Growth and properties of diamond-like films deposited from cyclohexane—argon mixtures in low-temperature plasma

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The deposition of diamond-like films on polymer substrates from low-temperature cyclohexane—argon plasma was studied. The deposition rate was found to be proportional to the mass flow rate of cyclohexane vapor and independent of the mass flow rate of argon. The microhardness of the films and the light absorption coefficient in the blue spectral region depend on the ratio between the deposition rate and ion current density.

Key words: diamond-like films; deposition; properties; polymer substrate; low-temperature plasma.

Several methods for deposition of diamond and diamond-like films are known presently. Polycrystalline diamond films are synthesized at 800—1000 °C mainly from methane—hydrogen mixtures. In high-vacuum synthesis from atomic and ionic carbon beams, diamond-like films are deposited which contain no chemically bound hydrogen, but the long-range order in the arrangement of the carbon atoms typical of the diamond crystal lattice is absent. In this case, the temperature of the substrate is close to the boiling point of liquid nitrogen. The plasma chemical methods for film deposition from hydrocarbons make it possible to obtain solid coatings containing a considerable amount of chemically bound hydrogen in the form of CH_3, CH_2, and CH groups, as well as dangling bonds between carbon atoms. These films are called hydrogenated carbon films, *a*-C:H-films, or diamond-like films.

Methane is mainly used for synthesis of diamond and diamond-like films. Diamond forms from the products of methane conversion in a high-temperature medium or in plasma. In works published previously,[1—3] the deposition of polycrystalline diamond layers from complex hydrocarbon structures formed from methane in the gas phase and adsorbed layer was considered. We showed[4] that deposition of diamond-like films from methane and their properties in low-temperature plasma depend on the degree of methane conversion. Compounds whose structure is most similar to diamond are the most promising for preparation of diamond-like films. In fact, positive results were obtained in experiments with adamantane[5] and decalin. However, in low-temperature plasma, these hydrocarbons are polymerized in the bulk gas phase. The cyclohexane—argon system was chosen as the object of the study here. The partial pressure and mass flow rate of cyclohexane were much lower than the corresponding values for argon. Therefore, it can be assumed in the first approximation that cyclohexane molecules are adsorbed on the deposition surface and serve as the "building material" for the diamond-like film, while argon ions bombarding the surface link them to form the spatial skeleton.

The processes of chemical deposition in the low-temperature plasma depend on many parameters. In this work, the effect of the mass flow rate of cyclohexane vapor on the deposition rate and some properties of diamond-like films were studied.

Experimental

The method of two electrical discharges[4] was used for deposition of the diamond-like films. The first discharge with a frequency of 50 Hz was used for activation of the gas medium in the positive column of glow discharge. The second discharge with a frequency of 250 kHz, characterized by the density of the deposition current, was used to control the ion flux to the deposition surface. Use of nontraditionally low frequency compared to radio-frequency discharge is associated with the necessity of decreasing the effect of this discharge on the processes in the gas phase. It is known that the higher the frequency of the electrical discharge, the more efficient its effect on the gas phase is and the higher its temperature can be, which is undesirable in the case considered. A cylindrical quartz reactor 6 cm in diameter was used in the experiments. Internal electrodes of the hollow cathode type were placed on the edges of the reactor. Glow discharge was ignited between these two electrodes. The activation current was varied from 25 to 100 mA. The third electrode with a 150 cm^2 surface area was placed outside on the reactor surface, and the high-frequency field was fed to this electrode. The high- and low-frequency voltage sources were connected through a system of filters, which made it possible to determine independently the activation and deposition currents.

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Cyclohexane and argon vapor were conveyed through flowmeters into a long narrow pipe, where they were mixed. A trap with liquid nitrogen was placed at the output of the reactor, which prevented capture of cyclohexane in a forevacuum pump. Thus, the trap served as a "pump" for cyclohexane and the other hydrocarbons formed in the reactor. Therefore, the system in the reactor can be characterized by the total pressure and the mass flow rates of cyclohexane and argon vapor.

Dacron films 0.12 mm thick were used as substrates. They were placed on the internal wall of the reactor opposite the external electrode. The thickness of the coatings deposited was determined by the gravimetric method. The density of the deposited films, equal to 1.2 g cm^{-3}, was determined in preliminary experiments.

Deposition was characterized by the deposition rate, and the properties were characterized by the microhardness and the blue light absorption coefficient (λ = 470 nm).

The microhardness of the film—substrate system, which depends on the load applied, was measured by the Knoop method for a load of 10 g. The loading time was 15 s; for higher loading times the results remained unchanged. The comparison of the values of the microhardness with those measured on a nanoindentor showed good coincidence. The measurements on the nanoindentor for small loads showed that the microhardness of the diamond-like film itself was 2—3 times higher for load of 10 g.

The optical properties of the films were determined in the visible range using a spectrophotometer.

Results and Discussion

The data obtained for a total pressure in the reactor of 0.8 Torr, activation current of 100 mA, and deposition current density of 0.1±0.01 mA cm^{-2} show that the deposition rate is proportional to the mass flow rate of cyclohexane and is independent of the mass flow rate of argon within the 0.2—1.8 L h^{-1} range (Fig. 1). This dependence shows that the deposition rate is determined by diffusion of cyclohexane molecules from the reactor volume.

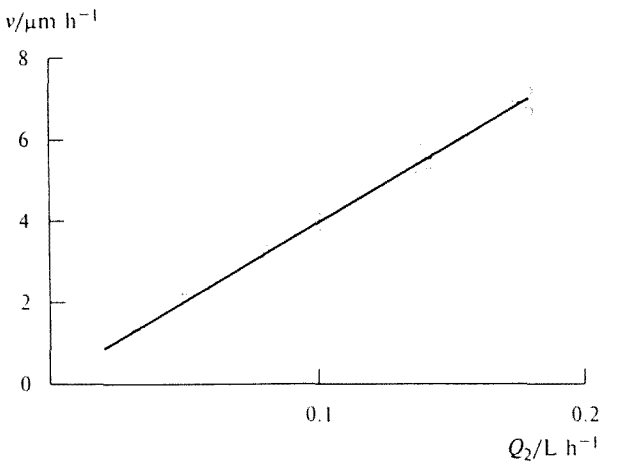

Fig. 1. Dependence of the deposition rate of diamond-like films on the mass flow rate of cyclohexane vapor.

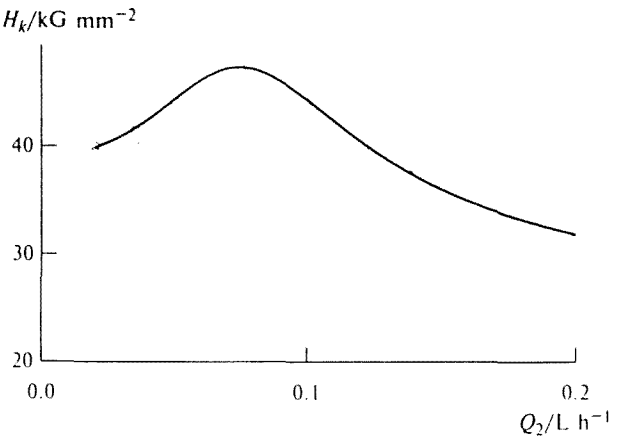

Fig. 2. Dependence of the microhardness of diamond-like films on the mass flow rate of cyclohexane vapor.

The dependence of the microhardness of the films obtained under the conditions indicated above on the mass flow rate of cyclohexane is presented in Fig. 2. Since the microhardness of the system depends on the thickness of the coating, the thickness of the films was chosen by variation of the deposition time in such a way that it would be approximately the same for all films and equal to 1.8±0.2 μm. The microhardness of the films has a maximum for a mass flow rate of cyclohexane equal to ~0.1 L h^{-1}. The existence of the maximum can be explained in the following way. The deposition current density, *i.e.*, the flow of ions to the surface, was kept constant, and the deposition rate increased. The ratio between the ion current and the deposition rate decreases as the mass flow rate of cyclohexane vapor increases. Probably, when the mass flow rate of cyclohexane vapor is high, the flow of ions to the surface is insufficient for formation of a stable spatial quasi-structure, and

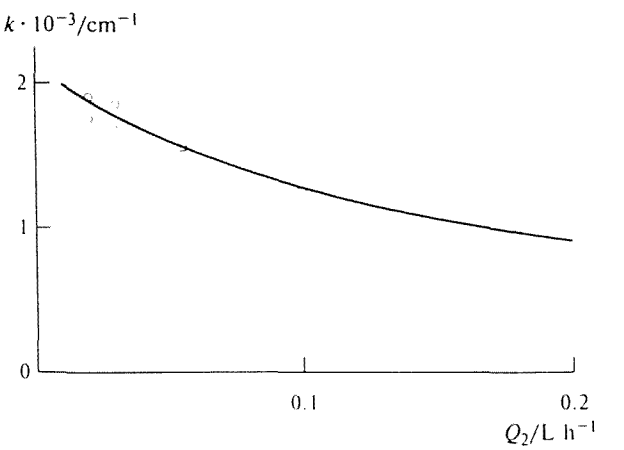

Fig. 3. Dependence of the light absorption coefficient (λ = 470 nm) on the mass flow rate of cyclohexane vapor.

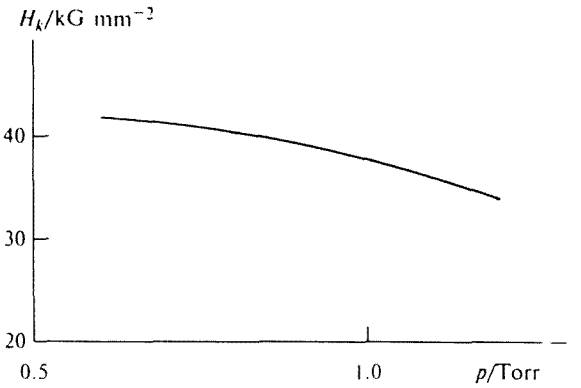

Fig. 4. Dependence of the microhardness of films on the total pressure.

therefore, the microhardness is low. It is likely that there is an optimum ratio between the ion current density and the deposition rate. When the deposition current changes, the position of the maximum changes, but its value remains almost unchanged. When the density of the deposition current increases to 0.2 mA cm^{-2}, the maximum shifts to the region of a cyclohexane vapor flow (0.14—0.15 L h^{-1}).

The blue light absorption coefficient decreases as the mass flow rate of cyclohexane increases (Fig. 3).

We previously assumed[6] that the value of the absorption coefficient is determined by graphite-like clusters. This concept was developed in the model suggested by J. Robertson.[7] For low deposition rates and a constant deposition current, the probability of the formation of clusters is higher due to radiation "shaking" of the surface under the action of the ion beam. For high deposition rates, the contribution of the polymer component increases, while k and the microhardness decrease. According to the data from Auger spectroscopy, the sizes of these clusters increase as the deposition current density increases and the deposition rate decreases.

For a constant mass flow rate of cyclohexane vapor and constant electrical discharge parameters, the deposition rate is independent of the total pressure in the range of 0.6—2.0 Torr. As shown in Fig. 4, the microhardness of the films decreases as the pressure increases. The blue light absorption coefficient also decreases as the pressure increases, which can be associated with a decrease in the ion energy. A change in the mass flow rate of argon has almost no effect on the deposition rate and properties of diamond-like films.

Thus, the deposition rate of a diamond-like film is proportional to the mass flow rate of cyclohexane vapor. The microhardness of the film and its optical properties depend both on the deposition rate and the ion current to the deposition surface.

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References

1. M. Frenklach, *J. Chem. Phys.*, 1992, **97**, 5794.
2. J. E. Butler and R. L. Woodin, *Phil. Trans. R. Soc. Lond. A*, 1993, **347**, 209.
3. S. Skokov, B. Weiner, and M. Frenklach, *J. Phys. Chem.*, 1994, **98**, 7093.
4. D. V. Fedoseev, Yu. N. Tolmachev, V. L. Bukhovets, and I. G. Varshavskaya, *Dokl. Akad. Nauk*, 1995, **345**, 498 [*Dokl. Chem.*, 1995, **345** (Engl. Transl.)].
5. D. V. Fedoseev, A. V. Lavrent'ev, and I. G. Varshavskaya, *Dokl. Akad. Nauk SSSR*, 1986, **291**, 917 [*Dokl. Chem.*, 1986, **291** (Engl. Transl.)].
6. D. V. Fedoseev, Yu. N. Tolmachev, I. G. Varshavskaya, and V. L. Bukhovets, *Abstract Book 5th European Conference on Diamond-like and Related Materials*, Italy, 1994.
7. J. Robertson, *Diamond and Related Materials*, 1995, **4**, 297.

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