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Modification of X-ray excited photoelectron and C *KVV* Auger spectra during radiative carbonization of poly(vinylidene fluoride)

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Abstract

Modifications of the photoelectron and C *KVV* Auger spectra during the long-term surface degradation of partially crystalline PVDF under simultaneous soft X-ray and electron followed by ion irradiation are reported. Deep radiative carbonization brings about the formation of carbynoid structures (chain-like carbon) in the surface, while the number of interchain cross-links is insignificant. As a result, the shape of the electron emission spectra of carbon in the carbonized sample essentially differs from that of graphite and PVDF. The ion bombardment of the carbonized sample destroys one-dimensional structure due to the formation of cross-links. Thus, carbon atoms transit into sp^2-hybrid state and, therefore, the photoelectron and Auger spectra show features characteristic for microcrystalline graphite.
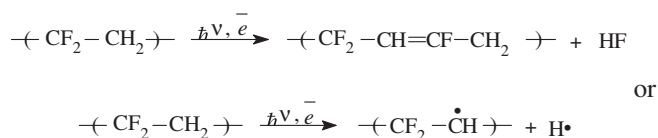
1. Introduction

One-dimensional carbon (carbyne) and carbynoid structures hold promise for a variety of technical applications, e.g. in optics, micro- and nanoelectronics, medicine and in some other branches of science and technology. The chemical dehydrohalogenation is a widely used method to synthesize carbynoid materials, starting from halogen-containing polymers [1]. Unfortunately, these materials are not chemically pure and structurally perfect one-dimensional carbon chains, but contain a lot of residual halogen and hydrogen atoms as well as oxygen, which appears due to side oxidation and substitution reactions. Because of high reactivity of carbon chains they form covalent cross-links during synthesis, thus producing two- and three-dimensional carbonaceous structures.

The effect of the surface degradation of poly(vinylidene fluoride) (PVDF) during its exposure to X-rays, ions, and electrons is quite well-known [2], though the detailed mechanism of this process is not fully understood yet. Mass spectra identify H_2, F, and HF as the elimination products, with no carbon-containing species being detected [3]. This means that the dehydrofluorination (DHF) of the sample surface occurs with the formation of carbon atoms whose valence state is different from that characteristic for pristine PVDF. Thus, the degradation process can be presented by simple schemes:

$$-(CF_2-CH_2)- \xrightarrow{\hbar\nu,\,\bar{e}} -(CF_2-CH=CF-CH_2)- + HF$$

or

$$-(CF_2-CH_2)- \xrightarrow{\hbar\nu,\,\bar{e}} -(CF_2-\overset{\bullet}{C}H)- + H\bullet$$

In the latter case, the formation of interchain cross-links is possible due to the recombination of polymeric carbon

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radicals:

$$-(-CF_2-\overset{\bullet}{C}H-CF-)- \quad + \quad -(-CF_2-\overset{\bullet}{C}H-CF-)- \quad \longrightarrow \quad \begin{array}{c} -(-CF_2-CH-CF-)- \\ | \\ -(-CF_2-CH-CF-)- \end{array}$$
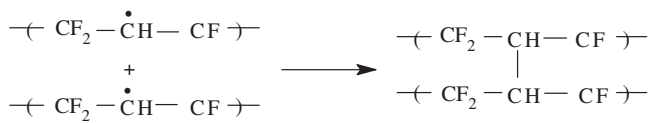
Morikawa et al. [3] analyzed photodegradation-induced changes in the photoemission spectra using ab initio molecular orbital calculations and found a high de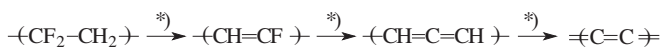gree of conjugation created in the degraded polymer due to the loss of fluorine atoms. Presumably, polyenes formed at low irradiation doses undergo further elimination at higher dose rates, evolving towards longer cumulene structures with the loss of hydrogen and fluorine.

$$-(-CF_2-CH_2-)- \xrightarrow{*)} -(-CH=CF-)- \xrightarrow{*)} -(-CH=C=CH-)- \xrightarrow{*)} =(-C=C-)=$$

*) depicts irradiation with photons, electrons, or ions.

The formation of double carbon–carbon bonds ($C=C$) in the polymer is confirmed by UPS [3], XPS [2,4] and IR-spectroscopy [4–6].

Modification of PVDF under high-energy heavy ion (Kr, $\sim 10^9$ ions/cm^2), X-ray and electron irradiation has also been studied by XPS [7]. Analyzing changes in the shape, intensity and energy position of C1s-line, the authors suggested a two-step mechanism for the polymer evolution after irradiation: (a) creation of allenes produced by DHF of the polymer backbone and (b) disappearance of the double bonds by addition of species (atoms or free radicals) generated under the beam. The desorption of hydrogen-fluoride molecules can be understood in the framework of the Manzel-Gomer-Redhead approach [8]. The (C–H) bond could be excited to an antibonding state (C–H)*. In the polymer backbone, hydrogen-like bonds exist between H and F atoms in certain configurations. The weakening of the (C–H) bond upon excitation could reinforce the (H–F) bond and in turn lead to the desorption of the HF molecules.

Le Moël et al. [9] studied electronic and structural modifications of PVDF under high-energy oxygen ion irradiation [10]. The authors performed a peak synthesis of C1s components based on up to 10 Gauss–Lorentz functions. The C1s core level spectra of the irradiated PVDF samples show a parallel reduction in –CF$_2$– and –CH$_2$– groups, which testifies to the elimination of the HF molecules and emergence of double $C=C$-bonds and allene or cumulene structures at higher doses [10].

Based on these findings, the radiative carbonization of PVDF can be considered as a new route of synthesizing one-dimensional carbon structures. Furthermore, one can anticipate evident application benefits in the future. The starting polymer not only exhibits piezoelectricity [11] but also pyroelectricity and ferroelectricity. Moreover, it possesses good mechanical flexibility [12], high chemical inertness [12] and excellent biocompatibility [13]. These properties of PVDF triggered further studies in a search for new applications. One of the latest developments is an application involving non-volatile ferroelectric random access memory (NVFRAM), since the ferroelectric properties of PVDF are considered to be suitable for such a device [14]. In this spirit, the surface modification of PVDF holds promise as a method for synthesizing new materials bearing a semiconducting layer on a dielectric substrate, which could exhibit a unique combination of properties.

The present paper reports on the studies of modifications of photoelectron and C *KVV* Auger spectra of partially crystalline PVDF during long-term degradation of its surface under soft X-ray and ion irradiation. One can expect the formation of nanoscaled carbon chains, graphite- or diamond-like clusters, or, most probably, a complex combination of different types of carbon valence states. The proportion of each of these phases can affect specific properties of the modified polymer surface, depending on the radiation dose. Thus, the determination of the valence states of carbon atoms and possibility to control their content by changing external conditions seems to be promising not only to study the degradation mechanism but in various practical aspects as well.

2. Experimental

2.1. Sample

The degradation experiment was performed using a partially crystalline film of PVDF Kynar (type 720, thickness 50 μM) produced by the extrusion method (Atofina, France). Compared to amorphous PVDF, the polymer chains in Kynar are much higher oriented. It is reasonable to assume in this case that the probability of crosslinking during the carbonization process should be appreciably lower. The reason for such an assumption is based on the fact of existence of large spaces (ca. 4.94 Å) between adjacent chains in crystalline PVDF. This value is sufficient to prevent an immediate collapse after the formation of "naked" fragments of one-dimensional carbon resulting from the DHF of PVDF.

The sample was exposed (ca. 7000 min) to X-ray radiation along with secondary electrons flux during XPS and C *KVV* measurements. Then partially carbonized PVDF film was exposed to an Ar$^+$ ion beam. To open the sample surface to ion flux, a box-like type of holder was replaced with a conventional one outside a vacuum chamber. Thus, carbonized film has been exposed to atmospheric air during ca. 1 h before ion irradiation. This operation has given opportunity for intermediate visual control of the sample after long-term exposure to soft X-rays and secondary electrons. Initially transparent and absolutely flat film has become non-uniformly brown and curved. The most intensively colored edge of the film has even rolled like a carpet and cracked perpendicularly to the roll axis close to the middle of it. Hence, the parts of the sample was installed in the conventional (open) holder keeping the previous orientation using an adhesive tape.

2.2. Technique

The spectra of electron emission were excited and measured using a home-made X-ray photoelectron spectrometer ES IFM [15] equipped with a coaxial magnetic analyzer and a non-monochromatic Al K_α (1486.6 eV) source. Apertures provide relative resolution value 7×10^{-3} which gives absolute value of ca. 2.2 eV for our spectra obtained with constant passing energy of 320 eV. Though the energy resolution in this case is relatively poor, the use of high passing energy allows one to speed up the spectra accumulation. This aspect proved to be crucial for reliable XPS and XAES monitoring of anticipated changes in the unstable surface of PVDF. The retarding voltage was applied to the sample holder, while the potential of a chamber of the energy analyzer was zero. This accelerated secondary electrons born in the aluminum filtering foil and the walls of a chamber, thus enhancing their role in degradation. The residual gases pressure was ca. 1.3×10^{-6} Pa.

Measurements included registration of the survey spectra in the 0–1270 eV binding energy interval, C1s (270–330 eV), F1s (670–730 eV), C KVV (1170–1270 eV) and valence electron spectra (0–45 eV). To minimize the effect of non-uniform electrostatic charging of the dielectric sample a specially designed box-like copper holder with two windows (one for X-rays and another one for emitting electrons) was used.

Ion irradiation was performed using unfocussed Ar^+ ions (1 keV) at a current of ~0.5 mcA to four consecutive doses: 0.2×10^{16}, 1.1×10^{16}, 3.9×10^{16} and 9.6×10^{16} ions/cm^2.

2.3. Fluorine content measurements

To measure fluorine content, a method based on the evaluation of yields of CF$_2$- and CF-groups in C1s-spectra was used. In fact, the position of C1s-peak for the former groups is shifted to 4.4–4.6 eV relative to the energy inherent in photoemission from carbon atoms having no chemical bonds with fluorine [2,16–18]. The yield from the latter groups is not directly observable [2,18]. It is natural to assume that a chemical shift is an almost additive factor, and one can expect their C1s-peak to be shifted close to 2.2–2.3 eV, as these groups contain only one fluorine atom. In both cases, the yield of the secondary shifts can be roughly considered to vary proportionally as well. Therefore, the experimental C1s-spectra were calculated as a sum of three model functions approximating these C1s-lines with maximum positions at 4.6, 2.3 and 0 eV, and a symmetrical and broad Gauss function centered at 9.4 eV to fit a background level on the side of higher binding energies. To subtract the yield of C1s-electrons excited by Al$K_{\alpha 3,4}$-photons, the correction of spectra was performed first. The dominant peak position for each C1s-spectrum was assumed as a zero point for binding energy. The shapes of C1s-peak of poly(ethylene) and F1s-peak of PVDF

proved to be absolutely identical for passing energy of 320 eV and were used to plot the model peaks. An example of this fitting is shown in the inset of Fig. 1. During the fitting, only heights of all peaks could vary, while the positions and widths were strictly fixed. This technique allows one to measure a relative content of CF$_2$- (X_1) and CF-groups (X_2) independently as a ratio of the area of the corresponding model peak to the total area of three model peaks (this area is proportional to the total number of carbon atoms involved in photoemission). Their variation under AlK_α X-rays exposure is also shown in Fig. 1.

The suggested technique allows one to measure relative concentration of fluorine only from the analysis of C1s spectra, whereas in standard routine the intensities of C1s, F1s and F2s photoelectrons must be measured separately. Kinetic energies of these groups of electrons are essentially different and, therefore, an account of their various attenuation lengths in a substance and, accordingly, various thickness of an analyzed layer of a surface is necessary. Furthermore, for the standard treatment it is necessary to know passing function of the spectrometer. Usually, its exact determination is a special and complicated problem.

There exists one more effect which makes the use of a conventional measurement of fluorine content quite dubious in our case. With increasing time of the PVDF carbonization, the density gradient directed in the depth of a sample appears and rises because the outer layers of the film absorb more secondary electrons and photons and, accordingly, eliminate more fluorine and hydrogen atoms. When evaluating fluorine content from the normalized intensities of the F2s and F1s photoelectrons, we usually assumed ratios of attenuation lengths for F2s, F1s and C1s photoelectrons to be different but constant. Actually, due to inhomogeneous modification of the sample density, the
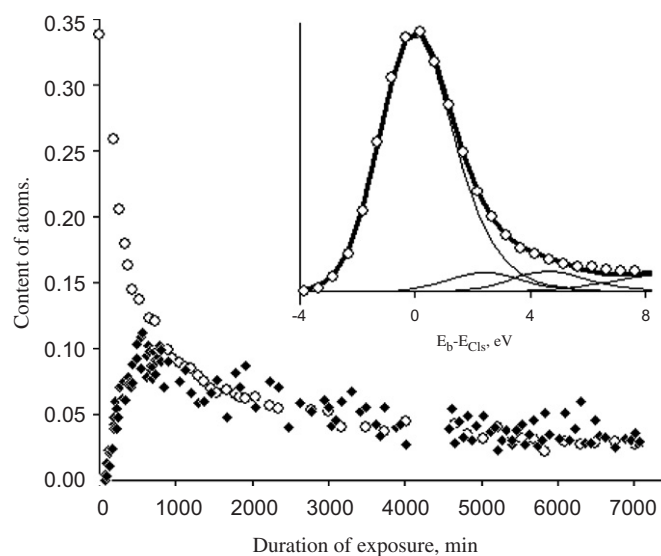

Fig. 1. Variation of content of CF$_2$- (○)and CF-groups (◆) vs. exposure time. An example of experimental C1s line deconvolution for separate determination of X_1 and X_2 is illustrated in the inset.

ratios F2s/C1s and F1s/C1s can vary with different rates. The F1s electrons possess lower kinetic energy (compared to F2s), and they are emitted from the near-surface polymer layer, which has lower density because of the degradation-induced gradient. Thus, the attenuation lengths of F1s electrons and their total yields can increase faster than those of F2s electrons during the irradiation. Furthermore, the attenuation lengths of C1s electrons elevates with intermediate rate. The latter effect leads to the overestimation for the value of the fluorine content measured from the F1s/C1s ratio and underestimation for that determined from the F2s/C1s ratio. These deviations are expected to increase with the duration of exposure. Fig. 2 shows the decline in the fluorine content in the course of XPS experiment determined using three different routines, thus evidently confirming the above considerations. Conventional measurements of the fluorine content using F1s/C1s and F2s/C1s ratios were performed as described previously [18].

3. Results and discussion

Fig. 2 shows the variation of the fluorine content plotted vs. duration of measurements determined by treatment of XPS spectra for different groups of electrons. The high elimination rate of fluorine atoms within first 1000 min can be explained when assuming that the dominating process at this stage of DHF is the formation of fluorine-substituted polyene chains corresponding to the decay of CF_2- and creation CF-groups (Fig. 1, first 1000 min). The evolution of these dependences upon irradiation is characterized by evident saturation at higher doses. We explain this fact by very low concentration of CF-groups and the formation of longer cumulene structures.

Previously, we have analyzed relative intensities of C *KVV* spectra of PVDF [17]. Our new data have confirmed the decrease of this parameter with the loss of fluorine atoms (Fig. 3) and can be explained by the sensitivity of the Auger spectra to the local hybridization of carbon atoms [19]. Thus, this effect can be considered as an indirect evidence for the modification of the carbon hybrid state [18] caused by DHF. The saturation of this dependence at lower content of fluorine corresponding to a longer time of exposure is presumably caused by the effects of the density gradient along with the low rate of DHF discussed above.

The direction of rolling (upwards to the X-ray source) of the most deeply carbonized edge of the sample is the most evident confirmation of the shortening of carbon–carbon bonds due to DHF of PVDF surface. This effect should occur in both cases: due to $CF_2 \rightarrow CF$ and $CF \rightarrow C^*$ transformations. The latter process could lead to the creation of chain-like carbon. However, one can expect not only the formation of nanoscaled chains, but also graphite-like clusters, or, most probably, a complicated combination of different carbonaceous phases. Although the formation of diamond-like carbon is not consistent with both the bond shortening and the variation of C *KVV* spectra, one cannot exclude it as a minor process that could occur due to extensive cross-linking of carbynoid fragments [20].

To elucidate the dominating nature of the species in the modified PVDF surface, the ion bombardment of the carbonized sample was carried out after 7000 min of X-ray irradiation. Since the sample has been exposed to atmospheric air prior to the ion irradiation, the first survey spectra obtained just after inserting it back into the chamber showed an increase in the oxygen content up to 9%. Possible chemical shifts due to covalent bonding between oxygen and carbon prevent determination of the fluorine content solely from the C1s line shape. Therefore, the content of fluorine and its variation in the sample surface due to ion irradiation has been measured from F1s/C1s and F2s/C1s ratios. These decreased with different
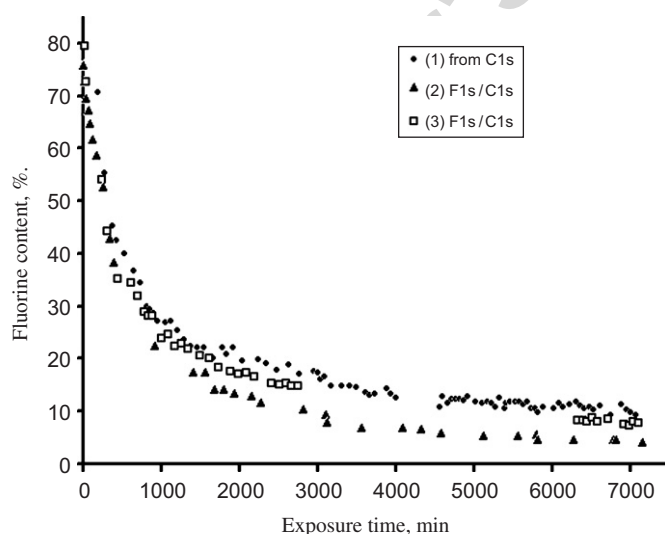

Fig. 2. Variation of the fluorine content in the PVDF surface vs. duration of X-ray and secondary electrons exposure measured by the treatment of XPS spectra for different groups of electrons.
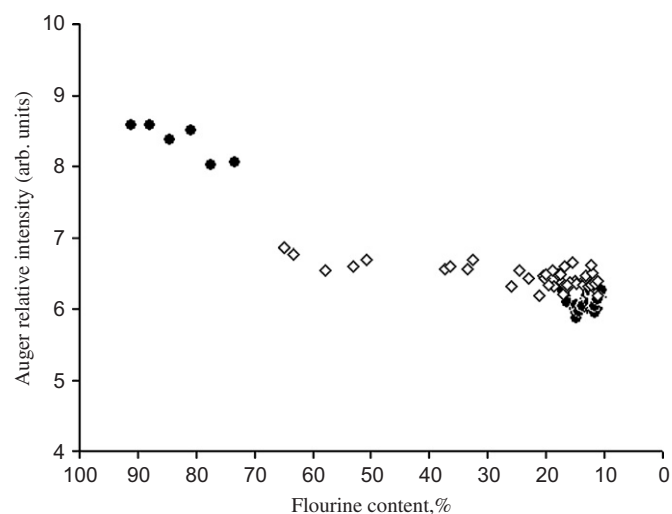

Fig. 3. Modification of relative intensity of C *KVV* Auger spectra vs. content of fluorine atoms in a sample. The data of two independent experiments are presented.

rates showing decrement of the fluorine content from 5% down to 3% (F1s/C1s) and from 6% down to 5% (F2s/C1s) with the dose increasing from 0.2×10^{16} to 9.6×10^{16} ions/cm^2, thus indicating the fluorine concentration profile increasing with depth. The ion bombardment did not significantly affect the relative intensity and the shape of the valence band photoemission spectra, while the C KVV and C1s spectra were noticeably changed.

Fig. 4 shows first derivatives of the Auger spectra normalized to the height of the main maximum. The alignment procedure was performed according to Speranza et al. [21]: all spectra were shifted along the binding energy scale to the position of a feature separating the most intensive part of the spectrum from its right shoulder (shown by a vertical line).

Considering the derivative spectra as the most familiar form of presentation, one can see that none of these spectra reveal the line-shape that one would call completely "graphitic". It can be seen from the spectra that the ion bombardment results in the shift of the major positive maximum towards lower binding energies. Moreover, the main peak becomes broader: its half-height width increases (cf. Fig. 5), which makes the spectrum looking more similar to that of highly oriented pyrolytic graphite (HOPG).

The spectra of core-level carbon electrons after the ion bombardment show appearance of a feature in the 5–10 eV energy interval, characteristic for carbon in sp^2-hybrid phase and corresponding to $\pi \rightarrow \pi^*$ interband transition; its intensity increases with increasing dose (Fig. 6). This effect can be explained by changes in the band-to-band transition spectrum due to the decrease in the band-gap width and modification of a combined density of states. Furthermore, with increasing irradiation dose, the wide satellite of energy losses ($\pi + \sigma$ plasmon) shifts to higher binding energy in
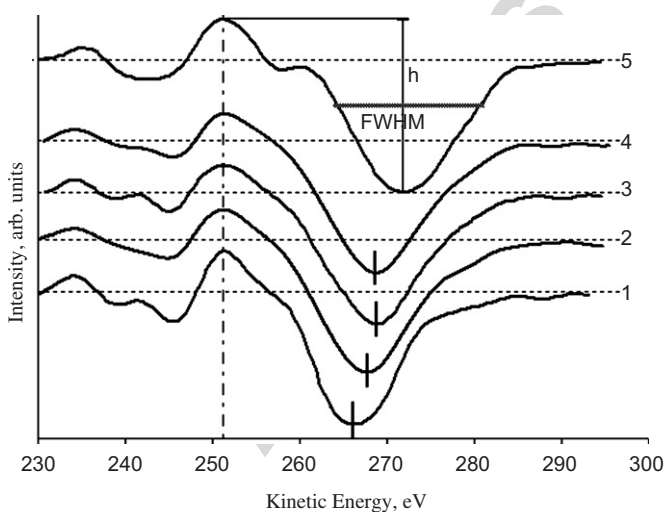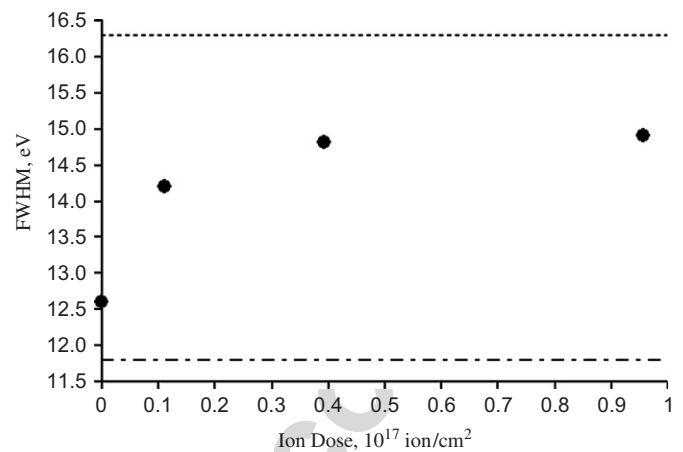

Fig. 5. Variation of the half-height width of the main peak in the C KVV derivative spectra vs. the dose of the ion bombardment. The dotted line shows the same parameter for HOPG, and the dot-and-dash line corresponds to the starting PVDF.
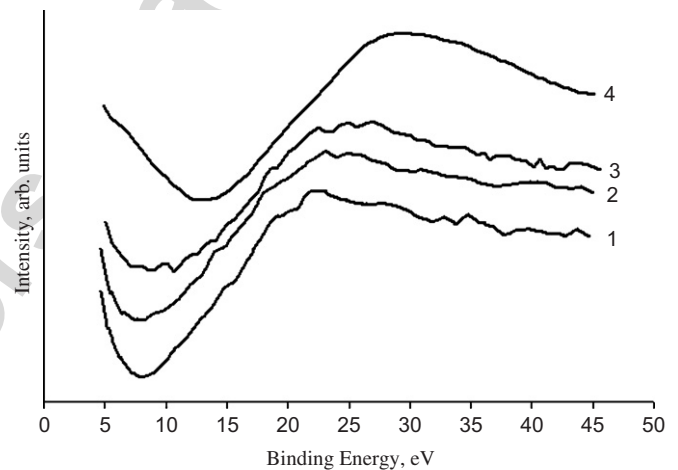

Fig. 6. Modification in the intensity of the C1s satellite vs. ion irradiation dose of partially carbonized PVDF: (1) after X-ray irradiation for ca. 7000 min; (2) after ion bombardment with a dose of 2×10^{15} ions/cm^2; (3) after a dose of 9.6×10^{16} ions/cm^2; (4) the satellite spectrum of HOPG. The spectra were normalized relative to the satellite maximum.

agreement with observations by Kudryavtsev et al. [22]. These facts, apparently, testify to the formation of interchain cross-links resulting in the transition of carbon atoms from sp- to sp^2-hybrid state.

4. Conclusions

The measurements of the photoelectron and Auger spectra have for the first time been carried out during long-term (7000 min) degradation of the surface of partially crystalline PVDF under soft X-ray radiation ($hv = 1486.6$ eV) along with secondary electrons. The results of the present study give a strong evidence for the formation of sp-hybridized carbon chains in the surface of PVDF during long-term radiative carbonization. The latter has been shown to bring about the formation of carbynoid structures in the surface, while the number of interchain

Fig. 4. Modification of first derivatives of the C KVV spectra of PVDF: (1) after X-ray irradiation for ca. 7000 min; (2–4) after ion bombardment with doses increasing from 0.2×10^{16} to 9.6×10^{16} ions/cm^2; (5) first derivative of the C KVV spectrum of HOPG. Horizontal dashed lines show a zero intensity level for each spectrum. FWHM, full width at half maximum.

crosslinks has been found to be insignificant. As a result the shape of the electron emission spectra of carbon in a carbonized sample essentially differs from that of graphite and original PVDF. The ion bombardment of the carbonized sample has been shown to destroy one-dimensional structure due to the formation of interchain crosslinks. The crosslinking causes the transition of carbon atoms into sp^2-hybrid state, and, therefore, the photoelectron and Auger spectra reveal features characteristic for graphitic carbon.

It has been mentioned in Section 1 that the surface modification of PVDF can become a promising method for synthesizing layered semiconductor–insulator materials. One can expect such materials to reveal unique electronic properties. Finally, the deposition of the PVDF layer onto various carbon substrates (e.g., diamond, graphite, glassy carbon) followed by its controlled carbonization could open up promising ways towards the creation of new hetero-structures for carbon-based electronics called C-tronics, and the present study is one of the first steps in this way.

Acknowledgments

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