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STUDY OF GRAPHENE FORMED IN THE ATMOSPHERE OF VAPORS OF AROMATIC HYDROCARBONS

B. A. Baitimbetova,[1] B. M. Vermenichev,[1] Yu. A. Ryabikin,[2]
Z. A. Mansurov,[3] and A. A. Abdikasova[1]

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For the first time graphene structures are obtained by reactive magnetron sputtering with the graphite cathode in vapors of one of the representatives of the wide class of aromatic hydrocarbons – naphthalene. The carbon grid of the molecular structure of aromatic hydrocarbons coincides with the graphene of the carbon grid. The paper presents the technique of obtaining graphene and results of investigations of its structural peculiarities by methods of Raman light scattering spectroscopy, electron paramagnetic resonance, and atomic force microscopy. Graphene peaks with the vibrational mode (2D-zone) at a frequency of ~2728 cm^{-1} are identified by the method of Raman spectroscopy. Results of investigations by the method of atomic force microscopy confirm the formation of graphene sheets and carbon nanotubes. Results of investigations are presented and discussed.

Keywords: graphene, structure of graphene, carbon nanotubes.

INTRODUCTION

Graphene possesses a number of interesting properties that allow it to be considered as a potentially promising material for nanoelectronics, optoelectronics, and some other applications [1, 2]. Plasma technologies play a huge role in obtaining products necessary for science and technology. An important integral part of the plasma nanotechnology is the magnetron sputtering of carbon films [3]. A new technique of obtaining graphene structures being integral parts of carbon films formed by magnetron sputtering is considered in the present work together with the influence of sublime vapors of aromatic hydrocarbons [4].

In a number of well-known traditional methods of obtaining thin film carbon structures by magnetron sputtering, the gas, for example, methane is flooded from a gas balloon through an inlet valve system with a gas pipeline into the working chamber of a vacuum installation where, being mixed with argon, it creates favorable conditions for synthesis of these materials. A salient feature of the suggested method of graphene structure manufacture is the application of solid aromatic hydrocarbons, for example, naphthalene, phenanthrene, anthracene, etc., with a close affinity to graphene structure. In this method the aromatic hydrocarbon – naphthalene whose vapors served as a reactive gas in the magnetron discharge was placed directly in the working vacuum chamber. A graphite disk separated from the water cooling chamber by an aluminum foil to prevent infiltration of cooling water through the pores of the graphite cathode was used as a cathode.

Naphthalene ($C_{10}H_8$) is an aromatic compound with a flat carbon skeleton in which all 10 carbon atoms are sp^2-hybridized state with 120° valence angles; pairing covers 2 cycles; the number of electrons participating in conjugation is equal to 10 ($4 \cdot 2 + 2 = 10$ π-electrons associated with 5 π-bonds) (Fig. 1).

The molecular structure of this aromatic hydrocarbon consists of two benzene rings surrounded by hydrogen atoms that are released in the magnetron discharge and are carried away by the vacuum pumping system, and the

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[1] K. I. Satpaev Kazakh National Technical University, Almaty, Republic of Kazakhstan; [2] Physical-Technical Institute, Almaty, Republic of Kazakhstan; [3] Combustion Problems Institute, Almaty, Republic of Kazakhstan, e-mail: baitim@physics.kz. Translated from Izvestiya Vysshikh Uchebnykh Zavedenii, Fizika, No. 3, pp. 101–105, March, 2015. Original article submitted June 23, 2014.

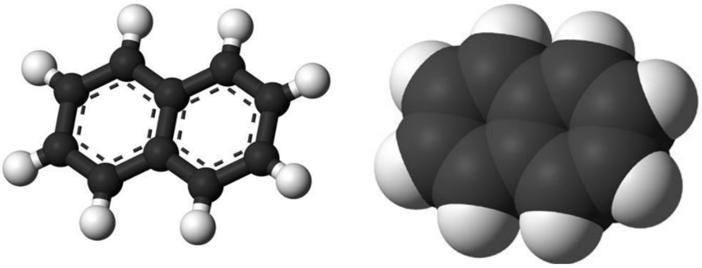

Fig. 1. Naphthalene structure.

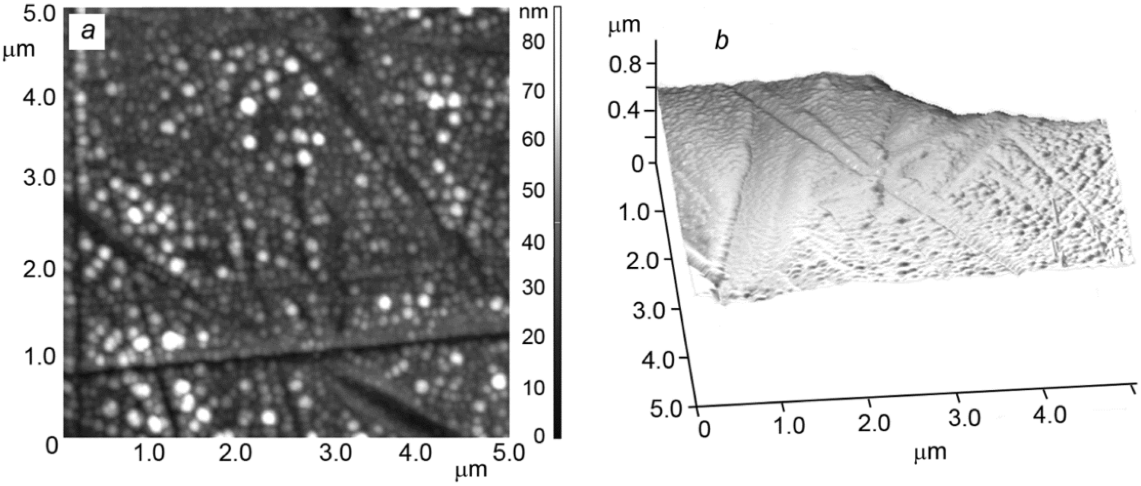

Fig. 2. Images of the graphene ribbons recorded by the method of atomic force microscopy: *a*) 2D image of graphene ribbons and *b*) 3D image of graphene ribbons.

skeletons of these molecular structures are analogous to the graphene cells. Depending on the substrate nature, carbon is deposited with different intensities with the formation of graphene and other carbon structures. Analogs of the given method of producing nanostructured carbon materials were not found, and a patent [5] was received.

Naphthalene was chosen as the most accessible and cheap aromatic substance. In our experiment, a piece of naphthalene was placed inside (at the bottom) of the vacuum chamber with initial pressure of $5 \cdot 10^{-5}$ Torr. For substances with high evaporation rates, a box with output aperture for emission of dosed vapors of evaporated material was provided. The aperture diameter was matched with the velocities of sublime substances.

In the presence of several grams of naphthalene at the bottom of the chamber, the pressure in the chamber was $5 \cdot 10^{-3}$ Torr; after flooding of argon, the pressure was decreased down to $6 \cdot 10^{-2}$ Torr. Under these conditions, a magnetron discharge was initiated at voltage of 200–300 V and current of 150 mA. Glass, quartz, aluminum plate, Fe–10Cr–18Ni–10Ti stainless steel, etc. were used for the substrates. Sputtering lasted from 30 min to 3 h. As a result, carbon films were formed comprising graphene structures, nanotubes, etc.

To study the morphology of the surface, scanning probe atomic force microscopy (AFM) was used. Below we present images of the stainless steel surface and thin carbon layers on it. More favorable conditions for the formation of graphene and nanotubes were provided on the substrate made from the stainless steel due to the presence of iron. Iron in this case was the catalyst for the formation of graphene ribbons and others carbon nanostructures (Fig. 2).

Raman light scattering spectroscopy is an efficient technique to identify the presence of graphene structures. It is well known that the number of graphene layers in the sample and their structural parameters can be unambiguously determined from the shapes and intensities of the spectral peaks [5–10].

TABLE 1. Parameters of the Raman Spectra of Carbon Films Fabricated in a Magnetron Discharge with Naphthalene

Serial No.	Substrates	*D*-line		*G*-line		2*D*-line		I_{2D}/I_G
		ω, cm^{-1}	FWHM, cm^{-1}	ω, cм$^{-1}$	FWHM, cm^{-1}	ω, cm^{-1}	FWHM, cm^{-1}	
1	Glass	1341	80	1580	32	2797	250	–
2	Aluminum plate	1332	76	1579	28	2795	279	0.57
3	Fe–10Cr–18Ni–10Ti stainless steel	1363	13	1579	15	2728	50	0.68

Note. Here FWHM denotes full width at half-maximum.

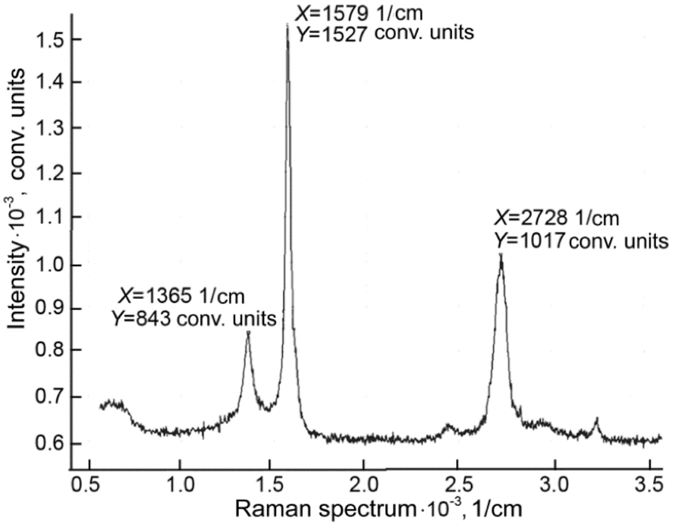

Fig. 3. Raman scattering spectrum of the carbon film on the stainless steel substrate.

The Raman spectra were measured with an MT-MDT Ntegra Spectra at room temperature. The spectra were excited by a semiconductor laser (λ = 473 nm). Results of Raman spectroscopy of the examined samples are shown in Fig. 3 and presented in Table 1. From Fig. 3 it can be seen that *G*-bands at 1350 and 1593 cm^{-1} caused by carbon nanotubes are observed in the spectra. The *D*-band in the region of 2500–2900 cm^{-1} was caused by the graphene ribbons. As can be seen from Fig. 2, the length of the graphene ribbons exceeds 5 μm. It is possible to expect that such long ribbons will find wide application in nanoelectronics.

The parameters of the Raman scattering spectra of the samples manufactured by the method of magnetron sputtering in the atmosphere of aromatic hydrocarbons are given in Table 1. In the last column, the ratio of the intensities of the 2D-band of graphene structures to the intensity of the graphite *G*-band is given. The Raman scattering spectra of the carbon film on the glass and aluminum substrates were also measured.

An analysis of the Raman spectra of carbon films demonstrates that the intensity of lines of graphene structures depends significantly on the nature of the substrates. The spectra of the carbon film on glass and aluminum substrates have comparatively low intensities in comparison with those on the stainless steel substrate. This is due to the fact that iron that plays the role of the catalyst for the formation of the graphene structures is comprised in the stainless steel.

The application of the method of electron paramagnetic resonance (EPR) to study the carbon films allowed the optimal conditions for forming graphene structures using the magnetron technology in the atmosphere of sublime vapors of aromatic hydrocarbons to be identified. In our experiments on the study of the intensity of EPR signal from unpared electrons on the sputtering time, the change of the intensity was observed under some conditions. Below we present some results of investigation of the carbon films by the EPR method. Measurements were performed at room

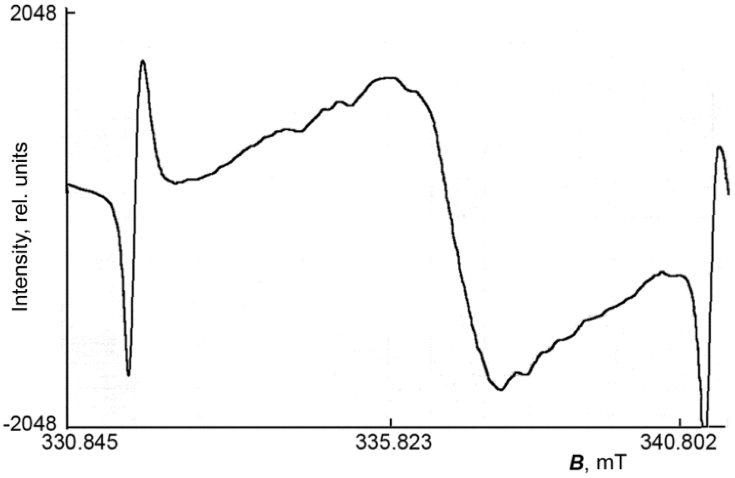

Fig. 4. EPR spectrum of the carbon films obtained in a magnetron discharge with naphthalene on the glass substrate. The sputtering time was 2 h 40 min.

temperature in the air atmosphere using an EPR spectrometer operating in the wavelength range 3 cm. The maximum sensitivity of the spectrometer was $5 \cdot 10^9$ spins/sample at 100 kHz magnetic field modulation frequency.

Mn^{2+} ions in MgO were used as a reference sample. A signal from the sample was registered between the 3rd and 4th components of the 6-line Mn^{2+} spectrum. The sample with sizes 3 × 5 mm was placed in an ampoule made from special glass which produced no EPR signal. When the resonant conditions were adjusted by changing the magnetic field within certain limits, the EPR signal was detected and the EPR spectrum was printed. The EPR spectrum of the sample was investigated as a function of the angle between the substrate plane and the magnetic field direction that was changed by sample rotation. The spectra were successively recorded at rotation angles of 0, 30, 60, and 90°.

It was established that the line width, the EPR signal amplitude, and the line *g*-factor changed insignificantly. This demonstrated that the carbon plate so obtained was amorphous in nature. The carbon films typically have complicated structures. They comprised graphene and graphene-like formations, nanotubes with different parameters, graphites of different organizations, and their oxides. Investigation of the EPR spectrum of the sample (Fig. 4) demonstrated that it has a single sufficiently intensive line with the *g*-factor equal to 2.00414–2.00416. Such value of the *g*-factor of the EPR spectrum is characteristic for graphene.

An analysis of the EPR line demonstrated that a small bend caused by contribution from the line with different g-factor to the total line is observed on the straight line connecting the extreme points of the spectrum. Depending on the rotation angle, the *g*-factor of this line changed from 2.00214 to 2.00244. Such values of the *g*-factor are characteristic for some graphite species, and their dependence on the rotation angle testifies to a certain degree of crystallinity of graphite comprised in the carbon film. The amount of graphite in the film was insignificant, namely, 7–10% of the graphene amount.

An analysis of the EPR spectrum of the carbon film produced during small sputtering time (Fig. 5) demonstrated that carbon nanotubes ($g = 2.0037$) were formed in it in addition to graphene. Moreover, their amount was approximately equal to that of graphene. In this case, the amount of graphite was about 10% of the total amount.

The width ($\Delta H = 16.4$ Oe) of the EPR line for the carbon film on the glass substrate in this case was greater than in the first case of preparation of the carbon film. It seems likely that the line broadening is due to the dipole-dipole interaction between graphene and nanotubes. The amplitude of signal from the carbon film on the aluminum substrate was 3 times smaller than that from the film on the glass substrate, and the line widths were 8 and 3 Oe, respectively. The bends observed in the spectrum allowed contributions from graphenes, nanotubes, and graphites in the ratios 2:3:1.4 to be determined. We failed to detect the EPR spectrum of the carbon film on the nickel substrate against the background of the strong signal of the ferromagnetic resonance (FMR) from nickel.

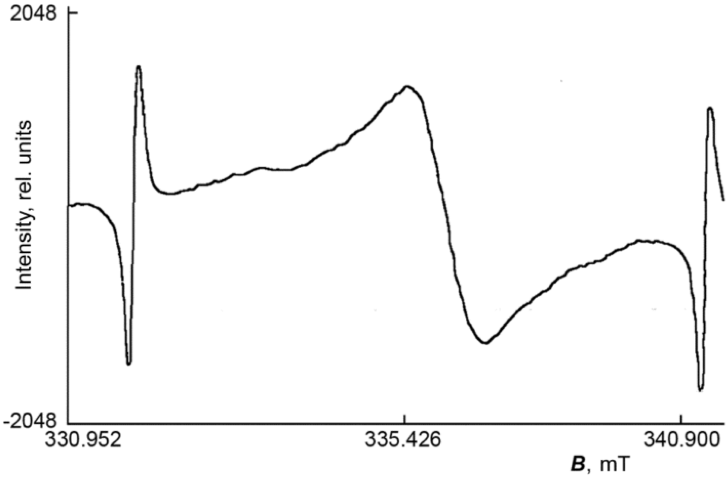

Fig. 5. EPR spectrum of carbon films produced in a magnetron discharge with naphthalene on the glass substrate. The sputtering time was 2 h.

CONCLUSIONS

For the first time, the graphene structures were fabricated by the method of reactive magnetron sputtering in vapors of solid naphthalene aromatic hydrocarbon. The method of the Raman spectroscopy was used to detect graphene peaks with the vibrational mode (*2D* zone) at a frequency of ~2728 cm^{-1} on the stainless steel substrate. Results of investigations by the atomic force microscopy confirmed the formation of graphene structures and carbon nanotubes. Investigation of the carbon film on the glass substrate demonstrated that the EPR spectrum consists of the single sufficiently intensive line with the *g*-factor equal to 2.00414–2.00416 characteristic for graphene. In addition, the contribution of the EPR line from the nanotubes was observed.

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