Electron spectroscopy of various nanostructured carbon films

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Abstract. X-ray photoelectron spectroscopy technique have been used to study carbon films obtained by means of ion-plasma deposition in the plasma of different chemical composition. The detailed analysis of electron spectroscopy data made it possible to determine the structure of the films and the influence of nitrogen and hydrogen admixture in plasma on the structural properties. Diamond-like films are obtained in pure argon plasma, graphite-like and carbon chain structures correspond to nitrogen and hydrogen addition respectively.

1. Introduction
Thin carbon films are promising objects for application in various heterostructures for micro- and nanoelectronics due to their unique physical, chemical and mechanical properties [1].

At the present time, nanocarbon films are obtained by different techniques including both high and low temperature deposition. The mean size of their structural element (cluster) has typical order of nanometers. At these nanocluster sizes the quantity of surface atoms is almost equal to the quantity of bulk ones, which significantly affects on the properties of the structure. All the three types of carbon bonds hybridization (sp\(^1\), sp\(^2\), sp\(^3\)) are present inside the clusters, on their surface and between them.

To study electrophysical properties of complex nanocarbon structures, it is necessary to use analytical techniques, which can give us information on both atomic and electronic structure of a sample. The most informative methods are electron spectroscopy techniques, which include such analysis techniques as X-ray Photoelectron Spectroscopy (XPS), Auger Electron Spectroscopy (AES) and Electron Energy Loss Spectroscopy (EELS). However, there is a lack of modern works related to investigation of carbon materials by electron spectroscopy.

Electron spectroscopy provides qualitative and quantitative information on chemical composition of material. More sophisticated application of the method can yield information about electronic structure of the studied object. For example, in work [2] Auger spectra were interpreted assuming that specific features observed in spectrum depend on the electron structure of carbon material. However, this interpretation of spectra is not straightforward, and accurate theoretical modelling is required.

In this work we present the results of experimental study of thin nanocarbon films by means of EELS and AES using the spectra interpretation technique described in paper [3].

2. Experiment
The samples were deposited by ion-plasma pulse arc sputtering of graphite (discharge power 1 kW, pulse duration ~ 1 ms) assisted with ion beam with the energy of 400 eV in an ultra-high vacuum chamber with an ambient pressure of 10\(^{-6}\) Torr [4]. The temperature of substrates did not exceed 30°C. The thickness of the deposited films was about 100 nm.
Before the deposition, silicon plates used as the substrates were cleaned by 1 keV Ar ion etching. Carbon films deposition was carried out at the working pressure of $8.5 \times 10^{-4}$ Torr in various gas atmospheres: in argon, in argon and nitrogen mixture (70/30) and in argon and hydrogen mixture (70/30).

3. Results and discussion

3.1. X-ray photoelectron spectroscopy

Photoelectron spectra provide information about the electronic structure of both surface and bulk phase of a sample. In the latter case, the information can be obtained by analyzing the spectrum of inelastic electron energy losses. Therefore, the consideration of x-ray photoelectron spectra was divided into two steps: analysis of carbon 1s line shapes and interpretation of electron energy loss spectra. In the spectra of each sample we observed a peak shifted by ~ 4 eV relatively to carbon 1s peak. This peak can be attributed to either carbon oxygen bonds presence on the surface or plasmon excitation. According to electron spectroscopy for chemical analysis data, all the three sets of the samples have the same oxygen concentration, but their loss spectra are greatly different. So we suppose this peak to arise due to plasmon excitation.

Figure 1 shows the electron energy loss spectra after subtraction of 1s electron elastic peak. The experimental spectra are shifted in such a way that the zero energy corresponds to 1s carbon peak position. For carbon materials, the energy range up to 10 eV is associated with excitation of weakly bound π- electrons, whereas the energy losses in the range of 20 - 30 eV are due to excitation of the whole electronic system (π+σ). It is known that the energies of collective electronic excitation are 27 eV in crystalline graphite and 35 eV in diamond. In contrast to diamond, there are non-hybridized π-orbitals in graphite, which correspond to plasmon energy 7 eV. In carbon materials having non-hybridized orbitals the values of π-plasmon energy are from 3.7 to 7 eV depending on the material structure. Low energies of the range correspond to quasi-one-dimensional carbon (polyacetylene and polydiacetylene) [5, 6]. π-plasmon excitation energy has a momentum-dependence, which is determined by the angle of electron exit relative to the carbon structure [5].

As can be seen from the figure, the spectra of the films obtained in different conditions differ from each other by the presence of π-plasmon peak and its energy. The data give evidence of existence of different carbon structures in the samples. The spectrum of the film deposited in pure argon plasma has no π-plasmon peak; hence, this film is a diamond-like one. In the spectrum of the film deposited in the Ar + N$_2$ plasma, we can observe the peak at the energy of 6 eV, position of which is close to the energy of π-plasmon in crystalline graphite. The 4 eV peak is a characteristic feature of electron energy loss spectrum of the carbon film obtained in hydrogen atmosphere.

![Figure 1. Electron energy loss spectra after subtracting C1s line](image-url)
Energy of $\pi$-plasmon excitation in the investigated film (6 eV) has lower values than in high-oriented graphite under the same electron exit angles. This can be explained with the existence of arbitrary oriented graphite clusters in the film structure. The peak corresponding to energy loss 4 eV unambiguously indicates to the presence of carbon chains in the film [6, 7].

High energy range of the spectra (> 10 eV) is associated with excitation of the whole electronic subsystem and determined by electron concentration and, accordingly, material density. As mentioned above, $(\pi+\sigma)$ plasmon energies in graphite and diamond are respectively 27 and 35 eV. In our case, the energy of $(\pi+\sigma)$ plasmons does not exceed 30 eV.

Such a low value of $\pi+\sigma$ plasmon energy can be explained by the size effect. For example, it was shown in [8] that electronic properties of the core and of the periphery of a diamond nanocrystal are significantly different. The energy loss spectrum of such a nanodiamond film has two maxima at energies 23 and 33 eV, corresponding to excitation of surface and bulk plasmons, respectively. In our case, the spectrum of the diamond-like film also has two components, shown in a dash line. The energy ratio of these components is approximately the same as one for surface and bulk plasmons. However, in contrary to an ideal diamond, in our case the maximum energy is 30 eV instead of 35 eV, which can be due to the low density of the diamond-like structure.

Generally, the loss function (spectrum) can be expressed as following:

$$S(E) = -\text{Im} \left( \frac{1}{\varepsilon} \right)$$

where $\varepsilon = \varepsilon_1 + i\varepsilon_2$ is a complex dielectric function of a sample, $\varepsilon_1$ corresponds to collective electron excitations; $\varepsilon_2$ corresponds to one-electron interband transitions between valence and conductive bands and is a convolution of electron state density or joint density of states (DOS).

Therefore, electron energy loss spectra can give us information about electronic structure of a sample. In order to obtain this information, it is necessary to determine one-particle excitations using the experimental spectrum with Kramers-Kronig’s relation:

$$S'(E) = -\text{Re} \left( \frac{1}{\varepsilon} \right) = 1 - \frac{2}{\pi} p \int_0^\infty \frac{E' S(E') dE'}{(E')^2 - E^2}$$

where $p$ means the principal value of the integral.

The calculated real $\varepsilon_1$ (dash line) and imaginary $\varepsilon_2$ (solid line) parts of the dielectric function of the films are shown in figure 2. The spectra were normalized using the measured value of optical refractive index $n=2.2$ ($\varepsilon_1 = n^2$), the value of which was determined by ellipsometry. The curve representing joint density of states for diamond-like film demonstrates the presence of band gap (zero values of density in the region of 0-2 eV). The exact width of the band gap cannot be obtained from this spectrum because of the high noise in this energy range. The spectrum of joint DOS has a maximum at the energy of 12.8 eV, a plateau centred at 7 eV and a feature at 10.5 eV. Each of them represent an electron transition and such a picture is well consistent with the energies theoretically calculated on the base of a convolution of valence and conduction bands of diamond-like films (α-C:H) [9]. The presence of $\pi$-states at 7 eV can be explained by nanodiamond film structure with a layer having deformed sp$^{3/4}$ hybridized bonds being formed on the surfaces of nanoclusters. These bonds have binding energy lower then sp$^3$ bonds, and the corresponding electronic states lie near the upper edge of the band gap.

Joint DOS of graphite-like film is similar to graphite one [10] and has specific interband transitions denoted $\pi+\pi'$ and $\pi+\sigma'$ in the figure (dot-dash line). In [10] the spectra are recorded from the highly oriented graphite for different exit angles. For comparison, the spectrum of electrons exiting normally to the base plane of graphite is also shown. The spectra are shown in the same scale and without normalization. In this case, we can speak of the existence of a nonzero band gap, which is in agreement with our results for the film. The displacement of $\pi$ electron excitation peak to higher energies can be explained by deformation of graphite bonds and formation of sp$^{3/4}$ orbitals, which means a shift toward diamond sp$^3$ bonds.

Joint DOS of the film deposited in the Ar+H$_2$ plasma corresponds well to joint DOS of one-dimensional or quasi-one-dimensional systems, which have maxima at the edges of both valence and conduction bands. The insert in figure 4 represents the band structure of an infinite carbon chain
calculated by the LCAO method [11]. Thus, in the spectrum there should be the maxima corresponding to the two types of transitions marked by arrows. The first maximum is due to the transition from the top of valence band to the bottom of conduction band (through the forbidden band), the second one represents the transition between the band edges. As can be seen from figure, the experimental curve is in a good agreement with the calculated data. The second transition on the experimental curve is broadened, since the width of the valence band is much larger than the width of the conduction band.

Thus, a diamond-like carbon film with a small number of defected sp\(^3\)-x bonds in a band gap can be obtained in pure argon atmosphere. The spectrum of the film deposited in nitrogen plasma is very similar to the spectrum of graphite single crystal, which does not have a band gap. Adding hydrogen into the plasma leads to formation of chain structures characterized by specific position of the \(\pi\)-plasmon peak.

3.2. Auger spectra analysis
The shape of carbon KVV peak heavily depends on the structure of carbon materials. Figure 3 depicts Auger C KVV spectra of the investigated samples. Here, the energies are measured from the Fermi level of carbon. As can be seen from the figure, the position of the main maximum is in the energy region of 20 - 25 eV for all three samples. A wide maximum at 40-50 eV arises from the Auger electrons, which lose their energy for plasmon excitations (20-30 eV).
analysis of presented spectra is not possible because of the significant background of inelastically scattered electrons and plasma losses.

![Figure 3. Auger spectra of deposited carbon films](image)

**Figure 3.** Auger spectra of deposited carbon films

![Figure 4. Experimental Auger spectra after inelastic and plasma losses background subtraction](image)

**Figure 4.** Experimental Auger spectra after inelastic and plasma losses background subtraction

Figure 4 shows the experimental Auger spectra after inelastic and plasma losses background subtraction. For comparison, theoretical spectrum is also presented in the figure. As it can be seen, the spectra of the samples differ from each other in the energy range from Fermi energy to the energy of spectrum maximum. Besides, there is an additional maximum at the energy of ~35 eV in the spectrum of the film deposited in argon and hydrogen mixture.

To explain the features of C KVV Auger peak of the investigated samples we used the one-electron approach in which the Auger lineshape of solids is determined by self-convolution of the density of valence electron states.

The valence band of graphite is made up of σ- and π-subbands, whereas only σ-electrons form the diamond valence band. Thus, the shape of KVV Auger peak can be derived from following expressions:

For graphite

\[
I(E) = (\sigma + \pi) \ast (\sigma + \pi) = \sigma \ast \sigma + 2\pi \ast \sigma + \pi \ast \pi
\]

and for diamond

\[
I(E) = \sigma \ast \sigma
\]

where \(\ast\) denotes a self-fold procedure.

Because of \(sp^3\)-hybridization of σ-orbitals in diamond, self-convolution of its σ-band can be decomposed as

\[
\sigma \ast \sigma = s \ast s + s \ast p + p \ast p
\]

The partial density of states was calculated within the framework of density functional theory (DFT) [12] using the plane wave basis set. As π-subband is closer to the Fermi level than σ-subband, the low energy region of Auger spectrum is determined mainly by the \(\pi^*\pi\) term. Figure 4 depicts the theoretical spectrum for diamond shown as the dashed line. The components of the spectrum are shown with dotted lines.

As can be seen from the figure, there is a large difference between the experimental and theoretical spectra in the low energy region which corresponds to \(\pi\)-subband. To analyse this difference we subtracted the theoretical spectrum from the experimental ones. The curves obtained are presented in figure 5.
First, note a wide and asymmetric peak on self-convolution curve of $\pi$-subband. Its asymmetry can be explained by the contribution of multi-particle effects accompanying Auger process. The ionization of 1s core level increases the effective nuclear charge experienced by valence electrons. This causes relaxation of the valence band represented by excitation of a valence electron into an unoccupied orbital above the Fermi level (formation of an exciton associated with long-lived holes in the valence band) [13]. As the result, we observe some broadening of $\pi$-subband, which can be decomposed into two Gaussian lines (Figure 5, $\pi$ and $\pi_{ex}$).

4. Conclusion
Electron spectroscopy methods are sufficiently sensitive to local structure of amorphous nanocarbon. The results showed that theoretical analysis of both photoelectron and Auger spectroscopy data makes it possible to identify $sp$, $sp^2$ and $sp^3$ hybridised bonds in carbon nanocrystals. Absence $\pi$-plasmon peak approves that diamond-like carbon films are obtained under pure argon atmosphere. Nitrogen addition into plasma leads to dramatic increase of graphite-like phase having $\pi$-plasmon with the same energy as the graphite one. With hydrogen addition, the film structure corresponds to carbon chains; it is indicated by both $\pi$-plasmon position and joint density of states shape.

References
[1] Avjya K E, Matevosyan L A, Ohanyan K S and Petrosyan L G 2016 Instrum. Exp. Tech. 59 60
[2] Shikin A M, Prudnikova G V and Adamchuk V K 1994 J. Elect. Spec. Rel. Phen. 68 413
[3] Ramaker D E 1991 Crit. Rev. Solid State Mater. Sci. 17 211–76
[4] Streletskii O A, Ivanenko I P, Khvostov V V, Savchenko N F, Nishchak O Yu and Aleksandrov A F 2016 Phys. Solid State 58 2119–25
[5] Ritsko J J, Mele E J, Heeger A J, MacDiarmid A G and Ozaki M 1980 Phys. Rev. Lett. 44 1351
[6] Ritsko J J, Crecelius G and Fink J 1983 Phys. Rev. B. 27 4902
[7] Kudryavtsev Yu P, Eysyukov S E, Babaev V G, Guseva M B, Khvostov V V and Krechko L M 1992 Carbon 30 213
[8] Baitinger E M, Belenkov E A, Brzhazinskaya M M and Greshnyakov V A 2012 Phys. Solid State 54 1715–22
[9] Zajičkova L, Franta D and Nečas D 2011 Thin Solid Films 519 4299–308
[10] Stephan O, Taverna D and Kociak M. 2002 Phys. Rev. B. 66 155422
[11] Babaev V G, Guseva M B, Novikov N D and Khvostov V V 2006 Polymers: Synthesis, Properties, and Applications ed. F Cataldo (CRC Press) pp.219–52
[12] Kohn W 1999 Rev. Mod. Phys. 71 1253
[13] Perfetto E, Cini M, Ugenti S, Castrucci P, Scarselli M, De Crescenzi M, Rosei F and El Khakani M A 2007 Phys. Rev. B. 76 233408