Photoluminescence of Si\(^{+}\) and C\(^{+}\) implanted polymers

T Tsvetkova\(^{1,5}\), S Balabanov\(^{1}\), L Avramov\(^{2}\), E Borisova\(^{2}\), I Angelov\(^{3}\) and L Bischoff\(^{4}\)

\(^{1}\)Georgi Nadjakov Institute of Solid State Physics, Bulgarian Academy of Sciences, 72 Tzarigradsko Chaussee, 1784 Sofia, Bulgaria
\(^{2}\)Emil Djakov Institute of Electronics, Bulgarian Academy of Sciences, 72 Tzarigradsko Chaussee, 1784 Sofia, Bulgaria
\(^{3}\)Institute of Organic Chemistry, Bulgarian Academy of Sciences, Acad. G. Bonchev Str., Bl. 9, 1113 Sofia, Bulgaria
\(^{4}\)Forschungszentrum Rossendorf e.V., P.O.Box 510119, D-01314 Dresden, Germany

E-mail: tania_tsvetkova@yahoo.co.uk

Abstract. Visible photoluminescence (PL) of ion implanted polymers was studied. Different polymer materials were used for the purpose: polypropylene (PP), poly-tetrafluor-ethylene (Teflon), ultra-high-molecular-weight-polyethylene (UHMWPE) and UHMWPE+Bi. Ion implantation with Si\(^{+}\) and C\(^{+}\) was performed at energies of 30 keV with doses in the range \(10^{13} - 10^{17} \text{ cm}^{-2}\). The results show that a PL enhancement (PLE) effect may occur for some polymer materials if proper implantation energy and doses are employed, the effect in the case of some polymer materials implanted with Si\(^{+}\) and C\(^{+}\) being considerable. While the effect is observed for all doses of C\(^{+}\) implanted in UHMWPE, PLE is only observed for the lowest dose of Si\(^{+}\) (\(D=1\times10^{15} \text{ cm}^{-2}\)) implanted in Teflon, the further dose increase resulting in PL quenching only, presumably due to processes of structural degradation. The appearance of ultra-violet (UV) range PL in the case of Si\(^{+}\) implanted UHMWPE could be originating from the formation of Si-related new defect sites, but more data are needed to explore this effect further into the deeper UV range (\(\lambda<350 \text{ nm}\)).

1. Introduction

The ion implantation technique is an attractive tool for material properties modification of polymers due to the possibility for precise control of the technological parameters both for fundamental research purposes and for various possible applications. The optical, electrical, mechanical and chemical properties can be selectively modified using ion bombardment [1]. Important advantages of the ion implantation method, compared to the other doping methods, are the possibility for precise dopants concentration control, the ability to resolve their spatial distribution – in-depth dopant profiling by designing the implantation parameters, and surface localization by using masks or focused ion beams.

The understanding of the structural re-arrangements effect on the relevant optical properties of ion-bombarded polymer surfaces reveals new approaches to the design of devices with desired parameters, e.g. for applications of high-performance polymers for optical filters, absorbers, reflectors, luminescent devices, etc. [2]. This knowledge is of considerable importance for the application of the ion beam synthesis (IBS) techniques to produce new compounds and advanced materials in the

\(^{5}\) To whom any correspondence should be addressed.
irradiated polymer surfaces by implanting ions of various chemical elements [3,4]. The optical properties of ion implanted polymers, being of particular interest for modern optoelectronics and photonics, have been extensively explored [5,6].

The aim of the present work was to apply the ion beam technique to produce polymer materials yielding interesting photoluminescence (PL) properties. In particular, it was of interest to study the PL dependence on the ion implantation conditions and implanted ion species.

2. Experimental

Various polymers, commercially available as bulk samples with thickness of 2 mm, were studied: ultra-high-molecular-weight-polyethylene (UHMWPE), polypropylene (PP), and poly-tetrafluoroethylene (Teflon). The samples were shaped as squares (side of 10 mm) or circles (diameter of 10 mm).

Ion implantation with Si⁺ was performed at room temperature (RT) and relatively low ion beam energy (E = 30 keV), with ion doses ranging from D=1.10¹⁵ to D=1.2.10¹⁷ cm⁻², using a 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 2μA/cm². The pressure in the target chamber was kept under 10⁻⁶ Pa during implantation. Additionally, implantation by carbon ions was performed with the aim to distinguish the Si⁺ implants induced effects from those introduced by self-ion implantation.

The photoluminescence (PL) measurements were performed at RT using two different excitation sources – Ar laser (λ_ex = 488 nm) and N₂ laser (λ_ex = 337 nm). The N₂ laser was used to obtain PL spectra of some of the UHMWPE samples. The laser power used was 14 μJ/pulse, with 10 Hz repetition rate. The detector was a Sony ILX511 2048-element linear silicon CCD array, with estimated sensitivity 86 photons/count, signal-to-noise ratio 250:1, and effective range 200-1100 nm.

The PL spectra excited by the Ar⁺-laser (Spectra Physics 171) were registered by an optical multi-channel analyser (2048 channels) coupled with a Ocean Optics S2000 spectrometer. The entrance slit was set at 100 μm. The samples were illuminated by a laser beam with diameter of about 1 mm and power 10 mW and 30 mW @ TEM₀₀. During the integration cycle of 5 seconds we did not observe any nonreversible temperature changes, degradation or damages to the polymer materials.

3. Results and discussion

Figure1(a) shows the PL spectra of Si⁺ implanted UHMWPE samples (E=30 keV, D=1×10¹⁵–2.5×10¹⁶ cm⁻²). For PL excitation, an N₂ laser (λ_ex=337 nm) was used and the PL spectra were measured in the range 350 – 650 nm. The Si⁺ ion implantation results in PL quenching in the whole visible range of the spectrum, while emergence of an UV range (λ~350 nm) PL signal is observed, increasing with the dose. No such UV range PL effect is found for the case of C⁺ implantation in the same polymer material (UHMWPE), as shown in figure1(b). Instead, only visible range PL is registered, with C⁺ implantation resulting just in its modification in the same range. The PL spectral changes observed in the case of Si⁺ implanted UHMWPE, and the UV range emission emergence in particular, could be originating from Si⁺–related defect complexes [7].

![Figure 1. PL (λ_ex=337 nm) spectra of Si⁺(a) and C⁺(b) implanted UHMWPE samples at ion beam energy E=30 keV and different doses. PL of reference samples is also given.](image_url)
When PL measurements are performed with the same material (UHMWPE) employing an Ar$^+$ laser as the excitation source ($\lambda_{\text{ex}}= 488 \text{ nm}$), the visible range PL modification effects for the two kinds of ions, Si$^+$ and C$^+$, are again very different (figure 2). While there is a considerable photoluminescence enhancement (PLE) of the emission for the C$^+$ implanted UHMWPE samples compared to the reference sample (figure 2(a)), the Si$^+$ implantation results in significant PL quenching for all implantation doses used (figure 2(b)). This difference could be explained bearing in mind the higher mass of the Si$^+$ ions, compared to the C$^+$ ones, hence a greater degree of radiation induced defects is introduced by the Si$^+$ implants, resulting in increased disorder and related processes of degradation of the polymer structure [8].

Bombardment with the lighter C$^+$ ions, accompanied by a considerable energy dissipation in the polymer surface, is more likely to induce increased cross-linking and hence a more ordered structure of the polymer material [9].

![Figure 2](image2.png)

**Figure 2.** PL ($\lambda_{\text{ex}}=488 \text{ nm}$) from UHMWPE samples implanted at E=30 keV by: (a) C$^+$ at ion doses: $D_1=1\times10^{13}$; $D_2=5\times10^{13}$; $D_3=5\times10^{14}$; $D_4=1\times10^{15} \text{ cm}^{-2}$; $D_0$-unimplanted polymer; and (b) Si$^+$ at 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 polymer.

![Figure 3](image3.png)

**Figure 3.** PL ($\lambda_{\text{ex}}=488 \text{ nm}$) from Si$^+$ implanted (E=30keV) PP (a) and Teflon (b) samples with ion doses: $D_1=1\times10^{15}$; $D_2=5\times10^{15}$; $D_3=2.5\times10^{16}$; $D_4=1.2\times10^{17} \text{ cm}^{-2}$; $D_0$-reference.
For Si\textsuperscript{+} implants in PP (figure 3(a)), only PL quenching is registered for all available doses, as already the lowest dose (D= 1×10\textsuperscript{15} cm\textsuperscript{-2}) is obviously inducing degradation processes. Some noticeable PLE is however observed for Si\textsuperscript{+} implants in Teflon (figure 3(b)), but it is only present for the lowest dose available (D=1×10\textsuperscript{15} cm\textsuperscript{-2}) while a further dose increase results in PL quenching only, presumably due to processes of structural degradation as discussed above.

The PL dependence on the ion dose is shown in figure 4, where the difference in the PL behavior, resulting from Si\textsuperscript{+} implants in Teflon (figure 4(a)) and the one induced by the C\textsuperscript{+} implants in UHMWPE (figure 4(b)), is displayed. While considerable PLE is found even for the higher C\textsuperscript{+} ion doses available, for the Si\textsuperscript{+} implants PLE is only recorded for the lowest dose used (D=1×10\textsuperscript{15} cm\textsuperscript{-2}). The reproducibility of the above given results is within a relatively small error (±2.5\%), hence no error bar has been introduced in the figures. Thus, self-ion implantation (C\textsuperscript{+}) implants is accompanied by a lower rate of disorder introduced in the ion bombarded polymer matrices, with possibilities to accommodate higher C\textsuperscript{+} doses while preserving significant PLE with further implications for possible applications.

4. Conclusion
The interesting PLE effect observed in the case of some polymers implanted with Si\textsuperscript{+} and C\textsuperscript{+} is of considerable magnitude, with some specifics for the different polymer materials. While the effect is observed for all doses of C\textsuperscript{+} implanted in UHMWPE, PLE is only observed for the lowest dose (D=1×10\textsuperscript{15} cm\textsuperscript{-2}) of Si\textsuperscript{+} implanted in Teflon, a further dose increase resulting only in PL quenching, presumably due to processes of structural degradation. No PLE was observed in the case of Si\textsuperscript{+} implants in PP; instead PL quenching is registered for all available doses, as already the lowest doses are obviously introducing significant degradation processes. The emergence of UV range PL observed in the case of Si\textsuperscript{+} implanted UHMWPE could be originating from the formation of Si-related new defect sites, but more data are needed to explore the effect further into the deeper UV range (λ<350 nm). Additional Raman and X-ray photo-electron spectroscopy (XPS) measurements are needed to identify the structural changes associated with the PL effects observed in the implanted polymer materials. Better understanding of the registered ion beam induced PLE in some polymers has wide implications for future optoelectronic and photonic applications due to its relevance to their electroluminescence behavior.

Acknowledgements
This work was supported by an International Atomic Energy Agency project (No:1294/RBF). The support of Forschungszentrum Rossendorf e.V., Germany, is also acknowledged.

References
[1] Marletta G 1995 Materials and Processes for Surface and Interface Engineering (Dordrecht: Kluwer Academic Publishers) p 597
[2] Vargo T G, Gardella J A et al. 1993 Surface Characterization of Advanced Polymers ed L Sabbattini and P G Zambonin (Weinheim: VCH Publ. Co.) p 163
[3] Balabanov S and Krezhov K 1999 J. Phys D: App. Phys. 32 2573
[4] Evelyn A L, Ila D et al. 1999 Nucl. Instrum. & Meth. B 148 1141
[5] Stepanov A L 2004 J. Techn. Phys. 74 1
[6] 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
[7] Yu Y H, Li L, Lei Y M, Zhao J, Mao D S, Zou S C, Sundaraval B, Luo E Z, Wong S P, Xu J B and Wilson I H 2000 Ion Implantation Technology ed H Ryssel et al. (IEEE) p 765
[8] Baleva M, Zlateva G, Tsvetkova T, Balabanov S and Bischoff L 2009 J. Optoelectr. Adv. Mater. 11 1420
[9] Charlesby A 1960 Atomic Radiation and Polymers (Oxford: Pergamon Press)