Dose dependence of visible range diffuse reflectivity for Si$^+$
and C$^+$ ion implanted polymers

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Abstract. Detailed insight into the near-surface area of the ion beam modified polymer is supplied by the measured diffuse reflectivity spectra. The near-surface layer (50÷150 nm) of bulk polymer samples have been implanted with silicon (Si$^+$) and carbon (C$^+$) ions at low energies (E=30 keV) and a wide range of ion doses (D=5.10$^{12}$-2.10$^{17}$ cm$^{-2}$). The polymer materials studied were: ultra-high-molecular-weight polyethylene (UHMWPE), poly-propylene (PP), and poly-tetra-fluor-ethylene (PTFE). The diffuse optical reflectivity spectra $R_d = f(\lambda)$ of the implanted samples have been measured in the visible range ($\lambda$=400÷830 nm). In this paper the dose dependences of the size and sign of the diffuse optical reflectivity changes $\Delta R_d = f(D)$ have been analyzed.

1. Introduction

Polymers are currently used extensively because of their structural and material properties and are more and more sought for their electronic properties [1]. Technologies of polymer material modification by a beam of energetic ions (ion beam implantation) have wide applications in different fields from microelectronic to medicine [2-4]. The uses of different polymer materials for various application purposes are essentially defined by the type and amount of the implanted ions, which often substantially modify their mechanical, optical and electrical properties [5,6].

In this paper, a detailed insight into the near-surface area of the ion beam modified polymer material is provided by the diffuse reflectivity spectra measured. The near-surface layer of bulk polymer samples has been implanted with silicon (Si$^+$) and carbon (C$^+$) ions at low energies and a wide range of ion doses. The diffuse optical reflectivity spectra of the ion implanted samples have been measured in the visible range and the dose dependences of the size and sign of the diffuse optical reflectivity changes $\Delta R_d = f(D)$ have also been analysed.

2. Experimental

The samples studied in the work reported here consist of different polymer materials, commercially available (AtoHaas Europe) as bulk specimens with thickness of 2 mm, namely, ultra-high-molecular-weight polyethylene (UHMWPE), poly-propylene (PP), poly-methyl-methacrylate (PMMA) and
poly-tetra-fluor-ethylene (PTFE). All polymer materials are shaped as squares (side of 10 mm) or circles (diameter of 10 mm).

Ion implantation with Si\(^+\) and C\(^+\) was performed at room temperature (RT) and relatively low energies (E = 30 keV), with ion doses ranging from \(D = 5 \times 10^{12}\) to \(D = 2 \times 10^{17}\) cm\(^{-2}\), using Danfysik 1090 implanter. In order to keep the target temperature lower than 80 °C, at which the polymer can be decomposed, the beam current was kept under \(2 \mu\text{A/cm}^2\). The aim of the C\(^+\) implants was to distinguish self implantation effects from Si\(^+\) implants induced effects.

The thickness of the modified surface layer is defined by the range of the implanted Si\(^+\) and C\(^+\) ions in the polymer material \([7]\) (table 1). SEM results on the surface roughness changes with the ion dose, together with evidence of Si precipitates formation and clustering, have already been reported \([8]\).

The diffuse reflection spectra in the visible range \((\lambda = 400\text{–}800\ \text{nm})\) were obtained using a double-beam spectrophotometer type Shimadzu UV-190, with an integrating sphere and a standard reference sample of pressed MgO powder.

### 3. Results and discussion

Results of previous investigations \([9]\) have established that ion implantation with different ions in polymer materials leads to an increase of visible range diffuse optical reflectivity \(R_D\). Our results essentially confirm this tendency. Analyzing the spectral dependences of the diffuse optical reflectivity \(R_D\) (figures 1, 2, 4 and 5) for the polymer materials studied after Si\(^+\) and C\(^+\) ion implantation, it is observed that \(R_D\) increases considerably with the wavelength, i.e. with \(\lambda\) increasing from 350 nm to 525 nm.

This common behaviour could probably be related to the presence of an optical absorption edge for the polymer studied in this wavelength range. In relation to this, the \(R_D\) increase is attributed to the

![Figure 1](image1.png)  
**Figure 1.** Diffuse reflectivity spectra \(R_D = f(\lambda)\) for Si\(^+\) ion implanted UHMWPE samples at doses \(D = 1 \times 10^{13} \div 1.2 \times 10^{17}\) cm\(^{-2}\).

![Figure 2](image2.png)  
**Figure 2.** Diffuse reflectivity spectra \(R_D = f(\lambda)\) for Si\(^+\) ion implanted PTFE samples at doses \(D = 1 \times 10^{15} \div 1.2 \times 10^{17}\) cm\(^{-2}\).

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**Table 1.** Medium projected ranges \(R_p\) and struggling \(\Delta R_p\) for Si\(^+\) and C\(^+\) implanted in different polymers with \(E = 30\) keV.

| Material | UHMWPE | Teflon | PP |
|----------|--------|--------|----|
|          | \(R_p\) [nm] | \(\Delta R_p\) [nm] | \(R_p\) [nm] | \(\Delta R_p\) [nm] | \(R_p\) [nm] | \(\Delta R_p\) [nm] |
| Si\(^+\) ion | 65 | 14.5 | 44 | 15 | 68.5 | 15.3 |
| C\(^+\) ion | 122.6 | 25.8 | 96 | 33.2 | 128.8 | 27.1 |

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Figure 3. Dose dependences of the diffuse reflectivity change $\Delta R_D = f(D)$ at two different wavelengths – $\lambda_1 = 525$ nm and $\lambda_2 = 725$ nm – for Si$^+$ ion implanted UHMWPE and PTFE samples.

Figure 4. Diffuse reflectivity spectra $R_D = f(\lambda)$ for C$^+$ ion implanted UHMWPE samples at doses $D = 1.10^{14} \div 2.10^{17}$ cm$^{-2}$.

Figure 5. Diffuse reflectivity spectra $R_D = f(\lambda)$ for C$^+$ ion implanted PTFE samples at doses $D = 1.10^{14} \div 1.10^{15}$ cm$^{-2}$.

Figure 6. Dose dependences of the diffuse reflectivity change $\Delta R_D = f(D)$ at different wavelengths for C$^+$ ion implanted UHMWPE and PTFE samples.

deeper light penetration in the near-surface region. The increased amount of implanted ions at a certain depth below the polymer surface, depending on the ion energy, leads to the formation of a ‘buried’ layer with increased concentration of implanted atoms (figure 3 and figure 6). This creates conditions for processes of nucleation and growth of clusters concentrated mainly in the buried layer [8,10].

This process leads to a smaller or bigger $R_D$ increase, depending on the depth of the buried layer, the type of implanted ions, the optical transmittance of the polymer, as well as changes in its restructuring ability. The latter is also stimulated by the radiation effect related to the magnitude of the radiation dose [11].

At our implantation conditions (E=30 keV), an $R_D$ increase is observed for Si$^+$ and C$^+$ ion implantation in PP for doses above $D = 1.10^{14}$ cm$^{-2}$ (figure 7). In a number of cases high dose ion implantation in polymer materials leads to the building of clusters [12], with certain prevailing size,
and the formation of carbon-based chains with them. This process has been observed by a number of authors in different cases of ion implantation in polymers. In some cases, a drastic increase of the electrical conductivity has been observed after B⁺ ion implantation for doses above $D=1.10^{15}$ cm⁻² [13]. The maximal values of $\Delta R_D$ increase in our case are achieved at $D=1.10^{15}$ cm⁻² for Si or C implants, after which for the higher doses - $D=5.10^{15}$ cm⁻² and $D=2.5.10^{16}$ cm⁻², a considerable decrease of the diffuse optical reflectivity is registered, and finally stabilization of $\Delta R_D$ is obtained for doses between $D=2.5.10^{16}$ cm⁻² and $D=2.10^{17}$ cm⁻², both for Si and C implants in PP (figure 7).

The $R_D$ decrease observed described above could probably be related to the decrease in the amount of formed Si- or C-based clusters as a result of the irradiation which affects the less radiation stable PTFE and PP during continuous implantation processing [10]. For the case of C⁺ ion implantation in UHMWPE (figure 4), a typical $R_D$ decrease is found with the dose increase for wavelengths below $\lambda=525$ nm. As we have already pointed out, this effect is also related with the transmittance increase towards the longer wavelengths in the presence of particles considerably smaller than $\lambda$. As for the cases when the $R_D$ values for several spectral curves exceeds the $R_D$ for the non-implanted sample, they could probably be related to partial restructuring of the polymer matrices of materials with an absorption edge in the region of $\lambda=500$ nm. Partial graphitization effect at the implanted polymer surface could not be excluded as well for the highest doses of C⁺, i.e. $D=2.10^{17}$ cm⁻², as observed at $\lambda=725$ nm. A similar effect has also been studied in [14], where a wide peak formation and growth has been observed at 1560 cm⁻² in the Raman spectra, which is typical for amorphous carbon.

4. Conclusion
The $R_D$ changes observed in the spectral range $\lambda = 350 \div 450$ nm after Si⁺ and C⁺ ion implantation in PTFE and PP could be explained with the rather steep absorption edge slope in this wavelength region and the related transmission change. For the lower dose range ($D=5.10^{13}$ cm⁻² ÷ $1.10^{15}$ cm⁻²) the main factor defining the $R_D$ changes is related to the increased concentration of implanted Si and C atoms, which creates conditions for nucleation and growth of clusters, containing these elements, in the implanted buried layer.

For the higher Si⁺ and C⁺ ion doses ($D=1.10^{15}$ cm⁻² ÷ $2.10^{17}$ cm⁻²), in most cases a drastic $R_D$ decrease is registered, which could be related with the gradual formation of chains of clusters and further gradual saturation of the buried layer with implanted Si and C atoms. In the cases of the higher C⁺ ion implantation doses in UHMWPE (up to $D=2.10^{17}$ cm⁻²), a considerable $R_D$ increase is observed. This latter effect is mainly related to the increased graphitization in the near-surface area of the implanted polymer material.

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