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Carbon film deposition from high velocity rarefied flow

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ABSTRACT

The presented study is based on the idea of the activation of a gas-precursor high velocity flow by hot wire. The wire forms the channel for flow before expansion to substrate. The construction allows change of the specific flow rate, velocity, composition and temperature of a gas mixture by studying the film synthesis in conditions from free molecular to continuum flow at velocities from hundreds to thousands of m/s. At a high pressure, the film has typical and unusual hexagonal incorporations for diamond tetragonal particles. Raman spectrum with the pronounced diamond peak is typical for diamond-like film. X-ray diffraction points in the presence of lonsdaleite. Conditions of deposition were simulated by Monte Carlo method. Collisions with hot surfaces and chemical transformations were taken into consideration as well.

1. Introduction

The extending progress in studies of synthesis of diamond-like nanostructures is stimulated by foregoing and emergent last time applications of new materials, for which it is very important to have high hardness, low friction coefficient, large surface area, transparency in the visible spectrum range, high heat conductivity, superb dielectric properties and negative affinity, unique capacity for introduction of n-type structures, chemical inertness and biological compatibility. As consequence of this the emergence of a flood of publications (more than a thousand of papers) is not surprising. The research idea and the state of the art of searches one can understand from book and paper reviews [1–5]. Amid different methods of a carbon film deposition for a wide ratio of sp^3 and sp^2 hybridizations and peculiarities in crystalline and amorphous structures the hot wire chemical vapor deposition (HW CVD or Cat CVD) become firmly established as one of the best for comparatively low growth rate. The essential constraints of traditional HWCVD are narrow realms of flow rate variations, change of pressure in the deposition chamber and velocity of precursors.

It is possible to realize new approach using jet flows not coming far aside of usual HWCVD [6–10]. The using of a wire net with a high velocity gas flow has an important disadvantage because of destroying a high velocity flow and scattering back of activated particles. It was quantitatively shown in the result of computational modeling by Monte Carlo method [10]. Important scale problems were solved by creation of the reactor using the spiral from refractory material, inserted into chamber with inlet and outlet nozzles. The authors are not familiar with such constructor solutions. The mention may be made of examples like, when the jet source for deposition of microcrystalline silicon films was used [11], and description of instruments for hydrocarbon pyrolysis immediately for the diamond film deposition [12].

To date the study of deposition of diamond-like films with the above-mentioned reactor was performed at very low (less than 0.15 Pa) and high (2600 Pa) pressures, when the precursor gas was a mixture hydrogen and methane.

2. The scope of experiments

In Fig. 1 the simplified scheme of experiments is shown. The important elements are the nozzle, spiral, screen, and substrate. All arrangement is installed in the vacuum chamber with the volume of about 1 m^3 that is pumped by oil diffusion or only for-vacuum pump. Fig. 2 presents the results of the direct statistical simulation just to show by streamlines the picture of the hydrogen flow at very low (less 1%) concentration of methane. Such calculations allow a-priori to understand the flow character in the gas-dynamic tract. The possibilities of employment of different conditions for experiments are extremely wide: the temperature of the wire of 2300–2600 K, the substrate temperature of 300–1300 K, the pressure in the vacuum stagnation chamber of 0.01–3000 Pa; the gas flow rate of hydrogen of 50–2000 sccm, methane mole fractions in the carrier gas of 0.5–5%, and the distance of the substrate from the reactor of 5–30 mm. The delivery of any mixture, containing hydrocarbons (CH_4, C_2H_2, C_2H_4, C_2H_6, C_2H_5OH, C_2F_2 and others) in a mixture with carrier gases H_2, Ar, N_2 and others is not limited. Different substrates form molybdenum, steel, silicon and others can be positioned at any angle to the flow from 90° to 0°. Some parameters, for example, wide variations of the mass flow rate and the pressure in the chamber of deposition can't be attained in the usual HWCVD. As it is clear from preliminary experiments, the scope of the above-described conditions of experiments will allow to deposit thin carbon films of any properties from graphite to diamond ones. The

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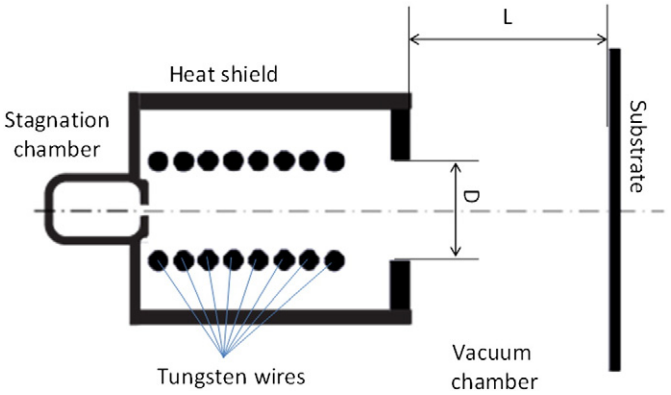

Fig. 1. Schematic image of activator for gas-jet deposition.

possibility to obtain films with new unknown properties is not unconceivable.

3. The direct statistical simulation of the flow (mixture $H_2 + CH_4$ and fragments)

Collision of molecules H_2 and CH_4 on the tungsten surface in the range of temperatures of 2300–2600 K is accompanied by the partial dissociation and inevitable excitation of the internal energy of molecules. The probability of H_2 decomposition by a single collision is approximately 0.24 [13]. In studies of chemisorption of methane on tungsten H.F. Winters [14] has determined the sticking coefficient equal to about 0.003 at temperature of 2400 K. In these experiments the chamber walls had room temperature that means methane molecules were not excited. It was shown later [15] that an increase in the vibrational energy leads to a dramatic enhancement of the sticking. Such situation takes place in our case. At low pressure the inelastic interaction between molecules and atoms can be neglected.

The lack of data on energy transformation by collisions of excited molecules with a hot surface bores difficulties for analysis. Taking into account the data of Holbland et al. [15], the value of sticking probability used was equal to 0.03. Of course the calculations were performed with rough assumptions. Nevertheless the modeling gives the useful important knowledge on an energy level of particles colliding with the substrate and some data on the gas composition in the vicinity of the substrate. The modeling of a gas flow from the sonic nozzle through the activator and around the substrate was performed by the direct simulation Monte Carlo method (DSMC) [16]. This method allows taking into account chemical reactions on walls in non-equilibrium rarefied flows. The geometry of the calculated space with all relative relations of sizes was chosen the same as in experiment. Hydrogen and methane enter into the reactor through the sonic nozzle with the diameter 0.5 mm with volume fluxes 100 and 5 sccm. The substrate is located on the distance 10 mm from the reactor. It is assumed, that the background pressure (0.013 Pa) is produced only by molecular hydrogen. The boundaries of the calculation area are located outside of the arrangement as it is seen in the field in Fig. 2. The hot wire temperature is 2400 K, the substrate temperature is 1200 K, and reactor wall temperature is 1700 K. It is assumed, that the probability of methane dissociation is increased ten times at following collisions after first one, having in mind the vibrational and rotational excitation.

The model of molecules with power repulsive potential (variable soft sphere) was accepted.

In Fig. 3 the distribution of temperature and velocity of the atomic hydrogen and carbon along the axes is shown. The peculiarity of these distributions is very low translational temperatures in the vicinity of substrate (below 500 K). The reason of this is the deep adiabatic expansion almost in the free molecular regime. Nevertheless the energy of atoms colliding with the substrate is very high: the velocity of C is 2 km/s and the velocity of H is even higher at 5 km/s. The flow regime in the region of the reactor exit up to the substrate is free-molecular. It means that the composition of the gas coming to the substrate forms only from particle–wall collisions. Such conditions are strikingly different from those for HWCVD. The deposition process should be completely different, and it is not studied yet. Another peculiarity of distributions is the negative value of atom velocities close to stagnation chamber. It is nothing but retrograde diffusion of hydrogen and carbon atoms.

4. Deposition at low pressure and low flow rate

These experiments were performed at the following conditions: temperature of the tungsten wire in the reactor is 2400 K, the flow rate of H_2 is 100 sccm, CH_4 — 1 sccm, the molybdenum substrate temperature is 1100 K, and the reactor–substrate distance is 10 mm. The heat shield was made from the beryllium oxide. The conditions used are very close to the above-posted calculations. It is worthy to note in the measurement of wire temperature. The tungsten–rhenium thermocouple with the

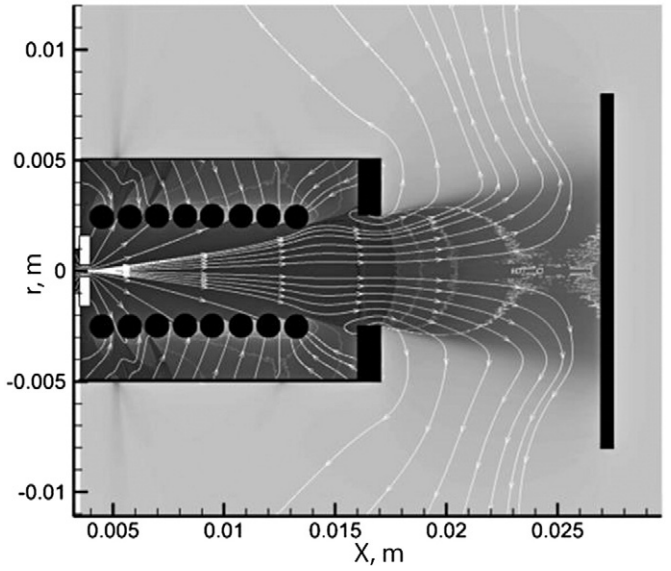

Fig. 2. The flow pattern of hydrogen. Mass flow and flow lines.

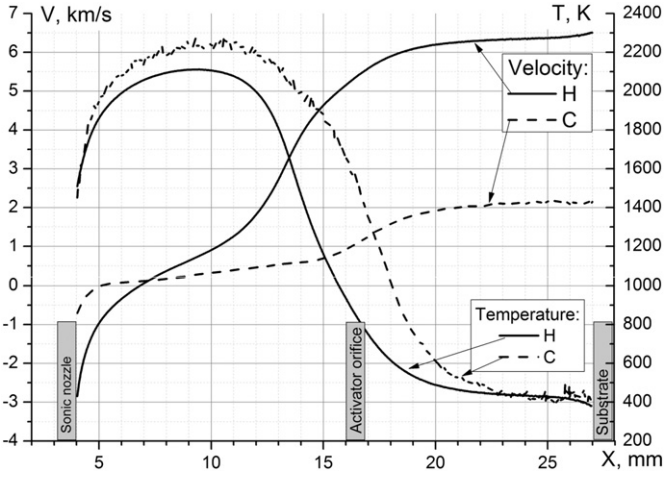

Fig. 3. Distribution of the mean velocity and temperature of the species along the stream for the low flow of gases.