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Formation of Diamond-Like Carbon Films by the Plasma-Chemical Decomposition of Hydrocarbons

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Abstract—The process of the formation of diamond-like carbon films on the surface of monocrystalline silicon is studied. The film is formed as a result of the plasma-chemical decomposition of hydrocarbons (propane, butane) and subsequent annealing in a vacuum. The carbon film is formed in the form of diamond-like nanoparticles with a diameter of about 8 nm. Silicon-carbon bonds are formed at the boundary of the silicon substrate and the carbon film, which ensures strong adhesion.

Keywords: plasma-chemical decomposition, hydrocarbons, diamond-like film, microhardness

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INTRODUCTION

Diamond-like coatings are one of the most effective ways to increase the service life of surfaces subject to friction [1–3]. The other characteristics of the materials, such as microhardness, resistance to aggressive environments, etc., can also be significantly improved [4, 5]. In this case, the thickness of the coatings can be quite small, about hundreds of nanometers, but sufficient to achieve the required characteristics [6]. Therefore, methods for forming such coatings are in demand in various high-tech areas, such as the oil and gas industry, automotive industry, and other industries [7–9]. Technologies for using diamond-like coatings to increase the capacity and number of cycles for lithium-ion batteries are being actively developed [10]. The application of such coatings often needs to be carried out not only on smooth flat surfaces, but also on surfaces with the developed morphology. Moreover, diamond-like coatings demonstrate strong biocompatibility [4, 11], which opens up wide possibilities for the use of materials with such coatings in medicine [12, 13]. Therefore, when creating coatings, preference is given to methods of deposition from the gas phase, such as pulsed laser deposition [14, 15], chemical vapor deposition [1], magnetron sputtering [11, 16], and film deposition using ion beams [17]. The described methods use various precursors, including expensive ones, for example, C60 fullerene powders [17], but methane is also considered as a precursor [18]. Given the high demand for the use of diamond-like coatings on an industrial scale, it is necessary to develop methods for their formation from the widely available inexpensive materials. Therefore, the aim of this study is to develop a method for the formation of diamond-like coatings by the method of plasma-chemical decomposition of hydrocarbons in the gas phase. Monocrystalline silicon was chosen as the model substrate, on which the physical and chemical properties of the obtained coatings are reliably studied.

MATERIALS AND METHODS

Technical propane was used as a source of hydrocarbons, in which the propane content was about 75% and the remaining gaseous hydrocarbons were about 25%. The use of technical propane allows us to significantly reduce the cost of the technology for forming diamond-like coatings.

The diamond-like coatings were formed on substrates of monocrystalline silicon with a polished surface. Before applying the coatings, the surface of the substrates was cleaned with argon plasma to remove any possible organic residues and the oxide layer. The cleaned substrates were placed in a flow-through gas cell, in which plasma was formed under the influence of laser pulses and, as a result of the plasma-chemical decomposition, a carbon-containing film was deposited on the surface of the substrate.

Carbon-containing films were formed on a substrate of monocrystalline silicon in a flow-through optical gas cell, through which a gas mixture of hydrocarbons was continuously passed at a rate of about 5 L/h. This ensures that there is no oxygen in the chemical reactor, which prevents the formation of carbon oxides. Nanosecond laser radiation was focused in the volume of the gas cell using a lens with a focal length of 150 mm, under the influence of which plasma was formed (Fig. 1).

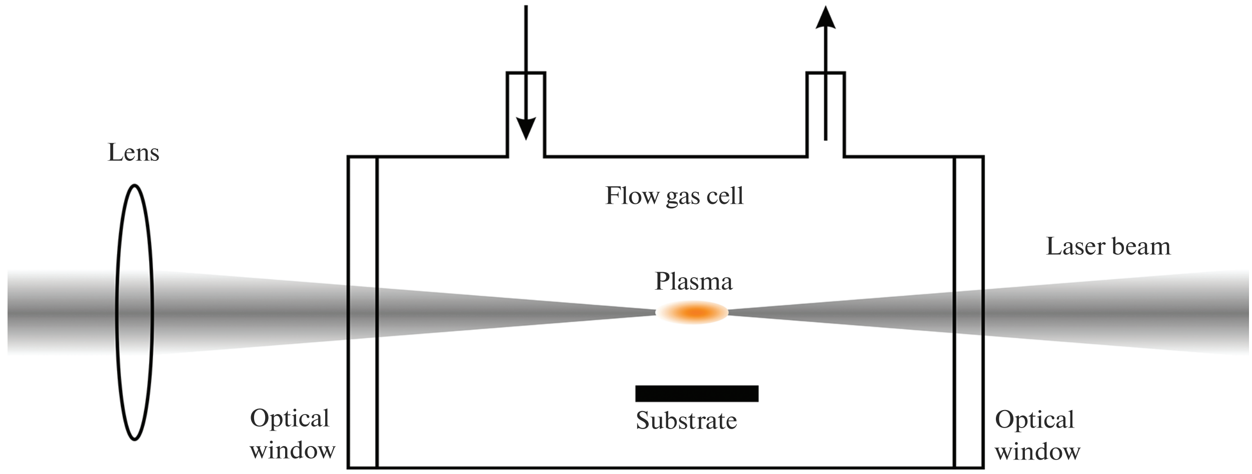

Fig. 1. Optical diagram of the formation of a carbon-containing film on the surface of a substrate using the plasma-chemical decomposition of hydrocarbons.

The laser plasma was initiated by nanosecond laser pulses from a Spit Light 2000 (InnoLas) Q-switched solid-state laser. Laser radiation characteristics: wavelength 1064 nm, pulse repetition frequency 1 kHz, pulse duration 7 ns, pulse energy 1 J.

The obtained samples of monocrystalline silicon with deposited carbon-containing films were placed in quartz ampules and pumped out to a vacuum of 10^{-3} mbar and annealed in a muffle furnace at a temperature of 500°C within 20 min.

The vibrational spectra of the obtained coatings were measured by the Raman scattering method using a Senterra spectrometer (Bruker) equipped with a confocal microscope. The Raman spectra were excited by focusing laser radiation with a wavelength of 532 nm and a power of 20 mW on the surface of the films using a 100× objective. The spectra were recorded in the backscattering configuration for 100 s with double averaging.

The fluorescence spectra of the films were measured using a LabRam HR800 spectrometer (Horiba) with a confocal microscope and focusing of the pump radiation through a 100× objective. The fluorescence signal was collected using the same objective and recorded for 5 s with double averaging.

X-ray photoelectron spectroscopy (XPS) was performed using an Escalab 250Xi integrated photoelectron and scanning Auger electron spectrometer (Thermo Fisher Scientific).

The surface morphology was studied by scanning tunneling microscopy (STM) using the Nanolab Research Platform installation equipped with an Omicron VT AFM XA 50/500 scanning probe microscope. The measurement was carried out under ultrahigh vacuum conditions ($1–2 \times 10^{-10}$ mbar).

The film thickness was measured using an MII-4M interference microscope using monochromatic radiation at a wavelength of 550 nm. The accuracy of the thickness determination was 10 nm.

Microhardness was measured using a PMT-3 microhardness tester by pressing a Vickers diamond tip with a square base of a tetrahedral pyramid into the test material. The load mass was 200 g, and the holding time, 20 s.

RESULTS AND DISCUSSION

As a result of the plasma-chemical decomposition of gaseous hydrocarbons, hydrogen atoms are eliminated and carbon-containing films are deposited on the surface of the substrate. The resulting films are characterized by intense fluorescence, which is observed upon excitation by photons with a wavelength of 532 nm (Fig. 2). Since none of the types of solid carbon, except for carbon cumulene chains, has its own fluorescence, its presence may indicate the formation of tholins in the plasma. Tholins are substances that are formed in the atmosphere from organic compounds (methane, ethane, etc.) under the influence of ultraviolet radiation from the Sun and are a mixture of organic copolymers.

The annealing of tholins at temperatures above 350°C leads to their decomposition and the formation of solid-phase carbon. In order to prevent the formation of carbon monoxide and carbon dioxide during the annealing of the obtained films, samples of substrates with carbon-containing coatings were placed in evacuated quartz ampoules and annealed. The obtained films were studied using Raman spectroscopy, XPS and STM.

Figure 3 shows the typical Raman spectrum of coatings on the surface of monocrystalline silicon sub-

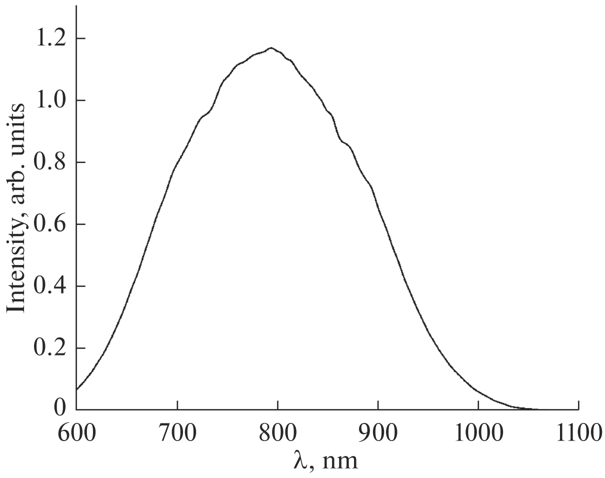

Fig. 2. Fluorescence spectrum of a carbon-containing film obtained by plasma-chemical decomposition of gaseous hydrocarbons.

strates. Note that fluorescence completely disappears after annealing. This indicates the absence of hydrocarbon fragments in the composition of the obtained coatings. All bands in the Raman spectrum with a wave number less than 1000 cm^{-1} correspond to the vibrational modes of monocrystalline silicon. Two bands in the range of 1000–2000 cm^{-1} are related to carbon film. Comparison of this spectrum with the published data allows us to attribute these bands to vibrations of carbon in diamond-like nanostructures with a diameter of about 5 nm [19]. The absence of a narrow vibrational band in the region of 1333 cm^{-1} in the spectra, characteristic of diamond, is explained by the small size of diamond-like nanoparticles [19].

To confirm the size of the particles forming the coating, a morphology study was conducted using the STM method (Fig. 4). It is obvious that the nanoparticles that form the coating are smaller than 10 nm and are on average 5–7 nm. Thus, the data obtained using the Raman and STM methods confirm the formation of a diamond-like coating on the surface of the silicon substrate with a grain size in the region of 5–7 nm.

The film thickness, which was determined using an interference microscope, for all samples obtained under the synthesis conditions described above was approximately 120 ± 10 nm. This value of the thickness of diamond-like coatings has a significant impact on the microhardness of the substrate, which will approach the values characteristic of single-crystal diamond only at thicknesses greater than 1 μm. For the studied samples, it was found that the microhardness varies from 12 GPa for monocrystalline silicon without a coating (the characteristic value) to 16 GPa for monocrystalline silicon with a diamond-like coating. Thus, it is confirmed that the obtained coatings lead to an increase in microhardness.

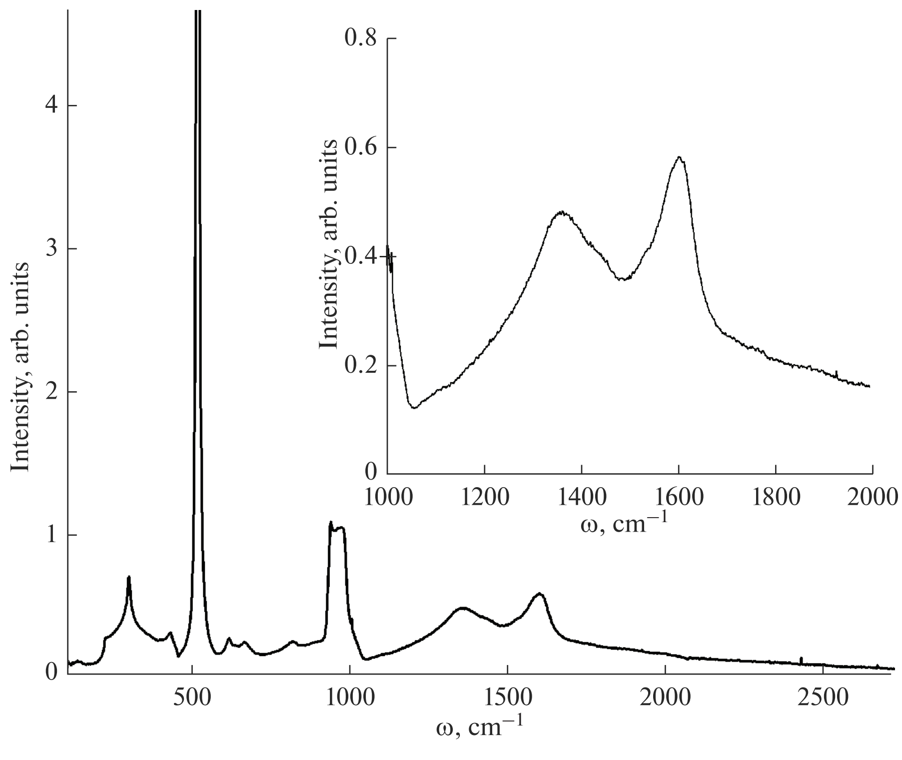

Fig. 3. Raman spectrum of a diamond-like coating on a silicon substrate. The insert shows an enlarged image of the spectrum in the range of 1000–2000 cm^{-1}.

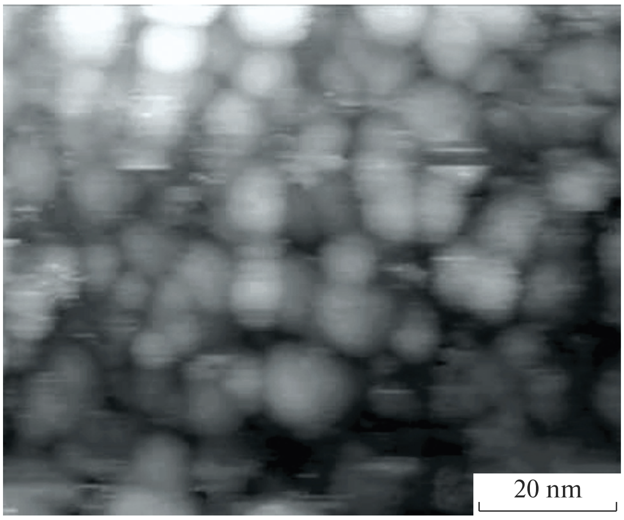

Fig. 4. STM image of the surface of a diamond-like coating on a silicon substrate.

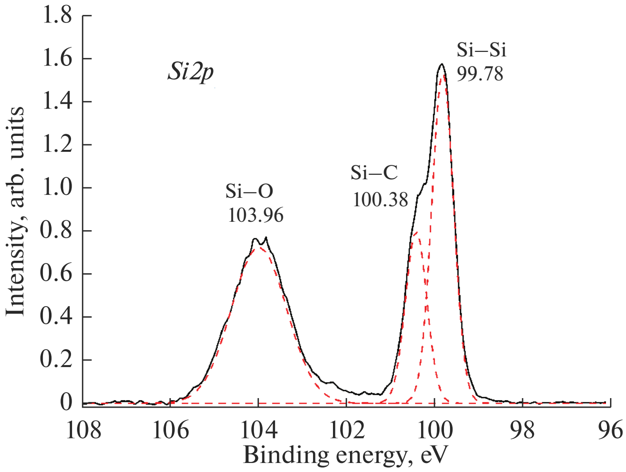

Fig. 5. XPS spectrum of single-crystal silicon with a diamond-like coating for the Si2*p* region.

One of the most important characteristics of a coating is its adhesion to the substrate surface. The greatest adhesion is usually observed for substances that form chemical bonds at the interphase boundary. X-ray photoelectron spectroscopy was used to identify the chemical bonds. The typical XPS spectrum for the obtained coatings is shown in Fig. 5. The spectra were decoded using the XPS database and the known published data [20]. For silicon atoms, Si–Si, Si–C and Si–O bonds were found (Fig. 5a). The presence of the Si–O bond is explained by the insufficiently effective plasma cleaning of the substrate surface from the silicon dioxide film. However, oxygen is partially removed and silicon-carbon bonds are formed at the interphase boundary of the silicon substrate and the diamond-like coating, providing a high degree of adhesion of the film to the substrate due to the covalent bond.

CONCLUSIONS

Carbon-containing films were obtained on the surface of monocrystalline silicon substrates using the method of the plasma-chemical decomposition of gaseous hydrocarbons. Presumably, the films formed in this way consist of tholins, which decompose upon annealing above 350°C. Annealing of the obtained films under vacuum conditions leads to the formation of diamond-like coatings on the surface of the substrates. The coatings consist of diamond-like nanoparticles with a diameter of 5–7 nm, which is confirmed by Raman spectroscopy and STM imaging data. The coating thickness averaged 120 ± 10 nm, and the Vickers microhardness was about 16 GPa. Silicon-carbon bonds are formed at the interphase boundary, which ensures the chemical bonding of the diamond-like coating to the silicon substrate. The proposed method allows the formation of diamond-like coatings on the surface of monocrystalline silicon.

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CONFLICT OF INTEREST

The authors of this work declare that they have no conflicts of interest.

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