EXPERIENCE IN THE SYNTHESIS OF DIAMOND FROM A SUPERSONIC MICROWAVE PLASMA JET


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Original Manuscript Submitted: 6/26/2019; Final Draft Received: 8/12/2019

In this paper, the traditional method of microwave plasma generation is used in combination with the formation of a high-velocity plasma flow from a resonant chamber into an evacuated deposition chamber. In the experiments, a modernized magnetron with power up to 3 kW at a frequency of 2.45 GHz is used. The calculations of the microwave plasma formation process make, in practice, it possible to estimate the optimal geometry of the discharge chamber for an acceptable distribution of the electromagnetic field in the discharge region. The gas-dynamic calculations give an estimate of the approximate content of atomic hydrogen at the deposition surface. The results of the work determine ways for further research on the synthesis of diamond from high-speed microwave plasma jets.

KEY WORDS: nanoparticles, diamond coatings, microwave plasma, gas jet

1. INTRODUCTION

The use of microwave radiation to activate gas mixtures containing hydrogen and carbon in the synthesis of diamond is well known (Bolshakov et al., 2012; Altukhov et al., 2011; Balmer et al., 2009). A common and significant feature of experiments in these works is the creation of a plasma cloud above a substrate, from which active fragments diffuse to the surface of the substrate. In this paper, the traditional method of microwave plasma generation is used in combination with the formation of a high-velocity plasma flow from a resonant chamber into an evacuated deposition chamber. This provides the following new possibilities:

1. Gas activation for a wide range of pressures, independent of the pressure in the deposition chamber during supersonic discharge from the nozzle;

2. Implementation of a wide range of specific mass flows to the substrate;

3. Gas-dynamic acceleration of heavy active particles such as C_mH_n in the flow of H_2 + H mixtures, followed by high-energy collisions of these particles with the surface; and


The method of using high-speed flow emerged out of studies on the deposition of polymer coatings from a gas flow (Rebrov et al., 2005; Safonov et al., 2018) and polycrystalline diamond coatings during expansion of gas mixtures from a cylindrical channel (Rebrov et al., 2009, 2017; Emel’yanov et al., 2017). In addition, devices for using high-speed flux in the deposition of diamond from a microwave discharge are in many respects similar to those used by developers of space thrusters with a working fluid created during the generation of microwave plasma (Rutledge et al.,
A significant advantage of plasma activation methods during the deposition of a polycrystalline diamond film is a high deposition rate (Cerio and Weimer, 1992).

2. EXPERIMENTAL FACILITY

Figure 1 shows a simplified diagram of the gas path. The antenna (2), which radiates electromagnetic waves from the magnetron, is placed in the chamber (1). The camera (1) is divided by the dielectric (quartz) barrier (3) to protect the antenna (2) from the plasma exposure. The geometry of the chamber is optimized such that the electric field intensity is at its maximum at the entrance to the nozzle (4). The gas mixture is fed through a channel (5). The substrate (7) is installed in the deposition chamber (6), temperature of which is regulated by water cooling through the channel (8) or by a resistor heater. Plasma expands through the nozzle (4) to the substrate (7) from the cloud (9), where the synthesis of the diamond coating takes place. Low pressure in the deposition chamber (6) is provided by a vacuum pump through a channel (10).

In the experiments, a modernized magnetron with power up to 3 kW at a frequency of 2.45 GHz is used, as well as hydrogen and methane supply systems with flow meters having an error of several percent, a vacuum pump with a pumping speed of 25 l/s, a baratron of the MKS PR4000B type for measuring pressure in resonant and deposition chambers, chromel–alumel thermocouples to measure the temperature of the substrate, a camera body, and the nozzle assembly. The diamond deposition was carried out at a consumption of hydrogen of 1–10 nl/min and methane from 1 to 2 mol% relative to hydrogen.

An important element in the experiments was the use of a pressure drop across the nozzle, which provided the supersonic flow of activated gas. This allowed adjusting the pressure in the deposition chamber, regardless of the pressure in the discharge chamber, and estimating the parameters in the critical section of the nozzle with a known gas flow rate, nozzle diameter, and pressure in the discharge chamber for flows close to equilibrium.

3. OPTIMIZATION OF THE MICROWAVE RESONANT CHAMBER

Numerical simulation is an important tool in optimization studies of chemical vapor deposition (CVD) devices. One key aspect of such optimization is correct simulation of the microwave energy distribution inside the resonant chamber. A well-known tool for simulation of microwave radiation is the COMSOL Multiphysics software package, which
was used previously to simulate the microwave plasma deposition of the diamond process (Alcantar-Peña et al., 2016) and microwave-powered space thruster devices (Gao and Bilén, 2008).

In the problem of optimizing the process of microwave plasma formation, an important role is played by the geometry of the waveguides and resonant volumes. To search for conditions that ensure the maximum electric field strength near the output nozzle, a series of numerical simulations of microwave radiation in a resonant chamber were carried out using the COMSOL software package for different chamber geometries. The simulations were carried out in an axisymmetric formulation. Microwave radiation was supplied through a coaxial port located at the bottom of the resonant chamber. The radiation frequency was set to 2.45 GHz, and the radiation power was set to 3 kW. The diameter and height of the resonant chamber corresponded to the dimensions of the experimental setup, which were equal to 100 mm and 145 mm, respectively. The walls of the chamber were considered perfectly conductive.

Figure 2(a) shows the obtained distribution of the electric field strength in the upper part of the resonant chamber with the geometrical parameters corresponding to the experimental setup (the nozzle is represented as a hole with a diameter of 1 mm in the center of the upper wall of the resonator chamber). Under such conditions, the field is not focused near the exit nozzle, but is uniformly distributed over the entire resonant chamber, and its intensity near the nozzle is 15 kV/m. It is well known that the plasma layer is capable of shielding the microwave field. This shielding may lead to significant disruption of the axial symmetry of the field distribution and to the subsequent displacement of the plasma cloud from the central axis of the exit nozzle, thus reducing the efficiency of the device. Therefore, it was decided to change the shape of the exit nozzle by adding a hemisphere or a truncated cone with a hole in it and having the same diameter as before (1 mm).

The results of the simulations for the nozzle in the shape of a truncated cone with a fixed large radius on the wall equal to 10 mm, different smaller radii, and a fixed height of 10 mm are shown in Figs. 2(b) and 2(c). It was found that the field focuses on the edge of the truncated cone, and as the smaller radius increases the field maximum moves away from the exit orifice, which leads to a decrease in the efficiency of the microwave heating. However, as the smaller radius of the truncated cone decreases its walls become closer to the outflowing gas jet, which should lead to more intensive recombination of atomic hydrogen in the gas stream flowing out of the nozzle.

To reduce the recombination of atomic hydrogen on the inner walls of the nozzle and at the same time maintain high field strength, it was proposed to use a nozzle in the form of a hemisphere. Three sphere radii of 5, 10, and 15 mm were considered (Fig. 3). The maximum field strength was observed at the sphere with the radius of 10 mm. The field value in this case reached 60 kV/m near the exit orifice; however, this was lower than the corresponding value for the truncated cone.

As a result of the simulations, it was found that the maximum amplitude of the electric field near the outlet was obtained with the truncated cone-shaped nozzle with the large and smaller radii of 10 and 2 mm, respectively. The field strength near the nozzle in this case reached 65 kV/m, which is about 3 times larger than in the unmodified case. The difference in the CVD efficiency between the hemisphere and cone nozzle shape needs further research that includes the process of thermal dissociation and the wall recombination of hydrogen.

**FIG. 2:** Distribution of the electric field for the case without a nozzle (a) and the cases with a nozzle in the form of a truncated cone with smaller radii of 4 mm (b) and 2 mm (c)
4. SIMULATION OF THE FLOW BEHIND THE NOZZLE

The task of modeling the flow behind the nozzle was performed to determine the parameters of the dissociated hydrogen between the nozzle and the substrate for the geometry used in the experiments. The results of these calculations are the data on the gas-dynamic separation of atomic and molecular hydrogen, and their speed and mass flows on the way to the substrate. Figure 4 shows the geometry of the channel behind the nozzle used in the calculations.

The calculations were carried out using the direct simulation Monte Carlo (DSMC) method (Bird, 1994) in the axisymmetric formulation (Morozov et al., 2016), under conditions equivalent to the experimental procedure. A mixture of atomic and molecular hydrogen was fed through a cylindrical nozzle with a diameter of 1 mm and length of 0.4 mm; behind the nozzle, the flow expanded into a cylindrical channel 15 mm long and 10 mm in diameter. At a distance of 5 mm from the channel exit the substrate was located. A background pressure of $2.7 \times 10^3$ Pa was set at the boundaries of the computational domain. The flow parameters corresponded to the stagnation temperature of 3800 K and pressure of $4 \times 10^4$ Pa. The dissociation degree was determined through the numerical density of hydrogen fractions using the following formula:

$$K_d = \frac{n(H)}{n(H) + 2n(H_2)}$$

In our case, the degree of dissociation was $K_d = 50\%$, according to the reference data (Vargafik, 1972).
The DSMC method assumes, as the boundary conditions, the interaction of molecules with a surface at the boundaries of the computational domain. The temperature of the channel walls was set at 1000 K, and the substrate temperature was set at 1200 K. At these temperatures, atomic hydrogen can be recombined to form molecular hydrogen. The data given in the literature on recombination probabilities lie within a wide range from 0.01 to 0.5 (Morozov et al., 2016; Plotnikov and Shkarupa, 2016; Rutigliano and Cacciatore, 2011). The calculations were carried out for three values of the recombination probability, $W$, of hydrogen on the channel surface: 1, 0.1, and 0.01. Figure 5 shows the distribution of the degree of dissociation of hydrogen, $K_d$, along the axis. Due to the large number of collisions of atoms with the surface, there is a weak influence of the probability of $W$ recombination on the degree of dissociation.

5. EXPERIMENTAL RESULTS

Figure 6 shows the Raman spectrum and morphology of the deposition obtained at the Center for Collective Use at the Rzhanov Institute of Semiconductor Physics for one of the experiments under the conditions adopted in the DSMC calculation (nozzle diameter, 1 mm; hydrogen flow rate, 3 nl/min; methane consumption, 1.5 mol% relative to hydrogen; pressure in the discharge chamber, $3.48 \times 10^4$ Pa; pressure in the deposition chamber, $2.7 \times 10^3$ Pa; and substrate temperature, 800 K). The photograph was obtained using a HITACHI SU8220 scanning electron microscope (SEM). The Raman spectrum indicates the presence of a diamond line on the spectrum. Diamond crystals with a face size of about 10 µm are visible in the SEM image, which corresponds to a deposition rate higher than 7 µm/h.
6. CONCLUSIONS

The results obtained open up a new outlook with fair promise for the synthesis of diamond films from a gas activated by microwave plasma. The calculations of the microwave plasma formation process make it possible, in practice, to estimate the optimal geometry of the discharge chamber for an acceptable distribution of the electromagnetic field in the discharge region. The gas-dynamic calculations give an estimate of the approximate content of atomic hydrogen at the deposition surface. The results of this work determine ways for further research on the synthesis of diamond from high-speed microwave plasma jets.

ACKNOWLEDGMENTS

The theoretical part of this study was carried out under state contract with the Kutateladze Institute of Thermodynamics of the Siberian Branch of the Russian Academy of Sciences (Contract Nos. AAAA-A17-117030110017-0 and AAAA-A17-117022850029-9). The experimental part of this study was financially supported by the Russian Foundation for Basic Research (Project No. 18-29-19069) and Integration Grant Sb RAS No. 47.

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