Influence of the substrate temperature on the jet diamond deposition

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Abstract. The gas-jet diamond deposition with the activation of H₂ + CH₄ mixture by microwave discharge has been implemented. The maximum crystal size was observed at the substrate temperature of 850°C. The dependence of a film structure on the substrate temperature has been established. Diamond coating was received at a low substrate temperature (524°C).

1. Introduction
Methods of synthesis of diamond films from the gas phase are known in the literature, and in particular, they are described in the collection edited by Asmussen and Reinhart (2002) [1]. For all the complexity of the influence of individual factors on the resulting coating, it has been established [1] that the substrate temperature determines the growth rate of individual faces (100, 110, 111) of diamond crystals. For a given fraction of carbon-containing gas as a mixture with hydrogen, and a substrate temperature of about 500-600°C, predominantly structures of tetrahedron are formed, and at a temperature of about 800°C the growth rate of flat faces increases. Such studies are given in [3-5]. In [3], it was shown that the speed increases by almost an order of magnitude with an increase in the substrate temperature from 550 to 850°C. When the substrate temperature changes, the size and shape of the peak on the Raman spectrum changes as well [6]. It indicates different crystallinity of the coating. These statements are valid for coatings obtained with various methods of gas activation: on hot metal wires, activation in the plasma torch jet and in microwave plasma.

We note some results for the growth of diamond films from a supersonic DC arc jet [7]. In this work, the possibility of obtaining a film at substrate temperatures of 180-360°C is shown when using a mixture of hydrogen with ethylene (C₂H₄) with an admixture of oxygen as a precursor. Diamond deposition at such low temperatures can be used for non-heat-resistant and, especially, biocompatible materials. In [8], the important fact of the dependence of the deposition rate on individual faces on the ratio of active components was noted. This explains the diversity of the structures formed at the same surface temperature, but with different methods of deposition. A very detailed analysis of the effect of substrate temperature on the deposition of nano-crystalline (NCD) and ultra-nano-crystalline (UNCD) films is given in [9]. The most important result of the study is that the composition, structure, and morphology of UNCD practically do not change if the substrate temperature varies from 530 to 770°C. On the contrary, with a decrease in temperature to 700°C or even lower, a sharp change in the structure of NCD films occurs. At the same time, the ratio sp²/sp³ of NCD films remains constant in the temperature range studied. Up to now studies of diamond deposition from high-speed flows of carbon-containing gas mixture are known: as activated by hot surfaces [10], as well as using a low-power microwave plasma reactor [11].
2. Experiments
The experimental results presented below relate to a new method of deposition of diamond coatings – the use of a high-speed jet of microwave discharge plasma. In this work, the features of the influence of the substrate temperature are established. The paper [12] is the first publication in the chosen field.

The schematic diagram of the experiment is shown in Fig. 1. Plasma is formed in the discharge chamber 2 (which is a gas-dynamic stagnation chamber), and expands through a nozzle 3 with a diameter of 1.5 mm into a vacuum chamber with a pressure of several torr towards the substrate 5. The magnetron power is up to 3 kW and the frequency is 2.45 GHz.

Figure 1. Scheme of the experimental site.

Hydrogen consumption in all experiments was 10 l/min; methane consumption was 0.1 l/min. The temperature of the substrate was regulated by water cooling and electric heater in the range of 400 - 1000°C. The molybdenum disk with a diameter of 28mm and a thickness of 0.45mm was used as the substrate. The chromel-alumel thermocouple was welded to its backside. The pressure in the discharge chamber and in the deposition chamber was measured by the MKS baratron PR4000B. The deposition time was chosen to be 1.5 hours to minimize the effect of the nucleation period and the initial film formation. The pressure in the resonant chamber was set at 300torr, and the pressure in the deposition chamber was 1 torr. The distance from the nozzle exit to the substrate was kept equal to 10mm.

3. Results
Figure 2 presents the SEM photographs of the surface of the obtained samples at different substrate temperatures. The density of nucleation of crystals weakly depends on the temperature of the substrate, since it is determined, first of all, by the surface properties. The size of the crystals increases with an increase in the substrate temperature, reaches a maximum in the temperature range of 850°C and then decreases as the temperature rises to 1000°C. With further increase in the temperature of the substrate, the deposition of the diamond coating stops. The film obtained at a low temperature of the substrate of 524°C contains crystals with minimal defects in the crystal structure. At higher substrate temperatures, a substantial background of sp² structures is seen. The characteristic Raman spectrum for a substrate at a temperature of 524°C in Fig. 3 contains a pronounced line of diamond 1332 cm⁻¹.
Figure 2. SEM photographs of the obtained samples at different substrate temperatures.
Figure 3. Characteristic Raman spectrum of the coating (Substrate temperature 524°C).

Conclusion
A gas-jet deposition method was implemented with the activation of the \( \text{H}_2 + \text{CH}_4 \) mixture by a microwave discharge in the braking chamber. A diamond coating was obtained at a low substrate temperature of 524°C, which is important when using such coatings for practical applications. The maximum crystal size was observed for a substrate temperature of 850°C. The dependence of the structure of the deposited film on the substrate temperature is established.

Acknowledgments
The work was carried out with the state budget support and the RFBR grant No. 18-29-19069

References
[1] Reinhard D K 2002 Diamond Films Handbook ed. by Jes Asmussen (Michigan State University)
[2] Farhat S, Silva F, Hassouni K, Gicquel A, Scott C D 1998 Proc. of the Fifth International Symposium on Diamond Materials (Pennington, NJ, USA: Electrochem. Soc) pp 1–19
[3] Ying X, Shen Y, Xue H, Jianhai L, Xing Z, Xu J, Zhang 1992 Diamond Opt (V SPIE) pp 1759:218–23
[4] Petrich R, Stenzel O 1994 Advances in New Diamond Science and Technology (Tokyo: MY) pp 387–90
[5] Seitz J R 1975 US Patent 3.895.313
[6] Barbosa D C, Barreto P R P, Ribas V W, Trava-Airoldi V J, Corat E J Encyclopedia of nanoscience and nanotechnology 13 (78) 59–782011
[7] Romanyuk A, Gottler H, Popov V 2001 Semiconductor Physics Quantum Electronics & Optoelectronics 4 (3) 187–91
[8] Qu Quan-yan, QIU Wan-qi, ZENG De-chang, LIU Zhong-wu, DAI Ming-jiang, ZHOU Ke-song 2009 Trans. Nonferrous Met. Soc. (China) 19 131–7
[9] Kulisch W, Petkov C, Petkov E, Popov C, Gibson P, Veres M, Merz R, Merz B, Reithmaier J P 2012 Physica status solidi 209 (9) 1664–74
[10] Emelyanov A A, Rebrow A K, Yudin I B 2014 Physica status solidi 211 (10) 2279–83
[11] Zhang Lei, Ma Zhibin, Wu Lifeng 2011 Inorganic Materials 47 (3) 255–61
[12] Rebrow A K, Isupov M V, Litvinchev A Yu, Burov V F 2018 J. of Appl. Mech. and Tech. Phys. 59 (5) 351 5–12