

FORMATION OF sp^2 -BONDS IN PARTIALLY CARBONIZED POLY(VINYLDENE FLUORIDE) FILMS BOMBARDED WITH Ar^+ IONS

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Introduction

Studies of chemical dehydrohalogenation of halogen-containing polymers are tightly connected with a problem of synthesis of carbyne [1]. This carbon allotrope is expected to manifest very unusual properties and to have a number of prospective applications. Unfortunately, extreme instability of carbyne structure does not allow produce perfect crystals. Instead only amorphous films with an appreciable content of non-carbon atoms are available. The dehydrohalogenation starts with a surface of the polymer film and is not complete even when the reaction is performed for prolonged periods of time. The structure of these samples changes with ageing. Hence, their properties depend on time of storage. One of the most probable mechanisms of both amorphization in the course of the synthesis and ageing effects is the formation of crosslinks between adjacent carbynoid chains. Our aim was to deliberately create them in the partially dehydrohalogenated polymer film by means of Ar^+ ion bombardment. As the crosslinking was expected to change hybridization of carbon atoms, we decided to employ XPS and XAES techniques, which are sensitive to the mode of valence orbitals superposition [2].

Experimental

The starting film was cast from a solution of poly(vinylidene fluoride) (PVDF) in N,N-dimethylformamide (DMF). The film was dehydrofluorinated by treating with a mixture of saturated (20%) KOH solution in ethanol with tetrahydrofuran (THF) in a 2:3 volume ratio at room temperature for 16 hours. The details of XPS and XAES measurements have been reported elsewhere [3]. The ion current during the Ar^+ -bombardment (20 μA) and the irradiated area of the specimen (10 mm^2)

correspond to the dose rate of $4 \cdot 10^{17}$ ions/ cm^2 per an hour. The ion energy was 1200 eV. The survey spectra of the pristine film and its modified surface were recorded after each 5 min of bombardment. The detailed study included registration of multi-scan emission spectra of valence, core, and Auger electrons. It has been conducted after 15, 30 and 45 min of bombardment, i.e. at doses ca. 10^{17} , $2 \cdot 10^{17}$ and $3 \cdot 10^{17}$ ions/ cm^2 . The whole series of measurements was accomplished within 3 days, and the sample was kept inside a vacuum chamber throughout that period. During the XPS/XAES measurements the residual gas pressure did not exceed 1 μPa , but it was not maintained strictly constant and rose up to 30 μPa over night hours, when a vacuum pump was off. During the ion irradiation the argon pressure was 50 mPa.

Results and discussion

The survey scan spectra have been recorded in order to study chemical composition of a pristine film surface and its modification caused by the ion bombardment. The dominant element was carbon. There were also fluorine, oxygen and a minor amount of nitrogen. Characteristic spectral lines of argon only were visible after the heaviest bombardment dose. To calculate contents of carbon, oxygen and fluorine their core 1s-lines were used. It was done mostly by a standard routine, taking into account an individual photoemission cross-section and a spectrometer passing function. The only peculiarity was concerned with the determination of integral intensity. In order to exclude usual ambiguity arising from the way of background subtracting and selecting the integration interval, we confined the latter by the region of binding energies from the spectra threshold to a maximum intensity (an "elastic" half of the core line). This is exemplified for C1s-line in Fig. 1 (I_1). As this interval is small enough, one has not to know an exact shape of the background. Instead, only the value of the threshold intensity should be subtracted. On the other hand, this restriction allows one to account

for only electrons that escape from the sample practically without energy losses. The character of inelastic scattering does not considerably differ when going from one element to another, if kinetic energies of their photoelectrons are of the same order of magnitude. Indeed, this is just the case. Hence, we believe our estimation to be close to the real content of the elements detected on the surface. The dose dependence of the content of fluorine (red) and oxygen (blue) is presented in Fig. 2. It shows an evident decrease in the number of fluorine and oxygen atoms. This decrease is sharp when the dose is small ($<1 \cdot 10^{17}$ ions/cm²) and becomes smoother at higher doses. The deviation of the points corresponding to the doses of 1 and $3 \cdot 10^{17}$ ions/cm² is unlikely to characterize an experimental error but rather changes in the surface composition during prolonged studies. These changes apparently arise due to complicated processes caused by two competing effects: the diffusion of fluorine from the bulk and the surface desorption when the pressure of residual gases (N₂, O₂, H₂O) is not constant.

We determined several parameters of electron emission spectra to monitor changes in the hybridization mode of carbon atoms. The energy interval Δ between the intensity maxima of a C1s-line itself and its high-binding energy satellite (Fig. 1) was found to suddenly be shifted towards the value typical of graphite in a 10^{17} to $2 \cdot 10^{17}$ ions/cm² dose range. This effect is shown in Fig. 3. The height of vertical bars corresponds to double standard deviation. In most cases the last value is large since the satellites are broad and their maxima are very poorly shaped. Nevertheless, this fact is obvious and has been a basis to declare the transformation of polymeric chains into a new state with a considerable amount of graphite-like (sp^2) bonds [3]. Unfortunately, this interpretation cannot be comprehensive because the effect observed may reflect the transition of some part of sp -bonded atoms into the sp^3 -state as well [4].

The latter possibility is denied, however, by the measurements of parameter $F=a/b$ (see Fig. 1). Its value has been determined after subtracting a linear yield of secondary electrons as the ratio of the inelastic background intensity in the region just behind a high-energy threshold of the CKVV-band to the maximum intensity of the latter. This ratio rises monotonously with the irradiation dose (Table 1). This effect neither can unambiguously define the route of the hybridization transition. The F -value of carbon allotropes was reported to increase in the following order: diamond – carbyne – graphite [2]. Thus the course of its dose dependence allows one to exclude the $sp \rightarrow sp^3$ process, but can testify to $sp^3 \rightarrow sp$ (probably, through an intermediate sp^2 -state) and/or $sp \rightarrow sp^2$ ones. We suppose them to dominate at

different stages of bombardment. The first process is more likely at low doses when the sample contains considerable proportion of sp^3 -bonded carbon atoms typical of pristine PVDF. The characteristic shape of the C1s-line observed earlier in non-irradiated film [3] shows a significant amount of carbon atoms chemically bonded with fluorine. The second process certainly occurs at higher doses, when more atoms in the chains have only carbon neighbors. In heavily irradiated film the crosslinking of adjacent chains takes place, thus resulting in the formation of sp^2 -bonds. This interpretation is consistent with a shift of the main feature of the first derivative of XAES upon irradiation [2]. To avoid an error in energy determination due to charging of the surface, the position of this feature (E_A) has been measured relative to the C1s-maximum (E_C). These data ($E_A - E_C$) are also presented in Table 1.

Another evidence of the change in the hybridization state is provided by parameter $S=I_2/I_1$ (see Fig. 1 and Table 1). The S value is known to increase in a sequence: carbyne – graphite – diamond [2]. During the irradiation of the sample up to a dose of $2 \cdot 10^{17}$ ions/cm² the parameter S decreased. At the heaviest dose it increased but did not reach its original value. Such behavior of S suggests two simultaneous but competing processes to occur, viz., $sp^3 \rightarrow sp^2 \rightarrow sp$ transitions due to elimination of fluorine, hydrogen, and oxygen, and the $sp \rightarrow sp^2$ modification associated with irradiation-induced crosslinking. The contribution of these effects significantly differs at different stages of irradiation. The first transition predominates at high rates of elimination of non-carbon atoms, i.e. at small cumulative doses (see Fig. 2). At higher doses this process subsides and becomes minor as the content of heteroatoms becomes low and almost constant (Fig. 2). The second process can be observed as an increase in parameter S . On the other hand, the second effect is expected to be weak at the first stage ($<1 \cdot 10^{17}$ ions/cm²) because the content of sp -bonds is small, but gets stronger at higher doses.

The most reliable evidence of the formation of sp^2 -bonds is provided by the analysis of XPS in a narrow energy interval in the proximity of the C1s-line (5 to 15 eV higher than E_C , Fig. 4). The spectra have been normalized using the integral intensity within an energy range between a threshold of the main peak and $E_C + 45$ eV (after subtraction of a constant component of the background, see Fig. 1). The minimum intensity value between C1s-line itself and its broad low-energy satellite monotonously rises with increasing the dose, thus suggesting an increased contribution of $\pi \rightarrow \pi^*$ transitions characteristic of sp^2 -bonded carbons and hydrocarbons. Not only the position of its maximum but also an entire shape of the satellite becomes similar to that of polycrystalline graphite upon heavy irradiation (Fig. 4).

The irradiation-induced structural changes in the film surface restrict the depth of the Ar⁺ implantation, where XPS lines of argon would become observable. This is a direct indication of hardening of the superficial layer. Finally, this modification results in the alteration of color of the film: a sharp border between shining black unexposed and pale grayish irradiated areas of the film were clearly observed.

Conclusions

The XPS and XAES analyses provide evidence for the significant modification of the hybridization mode of carbon atoms on the surface of partially dehydrofluorinated poly(vinylidene fluoride) films upon irradiating with Ar⁺ ions up to doses of 10¹⁷, 2·10¹⁷ and 3·10¹⁷ ions/cm². The main feature of this process is the formation of a significant amount of sp²-bonds. The effect revealed occurs as two steps. If the dose does not exceed 10¹⁷ ions/cm² the dominant process is the elimination or desorption of fluorine, hydrogen and oxygen-containing species from the film surface resulting in its further carbonization. This causes progressive sp³→sp² and sp²→sp¹ transformations of carbon atoms. At higher doses the

rate of surface purification becomes low and the irradiation-induced cross-linking of neighboring carbyne-like chains plays a significant role in the carbon hybrid transformation from sp¹ to sp².

References

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Table 1. Parameters of XPS and XAES spectra of the film surface exposed to different doses of the ion irradiation

Dose, 10 ¹⁷ ions/cm ²	0	1	2	3
<i>F</i> , arb. units	0.61	0.69	0.71	0.72
<i>E_A-E_C</i> , eV	934.7	935.6	933.9	932.5
<i>S</i> , arb. units	6.2	4.6	3.8	5.0

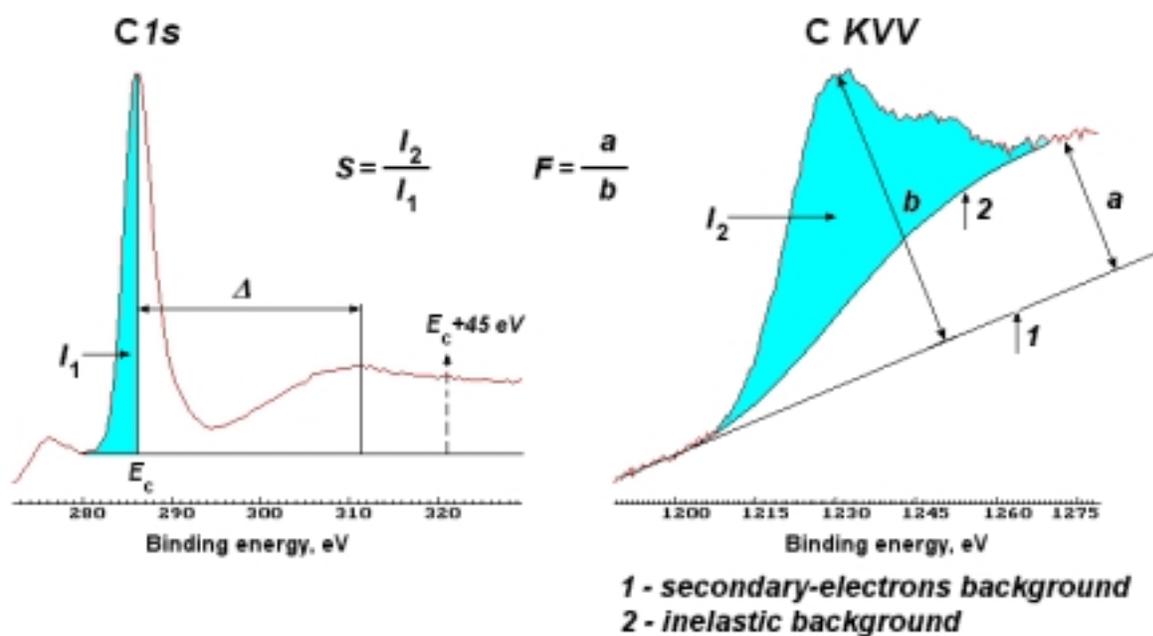


Figure 1. Schematic for the definition of spectral parameters.

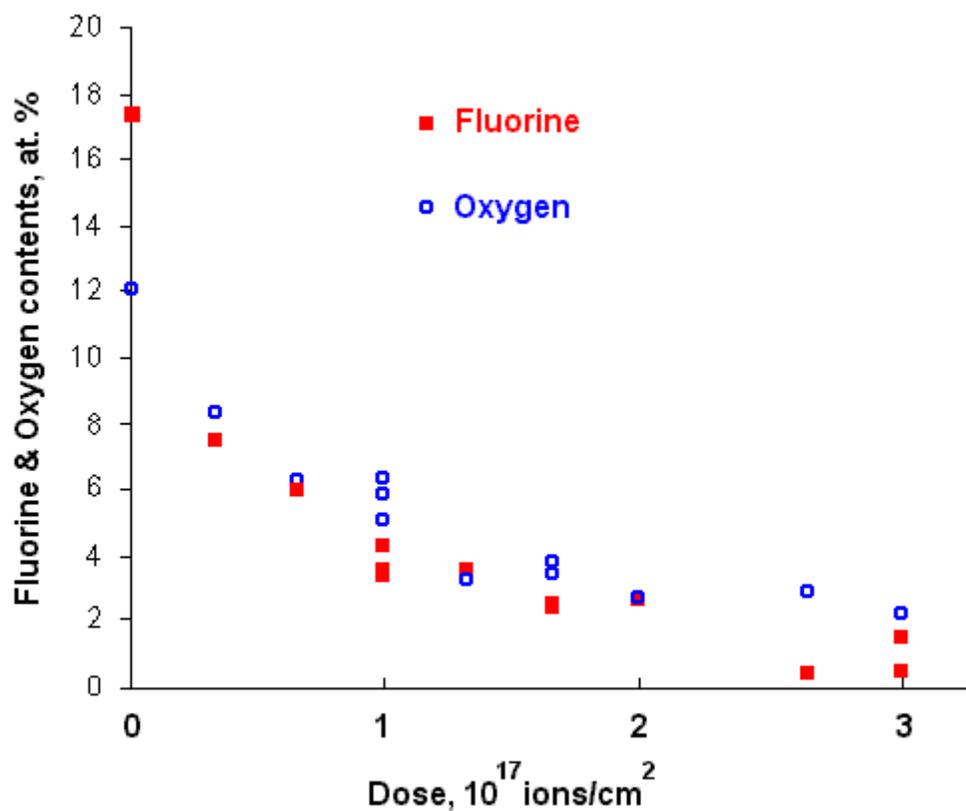


Figure 2. Dependence of fluorine and oxygen contents in the surface layer on the irradiation dose.

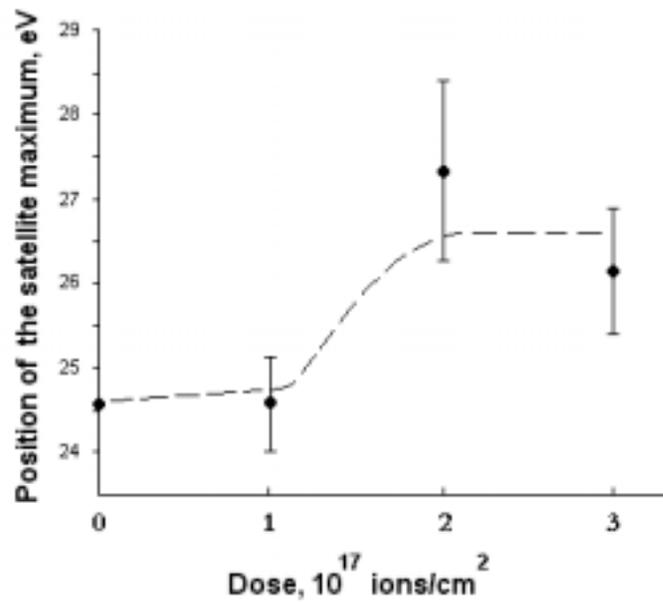


Figure 3. Position of the satellite maximum (relative to the C1s-line maximum) vs. irradiation dose.

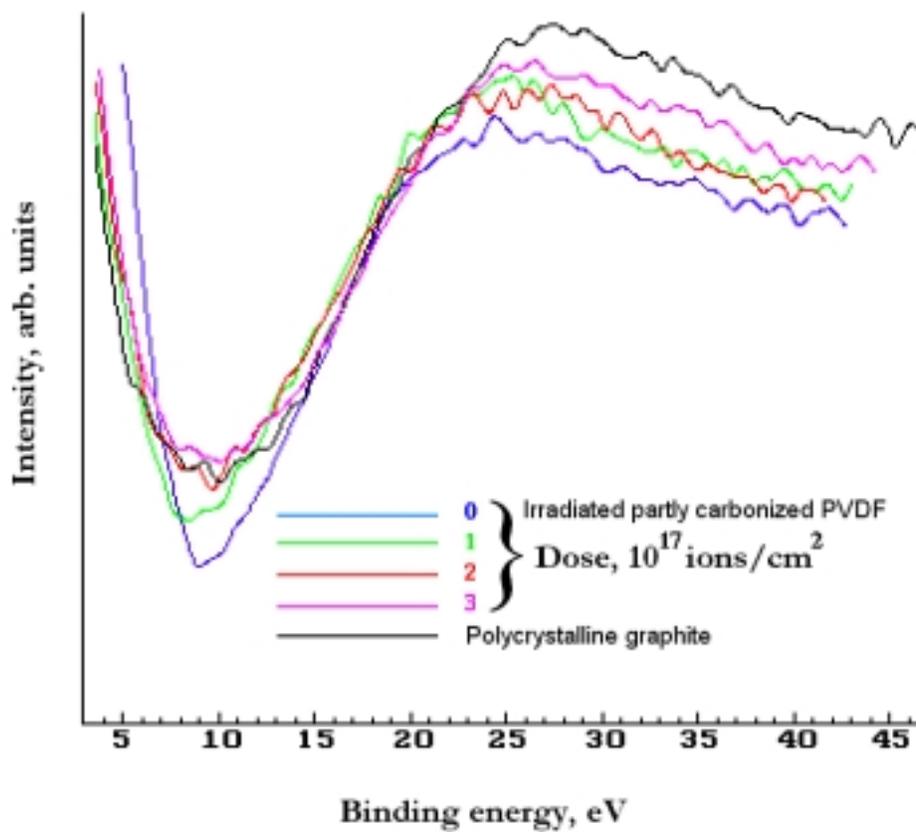


Figure 4. C1s-line satellites in the spectra of partially carbonized PVDF films recorded after various doses of the ion irradiation.