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Hot carbon nanoparticles in plasma volume during the plasma-assisted chemical vapor deposition of diamond films

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In the present paper, it is shown that the appearance of continuous Planck radiation in the emission spectrum of microwave plasma, during the plasma-assisted chemical vapor deposition of diamond films, may be associated with the formation of carbon nanoparticles in its volume. According to the spectrum recorded in the near infrared wavelength range, the temperature of these particles was determined to be $\sim 2600 \pm 100$ K. The obtained result indicates the possibility of the existence of carbon nanoparticles in the plasma's hot area.

Keywords: CVD diamond, plasma-assisted chemical vapor deposition, carbon nanoparticles, plasma spectroscopy.

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Due to a whole series of unique properties, diamond is a promising material in a wide spectrum of science and industry fields. In particular, the combination of record thermal conductivity and its chemical inertness and radiation resistance makes diamond a competitive material for use in various devices operating under extreme conditions, such as, for example, optoelectronic devices and powerful semiconductor microwave devices [1].

One of the most effective methods to produce both single-crystal and polycrystalline diamond films (DF) is plasma-assisted chemical vapor deposition method (PACVD) [2]. There are different methods for plasma activation of gas mix [3], but for DF use in electronics, the microwave activation method is preferred as the least contaminating for the deposited DF [4].

Multiple studies in this area show that the morphological structure of the crystalline DFs deposited by PACVD method is highly sensitive to the variation of physical parameters of the excited gas medium [4,5]. Therefore, it is important to monitor online the key physical parameters maintained in the process of DF growth both in the plasma volume and on the specimen surface. To provide for such monitoring, it is necessary to understand the key processes in the plasma, making it possible to optimize the DF growth conditions with the specified parameters, and to maintain these conditions for the entire deposition process.

This paper is dedicated to the study of the solid broadband radiation observed in the emission spectrum of plasma in plasma-chemical deposition of DF. Such radiation was observed previously in other papers [6–11] at various activation methods and conditions in the gas medium. Therefore, the analysis of the nature of such radiation may find the specific physical processes occurring in the gas volume under plasma excitation in various plants used for DF deposition.

The studies were conducted in the microwave reactor of resonant cavity type MWPACVD (see, for example, [4]), which structurally consists of a microwave generator (magnetron) with capacity of up to 1000 W, waveguide duct and volume cylindrical microwave resonant cavity with diameter of ~ 25.7 cm, a part of which is a CVD-reactor. Plasma (perceptible to the eye as a ball with diameter of ~ 4 cm) was formed in the resonance area above the substrate holder. Plasma spectra in the visible area (400–800 nm) were recorded using monochromator MS 3504i Solar TII with spectral resolution ~ 0.5 nm and photomultiplier tube (PMT) „Hamamatsu" R13456. In the infrared (IR) area (900–1400 nm) the spectra were recorded using InGaAs PIN-photodetector and monochromator MDR12 with IR-lattice. All spectra presented in the paper were obtained from the central area of the plasma. The spectral sensitivity of optical systems was calibrated using a reference source of radiation with a tungsten filament SIRSh 6-40 and high pressure LPP-source of radiation Xe ISTEQ-65 with the known quasi-continuous spectrum in the area of $0.25-2.5\,\mu$m.

Fig. 1, *a* shows the pure hydrogen plasma spectrum (H_2) at pressure of 60 Torr and deposited microwave capacity ~ 800 W, which only showed the radiation of atomic and molecular hydrogen and did not show the intensive continuous radiation in visible or near IR-area. Besides, the IR-radiation of the substrate holder, the temperature of which in the experiment was maintained around 800 °C, also had no contribution to the observed spectrum.

After addition of 16 % ethanol vapors in the work mixture as a source of carbon, solid radiation would appear in the visible spectrum apart from the radiation lines of the Swan system (fig. 1, *b*), the intensity of which increases noticeably towards the boundary of the IR-area. The IR-area showed the maximum of such radiation at around ~ 1140 nm.

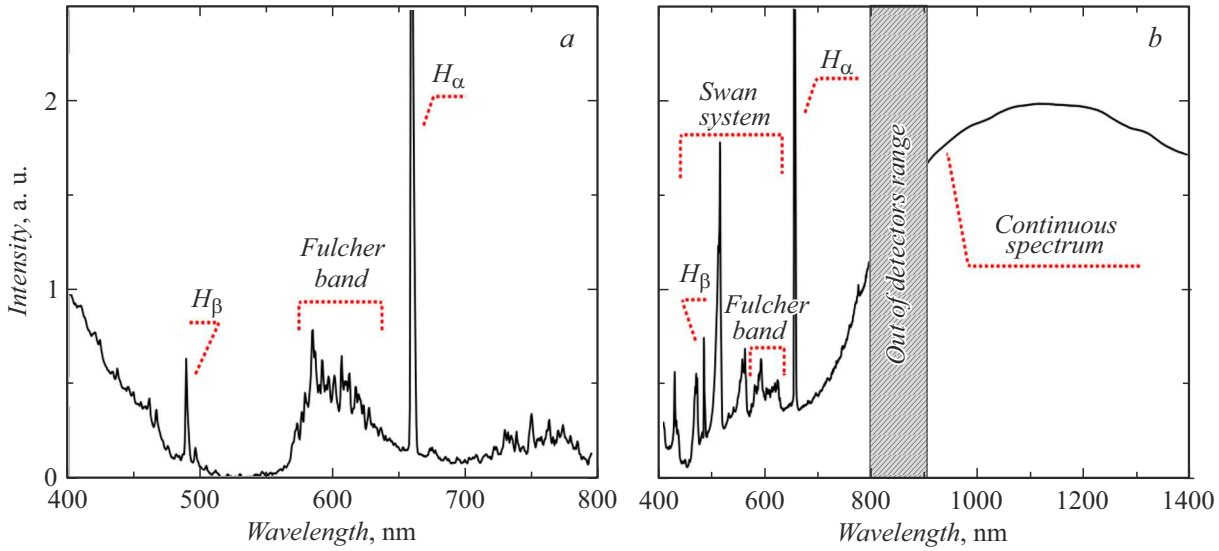

Figure 1. *a* — emission spectrum of pure hydrogen plasma; *b* — emission spectrum of mix 84 % H_2 and 16 % C_2H_5OH in the visible IR-area (dashed area — zone of severely suppressed sensitivity of PMT and InGaAs PIN-photodetector). Pressure in the reactor is 60 Torr, microwave capacity - $\sim$ 800 W.

The shape of the observed solid spectrum is close to the shape of the Planck spectrum, which indicates a considerable reabsorption of radiation in the plasma in the entire range of wavelengths. In case of atoms and simple molecules, this requires very high concentrations corresponding to the pressure of hundreds of atmospheres. Concentrations of atoms and molecules arising from alcohol dissociation under these conditions are lower by many orders of magnitude. Such Planck spectrum may be explained by the presence of solid-state carbon nanoparticles in the volume, the concentration of which provides for reabsorption of the recorded radiation in the plasma volume.

Note that the formation of carbon nanoparticles under PACVD-deposition of DFs was observed previously too. For example, in paper [12] the activation of low pressure gas mix of dichloromethane and trichloromethane with oxygen by a microwave-charge led to formation of diamond-like particles with diameter of $\sim$ 50 nm. Besides, in paper [13] the negatively charged carbon nanoparticles formed in the DF plasma-chemical deposition reactor, were recorded by the method of continuous displacement feed to the substrate and measurement of the corresponding current of such particles. In papers [6,14] it was assumed that the carbon „soot“ formed in the volume (the definition of the particles introduced by the authors) could be concentrated only in a rather narrow layer at the boundary of the plasma with temperature of less than 1900 K.

Assuming that the solid spectrum is related to the emission of carbon nanoparticles from the plasma volume, and that this spectrum is close to the spectrum of emission of the absolute black body (ABB), the average temperature of the particles may be assessed using the maximum of its intensity. The ABB continuous spectrum maximum position in the spectral range 900–1400 nm corresponds to ABB

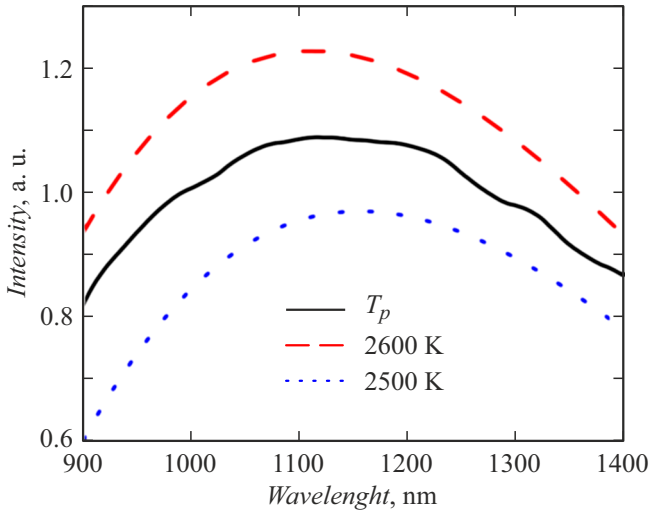

Figure 2. IR spectrum of plasma emission. The dashed line corresponds to Planck function for $T_p = 2600$ K, the dotted line — for $T_p = 2500$ K. The solid line was obtained experimentally.

temperatures in the field of 2400–3000 K. Fig . 2 shows the detailed IR-spectrum of plasma emission with maximum of $\sim$ 1140 nm (solid line), which corresponds to temperature of around $T_p \sim 2550$ K. For illustration purposes, the dotted and dashed lines also show the estimated spectra of Planck emission for 2500 and 2600 K temperatures. The position of the maxima in the spectra is quite well defined. In general with account of the repeatability of the spectroscopic measurements, the error of particle temperature detection may be estimated as $\pm$100 K.

Therefore, in the process of plasma-chemical deposition of DFs the solid spectrum of excited plasma emission is

observed, which is close in its shape to the Planck one. It was shown that the presence of this spectrum may be explained by the presence of the hot carbon nanoparticles with temperature of $\sim 2600 \pm 100$ K in the central area of the plasma. Observation of such hot particles is of interest for clarification of the mechanism of such particles formation and their possible effect on the speed of growth and properties of the produced DF.

It should also be noted that the observed emission of carbon particles may be used for online monitoring of the conditions of AF deposition technological process.

Conflict of interest

The authors declare that they have no conflict of interest.

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