Experiments with a further decrease in the supply of hydrogen led to a decrease in the size of the synthesized crystals. Increasing the distance between the cut of the channel and the substrate to 0.002 m resulted in a decrease in the size of the synthesized diamonds to 8 µm (for a flow rate of 150 sccm H$_2$ + 10 sccm CH$_4$).

1.2. Probe at the exit.

In this case, the zone of decomposition of methane is only 0.012 m. Therefore, in order to reduce the zone of mixing of the flow from the probe and the concurrent flow, small flow rate of hydrogen through the probe up to 150 sccm was considered. In experiments with a flow rate of 150 sccm H$_2$ + 10 sccm CH$_4$, diamonds with a size of 10–20 µm were obtained. In the experiment with zero hydrogen supply (0 + 10 sccm CH$_4$), diamonds up to 25 µm in size were obtained.

Figure 4. The flow of the gas mixture near the substrate for the three positions of the probe (Xz=0, Xz=0.011, Xz=0.002 m) (a) and for flow rates of hydrogen through the probe located in the center of the channel (b) (Q=0 sccm, 500 sccm, 750 sccm and 1500 sccm).
The use of the probe feed allows investigating the influence of the main parameters (temperature, time and conditions of methane decomposition) with an insignificant change in the amount of atomic hydrogen on the rate of synthesis of diamonds. Thus, the experiment confirms the possibility of increasing the rate of synthesis of diamonds using the probe supply of a mixture of methane with hydrogen. In particular, diamonds with a size up to 40 microns (500 sccm H₂ + 15 sccm CH₄) were obtained at the central location of the probe.

Conclusions
The present work is devoted to numerical and experimental investigation of the probe supply of “cold” methane on the growth of diamond structures during gas-jet deposition. The direct simulation Monte Carlo method for numerical analysis of gas-dynamic aspect of these experiments was applied. A one-dimensional approach based on the solution of equilibrium chemical kinetics equations was used to analyze gas-phase methane decomposition. The analysis results of experiments on the diamond gas-jet synthesis from methane and hydrogen mixture flows are presented. It is shown that reducing the residence time of methane in the zone of active defragmentation allows increasing the rate of synthesis of diamond structures. The obtained results can be useful for investigation of gas-jet deposition of diamond structures.

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