Deposition of diamond from the jet activated in the microwave discharge of gases

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Abstract. The present work is devoted to a numerical and experimental investigation of the effect of conditions of methane decomposition on the growth of diamond structures during gas-jet deposition. The results of experiments on the diamond gas-jet synthesis from methane and hydrogen mixture flows are presented. The direct simulation Monte Carlo method in cylindrical geometry for numerical analysis of these experiments is applied. A one-dimensional approach based on the solution of equilibrium chemical kinetics equations is used to analyze gas-phase methane decomposition. The conducted research has shown that at a decrease in methane decomposition time in the absence of high temperatures of the fed mixture it is possible to receive higher rates of growth of diamond structures. The obtained results can be useful for optimization of gas-dynamic sources of activated gas diamond synthesis.

1. Introduction
The use of microwave radiation to activate gas mixtures containing hydrogen and carbon for the synthesis of diamond has been the subject of a large number of works, in particular [1-3]. As a rule, the authors create a plasma cloud above a substrate to activate gas molecules and diamond crystals formation on the surface of a substrate.

Successful production of a high-quality single-crystal diamond using chemical vapor deposition methods was reported in [4, 5]. The authors of the US patent [6] proposed a method and device for producing colorless single crystal diamonds with a high growth rate by CVD method with microwave activation of components. The goals were achieved including by ensuring minimal gradients of the concentration components and the surface temperature of substrates. The wide range of possible applications of diamonds continues to stimulate researchers to develop new diamond deposition techniques for various applications.

The present work is devoted to the development of the gas-jet method of deposition of diamond structures from a mixture of hydrogen and methane activated in a microwave discharge.

2. Description of the experimental setup
Figure 1 shows a diagram of the reactor used in the experiments. An antenna 2 is installed in the reactor vessel 1, which emits electromagnetic waves from a magnetron. The chamber is divided by a dielectric partition 3 (quartz) to protect the antenna from plasma exposure. The plasma expands from discharge chamber 4 to the deposition chamber through the nozzle 5. The geometry of the discharge chamber is optimized so that the electric field is maximal at the entrance to the nozzle. Substrate 6 is installed in the deposition chamber, and its temperature is controlled by water cooling in case of excessive heat flux from the activated gas or by heater 7. The initial gas mixture is supplied to the
discharge chamber through line 8. A vacuum pump through the channel provides low pressure in the deposition chamber.

![Diagram of the microwave reactor with a substrate in the deposition chamber.](image)

**Figure 1.** Scheme of the microwave reactor with a substrate in the deposition chamber.

Molybdenum 0.25 mm thick foil was used as a substrate material. Before the experiment, the surface of the substrate was treated with a plasma jet of a mixture of atomic and molecular hydrogen. The substrate temperature was measured with a welded chromel-alumel thermocouple and was maintained at 950°C in all experiments. The pressure was measured in the discharge chamber and in the deposition chamber by the MKS PR4000B type baratron. The deposition time was 1.5 hours. A more detailed description of the setup and experimental procedure is given in [7].

In this study, a cone molybdenum nozzle with a critical cross-section diameter of 2 mm at the apex and a solution angle of 110° was used. The height of the cone was 2.8 mm, and the diameter of the base was 10 mm. The hydrogen flow rate of 8000 sccm, the methane flow rate of 80 sccm, and the substrate temperature of 950 °C were kept constant during the experiments. The pressure in the discharge chamber was set equal to 169 torr at such gas flow rates, and the pressure in the deposition chamber had values of 10, 20, 40 and 80 torr.

The papers [7–10] contain information on the optimization of the process of microwave plasma formation in the configuration under consideration. The interaction of a supersonic jet with a substrate is considered in [9].

### 3. Results of work and discussion

A review of the literature on the use of microwave radiation for the synthesis of diamond structures is presented in [3]. Important parameters determining the quality and growth rate of diamond structures are the composition of the initial mixture, pressure in the discharge chamber, microwave power, substrate temperature, and gradients of the activated components of the substrate and its temperature. Numerous experimental studies have established that the optimum substrate temperature for diamond synthesis is close to 1000°C. The ratio between the flows on the substrate of atomic hydrogen and fragments of methane decomposition is decisive in the synthesis of diamond structures. In particular, one can change the deposition rate from one to tens of microns/hour [3] changing these parameters.
One of the advantages of the considered circuit is the ability to change the conditions in the deposition chamber without changing it in the discharge chamber at a supersonic pressure drop on the nozzle. In the series of experiments performed, the pressure in the deposition chamber varied from 10 to 80 torr. The considered pressure range provided supersonic flow from the nozzle.

The main goal of this work is an experimental research of the effect of pressure in the deposition chamber on the synthesis of diamond structures at constant flow rate of the working mixture and substrate temperature. Previous studies have shown that the use of 1% methane in hydrogen is optimal: a lower amount of methane leads to a lower rate, and a larger one leads to a deterioration in the quality of the film.

Figure 2 shows SEM photographs of coatings obtained by a scanning electron microscope. A continuous film was not formed at the minimum pressure in these experiments (Fig. 2a). Separate diamond crystals with a characteristic face edge size of up to 10μm precipitated. At a pressure of 20 torr and above, a dense diamond film covered the entire surface with a maximum thickness in the center.

Figure 2. SEM photographs of films obtained at a pressure in the deposition chamber: a) 10torr, b) 20torr, c) 40torr, and d) 80torr.
Figure 3. Raman spectra films obtained under pressure in the deposition chamber:
a) 10 torr, b) 80 torr.

Figure 3 shows the Raman spectra of the resulting coatings. The peaks at 1331 cm\(^{-1}\) and 1332 cm\(^{-1}\) indicate the predominant formation of diamond on the substrate, and a weak signal of about 1535 cm\(^{-1}\) is due to an admixture of graphite.

Figure 4. The growth rate of a diamond crystal facet depending on the pressure in the deposition chamber.

The dependence of the growth rate of diamond crystal faces on the pressure in the deposition chamber is shown in Fig. 4. An increase in pressure in the deposition chamber leads to an increase in
density in the gas stream and in the compressed layer at the deposition surface, and a decrease in the
gradient of radial concentrations of the building material at the substrate and surface temperature.
Diamond synthesis under conditions with smaller gradients of temperature and concentration of
activated gas components on the surface of the substrate will occur with high growth rates. The
influence of parameter gradients on crystal size growth is taken into account by the authors of the
patent [6] and others. In addition, an increase in the density of the polycrystalline coating of the
substrate surface with increasing pressure (Fig. 2) indicates a simultaneous increase in the mass rate of
diamond deposition on the surface.

Conclusion
The proposed new CVD microwave gas-jet deposition method of diamond has certain advantages over
traditionally used methods due to the separation of activation and deposition zones. A supersonic jet
protects the activation zone from the deposition zone, where gas-phase reactions occur in the flow and
there is gas-dynamic interaction of activated gases with the surface. This is especially important when
studying processes on the substrate itself.

Dependences of the morphology of coatings on the pressure in the deposition chamber have been
obtained. It is shown that the growth rate of coatings and the sizes of crystal faces increase with
increasing pressure. The previously observed tendency for crystal sizes to grow under conditions of
lower gradients on the substrate has been indirectly confirmed.

The Raman spectra of the coatings obtained indicate the presence of an amount of graphite
impurities on the polycrystalline diamond coating on the molybdenum substrate.

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