EVALUATION OF DISORDER AND DETERMINATION OF MASS DENSITY OF ION-MODIFIED THIN CARBON FILMS BY XPS

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Abstract. In this work, thin carbon films were deposited on the surface of armco-iron using magnetron sputtering of a carbon target in an Ar+ working gas environment. Then the carbon films were implanted with argon and nitrogen ions. In order to clarify the content of differently hybridized (i.e., in different chemical states) carbon atoms in the deposited material, the method of analyzing the photoelectron energy loss spectra was used in this work. It is shown that the satellite structure of c1*s* spectra, when analyzed jointly with XPS of the c1*s* core level, confirms the formation of a disordered structure of the carbon film and allows one to determine the mass density of thin carbon films.

Keywords: *thin films, carbon, ion implantation, XPS, mass density*

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INTRODUCTION

Electron energy loss spectroscopy is one of the most informative methods for studying the electronic structure of carbon materials. In early works, for example [1], it was shown that the satellite structure accompanying the X-ray photoelectron (XRF) peak of C1s carries important information about the material. The π+σ plasmon loss peak of graphite at a distance of 27 eV from the main C1s peak was found to determine the mass density of graphite. Taking into account the relationship between the plasmon energy and the mass density of the material, it was determined that the density of fullerene is 2.03 g/cm^3, which is significantly different from the values previously obtained by X-ray structural methods [2]. A considerable number of works, including [3-5], have been devoted to the study of electron energy loss spectra. In a number of works, the values of the energies of the plasmon loss peaks Er in the spectra of carbon materials have been obtained. In particular, the position of the loss peaks for different forms of carbon (graphite, diamond, amorphous carbon, glass carbon) was determined [6, 7], and some of the experimental data were obtained by EELS (Electron energy loss spectroscopy) methods when bombarding surfaces with a monoenergetic electron flux. In the review paper [8] it is shown in detail that from the analysis of plasmon loss spectra it is possible to determine both mass and atomic density of carbon materials, in particular, thin films of amorphous carbon.

Significant information can be obtained from the analysis of the shape of core level photoelectron spectra, Auger electron spectra, and valence band spectra. In paper [9] back in 1977, the causes of XPS peak asymmetry were identified. In papers [10 – 13], the nature of O1 *s* , Si2 *p* -spectra broadening is discussed in detail, concluding that the main factors are phonon broadening, which leads to temperature-dependent symmetric Gaussian line broadening, and vibronic splitting of the excited state, first noted in [14], which leads to temperature-independent asymmetric line broadening. Since the charge density at the atom affects the binding energy of core level electrons, any changes in the chemical environment, including angular coordination and minor changes in interatomic distances, directly manifest in the XPS spectrum as chemical peak shifts [15, 16]. The composition, structure, and properties of carbon films have been the subject of numerous studies for many years (see, for example, [17, 18])

A feature of the XPS method is the minimal (3 – 5 nm) depth of the analyzed layer, determined by the electron mean free path in the material [19, 20], therefore this method can provide information about the uppermost layers of carbon films. Despite the long history of application, problems in interpreting XPS results, including problems in analyzing C1 *s* spectra and their satellites, remain [21] .

The influence of radiation defects on the electronic structure of materials according to X-ray photoelectron spectroscopy data is considered in works [22, 23]. The authors associate shifts in XPS spectra on the binding energy scale (E_b) with changes in the average degree of covalency of interatomic bonds and effective atomic charges, while broadening is associated with disorder of chemical and radiation nature. There are XPS studies of radiation damage in a number of natural orthosilicates, in particular, olivine, which report radiation-induced reduction of metallic iron [24, 25]. In general, the combined application of Raman spectroscopy and XPS spectroscopy methods for analyzing the atomic and electronic structure of radiation-damaged materials is promising.

In connection with the above, the purpose of this work is a qualitative assessment of disorder and determination of the mass density of ultrathin surface layers of magnetron sputtered carbon films based on XPS data before and after implantation of argon and nitrogen ions with energy of 30 keV at doses $D=10^{17}$ ion/cm ^{2} .

EXPERIMENTAL METHODOLOGY

Carbon films with a thickness of 30±4 nm were deposited on the surface of Armco iron by magnetron sputtering on a "Cathode-1M" installation in an argon environment at direct current [26, 27]. A graphite sheet with a thickness of 2 mm was used as a target. According to energy-dispersive microanalysis data obtained on a Quattro S electron microscope, the oxygen impurity concentration in the target was ~0.3 at.%.

To clean the substrate surface from adsorbed contaminants and ensure better adhesion of the deposited coating, the substrate temperature was maintained at 200°C. The film thickness was verified by atomic force microscopy (AFM) on a SOLVER 47 Pro probe microscope in contact mode using a CSG10 probe.

The obtained carbon films were subjected to bombardment with singly charged Ar^+ or N^+ ions with energy $E = 30$ keV and a dose of $D = 10^{17}$ ion/cm ^{2} in an ion implantation setup based on USU-4 with a pulsed ion source "PION-1M". Implantation was carried out in a pulse-periodic mode with pulse duration of 1 ms and pulse repetition frequency of 100 Hz. The ion flux density in the pulse was $3.086 \cdot 10^{12}$ ion/cm ^{2} . Ion implantation was performed normal to the surface. The studied carbon film samples were placed in the central part of the implantation spot, which ensured uniform ion flux density on the film. It should be noted that the projected range of nitrogen ions in carbon material significantly exceeds the thickness of the magnetron sputtered carbon film.

Studies of ultrathin (1-3 nm) surface layers of carbon films by XPS method were conducted on a SPECS electron spectrometer with a Phoibos-150 energy analyzer using non-monochromatized MgKα radiation ($h\nu$=1253.6 eV). The spectra were obtained at a constant analyzer pass energy of 15 eV using the Large Area lens mode. The analyzed surface area is a spot with a diameter of 5 mm, i.e., the results obtained refer to the average value over this area. The analysis depth is determined by the mean free path of electrons and for carbon materials can be up to several nanometers. XPS spectra were measured with a scanning step of 0.2 eV. The experimental spectra were processed using CasaXPS software.

RESULTS AND DISCUSSION

The mass density of known carbon forms using previously certified samples of static synthesis nanodiamond powders (SSND, particles of 100 nm) [28, 29] and highly oriented pyrolytic graphite (HOPG), used for calibration of scanning probe microscopes of the SOLVER type, was determined using a brief analytical expression [8] :

$$\rho = 0.00312 \cdot (\varepsilon_p)^2 \ . \qquad (1)$$

Here ε_p equals the distance from the $\pi+\sigma$ loss peak to the maximum of the main C1s peak (in electron volts, Fig. 1). From the XPS data (Fig. 2a), mass density values of 3.62 g/cm^3 (ε_p=34.05 eV) for NASB and 2.27 g/cm^3 (ε_p=27.0 eV) for HOPG were obtained. This showed satisfactory agreement of carbon materials mass density values determined by XPS method with known reference data [30, 31] (3.513 and 2.26 g/cm^3, respectively). The features of the NASB energy loss spectrum in the region of lower energy losses may be associated with the presence of a disturbed ultrathin surface layer of NASB particles formed during the powder production process, which contributes to the overall X-ray photoelectron spectrum.

Fig. 1. Photoelectron energy loss spectra: *1* – HOPG, *2* – NASB.

Subsequently, these methodological results were used to characterize thin ion-modified magnetron films on iron surface.

The results of XPS and Raman spectroscopy show that magnetron sputtered films are, firstly, highly disordered. This is evidenced by significant broadening with asymmetrization of the core XPS C1 *s* peak, with values of full width at half maximum (FWHM) indicated in parentheses (Fig. 2a), and broadening of the G and D peaks in the Raman spectra (Fig. 2b).

Fig. 2. XPS C1 *s* -spectra (a) and Raman spectra (b): *1* – HOPG; *2* – polycrystalline graphite (target); *3* – carbon film on iron; *4* – carbon film on iron after argon ion implantation; *5* – carbon film on iron after nitrogen ion implantation. FWHM values are indicated in parentheses.

Fig. 3. N1 *s* -spectrum of carbon film after nitrogen ion implantation.

Secondly, magnetron carbon films before ion bombardment have significantly lower mass density (average 1.98 g/cm^3) compared to the known density of bulk graphite (2.26 g/cm^3), the target of which was used for magnetron sputtering. Experimental density values were obtained based on data ε_p, determined relative to the maximum peak of the C1 *s* core level. The same technique later allowed showing changes in the mass density of magnetron-sputtered thin carbon film during pulsed irradiation with ions of different mass and chemical activity. It was determined that pulsed irradiation with argon at E = 30 keV causes further disordering of the thin carbon material film (broadening of C1 *s* peaks in Fig. 2a, spectrum 4) and further reduction of its average mass density (to 1.81 g/cm^3). Thus, the average mass density of the magnetron film decreased by 8%. When irradiated with nitrogen ions, the mass density of the carbon film decreases to a lesser extent (to 1.86 g/cm^3). From the XPS spectrum of N1 *s* , it is evident that the main proportion of nitrogen atoms (up to 89 at.%) is embedded in two non-equivalent positions in the carbon film structure (Fig. 3). A small portion of nitrogen (less than 10%) is incorporated into the film, apparently without replacing carbon atoms, for example, in interlayer spaces or pores. According to SRIM (Stopping and Range of Ions in Matter) software data [33], the proportion of elastically reflected nitrogen ions from the carbon film surface is 2.8% and does not play a significant role. The proportion of elastically reflected argon ions from the carbon material surface is even smaller and amounts to 0.08%.

Fig. 4. π+σ satellites of C1 *s* -spectra of HOPG sample (1), carbon film on Armco iron (2), carbon film subjected to argon ion implantation with $E = 30$ keV, D = 10^{17} ion/cm^2 (3), carbon film subjected to nitrogen ion implantation with $E = 30$ keV, D = 10^{17} ion/cm^2 (4).

Fig. 4 shows the π+σ satellites of C1 *s* spectra of the studied samples after subtracting the background component using the Shirley method [32]. Spectrum 1 corresponds to the π+σ satellite of the C1 *s* spectrum obtained from HOPG in the direction normal to the graphene plane. The π+σ satellite corresponds in its main parameters of energy loss (~27.15 eV) to the graphite satellite. The low-intensity line on the left at 35 – 36 eV can be attributed to carbon in areas with disturbed structure. The peak on the right is a satellite from the surface layer of carbon material, for example, interacting with adsorbed oxygen or nitrogen.

Spectrum 2 corresponds to the π+σ satellite of the C1 *s* spectrum of the magnetron carbon film. The carbon film obtained by magnetron sputtering is less dense. The energy loss ε_p =25.22 eV. The film base is disordered carbon with *sp* 2 hybridization.

Spectrum 3 is the π+σ satellite of the C1 *s* spectrum of the carbon film after irradiation with argon ions with $E = 30$ keV, D = 10^{17} ion/cm^2. The density of the graphite component decreases. The position of the peak maximum shifts slightly towards lower energy losses ε_p, and the film itself is inhomogeneous, as a clear component with ε_p near 33 eV appears in the loss spectrum, which can possibly be associated with the presence of regions with tetrahedral coordination of carbon atoms.

Spectrum 4 corresponds to the π+σ satellite of the C1 *s* spectrum of the carbon film after irradiation with nitrogen ions with $E = 30$ keV, D = 10^{17} ion/cm^2. The π+σ loss satellite is very similar to the satellite spectrum of the original magnetron film, but a slight increase in the density of the original film and traces of a component at $\varepsilon_p = 32$ eV can be noted.

The main difference between magnetron-sputtered and ion-modified thin carbon films is the absence of the shake-up satellite ($\varepsilon_p = 7$ eV) in the loss spectra.

CONCLUSION

Analysis of C1 *s* -spectra and π+σ loss spectra from the C1 *s* -peak allows to evaluate the disorder, homogeneity, and mass density of the magnetron carbon film.

It is shown that the magnetron sputtered thin (30±4 nm) carbon film is initially disordered with an average mass density lower than the density of the graphite target, and the implantation of argon and nitrogen ions leads to further disordering of the film. Bombardment with argon and nitrogen ions does not lead to a significant change in the average mass density of the "graphite" component of the magnetron sputtered carbon film. At the same time, bombardment with argon ions with an energy of 30 keV to a dose of 10^{17} ion/cm^2 leads to film heterogeneity in structure, which contains a fraction of tetrahedrally coordinated (diamond-like) carbon in regions with higher mass density. The main difference between magnetron sputtered and ion-modified thin carbon films is the absence of shake-up π-peaks ($\varepsilon_p = 7$ eV) in the loss spectra.

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CONFLICT OF INTERESTS

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

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