X-ray photoelectron study of Si\(^+\) ion implanted polymers

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Abstract. X-ray photoelectron spectroscopy was used to characterize different polymer materials implanted with low energy Si\(^+\) ions (E=30 keV, D= 1.10\(^{17}\) cm\(^{-2}\)). Two kinds of polymers were studied – ultra-high-molecular-weight poly-ethylene (UHMWPE), and poly-methyl-methacrylate (PMMA). The non-implanted polymer materials show the expected variety of chemical bonds: carbon-carbon, carbon being three- and fourfold coordinated, and carbon-oxygen in the case of PMMA samples. The X-ray photoelectron and Raman spectra show that Si\(^+\) ion implantation leads to the introduction of additional disorder in the polymer material. The X-ray photoelectron spectra of the implanted polymers show that, in addition to already mentioned bonds, silicon creates new bonds with the host elements – Si-C and Si-O, together with additional Si dangling bonds as revealed by the valence band study of the implanted polymer materials.

1. Introduction

Polymers ultra-high-molecular weight poly-ethylene (UHMWPE) and poly-methyl-methacrylate (PMMA) find various applications. They are currently used extensively because of their structural and material properties and are especially attractive lately for their electronic properties [1]. Technologies of modifying polymer material properties by a beam of energetic ions (ion beam implantation) have found wide applications in different areas from microelectronics to medicine [2-4]. The possibilities for various application purposes of different polymer materials are essentially defined by the type and amount of the implanted ions, which often substantially modify their mechanical, optical and electrical properties [5,6]. Particularly attractive, from both fundamental view and applications related implications, are the interesting photo-luminescent properties of these materials induced by low energy Si\(^+\) ion beam implantation [7,8]. The underlying Si\(^+\) ion beam induced structural properties modifications, defining the optical changes and related photo-luminescent properties, are also of particular interest with view of further photo-luminescence enhancement and optimization.

In this paper, X-ray photoelectron spectroscopy (XPS) methods, combined with Raman spectroscopy measurements, have been used to characterize the Si\(^+\) ion beam induced structural properties modifications of the polymer materials studied.
2. Experimental
Poly(methyl-methacrylate) (PMMA) and ultrahigh-molecular-weight polyethylene (UHMWPE) samples, commercially available in the form of bulk samples with thicknesses of 2 mm and shaped as squares (sides of 10 mm) and circles (diameters of 10 mm), were studied in the present work.

A Danfysik 1090 ion implanter was used for the Si⁺ implantation at room temperature (RT). The implantation was carried out at relatively low energies (E = 30 ÷ 50 keV) and a wide range of ion doses (D = 10¹³ ÷ 10¹⁷ cm⁻²). The beam current was kept under 2 µA/cm² during the implantation process, so that to maintain the target temperature below 80°C – the temperature at which the polymer material starts to decompose. A high vacuum (of the order of 10⁻⁶ Pa) was maintained in the target chamber during implantation.

The XPS studies were carried out on an ESCALAB MK II (VG Scientific) electron spectrometer with base pressure in the preparation and analysis chambers of 2×10⁻⁸ Pa and 1×10⁻⁸ Pa, respectively. The photoelectrons were excited using X-ray source Mg Kα (hv=1256.6 eV). The surface sensitivity was estimated as ~ 10 monolayers. A strip of gold, deposited on the surface of the sample, was used as a binding energy (BE) reference. The BE of Au 4f⁷/₂ was assumed to be 83.8 eV. This allowed a determination of the binding energies of the C 1s, O 1s, Si 2p and Si 2s peaks with an accuracy of ±0.1 eV. The depth profiling was carried out by sputter etching at 90° using a defocused Ar⁺ ion beam of 3 keV energy and a current density of 16 µA.cm⁻².

The room temperature infrared (IR) transmittance spectra were measured in the range 500 to 2000 cm⁻¹, using a UR-20 double-beam spectrometer. The Raman spectra were taken at room temperature using a SPEX 1403 spectrometer equipped with a photomultiplier working in a photon counting mode and a spectral resolution of 4 cm⁻¹. The 488 nm Ar⁺ laser line was with a power as low as 10 mW because the thermal stability of the PMMA was only 65°C.

3. Results and discussion

3.1. X-ray photoelectron spectra

The XPS spectra of Si2p for UHMWPE are presented in Figure 1. For the unimplanted UHMWPE (Figure 1a) no significant peaks are revealed in the spectra recorded on the surface and in depth after different intervals of argon ion sputtering.

Figure 1b shows Si2p spectra of the implanted UHMWPE. Pronounced peak at 100.3 eV characteristic of Si-C bonds in C₂H₄/Si groups [9] is visible in the spectra. Maximum amplitude of that peak is found in the second line recorded after 120 min Ar ion sputtering meaning that the maximum concentration of Si ions is at some depth where they have lost their energy. After 180 min sputtering the peak is centered at 101.2 eV characteristic of silicon atoms in Si-C groups [10] due to implanted Si⁺ ions bonded to the backbone of the polymer.
In Figure 2 the XPS spectra of C1s are presented for UHMWPE. Figure 2a shows C1s spectra of unimplanted UHMWPE. At the surface a large peak at 285.4 eV is visible characteristic of C atom in -CH2- groups [11] associated with a bend at 288.0 eV due to C atom in -C(O)O groups [11] which are possibly formed by oxidation. In depth the sample position of the peak shifts to lower binding energies (284.0 eV) characteristic of (-C6H2(CH3)2O-)n groups [12].

Figure 2b shows C1s spectra of implanted UHMWPE. At the surface a large peak at 285.0 eV is visible characteristic of C atom in -C(O)O groups [11] which are possibly formed by oxidation. In depth the position of the peak shifts to lower binding energies (283.9 eV) typical of silicon carbide [14].

The XPS spectra of O1s for UHMWPE are presented in Figure 3. In Figure 3a the O1s spectra of unimplanted UHMWPE are shown. The peak at the surface is centered at 532.5 eV characteristic of (-CH2)4O-)n groups [13]. This peak diminishes in the bulk of the sample showing surface oxidation.

Figure 3b shows O1s spectra of implanted UHMWPE. The peak recorded from the surface is centered at 533.0 eV characteristic of (-(CH2)4O-)n groups [13]. This peak due to surface oxidation diminishes after 120 min Ar+ sputtering. At depth reached after 180 min a new peak at 532.2 eV appears showing (-Si(CH3)2-C6H4-Si(CH3)2-O-)n groups [15]. In depth these bonds almost coincide with the maximum amplitude of Si peak in depth (Figure 1b).

The XPS spectra of Si2p for PMMA are presented in Figure 4. No significant peaks are revealed in the spectra recorded at the surface and in depth for the unimplanted PMMA (Fig.4a). Figure 4b shows Si2p spectra of implanted PMMA. No peak is visible in a line recorded at the surface. After 60 min sputtering a large peak at 108 eV dominates. This peak is Si2p satellite at 108.4 eV [16] due to (-Si(CH3)2-C6H4-Si(CH3)2-O-)n, -(Si(CH3)2-O-)n groups. In depth the sample recorded peaks are centered around 101.9 eV, due to (Si(CH3)2-C6H4-Si(CH3)2-O-)n groups [16]. The peak at 104.7 eV is due to silicon oxide [17].
In Figure 5 the XPS spectra of C1s are presented for PMMA. Figure 5a shows C1s spectra of unimplanted PMMA. In the line recorded at the surface the C1s peak at 285.00 eV [15] is characteristic of CH2C(CH3)(C(O)OCH2CH2CH3)\textsubscript{n} groups while the bend at 290.35 eV is due to ((-CH2CH2-)\textsubscript{x})-CH2CH2OC(O)O-)\textsubscript{n} groups [10]. In depth of the sample the position of the peak shifts to lower binding energies (284.1 eV) characteristic of (-C\textsubscript{6}H\textsubscript{2}(CH\textsubscript{3})2O-)\textsubscript{n} groups [12].

Figure 5b shows C1s spectra of implanted PMMA. The C1s peak recorded at the surface and centered at 285.00 eV [15] is characteristic of CH2C(CH3)(C(O)OCH2CH2CH3)\textsubscript{n} groups while the bend at 290.35 eV is due to ((-CH2CH2-)\textsubscript{x})-CH2CH2OC(O)O-)\textsubscript{n} groups [12]. After 60 min argon ion sputtering both peaks are suppressed - with the one centered at 288 eV predominating. In depth of the sample the peaks of the spectra tend to shift to lower binding energies characteristic of silicon carbide [10].

Figure 6a shows O1s spectra of unimplanted PMMA. The O1s peak recorded from the surface is due to oxidation and diminishes after 120 min argon ion sputtering. In depth of the sample a new contribution with centre at 533.0 eV characteristic of (-(CH\textsubscript{2})\textsubscript{4}O-)\textsubscript{n} groups [13] appears.

Figure 6b shows O1s spectra of implanted PMMA. The O1s peak recorded from the surface is centered at 285.00 eV characteristic of (-CH\textsubscript{2})\textsubscript{3}O-)\textsubscript{n} groups [13]. This peak is due to surface oxidation and diminishes after 60 min argon ion sputtering while a new peak at 538.8 eV appears showing presence of (CH\textsubscript{3})\textsubscript{2}CHOCH\textsubscript{3} groups [13]. In depth of the sample a new peak centered at 533.0 eV characteristic of (-CH\textsubscript{2})\textsubscript{3}O-)\textsubscript{n} groups [17] appears.

### 3.2. Infra-red and Raman spectra

The IR spectra of the unimplanted and Si\textsuperscript{+} implanted, at a dose of D\textsubscript{3}=1.10\textsuperscript{17} cm\textsuperscript{-2}, polymethyl-methacrylate (PMMA) substrates are compared in Figure 7. As seen, the absorption of the implanted sample is higher and some features, though not intense because of the small thickness of the modified region, can be resolved. The spectra are displayed in the region from 800 to 2000 cm\textsuperscript{-1}, since in the range from 500 to 800 cm\textsuperscript{-1} they are highly transparent. The features in these spectra are much strongly pronounced and the absorption is comparatively higher. The spectrum of the implanted PMMA substrate is also more transparent in the range 1700 - 1750 cm\textsuperscript{-1}. Stretching vibrations of the C=O bonds at 1720 cm\textsuperscript{-1} and 1780 cm\textsuperscript{-1} [18] are reported for polyimide layers. Then, the transparency increase of our samples around these frequencies can reasonably be attributed to the breaking of C=O bonds.
In Figure 8, the Raman spectra of the unimplanted and implanted with $D=1.10^{17}\text{cm}^{-2}$ PMMA substrates are shown, in the range from 200 to 2000 cm$^{-1}$. Because of the low scattering volume of the implanted regions, no significant difference between the spectra of unimplanted and implanted samples is seen. The only unambiguous statement concerns the increase in the scattered light intensity in the range close to 1550 cm$^{-1}$, shadowed in Figure 8. The subtraction of the unimplanted sample spectra from those of the implanted ones gave the spectrum, displayed in the inset in the same figure. It is seen that the difference in the spectra is governed by a broad band peaked at about 1550 cm$^{-1}$.

The only unambiguous statement, as it concerns the formation of new bonds, is the presence of C=C bonds. It is confirmed by the IR transmittance, as well as by the Raman spectra. The formation of graphite-like and carbon-rich amorphous structures results in the appearance of broad absorption bands in the infrared spectrum at about 1350 cm$^{-1}$ and at about 1550 cm$^{-1}$, known as D (disorder) and G (graphite) bands, respectively. The bands are usually assigned to the graphitic $sp^2$ hybridized C bonds. The G band corresponds to vibrations in the graphitic micro-particles and the D band to in-plane vibrational modes at the particle surface [19]. The experimental transmittance spectra displayed in Figure 7 show unambiguously an increase of the absorption of the implanted sample in the range 1300 and 1550 cm$^{-1}$, which is an indication of the presence of amorphous and microcrystalline graphite. It is seen, from the inset in Figure 8, that the difference in the Raman spectra of implanted and unimplanted samples is governed by a broad band peaked at about 1550 cm$^{-1}$. These spectra look like the spectrum of a network with graphitic $sp^2$ hybridized C bonds, see for example [20].

A wide variety of SiC phonon band profiles are observed, depending on the growth conditions. The frequencies of the transverse optical (TO) phonons for the different polytypes in which the material crystallize are close, and lie in the range $766 – 780\text{ cm}^{-1}$ [21]. Thus, the feature at 780 cm$^{-1}$ in the spectrum of the implanted PMMA sample can be related to the SiC fundamental phonon absorption. The noticeable feature at 740 cm$^{-1}$ in Figure 7, as well as that at about 850 cm$^{-1}$, may be due to morphological factors as grains of different sizes and shapes, as well as to plasmon-phonon coupling [22]. A possible explanation of the increased absorption at 1650 – 1700 cm$^{-1}$ is the two-phonon SiC one. It is worth mentioning also that the behaviour of the spectra of the implanted PMMA samples in the range 900 – 1250 cm$^{-1}$ is very similar to that of polycarbosilane (PCS), heated at 873 K [22].

It is well known that although optical phonons in covalent semiconductors, and Si in particular, are not infrared active, these semiconductors absorb infrared radiation. The absorption is interpreted as a multiphonon one [23]. The most intense peaks in the experimental absorption spectra of Si are observed at 600 – 610 cm$^{-1}$ and at about 1100 cm$^{-1}$ [24]. Less intense two-phonon absorption is detected also, at about 700 and 850 cm$^{-1}$ [18]. Low intensity features at 610 and 1080 cm$^{-1}$ in the spectrum of the implanted PMMA sample, marked with arrows in Figure 7, then can be attributed to the absorption of unreacted Si atoms.
4. Conclusion
The XPS, IR and Raman spectra show that Si+ ion implantation leads to the introduction of additional disorder in the polymer material. XPS spectra of the implanted polymers show that in addition to the already mentioned bonds silicon creates new bonds with the host elements atoms – Si-C and Si-O, together with additional Si dangling bonds, as revealed by the valence band study of the implanted polymer materials. The unambiguous statement, that follows from the investigations, is that the implantation of Si into PMMA leads to the formation of amorphous and nanocrystalline graphite, while the presence of SiC particles and unreacted Si atoms also looks possible.

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References
[1] Frank W F X, Kulisch J, Franke H, Ruch D M, Brunner S and Lessard R A 1991 SPIE 1559 344
[2] Marletta G 1995 Materials and Processes for Surface and Interface Engineering (Dordrecht: Kluwer Academic Publishers) p 597
[3] Sloof L H, van Blaaderen A, Polman A, Hebbink G A, Klink S I, van Veggel F C J M, and Hofstraat J W 2002 Appl. Phys. Lett. 91 3955
[4] Sum T C, Bettiol A A, Seng H L, Rajta I, van Kan J A and Watt F 2003 Nucl. Instrum. & Methods B 210 266
[5] Toth A, Bell T, Bertoti I, Mohai M and Zelei B 1999 Nucl. Instr. & Methods B 148 1131
[6] Evelyn A L, Ila D, Zimmerman R L, Bhat K, Poker D B, Hensley D K, Klatt C, Kalbitzer S, Just N and Drevet C 1999 Nucl. Instrum. & Methods B 148 1141
[7] Tsvetkova T, Balabanov B, Avramov L, Borisova E, Angelov I, Sinning S and Bischoff L 2009 Vacuum 83 S252
[8] Tsvetkova T, Balabanov S, Avramov L, Borisova E, Angelov I and Bischoff L 2010 J. Phys.: Conf. Series 223 012033
[9] Stinespring C D and Wormhoudt J C 1989 J. Appl. Phys. 65 1733
[10] Laoharojanaphand P and Lin T J, Stoffer J O 1990 J. Appl. Polymer Sci. 40 369
[11] Clark M B Jr, Burkhardt C A and Cardella J A Jr 1989 Macromolecules 22 4495
[12] Beamson G and Briggs D 1992 High Resolution XPS of Organic Polymers: the Scienta ESCA300 Database
[13] Bhatia Q S and Burrell M C 1991 Polymer 32 1948
[14] Mizokawa Y, Geib K M and Wilmsen C W 1986 J. Vac. Sci. Technol. A 4 1696
[15] Patel N M, Dwight D W, Hedrick J L, Webster D C and McGrath J E 1988 Macromolecules 21 2689
[16] Schmitt R L, Cardella J A, Magill J H and Chin R L 1987 Polymer 28 1462
[17] Paparazzo E, Fanfoni M and Severini E 1992 Appl. Surf. Sci. 56 866
[18] Lim H, Lee Y, Han S, Cho J and Kim K 2001 J. Vac. Technol. A 19 1490
[19] Collins R J and Fan H Y 1955 Phys. Rev. 93 265
[20] György E, Mihailescu I, Baleva M, Abrashev M, Trifonova E P, Szekeres A and Perrrone A 2003 Mat. Sci. & Eng. B 97 251
[21] Freitas J A Jr. 1995 Properties of Silicon Carbide, ed G L Harris, EMIS Data Reviews Series No. 13 29
[22] Mutschke H, Andersen A C, Clement D, Henning T and Peiter G 1999 Astron. Astrophys. 345 187
[23] Lax M and Burstein E 1955 Phys. Rev. 97 39
[24] Nakayama N, Tsuehiya Y, Tamada S, Kosuge K, Nagata S, Tahakiro K and Yamaguchi S 1993 Jap. J. Appl. Phys. Lett. 32 L1465