Optical properties of Si\(^+\) implanted PMMA

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Abstract. In the present work, low energy ion beam irradiation was used for surface modification of polymethyl-methacrylate (PMMA) using silicon (Si\(^+\)) as the ion species. After high doses ion implantation of Si\(^+\) in the polymer material, a characterization of the optical properties was performed using optical transmission measurements in the visible and near infra-red (IR) wavelength range. The optical absorption increase observed with the ion dose was attributed to ion beam induced structural changes in the modified material.

1. Introduction
In recent years there has been growing interest to the modification of surfaces and thin layers of polymers. The ion beam technique is widely used, as it is a flexible and powerful tool for surface engineering of different materials, including polymers. The increased attention to the ion implantation of polymer materials is due to the possibility to control precisely the technological parameters for fundamental research purposes, and also in view of some possible applications to device fabrication. Thus, optical, mechanical, electrical and chemical properties can be selectively modified using ion bombardment [1]. The ion irradiation of polymers is followed by various processes, such as: macro-molecular destruction, cross-linking, free radicals formation, carbonization and oxidation [2-4]. Therefore, understanding the influence of certain structural re-arrangements on the suitable properties of polymers opens a way to design devices with required parameters, involving such applications as optical filters, absorbers, reflectors, etc. [5].

The net result of ion beam treatment of polymer materials is that it leads to alteration in their physical and chemical properties, i.e. modification of the electrical and optical properties, changes in the surface wettability and adhesive bonding, as well as improvement of surface hardness and wear resistance. Some of the beam-induced chemical effects involve: reduction of crystallinity, partial graphitization of the surface layer, formation of unsaturated C=\(\mathring{\text{C}}\) bonds, formation of methyl groups due to chain scission, etc. [6,7].

In the present work, low energy ion beam irradiation was used for surface modification of polymethyl-methacrylate (PMMA) using silicon (Si\(^+\)) as the ion species. The ion bombardment effects

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on the optical properties of the polymer materials were investigated using optical transmission measurements in the visible and near infrared (IR) wavelength range.

2. Experimental
Polymethylmethacrylate (PMMA) samples, available commercially as bulk samples with a thickness of 2 mm, were studied. All samples were shaped as squares (side of 10 mm) or circles (diameter of 10 mm).

Danfysik 1090 ion implanter was used to carry out the Si⁺ ion implantation at room temperature (RT) and relatively low energies (E = 30–50 keV), with ion doses ranging from D = 1×10¹³ cm⁻² to 1.2×10¹⁷ cm⁻². The ion beam current was kept under 2 μA/cm² during the implantation process, so as to maintain the target temperature below 80°C, at which the polymer material starts to decompose. The pressure in the target chamber was kept under 10⁻⁶ Pa during implantation.

The optical transmission and reflection spectra of the PMMA samples were measured by double-beam spectrophotometers Specord UV-VIS (400–800 nm) and Cary 5E (330–3300 nm).

3. Results and discussion
The optical transmission spectra of Si⁺ implanted (E = 50 keV) PMMA samples are presented in figure 1(a). Wide range of ion doses were used: D = 10¹⁴ – 10¹⁷ cm⁻². There is no significant change in the optical transmission for the lower doses – up to D₃ = 1×10¹⁵ cm⁻² – while a well expressed increase in the absorption is observed with the further dose increase, reaching quickly saturation at D₄ = 3.2×10¹⁵ cm⁻² and higher doses. Similar behavior in the IR absorption is also observed in figure 1(b).

Figure 1. Optical transmission (a) and IR (b) spectra of Si⁺ implanted PMMA at ion beam energy E=50 keV and different ion doses: D₁ = 1×10¹⁴; D₂ = 3.2×10¹⁴; D₃ = 1×10¹⁵; D₄ = 3.2×10¹⁵; D₅ = 1×10¹⁷ cm⁻²; D₀ - unimplanted PMMA.

A more gradual increase in the absorption with the dose is registered for Si⁺ implanted PMMA samples at lower energy (E = 30 keV) and relatively low doses (D = 1×10¹³ + 2.5×10¹⁶ cm⁻²) – figure 2. In this case, noticeable absorption increase is observed at a similar low dose (D₁ = 1×10¹⁵ cm⁻²), but then continues to increase gradually with the dose, without reaching saturation.

Figure 2. Optical transmission spectra of Si⁺ implanted PMMA at ion beam energy E=30 keV and different ion doses: D₁ = 1×10¹³; D₂ = 5×10¹³; D₃ = 2.5×10¹⁴; D₄ = 1×10¹⁵; D₅ = 5×10¹⁵; D₆ = 10¹⁶ cm⁻²; D₀ - unimplanted PMMA.

Figure 3 presents the transmission spectra in the visible range for two PMMA samples implanted at two different energies with the same ion dose, D = 1×10¹⁵ cm⁻². Slightly greater absorption is observed for the sample implanted with E = 30 keV, as compared to the one for E = 50 keV, probably due to the slightly larger peak concentration in the Si⁺ ions distribution for the lower energy and the same ion dose [8].

Figure 3. Optical transmission spectra in the visible range for two PMMA samples implanted at energies E=30 and 50 keV with the same ion dose, D = 1×10¹⁵ cm⁻². Slightly greater absorption is observed for the sample implanted with E = 30 keV, probably due to the slightly larger peak concentration in the Si⁺ ions distribution.
Figure 3. Optical transmission spectra of Si\textsuperscript{i+} implanted PMMA samples with ion dose \(D = 1\times10^{15}\text{cm}^{-2}\) at two different ion energies: \(E_1 = 50\text{keV}\) and \(E_2 = 30\text{keV}\).

Figure 4. Optical transmission (a) and IR (b) spectra of Si\textsuperscript{i+} implanted PMMA at ion beam energy \(E = 30\text{keV}\) and different ion doses: \(D_1 = 1\times10^{15}\); \(D_2 = 5\times10^{15}\); \(D_3 = 2,5\times10^{16}\); \(D_4 = 1,2\times10^{17}\text{cm}^{-2}\); \(D_0\) - unimplanted PMMA.

A more pronounced effect of absorption increase with the dose, again without reaching saturation, is shown in figure 4 for still higher ion doses \((D = 1\times10^{15} \div 1.2\times10^{17}\text{cm}^{-2})\) at a lower energy \((E = 30\text{keV})\), i.e. an even higher peak concentration in the Si\textsuperscript{i+} ions distribution. This is demonstrated both in the visible (figure 4(a)) and IR (figure 4(b)) range.

Using the transmission data one can derive the dependence \(T(D)\), i.e. the transmittance v/s the ion implantation dose (figure 5) for one wavelength in the visible range – 500 nm, and for one in the IR – 1300 nm. \(T(D)\) for the other wavelengths in respective ranges are essentially the same. As seen in figures 5 (a,b), \(T(D)\) decreases in a non-monotonic way, in contrast to the behavior observed in other implanted polymers at comparable doses [9-11].

This declination type of behavior seems as a ‘break in transmission’ and occurs at a certain ‘breaking dose’, \(D_B\). In fact, at a slightly lower dose the photoluminescence (PL) of Si\textsuperscript{i+} implanted PMMA is enhanced, and at \(D \geq D_B\) it is continuously quenched [12]. Presumably, the increased defect introduction, above some critical concentration, results in an increased degree of structural disorder.

It appears that \(D_B\) is related to the energy of implantation. \(T(D)\) obtained from transmission spectra of another set of PMMA samples, also implanted with Si\textsuperscript{i+} but at lower energy \(E = 30\text{keV}\) (figures 5(c,d)), do not exhibit any declination behavior.

Figure 5. Dose dependence of the optical transmittance (T) for Si\textsuperscript{i+} implanted PMMA samples with: ion energy \(E = 50\text{keV}\) at \(\lambda_1 = 500\text{nm}\) (a) and \(\lambda_2 = 1300\text{nm}\) (b); and ion energy \(E = 30\text{keV}\) at \(\lambda_1\) (c) and \(\lambda_2\) (d).
Figure 5(c) includes also the dependence $T(D)$ (solid circles) for an additional set of PMMA samples coming from another source with probably different impurities content, crystalline to amorphous phase ratio, etc., which is the reason for the lack of complete overlapping between the results of the two sets of samples implanted with the same energy and range of doses. Otherwise, the reproducibility of the above given results is within a relatively small error ($\pm 1.5\%$, hence no error bar has been introduced in the figures.) As is seen, $T(D)$ decreases gradually. In our view, the lack of declination means that the polymer surface in this case is not so hardly structurally modified as for the Si$^+$ implantation at $E = 50$ keV. Probably, for the higher energy case, some critical level of energy deposition into the surface layer is reached, so that greater destruction occurs via a mechanism resulting in a significant change of the defect states density.

4. Conclusion
The results obtained in this work demonstrate that the optical absorption of Si$^+$ implanted PMMA could be significantly altered, both in the visible and the IR range, depending on the ion energy and dose. For higher energies, the ion beam induced absorption increase with the dose exhibits declination point type of behavior, which is absent in the lower energy case. This is presumably due to an increased defect introduction above some critical concentration causing an abrupt increase of structural disorder.

Additional experiments with Raman and X-ray photo-electron spectroscopy (XPS) are in run to help identify the ion beam induced structural changes associated with the observed optical properties modification. The correlation between the Si$^+$ implantation effects on the optical and PL behavior of ion implanted polymers is also of interest in view of further uses in optoelectronics and photonics.

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