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AMORPHOUS, VITREOUS, POROUS, ORGANIC, AND MICROCRYSTALLINE SEMICONDUCTORS; SEMICONDUCTOR COMPOSITES

Optical Study of Platinum-Modified Amorphous Carbon

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Abstract—Films of amorphous carbon *a*-C and a platinum-modified amorphous carbon composite *a*-C–Pt, produced by magnetron sputtering in a wide range of thicknesses and modifying platinum concentrations in the optimal mode for the catalytic activity of *a*-C–Pt, have been studied by ellipsometry, and FTIR and Raman spectroscopies. It is demonstrated that (i) platinum clusters are incorporated into the system of graphene planes of amorphous carbon without any significant transformation of the carbon structure itself and (ii) an increase in the amount of modifying platinum in an *a*-C–Pt film leads to a decrease in the size of graphene clusters.

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1. INTRODUCTION

Amorphous carbon (*a*-C) attracts the attention of researchers by its interesting physical properties and possible applications in photonics and electronics. This material possesses a high strength, high dielectric constant, and high optical transparency in a wide spectral range, chemical stability, controllable optical absorption edge, and effective photoluminescence at room temperature. At the same time, *a*-C is a low-cost and ecologically acceptable material.

In recent years, steadily increasing attention has been attracted to the composite amorphous carbon containing metallic additives: gold [1], titanium [2], chromium [3], iron, cobalt, and copper [4–6]. A metal is introduced in amounts comparable with the content of carbon and modifies the amorphous carbon matrix by creating metal nanoclusters, rather than becoming a substitutional impurity. The properties of these nanoclusters and their effect on the way in which the matrix is modified depend on the nature of a modifying metal and on the chemical interaction of the metal with carbon atoms. It has been shown by transmission electron and atomic-force spectroscopies that, at comparable amounts of the metal and carbon, the typical sizes of metallic clusters are within 1–5 nm for gold [1], 0.6–0.8 nm for copper [4], and 2–15 nm for cobalt, with the distribution of the cluster size having a maximum at ~7 nm [7]. Platinum is of particular interest as a carbon-modifying impurity because this metal is a known catalyst of numerous chemical processes [8]. In this case, the carbon film can serve as a support of such a catalyst.

The aim of this study was to examine the optical properties of layers of platinum-modified amorphous carbon *a*-C–Pt, produced by magnetron sputtering. It continues a series of studies concerned with the interaction of metallic clusters with the amorphous carbon matrix [7, 9–11].

2. EXPERIMENTAL

2.1. Sample Fabrication Technology

Amorphous carbon *a*-C layers were thin films transparent in the visible spectral region. The layers were deposited by dc magnetron sputtering of a graphite target in the atmosphere of argon on an O1NI-7-006 Oratoriya 5 industrial installation. The procedure used for sample fabrication was described in more detail in [12].

To introduce platinum into amorphous carbon, i.e., to obtain the *a*-C–Pt composite, layers were deposited onto silicon substrates by joint sputtering of graphite and platinum. The concentration of platinum introduced into carbon films was varied by changing the area of the platinum target and the sputtering time.

2.2. Methods for Optical Studies

The thicknesses of amorphous carbon and platinum-modified amorphous carbon films were determined using an MII-4 interference microscope and multiple-angle ellipsometry. The optical constants of composite *a*-C–Pt films on silicon substrates and their uniformity over their area were also determined by multiple-angle ellipsometry. The ellipsometric measurements were performed using an LEF-3M zero

Table 1. Information about samples

Sample no.	Amount of Pt/C (RBS)*	Pt*, cm^2 min	Deposition time, min	Amount of Pt in the target, cm^2	Refractive index, n_{eff}	Extinction coefficient, k_{eff}	Thickness d, nm	Method used in d measurements
1	–	–	40	–	1.77	0.014	60.8	Ell*
2	–	–	60	–	1.80	0.009	79.2	Ell
3	–	–	180	–	1.55	0.037	222	Ell
4	–	–	480	–	1.7	0.2	761	Ell
5	–	–	630	–	1.55–1.64	0.06–0.11	816	Ell
6	–	≤0.03	270	Background			660	IM*
7	–	20	10	2	2.10	0.67	114	Ell
8	–	22.5	3	7.5	2.01	0.16	33	Ell
9	–	30	3	10	2.34	0.52	45	Ell
10	–	30	3	10	2.37	0.75	58	Ell
11	–	39.5	6	6.5	–	–	110	IM
12	–	40	20	2	–	–	130–170	IM
13	0.44	180	90	2	–	–	360	IM
14	0.56	270	90	3	–	–	410	IM
15	0.88	405	90	4.5	–	–	600	IM

Note: RBS, Rutherford backscattering; Ell, thickness determination by ellipsometry; and IM, thickness determination by interference microscopy. The column for Pt gives the product of the platinum target area by the deposition time.

ellipsometer ($\lambda = 632.8$ nm) at three angles of incidence, $\varphi = 55°$, $60°$, and $65°$ [13]. The calculations were performed for the following configuration: external medium, uniform isotropic film (or a film with n and k linearly varying across the film thickness), and substrate. The refractive index n, extinction coefficient k, and film thickness d were calculated by a search for unknown parameters, with the error function F calculated by the least-squares method [14].

Pure amorphous carbon *a*-C and that modified with platinum, *a*-C–Pt, were characterized by the methods of IR absorption (FTIR) and Raman scattering. FTIR transmission spectra of *a*-C and *a*-C–Pt films were measured using a Shimadzu spectrometer in the spectral range 400–4000 cm^{-1} with a resolution of 8 cm^{-1} and number of scans equal to 100. The intensity of Raman scattering was measured with a Renishaw Ramanscope spectrometer in the backscattering configuration, with unpolarized excitation at a wavelength of 632.8 nm. The spot diameter was 10 μm, and the resolution was ~0.5 cm^{-1}. The content of platinum was found using the methods of Rutherford backscattering and instantaneous nuclear reactions [15].

3. EXPERIMENTAL RESULTS AND DISCUSSION

3.1. Ellipsometry

The values obtained for the film thicknesses d, refractive index n, and extinction coefficient k are listed in Table 1 in relation to the sputtering time and platinum target area. The values of n for films with different thicknesses d were found to be 1.55–1.75 for *a*-C, in good agreement with [11], and 2.01–2.37 for *a*-C–Pt. The values of k were in the range 0.01–0.11 for *a*-C and 0.16–0.75 for *a*-C–Pt. To assess the uniformity of the films, measurements were conducted at different points over the sample area. The thickness scatter did not exceed 1 nm for each film, with $\Delta n \approx 0.015$.

3.2. IR Absorption

Transmission spectra of a sample of unmodified amorphous carbon (*a*-C) and platinum-containing samples (*a*-C–Pt) are shown in Fig. 1. The main absorption bands in the spectra of the films are at 1360–1460 cm^{-1} (CH–, CH$_2$–, and CH$_3$– bonds with sp^2 and sp^3 hybridization), 1400–1950 cm^{-1} [C=C bonds in sp^2 states and absorption bands of water (bending vibrations of H–O–H) that appeared in a film in the course of its deposition], 2800–3000 cm^{-1} (CH–, CH$_2$–, and CH$_3$– bonds in the sp^2 and sp^3 states), and 3500–3900 cm^{-1} [bands of water (stretching vibrations of O–H) absorbed by the film in the course of its deposition] [15]. The fact that there are hydrocarbon-related bands in the spectrum indicates that the films contain hydrogen that appeared because of the presence of hydrogen in the sputtering chamber as an impurity gas. Spectra of fairly thick film deposited in the course of more than 180 min also contain a very weak absorption band at 2050–2250 cm^{-1}, commonly attributed to nitride bonds. This may indicate that the films contain nitrogen that appeared because of the presence of nitrogen in the working chamber as an impurity gas [16]. According to another version, this band can be attributed to two-phonon transitions in diamond nanoclusters within *a*-C in the presence of ultradispersed metallic formations [17, 18].

The doublet observed at 2325 and 2350 cm^{-1} is due to the parasitic signal associated with atmospheric CO_2.

The frequencies of the absorption line obtained in decomposition of the absorption spectra into Gaussian components are listed in Table 2 for the ranges 2800–3000 and 1300–1900 cm^{-1}. It can be seen that the frequencies well coincide with published values.

The difference of the frequencies of vibrations responsible for the corresponding absorption bands of amorphous carbon obtained in this study from published values may be due to the following [19]. First, the *a*-C film deposited by ion-plasma sputtering is stressed. The stress depends on the energy of particles impinging upon the substrate in the course of growth, substrate heating, and other specific features of the technological process and may vary between different techniques, which lead to a shift of the vibration frequencies. Second, defects appear in a growing film and may lead to generation of dangling bonds and centers of various types and to deformation of rings in the structure of graphite-like clusters. Third, the uncontrollable presence of impurity gases may distort the symmetry of carbon sp^2 and sp^3 bonds, which can also shift the absorption bands in the spectra of samples obtained in various technological processes [20].

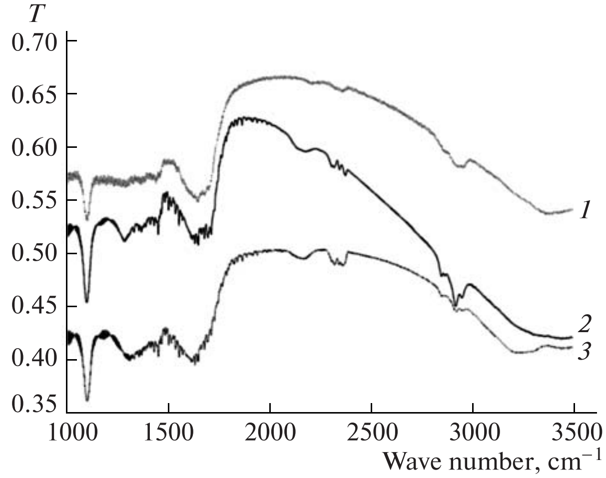

Fig. 1. FTIR transmission spectra of *a*-C. (*1*) FTIR spectrum of a platinum-free sample, (*2*) FTIR spectrum of a sample with a Pt/C atomic ratio of 0.03, and (*3*) FTIR spectrum of a sample with a Pt/C atomic ratio of 0.44.

Table 2

Mode	Mode frequency obtained in this study for platinum-free samples, cm^{-1}	Mode frequency according to published data, cm^{-1}	Mode frequency obtained in this study for samples with platinum, cm^{-1}	Reference
sp^3CH_3	2962	2950–2970	2959	[26, 23]
sp^2CH_2, CH	2932	2925–2950	2921	[26, 27, 24]
sp^2CH	2908	2910	2912	[28]
sp^2CH_2, CH_n	2852	2850	2854	[28, 23]
C=N	–		2188	[23, 29, 17]
N^{2+} structure	–		2151	[29, 17]
			1759	
C=O in C=O and HC=O bonds	1721		1723	[30]
	1694		1693	
C=C	1653	1654	1652	[26, 16]
C=C	1617	1630	1613	[31]
$sp^2C=C$	1568	1580	1559	[15]
$sp^2C–H$, sp^2CH_2	1438	1450, 1440		[32, 16]
	1420		1423	
	1401			
CH_3	1367	1372	1370	[15, 16]
			1331	
			1313	

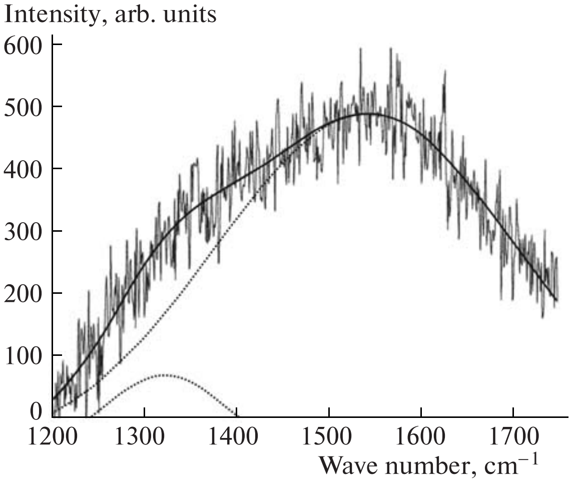

Fig. 2. Raman spectrum of a platinum-free sample.

Introduction of metallic platinum into the carbon matrix gives rise to metallic clusters that are foreign to the matrix, which is manifested in the fact that the spectrum is changed. As can be seen in Fig. 1, the FTIR transmission spectra of platinum-containing *a*-C films for the most part coincide with those of platinum-free films. Significant differences are observed at 1300–1500 cm^{-1}. It can be seen in Fig. 1 that, as in the case of cobalt [15], a pronounced increase in the absorption intensity is observed in this region. The results of the decomposition of this part of the spectrum into Gaussian components are listed in Table 2. It can be seen that the frequencies of the vibration mode are rather close for platinum-containing and platinum-free samples. This indicates that the introduced platinum is incorporated into the system of graphene planes and amorphous carbon chains, but the carbon structure itself is not transformed significantly.

3.3. Raman Scattering

Raman spectroscopy is a known informative nondestructive method for the study of the bond configuration in a carbon material. In the case of amorphous carbon, mostly two bands are observed in the Raman spectrum: D band with a frequency of about 1350 cm^{-1} and G band with a frequency of about 1560 cm^{-1}, associated with sp^2 bonds. The G band is due to the stretching mode of pairs of sp^2 bonds in carbon rings and chains, and the D band is due to breathing modes in carbon chains [10, 16]. The presence of the D band results from violation of the wave-vector selection rule in phonon transitions for the case of small crystallites in the presence of structure-disturbing factors, e.g., foreign inclusions. The intensity of the D band can to a certain extent serve as a measure of the structural disorder.

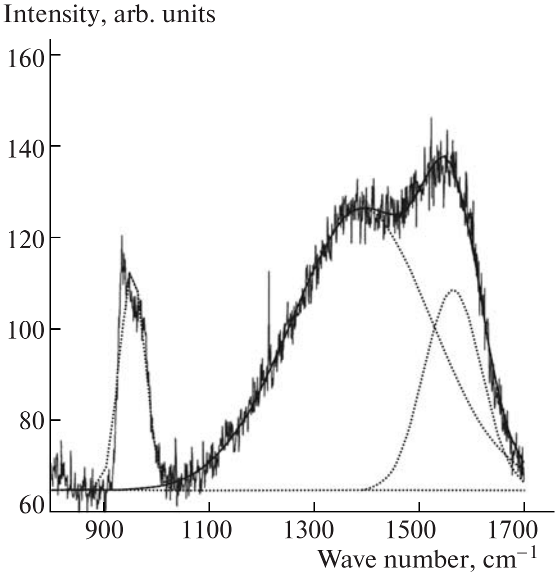

Fig. 3. Raman spectrum of a sample with platinum, Pt/C = 0.24.

Figure 2 shows the Raman spectrum of a Pt-free *a*-C sample. The spectrum is typical of amorphous carbon [10]. The D band is substantially weaker than the G band and only makes the spectrum asymmetric, being a shoulder of the G band. Decomposition of the spectrum into two Gaussian components yields bands peaked at 1370 ± 10 and 1551 ± 7 cm^{-1}, which corresponds to the frequencies of the D and G bands, respectively. The full widths at half-height (FWHM) of the D and G bands are 145 and 245 cm^{-1}. The ratio of peak intensity is $I_D/I_G = 0.64 \pm 0.3$. This ratio can be used to estimate the size of graphene clusters. In accordance with [21, 22], $I_D/I_G = \gamma L_a^2$ at small sizes of the graphene clusters. Here, L_a is the cluster size, and $\gamma = 5.5 \times 10^{-3}$ Å^2 at an excitation wavelength of 515.5 nm is obtained by means of formula matching at 20 Å [23, 24]. Then, the estimate of the cluster size for the carbon film is $L_a \approx 10$ Å.

Figure 3 shows a Raman spectrum of a platinum-containing sample. The shape of the spectrum substantially changes, compared with that of the platinum-free sample. The intensity of the D line increases several-fold. The ratio I_D/I_G becomes considerably larger (see Table 3). The D band is broadened, and the G band becomes narrower. As also for amorphous carbon samples containing copper and cobalt [10, 25] or an admixture of nitrogen [10], the band peaks are shifted to higher frequencies. Estimates of the average sizes of graphite-like clusters for this case are listed in Table 3.

The mechanism by which metallic particles are introduced into an amorphous carbon film in the course of its deposition was analyzed in [10] in terms of the theory developed in [21]. The shift of the peak of the G band to higher frequencies upon the introduction of platinum indicates that carbon bonds in the carbon matrix are ruptured and finer nanoclusters

Table 3

Sample	Pt, cm^2 min	d, nm	I_D/I_G	L_a, Å
5	0	816	0.64	10.8
8	20	114	1.4	16
11	39	110	1.17	14.6
13	40	130–170	0.83	12.3
15	380	600	0.58	10.3

Note: The column for Pt gives the product of the platinum target area by the deposition time; d, film thickness; I_D/I_G, intensity ratio of the D and G bands in the Raman spectrum; and L_a, size of graphene nanoclusters.

with a structure of rings or shorter chains are formed in the system of carbon sp^2 bonds of the structure. The narrowing of the G band is possibly a consequence of increasing disorder in the entire system, and the change in the intensity of the D band means that the graphitization of the film becomes more pronounced upon introduction of platinum.

4. CONCLUSIONS

The study of an admixture-free amorphous carbon and amorphous carbon modified with platinum by means of ellipsometry, and FTIR and Raman spectroscopies demonstrated that platinum clusters are incorporated into the system of graphene planes in amorphous carbon. As in the case of modification of amorphous carbon with cobalt and copper [14], modification with platinum leads to fragmentation of the chain and ring structures of graphite. Estimation calculations of the size of graphene clusters for unmodified amorphous carbon and that containing platinum in amounts comparable with that of carbon were performed. It was demonstrated that, as the content of platinum increases, this size decreases from 1.6 to 1 nm and approaches the value characteristic of pure amorphous carbon.

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