Effective cooling of substrates with low thermal conductivity under conditions of gas-jet MPCVD diamond synthesis

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Abstract. The paper presents the results of an experimental study of heating molybdenum and silicon substrates under the conditions of gas-jet deposition of diamond structures using the precursor gases of a microwave discharge to activate. A cooled substrate holder using a metal melt to improve heat removal by reducing the thermal resistance between the substrate and the substrate holder has been developed. The use of the melt allowed lowering the temperature of the silicon substrate under the conditions of gas-jet deposition to a level that ensures the preservation of its structure. The developed substrate holders were used to carry out gas-jet synthesis of diamond structures on molybdenum and silicon substrates.

1. Introduction
The deposition of diamonds on materials with low thermal conductivity, such as silicon, silicon carbide, sapphire, quartz, zirconium dioxide, zinc sulfide, etc. is of great technological importance for many applications (infrared windows, an electron emitter, a material for heat dissipation in electronic devices) and for solving other technical problems [1]. At present, chemical vapor deposition using microwave discharge to activate gas mixtures (Microwave Plasma Chemical Vapor Deposition - MPCVD) containing hydrogen and carbon is widely applied to obtain a diamond film of a good quality [2, 3]. A common feature of this approach is the creation of a plasma cloud above the substrate, from which active fragments participating in the formation of diamond crystals diffuse to the surface. The MPCVD method was further developed in [4-6] for the deposition of diamond structures using a microwave discharge to activate gases. The use of jet supersonic plasma expansion opens up the possibility of activating the initial gas mixture in the discharge chamber in a wide range of specific mass fluxes to the substrate without the pressure in the deposition chamber affecting this process. The use of jet delivery of active components creates the prerequisites for high rates of diamond synthesis on it. In [6], the rate of diamond deposition by this method is 78 µm/h. In [7, 8], a numerical analysis of flows of gas mixtures formed under conditions of gas-jet deposition is carried out. In [5, 9], numerical methods are used to study methods of optimizing the process of microwave plasma formation in the considered configuration. The results of a detailed study of diamond structures synthesized by the gas-jet method are presented in [10, 11].

In most cases, the deposition of diamond coatings is carried out on a substrate with a temperature of 700 - 1000°C. However, the high temperature of the substrate limits the production of diamond films on thermally unstable materials with low thermal conductivity, which are used in many industrially important fields. Consequently, the development of methods for the deposition of diamond coatings on the surface of materials with low thermal conductivity and at low temperatures will expand the range of substrate materials used, including such materials as silicon, silicon carbide and others. The most
important task in the synthesis of diamond on a substrate with low thermal conductivity under conditions of its heating by a jet of activated gas is to ensure effective cooling due to the contact of the substrate with the cooled base. The results of studies of diamond growth at low substrate temperatures are considered in [12, 13].

The presented work is devoted to the development of approaches for efficient heat removal from a substrate under conditions of gas-jet diamond deposition. To solve this problem, it is proposed to place the substrate on a molten metal, which will significantly reduce the contact resistance, ensure its constancy and control the temperature of the substrate when it is heated by an activated gas.

2. Experimental technique, description of the substrate holder design
The scheme for the deposition of a diamond coating from a high-temperature jet of gases activated in a microwave discharge contains the discharge and deposition chambers [6]. The gas flow from the discharge chamber through the nozzle with the formation of a supersonic flow enters the deposition chamber, where the substrate is located. This scheme eliminates the influence of a change in pressure in the deposition chamber on the processes in the discharge chamber. This circumstance allows the study of nucleation and growth of diamond structures for a wide range of substrate temperature almost without changing the parameters of the activated gas flow entering the substrate surface. An axisymmetric jet of a gas mixture has a pronounced radial distribution of temperature and density, and in this regard, conditions arise for elevated temperatures in the center of the substrate [6, 8]. The temperature of the substrate will be determined by the thermal parameters of the gas flow, the thermophysical properties of the substrate material, and the design of the substrate holder. The development of methods for the synthesis of diamond on materials with low thermal conductivity necessitates the creation of substrate holders that will ensure the uniformity of the temperature field of the surface and the required temperature range of the substrate surface. The experience of gas-jet deposition of diamond coatings on molybdenum and silicon substrates has shown that heating a molybdenum substrate with an activated gas may be insufficient to reach the required temperature, while silicon substrates may be destroyed by overheating. To solve these problems, substrate holders have been developed, which should provide the desired temperature regime of the substrate for materials with different thermal conductivity during the deposition of diamond coatings.

The design of the holder for a material with high thermal conductivity is shown in Fig. 1.

![Figure 1](image.png)

**Figure 1.** Holder 1 - substrate, 2 - base, 3 - clamp, 4 - transition disk, 5 - cooling unit, 6 - water cooling channel, 7 - wire heater in ceramics, 8 - thermocouples (substrate, base surfaces).

A substrate in the form of a plate 1 made of molybdenum foil 0.4 mm thick and 12x12 mm in size is located on a molybdenum base 2 with a diameter of 12 mm and a height of 15 mm, which is a continuation of a molybdenum transition disk 4 with a diameter of 30 mm and a thickness of 5 mm. The substrate 1 is tightly pressed against the surface of the base 2 by a clamp 3 made of tungsten wire with a diameter of 1 mm. When heated, the pressing force of the substrate to the base increases due to the temperature increase in the length of the spiral and twisting of the clamp turns. There is a 1.5mm hole in the center of the base for the thermocouple wires. The thermocouple junction 8 is fixed in a
groove on the upper boundary of the base 2. The temperature of the substrate is measured by a thermocouple welded to it from the shadow side (not shown in Fig. 1), the wires of which are led out through the channel together with thermocouple 8. In addition, it is possible to measure the temperature surface of the substrate with an optical pyrometer. Base 4 with a substrate is installed in a socket with a diameter of 35 mm and a depth of 8 mm in block 5, which is equipped with a circuit 6 with water cooling and a heater 7. The heater is made of two-core molybdenum wire with a diameter of 0.5 mm, which is placed in a two-channel ceramic tube with a diameter of 3 mm made of aluminum oxide. Heating of the substrate under the conditions of the gas-jet method of deposition of diamond structures occurs due to interaction with an activated high-temperature gas and surface exothermic reaction during the formation and growth of diamond. Heater 7 allows you to set the required temperature of the substrate with insufficient heating by the gas flow. To synthesize diamond on a silicon substrate, a substrate holder 2 was developed with efficient heat removal by significantly reducing the contact thermal resistance (Fig. 2).

Figure 2. Holder 2 (for low thermal conductivity substrate). 1 - substrate, 2 - base, 3 - clamp, 4 - transition disk, 8 - thermocouples (substrate, base surfaces), 9 - protective substrate, 10 – the melt of Rose.

Substrate 1 and protective substrate are silicon wafers 0.5 mm thick and 12x12 mm in size. They are located on a base 2 made of copper with a diameter of 12 mm with an internal cavity of 8 mm in diameter and 19 mm in depth. Base 2 with a height of 15 mm is a continuation of copper disc 4 with a thickness of 5 mm. Substrates 1 and 9 are tightly pressed to the base 2 by a clamp 3 made of tungsten wire 1 mm in diameter. The tightness of the cavity 10 during heating is ensured by an increase in the pressure due to the thermal expansion of the wire length. In the center of the copper disk 4 there is a hole with a diameter of 1.5 mm for the hermetically sealed leads of the thermocouple 8, the junction of which is located in the molten solder at a distance of 0.5 - 1 mm from the lower surface of the protective substrate 9. Before installing the disk 4 into the socket of block 5 (Fig.1) the cavity is filled with low-temperature melt 10 - Rose alloy (50% Bi + 25% Su + 25% Pb). The use of the alloy is due to the need to ensure good thermal contact of the substrate with the base, which must remain constant during the synthesis of the film. A gas jet in the experiment, directed against the force of gravity, heats the substrate and melts the alloy in the bath, which adheres tightly to the substrate and, due to the force of gravity, fills the gap that appears between the substrate and by the bath. In this way, a constant contact thermal resistance is established and, thus, there is no point overheating of the substrate. The use of the protective substrate 9 allows avoiding the destruction on the working substrate from the side of the melt, and the presence of the interface between the substrates does not make any noticeable changes.
3. Results and discussion

Experimental conditions for gas-jet diamond deposition: hydrogen flow rate of 3000 - 10000 sccm, microwave discharge power of up to 3 kW. The diameter of the activated gas jet at a pressure of 40 torr in the deposition chamber was about 10 mm. In this case, the power of the heat flux to the substrate was 500-1500 W. Under these conditions, the temperature of the molybdenum substrate reached 1000°C. Experiments were carried out with the substrate holder 1 (Fig. 1) for heating a silicon substrate 0.5 mm thick. In some of experiments the silicon substrate was significantly overheated up to destruction. The main result of these experiments was the impossibility to reduce the surface temperature of the silicon substrate to avoid destruction under the consider conditions.

Note that under the considered conditions for the synthesis of a diamond coating, the surface temperature of the silicon substrate is significantly higher than the temperature of the molybdenum substrate. In addition, heating of the silicon substrate sometimes resulted in unpredictable destruction and burning of a hole in the center of the substrate with a diameter of up to 1–2 mm. From the analysis of the results of the silicon substrate heating, it follows that the burnout and destruction of the silicon substrate occurs due to uneven radial thermal expansion under the influence of the gas jet. The flexure of the substrate in the center leads to a significant increase of the thermal contact resistance at the interface between the substrate and grounds. This leads to a sharp decrease in heat transfer from the substrate, and destroys the material. The most effective way to cool the substrate is to ensure a constant maximum thermal contact of it with the base 2, through which the heating system 7 contacts the block 5 cooled by water. It is known that any interface between two media has thermal resistance, and a temperature jump appears at the interface between the media. In the simplest case, this phenomenon is associated with the roughness of surfaces and their poor contact, as well as with the difference in the density of the two media, which causes phonon scattering at the interface. In reality, the passage of phonons is also hampered by the presence of various imperfections (roughness, grain boundaries, etc.) [14].

Contact thermal resistance is an important factor in many heat transfer applications. As a result, when two bodies are pressed against each other, contact occurs only at a finite number of points separated by relatively large gaps. At low compressive forces, the actual contact area can be only about 5% of the total surface [15]. Consequently, the temperature drop across a contact will increase in proportion to the decrease in the contact area, i.e., almost 20 times. Decrease of contact thermal conductivity leads to an equilibrium thermal state of the system at higher temperatures of the surface receiving the heat flux. This necessitates the creation of conditions for the elimination of contact thermal resistances.

One of the best ways to increase the contact area is to place a heat-conducting liquid metal between the contacting bodies. The use of liquid metal to ensure the maximum contact area between the silicon substrate heated by the gas flow and the cooling block, in our case, allows achieving the required temperatures while maintaining the structure of the substrate material. When introducing the melt, the appearance of a geometric gap at the interface between the substrate and the melt is eliminated, the thermal resistance remains constant, random temperature jumps disappear, and thus the structure of the silicon substrate is preserved during heating.

Table 1. The results of temperature measurements of the base \( T_{\text{base}} \) and substrates at different flow rates of hydrogen.

| Hydrogen flow rate, sccm | 3000  | 4000  | 5000  | 6000  | 8000  | 10000 |
|-------------------------|-------|-------|-------|-------|-------|-------|
| \( T_{\text{base}}(\text{Mo}) \), °C | 100   | 150   | 250   | 300   | 550   | 700   |
| \( T (\text{Mo on Mo}) \), °C | 200   | 350   | 450   | 650   | 850   | 1200  |
| \( T (\text{Si on Mo}) \), °C | -     | -     | 650   | 850   | 1200  | -     |
| \( T (\text{Si on Rose alloy}) \), °C | -     | -     | 450   | 600   | 800   | 1000  |

To define the effect of thermal resistance on heating the substrates, the experiments were carried out for 0.4 mm thick molybdenum substrates and 0.5 mm thick silicon substrate under gas-jet flow
with a heat flux power of 500-1500 W. Using the substrate holder 1 (Fig. 1), the heating of molybdenum substrates based on molybdenum (Mo on Mo) and silicon substrates on a molybdenum base (Si on Mo) was studied. Using the substrate holder 2 (Fig. 2), the heating of the silicon substrate on the Rose alloy (Si on the Rose alloy) was studied. The temperatures of the base and Rose alloy were measured with thermocouple 8 (Fig. 2). The measurement results are shown in Table 1.

In the experiment, the hydrogen flow was set in the range of 3000 – 10000 sccm. The pressure in the deposition chamber was maintained at 40 Torr, and the base temperature was measured for alternately installed molybdenum and silicon substrates. The temperature of the molybdenum substrate was controlled by a thermocouple welded on the shadow side. The surface temperature of the silicon substrate above 600°C was measured with an optical pyrometer, and at lower temperatures it was estimated from the readings of a chromel-alumel thermocouple placed inside the melt under substrate 1 at a distance of 2 mm from the contact of the substrate with the melt. In these experiments, the protective substrate 9 was not used. The data presented in Table 1 show that at the same hydrogen flow rates, the value of the contact thermal resistance has a significant effect on the temperature of the substrate surface. For example, for a hydrogen flow rate of 8000 sccm, the surface temperature of the silicon substrate in contact with the Rose alloy has a value of 800°C, and in contact with the molybdenum base it reaches 1200°C. With a further increase in the hydrogen flow rate to 10000 sccm, in the first case, the substrate is retained when the temperature increases to 1000°C, and in the second case, the destruction of the material structure is observed. The developed substrate holder 2 was successfully used to obtain diamond structures by the gas-jet method. Figure 3 present the SEM photograph of diamond structures obtained on a silicon substrate on a Rose alloy.

Figure 3. SEM photograph of obtained diamond structures.

Diamond deposition was carried out for 90 minutes. A silicon substrate 12x12 mm in size and 530 μm thick was attached to a substrate holder at a distance of 30 mm from the critical diameter of the conical nozzle. The flow rate of the mixture was 8000 sccm for hydrogen flow with the addition of 80 sccm of methane. The pressure in the deposition chamber was maintained at 40 Torr. The substrate temperature in the central region of deposition was about 850°C. A protective substrate was used to preserve the structure of the back side of the substrate, but on the other hand, it led to higher heating temperatures of the surface of the substrate 1 by about 200°C. For comparison, the data on temperature without a protective substrate are given in Table 1. To control the temperature level, we additionally used a chromel-alumel thermocouple located inside the melt under the substrate at a distance of 2 mm from the contact of the substrate with the melt. The thermocouple readings during the diamond film deposition experiment showed a melt temperature in the range 290-300°C.

4. Conclusion
The paper presents the results of an experimental study of heating molybdenum and silicon substrates under the conditions of gas-jet deposition of diamond structures using the precursor gases (hydrogen and methane) of a microwave discharge to activate. A cooled substrate holder using a metal melt to improve heat removal by reducing the thermal resistance between the substrate and the substrate
holder has been developed. The data on the temperature of the substrate and substrate holder were obtained in a series of experiments with different flow rates of the supplied hydrogen. The use of the melt allowed lowering the temperature of the silicon substrate under the conditions of gas-jet deposition to a level that ensures the preservation of its structure. The developed substrate holders were used to carry out gas-jet synthesis of diamond structures on molybdenum and silicon substrates.

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