Synthesis of diamond structures from the coaxial flows of H_2 and H_2+CH_4 mixture

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Abstract. The work presents the results of experiments on the diamond gas-jet synthesis from methane and hydrogen mixture, flowing from coaxial channels under the following conditions: temperature of the hydrogen activating surface of 2400 K, pressure in the deposition chamber of 20 Torr, different gas fluxes, and different CH_4 concentrations. The Direct Simulation Monte Carlo method for numerical analysis of experiments was applied.

1 Experiment

Spitsyn [1] was among the first researchers who studied chemical crystallization of diamond during the separate feed of interacting flows at the beginning of 1970s. A growth rate of 1 μ/h was attained on a diamond nucleus crystal using the flows with activated H_2 and CH_4. The low rate can apparently be explained by insufficiently high temperature of the tungsten activating surfaces and by inevitable effect of carbonization, viz., the deterioration of catalytic properties of the tungsten surfaces. The information on the effect of carbonization of the surface on the synthesis of diamond coating can be found in [2]. In the case of hot-wire chemical vapor deposition (HWCVD), the activated mixture of hydrogen and hydrocarbons is formed in single collisions of initial gas molecules with hot surfaces of heated wires. When the initial gas flow is activated on an extended high-temperature surface, multiple collisions lead to deep dissociation of hydrogen and decomposition of methane. This concept was realized in [3–7].

For the gas-jet deposition of diamond structures, the reactor with a high degree of dissociation of the hydrogen flow was elaborated and manufactured. The detailed description of this reactor (Figure 1) is presented in [7]. The experiments were performed under the following conditions: the pressure in chamber was 20 Torr, and temperatures of the tungsten tube, substrate, and tungsten capillary were 2400, 1300, and about 2400 K, respectively. The hydrogen flow rate in the annular channel of the tube 1 was 1500 sccm; the flow of mixture H_2 + CH_4 with CH_4 concentration of 0.3-1% was delivered through capillary 5 with hydrogen flow rate of 500–1500 sccm.

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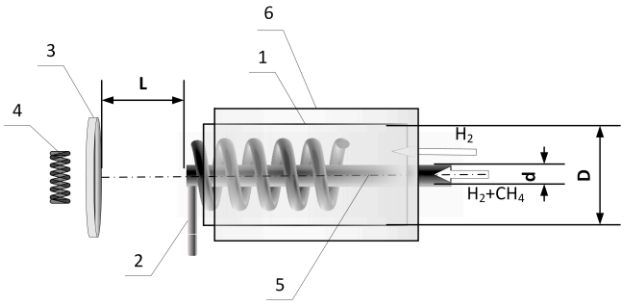

Fig. 1. Two-channel activator with a heating spiral in the hydrogen channel: (1) activator tube; (2) tungsten spiral; (3) substrate; (4) heater; (5) tungsten capillary, and (6) heat screen.

The example of crystals when the flow of methane is 8 sccm is shown in Fig. 2a. The increase of the methane concentration leads to the growth of diamond crystals (Fig. 2b). These results of experiments were obtained for hydrogen flow through a capillary 1500 sccm.

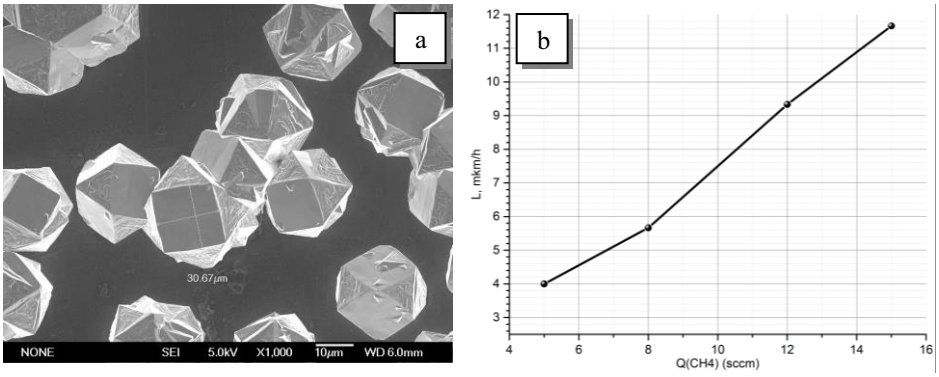

Fig. 2. a) SEM photo of crystals; b) the growth rate of crystals.

2 Gas-dynamic modelling

To understand peculiarities of deposition from such coaxial source the simulation of the flow was performed by Direct Simulation Monte Carlo method [8, 9] for conditions of experiments. One of the main results was the data on atomic hydrogen flows in the space from source exit to the substrate. The calculations were performed for the mixture of H_2, H and CH_4. Algorithm parameters were chosen according to recommendations of [10].

The calculation domain includes channels formed by cylinders with diameters of 3 and 13 mm, and space surrounding the substrate, which is located at the distance of 10 mm (Figure 3a). The used temperatures were 2400 K for spiral and internal cylinder, 1800 K for external cylinder, 1300 K for the substrate. Hydrogen flow rate was 1500 sccm in both channels, and methane flow rate was 5 sccm in a capillary. Data for heterogeneous reactions were used from [11- 13]. The hydrogen dissociation in the capillary was neglected because of carbidization of internal surface [2, 3].

Three stream lines in Figure 3a give contours of the atomic hydrogen flow in the computational domain. The radial distribution of the dissociation rate ($K = n_H/(2n_{H2}+n_H)$),

where n_{H2} and n_H are the number densities) (Figure 3b) shows very fast smoothing K inside the jet with approaching a substrate.

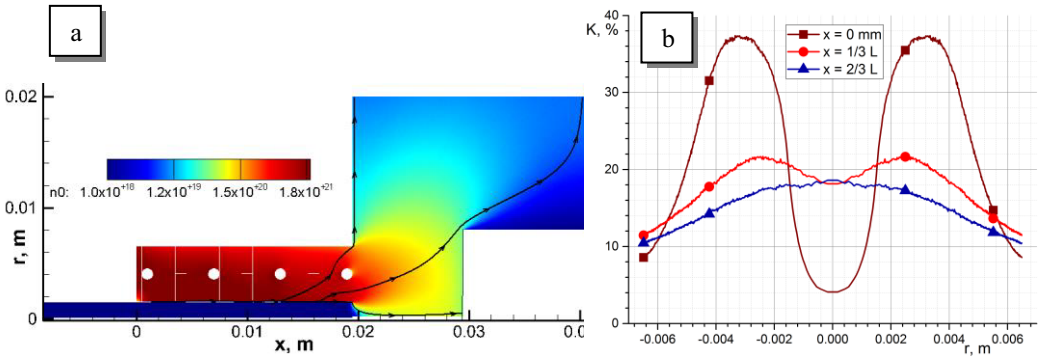

Fig. 3. a) Distribution of density(m^{-3}) and streamline of H; b) radial distribution of hydrogen dissociation at different distances from cylinders exit.

It is explained by high diffusion velocity of atomic hydrogen. The illustration of the radial distribution of specific flow nV and density for H_2 and H is given in Figure 4 a, b.

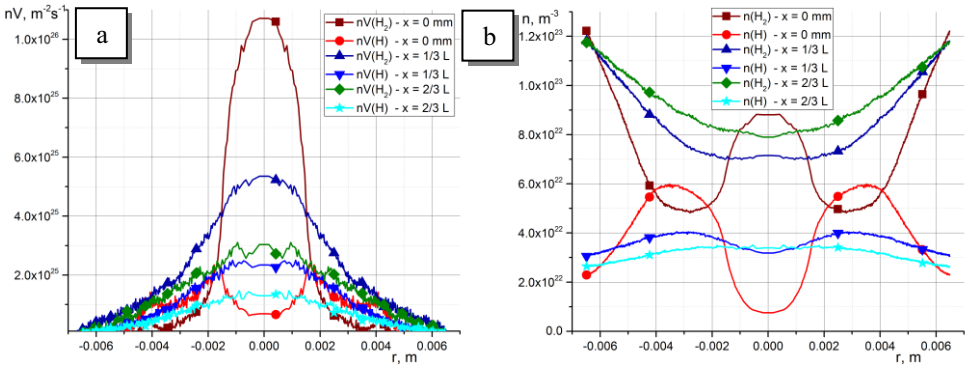

Fig. 4. Radial distribution of nV (a) and densities (b) of H_2 and H.

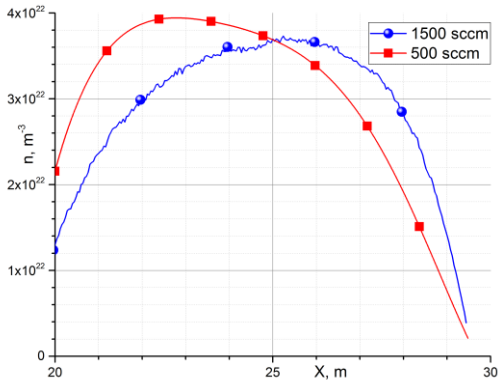

Fig.5. Atomic hydrogen distribution along the flow axis by different H_2 flux through the capillary.

Peculiarities of diamond deposition become clear from the comparison of axial distribution of atomic hydrogen density at different flow rates (and velocities) through the central channel. In Figure 5 one can see high enrichment of the zone upstream the substrate by atomic hydrogen at higher hydrogen flux through the capillary. It explains more intensive diamond deposition at high mass flux of H_2 through the central channel in performed experiments.

This work was supported by RFBR 15-08-01949 and by the grant of Presidium of the RAS II.2П/III.22-1.

References

1. B.V. Spitsyn, *Handbook of Crystal Growth* (Elsevier, Amsterdam, 1994)
2. M. Sommer, F. W. Smith, J. Mater. Res. **5** (11) (1990)
3. A. Emelyanov, A. Rebrov, I. Yudin, Phys. Status Solidi (A) **211**, 2279 (2014)
4. A. Rebrov, A. Emelyanov, S. Kosolobov, I. Yudin, Phys. Status Solidi (C) **12**, 931 (2015)
5. A.A. Emel'yanov, A.K. Rebrov, I.B. Yudin, J. Appl. Mech. Tech. Phys. **55**, 270 (2014)
6. A.K. Rebrov, A.A. Emelyanov, I.B. Yudin, Thin Solid Films **575**, 113 (2015)
7. A.A. Emel'yanov, A. K. Rebrov, I.B. Yudin, Technical Physics **61**, 12 (2016)
8. G.A. Bird, *Molecular Gas Dynamics and the Direct Simulation of Gas Flows* (Oxford: Clarendon Press, 1994)
9. M.S. Ivanov, S.V. Rogasinsky, Russian J. Numer. Anal. Math. Modelling **3**, 6 (1987).
10. M.Yu. Plotnikov, E.V. Shkarupa, Comput. Fluids **58**, 102 (2012)
11. A.A. Morozov, M.Yu. Plotnikov, A.K. Rebrov, I.B. Yudin, AIP Conference Proceedings of 30th Intern. Symp. on Rarefied Gas Dynamics **1786**, 050015
12. A.K. Rebrov, I.B. Yudin, AIP Conference Proceedings of 30th Intern. Symp. on Rarefied Gas Dynamics **1786**, 150012 (2016)
13. M.Yu. Plotnikov, E.V. Shkarupa, Vacuum **129** 31 (2016)