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# Formation Mechanism and Structure of Monatomic Carbon Films in Ethylene Decomposition on the Pt(111) Surface According to XPS Data

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**Abstract**—The interaction of ethylene with a Pt(111) single-crystal surface was studied using X-ray photoelectron spectroscopy. It was found that both two-dimensional flat graphite islands and curved fullerene-like carbon structures or nanotubes can be formed depending on the reaction temperature of ethylene and the presence of dissolved carbon in the bulk of the crystal. It was assumed that the size and curvature of the islands depend on the size of terraces on the single-crystal surface.

## INTRODUCTION

In recent years, the chemistry of carbon has been intensively developed because of the discovery of a number of new carbon modifications and structures: fullerenes, “onion” carbon, nanotubes, and filamentous carbon [1]. Experiments on the preparation of various carbon films and coatings have been performed for both corrosion control in materials and assemblies and the development of highly efficient electron emitters [2]. In this context, an understanding of the physical chemistry, in particular, the determination of the electronic and geometric structures of carbon films, is of paramount importance.

The use of a methane–hydrogen plasma is the most popular technique for the deposition of carbon films [3]. However, as a rule, rather thick films were formed with the use of hydrocarbon–hydrogen plasmas for the deposition of carbon films onto metal surfaces [3]. It is particularly important to know the state and structure of carbon at a transition layer (interface) in order to understand film growth mechanisms. Therefore, the study of monatomic films at the early stages of growth is of the greatest interest. In this context, note that the catalytic decomposition of hydrocarbons without exposure to plasma provides an opportunity to control the preparation of monatomic adsorption carbon layers [4–12].

Until recently, it was considered that carbon films on the surfaces of metals, including platinum-group metals, exhibit only the simple structure of graphite, and that no other carbon structures can be stable [5, 6]. Indeed, carbon rings were detected by low-energy electron diffraction (LEED) at high temperatures; this is considered to be a good test for graphite formation. However, LEED data published by Baron *et al.* [5] suggested the formation of graphite on only closely packed (111) or stepped surfaces with a small deviation of the plane from the surface. More complicated structures of

carbon layers were observed on open planes and more open planes.<sup>1</sup>

In recent studies, it was found that diamond-like films or even diamond microcrystallites can be formed on the surface of platinum under exposure to a methane–hydrogen plasma [3, 7, 8]. It was noted that a rough rather than smooth surface is required for the formation of diamond nuclei. Previously [9–11], it was found that aggregated carbon structures in the form of two-dimensional diamond-like films with a predominant  $sp^3$  hybridization of carbon were formed under the action of ethylene on the open reconstructible (110) and (100) planes of platinum.

Thus, it follows from published data [4–12] that two-dimensional diamond-like and graphite-like films can be formed depending on the surface structure of platinum. In this case, the structure of the two-dimensional graphite-like film was assumed to be flat by analogy with the structure of graphite. However, it follows from data obtained by Tontegode and coauthors [4, 6, 12] that two-dimensional graphite-like films on metal surfaces can exhibit unusual properties because of the formation of curved regions (blisters, as termed by the authors) due to intercalated heteroatoms and differences in the thermal expansion of the lattices of two-dimensional graphite-like films and metals. It follows from these data that, even on smooth closely packed surfaces of noble metals, the real structure of a graphite film can be composite rather than planar under the action of external factors.

The thermal decomposition of benzene, which is known to contain a structural unit of graphite (benzene ring), was used to prepare two-dimensional graphite-like films in [4, 12]. Therefore, the formation of structures other than two-dimensional graphite-like films

<sup>1</sup> Planes with high and higher Miller indices, respectively.

was highly improbable. In this context, we believe that the use of simpler ethylene-like aliphatic hydrocarbons is more promising for the formation of not only flat two-dimensional graphite-like films but also three-dimensional nanostructures.

In this work, we used X-ray photoelectron spectroscopy (XPS) to study the state of adsorption carbon layers obtained by ethylene decomposition on a Pt(111) surface. The data allowed us to interpret the formation of both flat and curved (bent) islands of carbon with  $sp^2$  hybridization.

## EXPERIMENTAL

The experiments were performed on a VG ESCALAB HP instrument from VG Scientific (Great Britain). The vacuum system of the instrument included an analyzer chamber and a preparation chamber in which three-grid optics and an electron gun for LEED studies, as well as an ion gun used for surface cleaning by bombardment with  $Ar^+$  ions, were arranged. The differential evacuation of the analyzer and the X-ray source was provided; this allowed us to perform *in situ* XPS measurements by continuously passing gases over a sample at pressures of up to  $10^{-5}$  Torr.

The spectrometer was equipped with an Mg/Al dual-anode X-ray source, which allowed us to use the  $MgK_\alpha$  and  $AlK_\alpha$  primary radiation with photon energies of 1253.6 and 1486.6 eV, respectively, for excitation. The energy spectrum of photoelectrons was analyzed with the use of a hemispherical electrostatic analyzer.

The XPS spectra were recorded using constant analyzer pass energy ( $HV$ ). The survey spectra were measured at  $HV = 100$  eV. The precision spectra of the  $Pt4f$ ,  $C1s$ , and  $O1s$  lines were measured with an energy step of 0.1 eV at  $HV = 20$  eV; this provided the required resolution (the full width at half maximum peak height was 1.2 eV for the XPS  $Ag3d_{5/2}$  reference line). At the beginning and end of an experimental run, the spectrometer was calibrated using the  $Au4f_{7/2}$  ( $E_b = 84.0$  eV) and  $Cu2p_{3/2}$  ( $E_b = 932.7$  eV) standard lines [13]. The binding energy of the  $Pt4f_{7/2}$  line equal to 71.1 eV was used as an internal standard.

Specially designed sample holders were used in *in situ* experiments at temperatures of up to 1800 K. The holders allowed us to use simultaneously XPS and temperature-programmed reaction (TPR)/temperature-programmed desorption (TPD) techniques. The design of the sample holder used in this study was described in detail elsewhere [14]. A platinum crystal was mounted on tungsten "legs" made of wire 0.2 mm in diameter, which were welded to the lateral surfaces of the sample using spot welding. To prevent the position of the sample relative to the entrance slit of the analyzer from changing due to the thermal deformation of the assembly, tantalum springs were used in this assembly. The sample was heated by the resistive heating of the tungsten legs. The sample temperature was measured using

a Pt/Pt–Rh thermocouple, which was welded to the lateral surface of the crystal. The cold ends of the thermocouple were at a distance of ~5 cm, and they were in thermal contact with an element of the holder cooling system. The design of the holder allowed the sample to be heated up to 1800 K.

The sample temperature was controlled with a heat regulator interfaced with a computer. The spectrometer control program made it possible to record XPS spectra and mass-spectrometric data simultaneously. The indications of the thermocouple time synchronized with the signals of the XPS measurement unit and the mass spectrometer were also recorded in a data file.

Spectrokinetic curves were automatically recorded simultaneously using several XPS peaks. The  $C1s$  and  $Pt4f$  lines and a background intensity at 200 eV on the scale of binding energies were used to record the kinetic curves of carbon elimination from the Pt(111) surface.

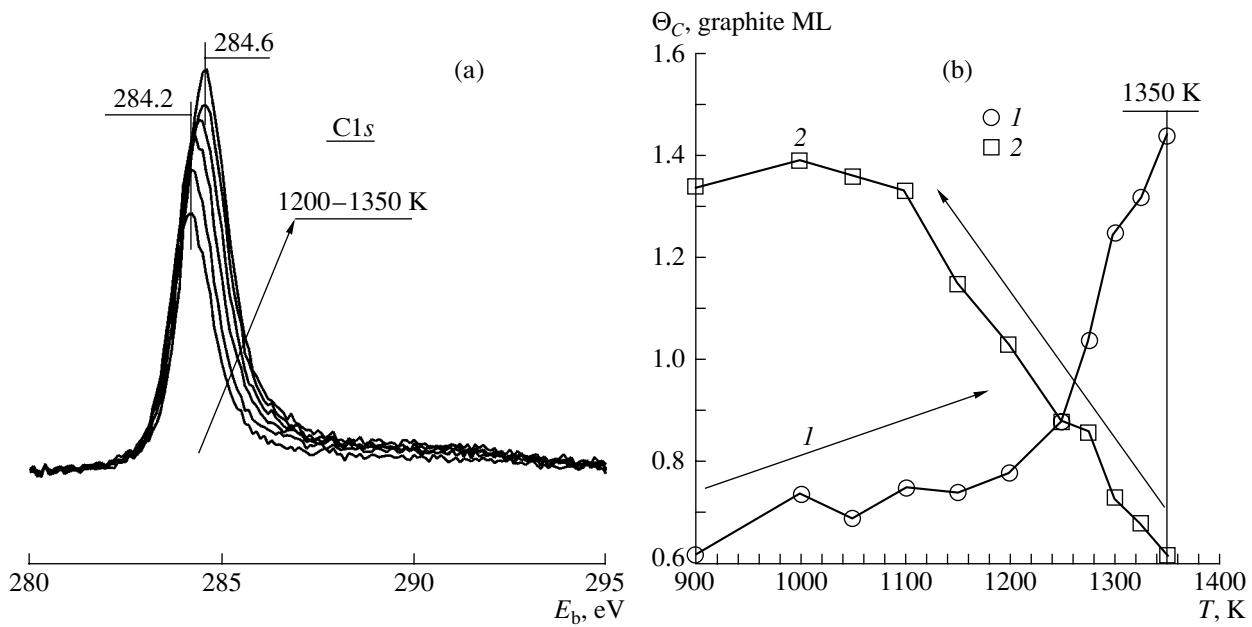
The surface of a platinum single crystal was cleaned using the alternating cycles of etching the surface with argon ions and the combustion of residual carbon with molecular oxygen followed by the reduction of the surface using high-temperature vacuum annealing at  $T = 1400$  K. The structure of the pure Pt(111) surface was characterized using LEED. The LEED technique was also used to determine the degree of ordering of a carbon adsorption layer.

## RESULTS

The TPR studies of the adsorption of simple hydrocarbons reliably demonstrated that, in the course of hydrogen removal from adsorption layers, elemental carbon was deposited on the surface at 700–800 K [10, 11, 15]. Because of this, to study adsorption layers that consisted of only elemental carbon, we performed our experiments at crystal temperatures higher than 800 K.

Figure 1a demonstrates the XPS  $C1s$  spectra measured after long exposures of the Pt(111) surface to ethylene over a temperature range of 1200–1350 K. These spectra were recorded at 900 K after heating the crystal in a flow of ethylene at a specified temperature for 30 min with subsequent cooling to 900 K. The spectra obtained after sample heating at 900–1200 K are identical to each other, and they are characterized by a main peak with  $E_b(C1s) = 284.2$  eV and a broad diffuse peak at 290 eV. These characteristics suggest the presence of carbon with  $sp^2$  hybridization [1, 16]. In other words, the adsorption film of elementary carbon obtained by the action of ethylene on the Pt(111) surface over a temperature range of 900–1200 K belongs to films with a two-dimensional graphite structure.

The heating of a crystal in ethylene at  $T > 1200$  K followed by cooling significantly changed the XPS  $C1s$  spectrum. As the treatment temperature was increased, the  $C1s$  peak intensity noticeably increased, and its maximum was shifted to greater binding energies by



**Fig. 1.** (a) XPSC1s spectra measured after the action of ethylene on the Pt(111) surface at  $T = 1200, 1250, 1275, 1300, 1325$ , and  $1350$  K for  $30$  min in a flow of ethylene at  $P = 5 \times 10^{-7}$  Torr. All the spectra were recorded at  $900$  K after the slow cooling of the sample at a rate of  $1$  K/s. (b) The temperature dependence of the coverage ( $\Theta_C$ ) of the Pt(111) surface with carbon: (1) data calculated from the C1s and Pt4f spectra; (2) data calculated from the C1s and Pt4f spectra measured in the *in situ* mode (sample treatment with a flow of ethylene at  $P = 5 \times 10^{-7}$  Torr in the course of stepwise cooling). Arrows indicate the sequence of experiments.

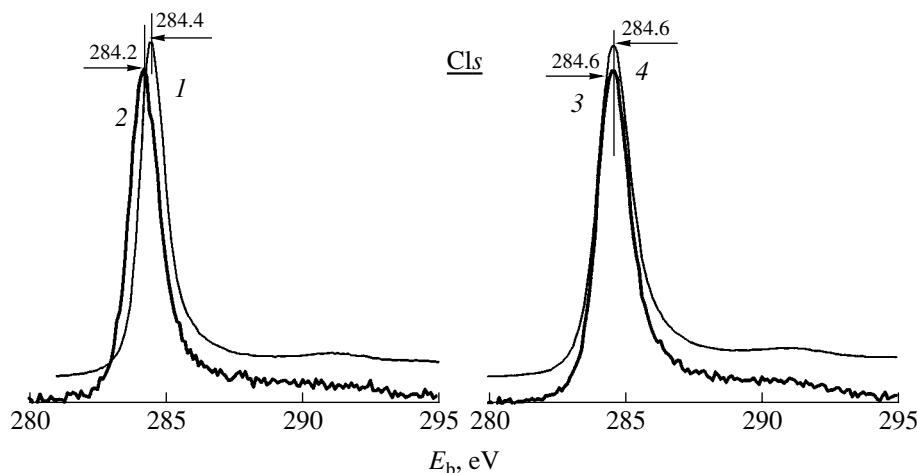
0.4 eV. The increase in the C1s line intensity unambiguously correlated with an increase in the surface coverage with carbon. The line shift is also a reliable indication of the structural transformation of the adsorption layer. The retention of the broad diffuse peak at  $E_b \sim 290$  eV indicates that the structural transformation occurred with the retention of the  $sp^2$  hybridization of carbon.

Figure 1b illustrates the results of the quantitative calculations of changes in the coverage ( $\Theta_C$ ) of the Pt(111) surface with carbon over a range of 900–1350 K. The  $\Theta_C$  scale was calibrated on a graphite monolayer (ML) basis (the packing density of carbon atoms in the basal plane of graphite is  $N_{ML} = 3.5 \times 10^{15}$  atom/cm<sup>2</sup>). Curve 1 in Fig. 1b was obtained by the treatment of spectra shown in Fig. 1a; that is, the experiments were performed by annealing the crystal in the presence of ethylene in the gas phase followed by cooling. It can be seen in Fig. 1b that annealing at  $T > 1300$  K almost doubled the coverage. To determine at which step  $\Theta_C$  increased (on treatment with ethylene immediately at the annealing temperature or in the course of cooling), Fig. 1b demonstrates a curve of changes in the coverage; this curve was obtained by the *in situ* recording of the C1s spectra (curve 2). These data were obtained after the preheating of the crystal at  $T = 1350$  K and stepwise cooling (30-min exposures at each temperature) to 900 K in a flow of ethylene. It can be seen that at 1350 K the coverage was equal to that found upon direct exposure to ethylene at  $T = 900$ – $1200$  K. On the cooling of the

crystal and the *in situ* recording of the spectra, an increase in the coverage was observed, and  $\Theta_C$  reached a maximum value at  $T \sim 1100$  K. The above experiments allowed us to conclude that the increasing coverage effect is associated with the process of cooling.

A comparison with the spectra of reference samples with a well-known structure was performed in order to identify the carbon structures observed. Figure 2a demonstrates the XPS C1s spectra of a carbon film prepared by ethylene adsorption at  $T = 900$  K and a highly oriented pure graphite (HOPG) single crystal. Figure 2b demonstrates the XPS C1s spectra of a film obtained after the high-temperature annealing of Pt(111) in ethylene ( $T = 1350$  K) and nanotubes with an average diameter of  $\sim 50$  Å. This comparison indicates that in the latter case the peak positions and line shapes are identical; this is a serious argument in favor of the formation of curved carbon structures on the Pt(111) surface.

The peak positions of HOPG and the film prepared without high-temperature annealing (Fig. 2a) differed by 0.2 eV, although the general line shapes were similar. We believe that the line shift for the adsorption film on platinum was associated with an increase in the effect of relaxation factors due to platinum, as well as with the fact that carbon plains small in length (of the order of hundreds of angstrom units) exhibited a shift toward low binding energies, as compared with lengthy planes of HOPG [17]. Thus, it is most likely that the reaction of ethylene and its decomposition on the



**Fig. 2.** Comparison between the XPS C1s lines of carbon deposits on the Pt(111) surface, which are given in Fig. 1a, and those of the reference samples of various allotropic modifications of carbon: (1) HOPG; (2, 3) adsorption carbon layers obtained on the Pt(111) surface at 900 and 1350 K, respectively; and (4) carbon nanotubes.

Pt(111) surface at  $T < 1200$  K resulted in flat graphite structures.

Because the Auger spectra of carbon are highly sensitive to the state and structure of carbon species, Fig. 3 compares the Auger spectra of two types of the prepared adsorption films on platinum with the spectra of the above reference samples. The CKLL spectrum of HOPG (spectrum 1) is characterized by the greatest splitting of components  $a$ – $e$ , whereas the spectrum of nanotubes exhibits minimum splittings. This is most clearly seen in a comparison between characteristics  $a$  and  $c$ . Lascovich and coauthors [18, 19] demonstrated that the difference between the kinetic energies of these components is the most sensitive structural characteristic of carbon materials and species. This is the parameter  $D = 22.2$  eV for HOPG and  $D = 18.7$  eV for nanotubes. A comparison demonstrated that the value of  $D$  for an adsorption film prepared on the low-temperature action of ethylene on the Pt(111) surface was almost the same as the value for HOPG graphite, which is equal to 21.2 eV. The parameter  $D$  for an adsorption film obtained after high-temperature heating is equal to 19.7 eV, which approaches the parameter  $D$  for nanotubes.

Thus, the qualitative analysis of CKLL Auger spectra is also indicative of the formation of both flat and curved carbon structures with  $sp^2$  hybridization.

Figure 4 demonstrates the kinetic curves of carbon elimination from adsorption layers obtained by ethylene degradation on the Pt(111) surface at  $T < 1200$  K (curve 1) and after heating at  $T = 1350$  K for 30 min (curve 2). The reaction with oxygen was performed at the same temperature (1000 K). As can be seen in Fig. 4, the rate of carbon elimination in the former case was much higher than that in the latter case. This fact suggests that the structure of the adsorption layer has a very strong effect on the activity of platinum toward

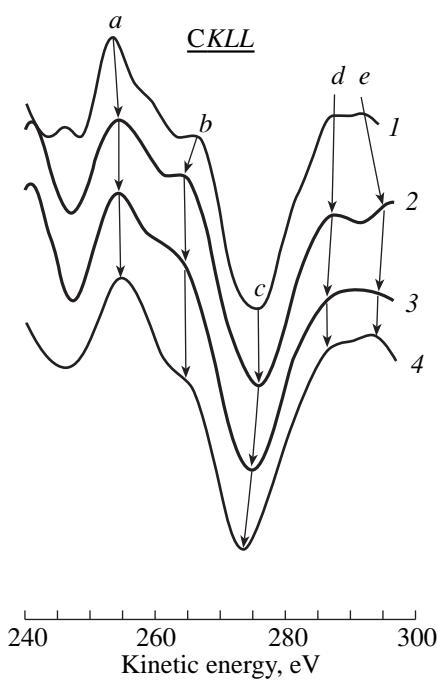
oxygen. The maximum rate of elimination of flat graphite structures was  $1.8 \times 10^{-3}$  ML/s, that is,  $6.3 \times 10^{12}$  atom  $s^{-1} cm^{-2}$ . Correspondingly, the reaction efficiency as a ratio of the number of reacted carbon atoms to the number of oxygen molecules collided with the surface was  $1.7 \times 10^{-2}$ . Analogous calculations for an adsorption layer obtained after the high-temperature annealing of a crystal in ethylene gave a rate of elimination equal to  $8 \times 10^{-5}$  ML/s or  $2.8 \times 10^{11}$  atom  $s^{-1} cm^{-2}$ ; in this case, the reaction efficiency was  $\sim 7 \times 10^{-4}$ .

## DISCUSSION

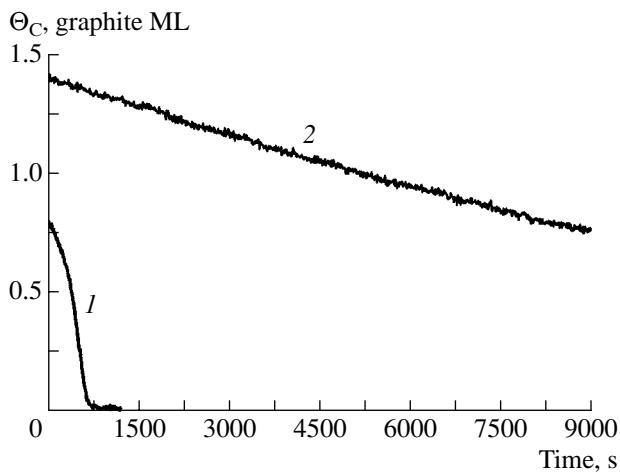
The above XPS data reliably indicate that the interaction of ethylene with the smooth closely packed (111) surface of platinum over a temperature range of 900–1350 K and an ethylene pressure range of  $10^{-10}$ – $10^{-2}$  Torr resulted in the formation of aggregated species of carbon in the  $sp^2$ -hybridized state. A structural rearrangement was observed in the range 1200–1350 K; because of this rearrangement, flat graphite-like carbon structures underwent a distortion and became similar to nanotube structures (or fullerenes). In other words, the layer of flat graphite structures changed to another structural state associated with the distortion of the flat graphite lattice. This result is consistent with published data [4, 12]. However, in the cited publications, it was believed that distortions occurred under the action of atoms and ions intercalated beneath graphite films to distort their flat structure. In our case, intercalated heteroatoms were absent.

What are the driving force and the mechanism of distortion of flat graphite structures? Initially, let us draw brief conclusions from the experimental findings.

First, data on carbon elimination indicate that the low-temperature decomposition of ethylene resulted in the formation of a discontinuous graphite film. This fol-



**Fig. 3.** Comparison of the Auger CKLL spectra of carbon deposits on the Pt(111) surface (see Fig. 1a) and of the reference samples of various allotropic modifications of carbon: (1) HOPG; (2, 3) adsorption carbon layers obtained on the Pt(111) surface at 900 and 1350 K, respectively; and (4) carbon nanotubes.



**Fig. 4.** Kinetics of elimination of carbon deposits on the Pt(111) surface, which were prepared by ethylene decomposition (1) at  $T < 1200$  K and (2) after heating the Pt(111) crystal at  $T = 1350$  K. Combustion conditions:  $P(O_2) = 10^{-6}$  Torr;  $T = 1000$  K.

lows from the high reaction efficiency ( $\sim 10^{-2}$ ) and the *s*-shaped kinetic curve of combustion (Fig. 4, curve 1). In the formation of a uniform graphite layer on the surface, its combustion was not observed at 1000 K. It is well known that the reaction of oxygen with graphite takes place at graphite island boundaries and depends

on the ratio between the numbers of atoms arranged along the perimeter and atoms within islands. This topochemical process is characterized by *s*-shaped kinetic curves. The island character also follows from the analysis of quantitative data (Fig. 1b), according to which the monolayer coverage with carbon was not achieved on low-temperature exposure to ethylene. Therefore, some platinum surface regions between the islands remained empty.

Second, experimental data suggest that the flat graphite islands were curved only after the preheating of a crystal in ethylene at a temperature higher than 1200 K in the course of slow cooling to  $T < 1100$  K. That is, the segregation of carbon dissolved in the bulk of platinum is required for curving. Hamilton and Blakely [20] found that the diffusion of carbon into the bulk of platinum occurred with a detectable rate at  $T > 1000$ –1100 K. Therefore, the effect of preheating consists in producing sufficiently intense carbonization of platinum with dissolved carbon. In this case, the higher the treatment temperature, the more intense the dissolution in the presence of ethylene as a carbon source. On cooling, segregation occurred, which is the reverse of diffusion. Segregation depends on temperature and carbon concentration in the bulk. The higher the bulk concentration of carbon, the higher the equilibrium surface coverage at a given temperature. This behavior of the test system was observed in our experiments and reported previously [20].

Thus, the curving of graphite islands resulted from segregation in the presence of ethylene in the gas phase. This segregation facilitates the egress of carbon atoms from the bulk to the surface.

The third important result is that the (111) surface of platinum is actually a stepped surface rather than an ideal crystal. In the sample preparation of a single crystal with the (111) surface orientation, we found that the deflection of the plane from the (111) surface was  $\sim 1^\circ$ , which corresponds to a terrace width of about 100 Å. It is believed that the role of steps consists in the activation and dehydrogenation of ethylene on them. The steps served as a kind of source of carbon atoms, which were either extruded to smooth terraces where carbon atoms underwent aggregation to graphite or diffused to the bulk of the crystal. It is likely that the maximum size of flat graphite islands should correspond to the terrace width, and the boundary atoms of islands have strong Pt–C chemical bonds. On heating the crystal, the diffusion of carbon took place through the dissolution of graphite islands beginning with boundary atoms localized at the steps. It is most likely that the reverse process of segregation also occurred by the egress of carbon atoms at the sites of structural distortions, that is, at the steps of the (111) surface. In this case, the egress of carbon atoms at the boundary of islands crowds the structure of the flat island at the boundary; because of this, the island began to curve and took the shape of a semicylinder in the form of a half-cut nanotube.

The results obtained by Dulot *et al.* [21] can provide support for the considerable role of steps. They found the formation of nonplanar structures stabilized at the steps of a Pd surface with the use of scanning electron microscopy.

Thus, we can formulate the necessary condition for  $sp^2$ -carbon structural rearrangement from flat graphite islands to a curved state:

(1) The surface should consist of terraces with a (111) orientation that alternate with steps. It is our opinion that the surface topography is of paramount importance for the formation of the structure and size of both flat and curved carbon structures.

(2) Dissolved carbon should be present in the bulk. The occurrence of the surface carbon–bulk carbon equilibrium is a fundamental property of carbon–metal systems. Therefore, depending on the temperature and the amount of carbon on the surface or in the bulk, the process can follow either a forward (diffusion) or a reverse (segregation) direction. To implement segregation in practice, the sample should be cooled after the intrusion of carbon into the bulk.

However, a number of questions are still open:

(1) What should be the size of the terraces? Probably, it should be close to the diameter of the nanotubes and amount to several tens of angstrom units.

(2) Is the presence of ethylene in the gas phase necessary for the segregation of carbon in the course of crystal cooling?

(3) What is the effect of the nature of hydrocarbons on the formation of both flat and curved structures of aggregated carbon? Does only ethylene possess the required properties?

Finally, it is reasonable to confirm the structural XPS data on carbon films on the Pt(111) surface with the use of direct structural analysis by scanning electron microscopy.

Thus, structurally different adsorption layers can be obtained with the use of catalytic ethylene decomposition on platinum. We found that both two-dimensional flat graphite islands and curved fullerene-like or nanotubular structures can be formed depending on the ethylene reaction temperature and the presence of carbon in a dissolved state in the bulk of the crystal. It is believed that the size and curvature of islands depend on the size of the terraces on the surface of the single crystal, and the driving force for the curving of flat graphite islands is the segregation of carbon.

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