Spectral distribution of UV range diffuse reflectivity for Si⁺ ion implanted polymers

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Abstract. The analysis of the UV range spectral characteristics can supply additional information on the formed sub-surface buried layer with implanted dopants. The near-surface layer (50÷150 nm) of bulk polymer samples have been implanted with silicon (Si⁺) ions at low energies (E=30 keV) and a wide range of ion doses (D=1.10¹³ ÷ 1.2.10¹⁷ cm⁻²). The studied polymer materials were: ultra-high-molecular-weight polyethylene (UHMWPE), poly-methyl-metacrylate (PMMA) and poly-tetra-fluoro-ethylene (PTFE). The diffuse optical reflectivity spectra R_d = f(λ) of the ion implanted samples have been measured in the UV range (λ = 220÷350 nm). In this paper the dose dependences of the size and sign of the diffuse optical reflectivity changes ΔRD = f(D) have been analysed.

1. Introduction
Polymer materials are presently attracting much attention due to their structural and material properties, and are more and more sought for their electronic properties [1]. The growing interest in the ion implantation technique as a tool for material properties modification of polymers is due to the possibility for precise control of the technological parameters [2-4]. Thus mechanical, optical and electrical properties can be selectively modified using ion bombardment [5,6].

Investigations of the diffuse optical reflectivity spectra provide detailed insight into the near-surface area of the ion beam modified polymer material. The analysis of the UV range spectral characteristics can supply additional information on the formed sub-surface buried layer with implanted dopants. The near-surface layer of bulk polymer samples have been implanted with silicon (Si⁺) 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 UV range (λ = 220÷350 nm) and the dose dependences of the size and sign of the diffuse optical reflectivity changes ΔRD = f(D) have also been analyzed.

2. Experimental
Samples of different polymer materials, commercially available (AtoHaas Europe) as bulk samples with thickness of 2 mm, are studied in the present work: 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 \( \text{Si}^+ \) was performed at room temperature (RT) and relatively low energies \( (E = 30 \text{ keV}) \), with ion doses ranging from \( D = 1.10^{13} \) to \( D = 1.2.10^{17} \text{ cm}^{-2} \), 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 thickness of the modified surface layer is defined by the range of the implanted \( \text{Si}^+ \) ions in the polymer material [7] (table 1). SEM results on the surface roughness changes with ion dose, together with evidence of Si precipitates formation and clustering, have already been reported [8].

Table 1. Medium projected ranges \( R_p \) and struggling \( \Delta R_p \) for \( \text{Si}^+ \) implanted in polymers \( (E=30\text{keV}) \).

| Material | UHMWPE | PMMA | Teflon |
|----------|--------|------|--------|
| \( R_p \) [nm] | 65 | 63 | 44 |
| \( \Delta R_p \) [nm] | 14.5 | 16.5 | 15 |

The diffuse reflection spectra in the UV range \( (\lambda = 220\div350 \text{ nm}) \) have been 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 are presented for the spectral dependences of the diffuse optical reflectivity \( R_{\Delta} = f(\lambda) \) in the UV range \( (\lambda = 220\div350 \text{ nm}) \) after \( \text{Si}^+ \) ion implantation in PMMA (figure 1) and UHMWPE (figure 3).

Figure 1. Diffuse reflectivity spectra \( R_{\Delta} = f(\lambda) \) for \( \text{Si}^+ \) ion implanted UHMWPE samples at doses \( D=1.10^{15} \div 1.2.10^{17} \text{ cm}^{-2} \).

Figure 2. Dose dependences of the diffuse reflectivity change \( \Delta R_{\Delta} = f(D) \) at different wavelengths for \( \text{Si}^+ \) ion implanted UHMWPE samples.

Figure 3. Diffuse reflectivity (UV) spectra \( R_{\Delta} = f(\lambda) \) for \( \text{Si}^+ \) ion implanted PMMA samples at doses: \( D=1.10^{15} \div 1.2.10^{17} \text{ cm}^{-2} \).
Analyzing the dose dependences for the two polymers (figures 2 and 4), it could be seen more clearly that a considerable increase of $\Delta R_D$ for PMMA is observed at implantation doses above $D = 5.10^{15}$ cm$^{-2}$. Analogous effect for UHMWPE is observed for implantation doses above $D = 1.10^{16}$ cm$^{-2}$. This could be related to partial penetration of light in the near-surface area. This effect dominates in spite of the increase of the light absorption, related to the increased amount of implanted atoms in the near-surface layer [9]. The observed effect is smaller for UHMWPE, for which $R_D$ has higher values also for the non-implanted samples compared to those of PMMA due to the different structure of the polymer material.

![Figure 4](image1.png)  
**Figure 4.** Dose dependences of $\Delta R_D=f(D)$ at: $\lambda_1=230$ nm, $\lambda_2=260$ nm and $\lambda_3=350$ nm for Si$^+$ ion implanted PMMA samples.

![Figure 5](image2.png)  
**Figure 5.** Diffuse reflectivity (UV) spectra $R_D= f(\lambda)$ for Si$^+$ ion implanted PTFE samples at doses $D=1.10^{15}\div1.2.10^{17}$ cm$^{-2}$.

The spectral dependences of the diffuse optical reflectivity $R_D= f(\lambda)$ and their changes after different doses of Si$^+$ ion implantation in PTFE (figure 5) represent substantial differences as compared to the results for PMMA and UHMWPE considered above. The sign of the $R_D$ change is opposite here, i.e. the increase of the implantation dose leads to considerable $R_D$ decrease, several times bigger than the $R_D$ change shown in figure 1 and figure 3, in absolute values. This is understandable, however, bearing in mind that for the PTFE non-implanted samples, the UV range is the region of maximal diffuse reflectivity since they behave as turbidity media [10]. Moreover, $R_D$ for this material is comparable with the values for the reference sample used in the spectrophotometer, prepared of pressed MgO powder.

Bearing in mind that the optical absorption coefficient is changing slightly in the UV range ($\lambda = 220\div350$ nm), the $R_D$ changes, i.e. $\Delta R_D$, could be attributed to processes of destruction of the polymer molecular structure. The increase of the amount of implanted Si$^+$ ions leads to increase in the optical absorption due to processes of clusters formation and their coalescence [8,11].

### 3. Conclusion

Comparing the results of Si$^+$ ion implantation in different polymer materials with substantially different optical properties, a conclusion could be reached that decisive factor for the $R_D$ increase in PMMA and UHMWPE is the increase of optical transmission with $\lambda$ increase in the region of the absorption edge. For the considerably bigger decrease of $\Delta R_D$ for PTFE in the same spectral region ($\lambda = 220\div350$ nm), a substantial role plays the increase of the optical absorption depending on the amount of the implanted Si atoms and the structure of the formed clusters. As a result of the radiation effects accompanying the implantation process, especially in PMMA and PTFE which are not highly radiation stable materials, processes of partial breaking of the polymer molecules are possible, together with increased carbon concentration in the near-surface layer in the form of C-C bonded graphitic carbon, especially for the case of the high Si$^+$ implantation doses ($D=5.10^{16} \div 1.2.10^{17}$ cm$^{-2}$).
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