



Effect of structural transformation of C⁺-ion implanted PMMA into quasi-continuous carbonaceous layer on its optical and electrical properties

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ABSTRACT

The samples of Polymethylmethacrylate (PMMA) have been implanted with 500 keV C⁺-ions at different ion fluences ranging from 9.3×10^{13} to 8.4×10^{14} ions/cm². The structural modifications are examined by Fourier Transform Infrared and Raman spectral studies. For the investigation of optical, electrical and surface morphological properties of implanted samples UV–Visible spectrometer, four probe apparatus and optical microscope have been employed. The FTIR spectra confirmed the cleavage of chemical bonds as a consequence of polymer chain scission, whereas, Raman studies revealed the transformation of PMMA structure into quasi-continuous amorphous carbon with increasing ion fluences. A continuous reduction has been observed in the optical band gap of PMMA from 3.16 to 1.42 eV. Moreover, the refractive index, extinction coefficient and electrical conductivity of implanted PMMA are found to be an increasing function of the ion fluence. The micrographic images revealed the signatures of ion-induced defects like cracking, dehydrogenation, stress and swelling on the surface of PMMA. These implanted samples have a potential to be used in the field of optical communications and thin plastic flexible electronics.

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1. Introduction

Since 21st century intrinsically conducting polymers have gained much interest in polymer electronics due to their native properties like electrical and photoconductivity, having ability of emission and absorption of light etc. [1]. Here, an effort has been made to modify the structural, optical and electrical properties of insulating polymer for its future utilization in plastic electronics and opto-electronic devices including photo-diodes, photo-voltaic cells, etc.

Polymethylmethacrylate (PMMA) is a broadly used thermoplastic polymer material. Due to various attractive properties like light weight, low cost, high mechanical strength, chemical inertness, good electrical insulation, ease of structure moldability, low water absorptivity [2] and excellent optical clarity [3], it is widely used in medical [4], optical, architectural and automobiles

applications. However, in order to extend its applications in plastic electronics, opto-electronics and optical communications there is still a need to improve optical as well as electrical properties of PMMA.

Though the extent of modifications in optical, electrical, mechanical and chemical properties of polymers depend on backbone structure as well as on their chemical composition [5]. The structure of PMMA is highly sensitive to energetic ions [6]. Thus, ion implantation is considered as an advantageous technique to transform the structure as well as chemical composition of PMMA in a controlled manner [7].

When an energetic ion interacts with the polymer target, it loses its energy in a series of processes involving chain scission, ionization of atoms, excitation of electrons, displacement or replacement of atoms, free radical formation, evolution of volatile gaseous species, formation of network of carbon-carbon multiple bonds, etc. [7–10]. Consequently, these ion-induced processes are responsible for improving the optical, electrical, mechanical and structural properties of a specific layer of thickness of the order of few hundred nanometers in implanted polymers without disturbing their

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bulk properties. However, the magnitude of modifications in above mentioned properties depends on structure of polymer and ion implantation parameters like mass, energy, ion fluence, etc.

Along with structural and chemical properties, ion implantation can also affect the refractive index of polymer. If the refractive index increases with implantation, then polymer can be considered as a bilayer system, comprising of a layer of high refractive index (implanted) above the layer of low refractive index (un-implanted). Such a combination of layers with different refractive indexes can be utilized in optical communication applications [11].

Thus, the structural transformation in polymer, as a result of high energy or high-fluence ion implantation, has been previously studied [12–15]. Recently, interest has been growing in the modification of structural and physical (optical, electrical, etc.) properties of polymer with medium-energy ions and at relatively low ion fluences to make them more economical. Here, we have attempted to modify the electrical conductivity of implanted PMMA in conjunction with its optical properties as a result of polymer structural transformation into a carbonaceous implanted layer with relatively low ion fluence.

2. Experimental details

The sheets of Polymethylmethacrylate (PMMA) of thickness ≈ 2 mm were obtained from Good fellow, UK. The sheet was cut into dimensions of 1.5×3 cm². The samples were ultrasonically cleaned for 20 min in distilled water prior to ion implantation. Five samples were implanted with 500 keV C⁺ ions with the fluence of 9.3×10^{13} ions/cm², 1.9×10^{14} ions/cm², 4.7×10^{14} ions/cm², 6.5×10^{14} ions/cm² and 8.4×10^{14} ions/cm² using 4 MeV Pelletron accelerator. The implantation was performed at room temperature under vacuum $\sim 10^{-7}$ torr. The ion beam area was 4 cm².

The ion penetration range, electronic (S_e) and nuclear (S_n) stopping powers for 500 keV carbon (C⁺) ions were estimated using SRIM (Stopping and Ranges of Ions in Matter) simulation (2013) [16]. The structural modifications in the implanted samples were investigated using Bruker Alpha-P Fourier Transform Infrared Spectrometer (Bruker Optics GmbH, Germany) equipped with an attenuated total reflectance (ATR) assembly. The FTIR studies were carried out in transmission mode in the wavenumber range of 500–4000 cm⁻¹. The Raman spectra were obtained in the wavenumber range 400–3250 cm⁻¹ using a Raman spectrometer (μ -Ramboss: Micro Raman measurement system, Dongwoo Optron Co. Ltd, Korea). A Continues Diode-pumped solid-state laser was used as an excitation source at wavelength 532 nm. The laser was focused on the sample surface with a 100 \times objective in the back-scattering configuration.

The optical properties of pristine and implanted PMMA were analyzed using Hitachi UV–Vis U-2800 spectrophotometer. For the measurements of electrical conductivity four-point probe apparatus with Keithley KI 6220 nano-voltmeter was used. The surface morphological examination of the implanted PMMA samples was performed using Olympus STM-6 optical microscope.

3. Results and discussion

3.1. SRIM/TRIM simulation

When energetic ion interacts with solid, it penetrates and collides with target atoms. During collision it transfers energy to electrons and nuclei of solid and finally comes to rest. These collisional processes are known as electronic and nuclear stopping powers, respectively. Before coming to rest, ion covers a specific distance inside the material known as ion range or ion penetration

depth. The implantation parameters as projected range, ion straggling, electronic (S_e) and nuclear (S_n) stopping powers for 500 keV C⁺ ions in PMMA are estimated using SRIM-2013 simulation software and are given in Table 1. The different stages of structural damage produced in C⁺-ion implanted PMMA are presented in Fig. 1 using the simulation code named Transport of Ions in Matter (TRIM (2013)) [16].

Fig. 1a shows the transverse view of possible ion trajectories in implanted PMMA. Table 1 shows that for 500 keV C⁺ ions the phenomenon of electronic stopping is dominating compared with the nuclear stopping phenomenon. However, both electronic and nuclear stopping play relative roles to the structural modifications in implanted material [18]. The energy lost by fast incoming ions is utilized in the breakage of chemical bonds, creation of electron-hole pairs and vacancies as well as in the formation of recoil atoms in the target material. The recoil atoms with sufficient energy lead to cascade collisions with other atoms and electrons. The 500 keV C⁺ ions deposit up to 91% of their initial energy directly to PMMA target during interaction and use about 9% of it in recoil cascades [16]. Thus, they play an important role in producing significant ionization along their trajectories. The free knocked-off electrons successively collide with other atoms and excite secondary electrons in a cascade process. During their passage deep into the material, the remaining energy of ions is lost in various other processes like nuclei displacements and cascade collisions, etc. and finally it comes to rest after covering a specific penetration range ($R_p \approx 1.46$ μ m).

During cascade collisions, vacancies and interstitial species are produced in the implanted layer. TRIM simulation for the total in-depth damage distribution produced in 500 keV C⁺-ion implanted PMMA is shown in Fig. 1b. The left-side axis (in green color) provides a view for 2D lateral plot of ion-induced damage distribution. The central axis (in red color) is for 2D depth plot whereas, the axis on the right side (in black color) shows the ordinate for 3D total in-depth damage distribution. The ion induced spatial damages are fluence dependent and the large number of damages in a localized region lead to chain scission, cleavage of chemical bonds and release of various volatile species with the production of double bonds and free radicals [7,19,20]. The release of volatile fragments (like H₂, CH₃, CO₂, etc.) of ion irradiated PMMA has been detected by Residual Gas Analysis (RGA) [21].

As a result, the lighter hydrogen atoms more easily escape from the shallow implanted layer of PMMA and leave behind un-paired free reactive electrons which can recombine with other electrons to form new covalent bonds [19,22]. The formation of free radicals and dehydrogenation processes in implanted PMMA are attributed to the formation of sp²-carbonaceous networks in the implanted layer, as shown in Fig. 1c.

3.2. FTIR spectroscopic analysis

Fig. 2 shows the FTIR spectra of pristine and C⁺ implanted PMMA. In spectrum 2a, the IR peaks at 840 cm⁻¹ and 986 cm⁻¹ are related to CH₂ and C-O-CH₃ rocking modes. The peaks at 1350–1450 cm⁻¹ show the presence of C-H bending vibrational modes [23]. The bands at 960–1270 cm⁻¹ and 1280–1400 cm⁻¹ correspond to C-O and C-C stretching vibrations [24] while a sharp peak at 1720 cm⁻¹ originates due to C=O stretching vibrations. The spectrum for pristine PMMA exhibits characteristic peaks at 2848 cm⁻¹, 2947 cm⁻¹, 2995 cm⁻¹ due to CH₂ stretching, CH₃ symmetric and CH₃ asymmetric vibrations, respectively [25]. These characteristic peaks confirm the monomer structure of PMMA.

However, the height of transmittance peaks reduces with increasing ion fluence from 9.3×10^{13} to 8.4×10^{14} C⁺/cm² in comparison with pristine sample. The continuous decrease in the

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