Surface topographical and structural analysis of Ag+-implanted polymethylmethacrylate

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ABSTRACT

Specimens of polymethylmethacrylate (PMMA) were implanted with 400-keV Ag+ ions at different ion fluences ranging from 1×10^{14} to 5×10^{15} ions/cm^2 using a 400-kV NEC ion implanter. The surface topographical features of the implanted PMMA were investigated by a confocal microscope. Modifications in the structural properties of the implanted specimens were analyzed in comparison with pristine PMMA by X-ray diffraction (XRD) and Raman spectroscopy. UV–Visible spectroscopy was applied to determine the effects of ion implantation on optical transmittance of the implanted PMMA. The confocal microscopic images revealed the formation of hillock-like microstructures along the ion track on the implanted PMMA surface. The increase in ion fluence led to more nucleation of hillocks. The XRD pattern confirmed the amorphous nature of pristine and implanted PMMA, while the Raman studies justified the transformation of Ag+-implanted PMMA into amorphous carbon at the ion fluence of $\geqslant 5 \times 10^{14}$ ions/cm^2. Moreover, the decrease in optical transmittance of PMMA is associated with the formation of hillocks and ion-induced structural modifications after implantation.

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1. Introduction

Ion implantation is a suitable means for altering the near-surface properties of a wide variety of materials including semiconductors and polymers. Because of having a good control over various implantation parameters such as ion energy, mass, fluence, and penetration depth, it has attracted much attention in the field of materials science [1]. After interaction with target atoms, the energetic ions dissipate their energy in elastic or inelastic collisions. During elastic collisions (nuclear collisions or nuclear stopping), the kinetic energy of implanted ions is transferred to the nuclei or target atoms, leading to the displacement of the target atoms from their original sites. The displaced atoms acquire sufficient energy to displace other atoms in cascade collisions. These collisions are dominant for low-energy implanted ions. On the contrary, inelastic collisions (electronic collisions or electronic stopping) cause ionization or excitation of target atoms due to high-energy ions.

On the basis of energy, ions can be divided into two categories: (1) the swift heavy ions with kinetic energy of about 50–250 MeV and (2) the low-energy ions with kinetic energy of the order of few hundred kiloelectron-volts [2].

The former ions deposit their energy in implanted layers through electronic excitations [3], and disrupt the chemical bonds between the polymer atoms producing free radicals. The swift heavy ions lead to irreversible chemical reactions in the implanted polymer in terms of cross-linking, chain scission, generation of sp^2 and sp^3 hybridization, and finally, amorphization or graphitization of the subsurface layer [4–6].

The swift heavy ions can also affect the surface topographical properties of materials. Many researchers have examined the modification produced by highly charged ions on the surface of a wide variety of materials, including CaF$_2$ [7], Mica [8], GaAs [9], Al$_2$O$_3$, and KBr [10], in terms of formation of craters, pits, and hillock-like structures.

Besides other materials, micro- and nanostructures can be grown on polymers by laser or swift heavy-ion implantation [11,12]. The polymer microstructures have gained much interest in a wide range

of applications, including biomaterials, microelectromechanical systems (MEMS), self-assembly, and microdevices [13].

Swift and heavy ions may produce sputtering as well as unwanted cracks on the surface of implanted polymer. In contrast to swift heavy ions, low-energy ions induce less damage to the polymer surface. Because ion penetration depth also depends on the energy of incoming ions, only surface properties of the implanted polymer can be modified using low-energy ions.

Besides ion energy, other important parameter is ion fluence. It has been reported that in case of low-energy metal ion implantation on polymers, metallic nanoparticles (NPs) nucleate at the high fluence of 10^{16}–10^{17} ions/cm^2 [14–16]. According to the literature, low-energy implantation with high fluence (10^{16}–10^{17} ions/cm^2) is required to transform the polymer into amorphous carbon [45,50]. However, ion implanter requires relatively longer processing time to attain such high fluence. On the contrary, high ion fluence can be achieved in short time by increasing the current density, but it is unfavorable for polymers to avoid thermal degradation.

In order to avoid sputtering and unwanted cracking in this experiment, polymethylmethacrylate (PMMA) is implanted with 400-keV Ag$^+$ ions at the fluence range of 10^{14}–10^{15} ions/cm^2. PMMA is highly sensitive to ion beam irradiation. Because of various excellent properties, such as thermal stability, chemical inertness, high optical clarity, low cost, light weight, and resistance to corrosion, it has gained much interest in different fields of science and technology. Ag$^+$ ions are selected to observe the near-surface effects of shallow implantation.

The purpose is to study the ion track formation and structural modifications in PMMA due to low-energy ions. Ion track formation in polymers is interesting because of not only fundamental phenomenon involving in ion implantation but also the formation of micro-/nanostructures around the ion tracks. Such structures improve the adhesion of implanted polymeric films with other materials and increase the probability of PMMA to be used in microdevices such as MEMS. The ion-induced structural modifications involving the formation of ion tracks and microstructures have been investigated here. These modifications in polymer structures can enhance their optical, electrical, mechanical, and thermal properties.

2. Experimental details

The as-received sheet of PMMA of thickness approximately 2 mm, Goodfellow Cambridge Ltd, UK, was cut into samples of dimension 2×1 cm^2. The samples were ultrasonically cleaned using distilled water for 20 min and then air-dried before implantation. The cleaned samples were mounted on a conductive disk using copper tape. The disk was set at ground potential to avoid surface charging during ion implantation. The samples were implanted with 400-keV Ag$^+$ ions at room temperature using a 400-kV NEC ion implanter. The Ag$^+$ ions were extracted from the sputter version of "CHORDIS" (Cold and Hot Reflex Discharge Ion Source, Model 921) ion source. The extracted ions were then accelerated up to 400 keV by increasing acceleration voltage. The implantation was performed at different ion fluences ranging from 1×10^{14} to 5×10^{15} ions/cm^2 under ultrahigh vacuum of the order of 10^{-8} Torr. The diameter of ion beam spot was approximately 3 mm. The ion beam was raster-scanned over the whole surface of samples to achieve uniform implantation.

The average penetration depth for Ag$^+$ ions was estimated 0.260 μm as per SRIM simulation [17]. The values of electronic and nuclear stopping were 4.65×10^2 and 1.12×10^3 keV/μm, respectively. In addition, the estimated values of longitudinal and lateral straggling were 339 and 305 Å, respectively.

The surface topography of the implanted specimens was examined using confocal microscope μSurf explorer, NanoFocus AG. The surface area of 50×50 μm^2 was scanned under confocal microscope. Structural studies were carried out using Bruker D8 Discover X-ray diffractometer with Cu-Kα radiation (1.54 Å) in the range of Bragg's angle 2θ ($10° \leqslant 2\theta \leqslant 50°$). In addition, Raman spectroscopy was performed using a Ramboss Raman spectrometer. An argon laser with wavelength of 514.5 nm was used as an excitation source. Raman spectra were obtained in the wavenumber range of 400–2400 cm^{-1} under ambient conditions. UV–Visible transmission spectra were obtained in the wavelength range of 300–900 nm using UV-1800 Shimadzu double-beam spectrophotometer.

3. Results and discussion

3.1. Topographical analysis

The surface topographical analysis is performed for the 400-keV Ag$^+$-implanted PMMA using confocal microscope. Confocal microscope is an ideal tool to obtain the three-dimensional (3D) view of surface topographical modifications, with high precision. Fig. 1 shows the 3D microscopic images of Ag$^+$-implanted PMMA at different ion fluences ranging from 1×10^{14} to 5×10^{15} ions/cm^2.

These microscopic images reveal the formation of ion tracks, micropores, and hillock-like-microstructures on the surface of PMMA after Ag$^+$ ion implantation. We define hillock as some protrusion of the size of few microns above the surface of the implanted PMMA. The surface topography of the implanted PMMA at the fluence of 1×10^{14} ions/cm^2 shows the formation of a few isolated hillocks with a height of 0.4–1.3 μm and basal diameter in the range of 0.78–3.13 μm (Fig. 1(a)). After implantation at 5×10^{14} ions/cm^2, the number of hillocks increases with different heights and basal diameters of about 1–2.5 and 1.42–4.52 μm, respectively (Fig. 1(b)). In addition to these localized hillocks, some smaller pores with average depth and diameter of 0.12 and 0.75 μm, respectively, are observed in the implanted surface of PMMA.

However, large hillocks with the height and basal diameter of approximately 0.5–3.5 and 2.04–5.28 μm, respectively, are observed on the surface of Ag$^+$-implanted PMMA at 1×10^{15} - ions/cm^2 (Fig. 1(c)). At this fluence, a sequential pattern of hillocks generate along the trail of incoming ions (marked on the microscopic image). A few pores of average diameter of 0.67 μm are also identified on the surface of Ag$^+$ implanted PMMA at 1×10^{15} ions/ cm^2. With an increment in ion fluence up to 5×10^{15} ions/cm^2, the entire surface is severely covered with hillocks as shown in Fig. 1 (d). The height and basal diameter of these nonlocalized hillocks are approximately 12–16 and 0.8–6.85 μm, respectively. Many small protrusions of height 2–4 μm are observed together with these large hillocks. The number, height, and diameter of hillocks are significantly increased with an increase in ion fluence, as shown in Fig. 1(d).

Ion tracks are the highly damaged zones in PMMA due to the implanted Ag$^+$ ions. In general, when an energetic ion traverses a material, it interacts with the electrons and nuclei of target atoms. Such interactions result in the deflection of energetic ion from its original path until it comes to rest. During these collision events, the initial kinetic energy of the ion is transferred to the target atoms, resulting in the production of atomic displacements, vacancies, free electrons, radicals, cations, and anions close to the path of the incoming ion. The mechanisms involved in the formation of ion tracks have been explained by several models. The two well-recognized physical models are the Coulomb explosion and thermal spike models [18]. Fleischer et al. [19] proposed the first model of the Coulomb explosion for the formation of tracks in solids. According to this model, the generation of high positive charge