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Photoluminescence and optical properties of He ion bombarded ultra-high molecular weight polyethylene

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ABSTRACT

Ion bombardment is a suitable tool to improve the physical and chemical properties of polymer surface. In this study UHMWPE samples were bombarded with 130 keV He ions to the fluences ranging from 1×10^{12} to 1×10^{16} cm^{-2}. The untreated and ion beam modified samples were investigated by photoluminescence, and ultraviolet-visible (UV–vis) spectroscopy. Remarkable decrease in integrated luminescence intensity with increasing ion fluences was observed. The reduction in PL intensity with increase of ion fluence might be attributed to degradation of polymer surface and formation of defects. The effect of ion fluence on the optical properties of the bombarded surfaces was characterized. The values of the optical band gap E_g, and activation energy E_a were determined from the optical absorption. The width of the tail of the localized states in the band gap (E_a) was evaluated using the Urbach edge method. With increasing ion fluences a decrease in both the energy gap and the activation energy were observed. Increase in the numbers of carbon atoms (N) in a formed cluster with increasing the He ion fluence was observed.

1. Introduction

Ultra-high molecular weight polyethylene (UHMWPE) is well known polymer, it exhibit wide range of excellent properties, such as high abrasion resistance, good chemical resistance, and relatively low cost make it a useful material in medicine, high technology engineering, biology, etc. Several methods are used to improve the properties of such material like ion bombardment, electron beam and gamma ray irradiations [1–4]. Because of the large linear energy transfer (LET), i.e. particle stopping power and easily adjustable penetration depth ion beams seem to be a very promising option. Ion bombardment (with high and low energy) of polymers leads to disruption of chemical bonds and eventually to ejection of hydrogen atoms [5] and formation of double bonds –C=C– initiates their clustering [6]. The release of the hydrogen from the material causes changes in the physical properties of the material such as mechanical, electrical and optical properties [7–12]. Following the disruption of original chemical bonds cross-linking and chain scission occurs. The latter cause ejection of polymer fragments with a wide distribution of molecular masses. Moreover, the contact of bombarded samples with the air leads to their rapid oxidation [13–16], which also changes material properties. Structural modifications occurring in the ion beam modified polymers may produce new electronic levels into the forbidden gap of its electronic band structure [17]. Photoluminescence is one of the powerful methods to monitor the modification of localized gap states in polymers [16], and can be used to obtain information about the nature of chemical bonds as well as defects and impurities presence [18,19]. Toth et al. [17] have studied the photoluminescence of UHMWPE bombarded by fast atom. They have observed a decrease in the integrated luminescence intensity and they have attributed this decrease to appearance of new non-radiative recombination levels caused by fast atom beam. In recent years, the optical and electrical properties of polymers have attracted much attention in view of their applications in many optical and electrical devices [20]. Also, the determination of activation energy is of great importance, especially when the material under investigation bombarded with ions.

The aim of this paper is to investigate the effect of He ion bombardment on the optical properties of UHMWPE. In the present study, significant changes of different amounts have been observed in optical response of the UHMWPE polymers after ion beam bombardment. The influence of ion bombardment on the photoluminescence behavior, optical band gap, activation energy and the production of carbon clusters are also studied.

2. Materials and methods

The UHMWPE studied was commercial Goodfellow (UK) product of molecular weight M_w = 120,000 g/mol, degree of

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crystallinity X_c = 65% and density of 0.95 g/cm^3. The samples used were flat, rectangular wafers of 1 mm thickness. Ion bombardment was carried out using Balzers MPB 202 RP ion implanter at Institute of Electronic Material Technology, Warsaw, Poland, using 130 keV He ions with the fluence ranging from 1×10^{14} to 2×10^{16} cm^{-2}. Beam density was maintained below 0.1 μA/cm^2 in order not to let the sample temperature rise. The ion irradiation parameters were determined using SRIM code (version 2008) [21]. The He ions penetrate ~1.14 μm in UHMWPE sample with an initial electronic (S_e) and nuclear (S_n) energy loss of 169.20 and 1.57 eV/nm, respectively. The depth distribution of the displaced atoms (damage) in UHMWPE bombarded with He ions at two different fluences calculated with the SRIM code is shown in Fig. 1.

Photoluminescence measurements have been focused on irradiation induced defects. Photoluminescence spectra were taken with RF-1501 SHIMADZU double monochromator spectrometer. All spectra were measured in reflection geometry and a special attention was paid to avoid stray light. Luminescence was excited by the light of high-pressure xenon lamp dispersed by a grating monochromator and detected by a photomultiplier through a second grating monochromator. PL emission spectra of the samples of pristine and ion bombarded were recorded with excitation wavelength of 350 nm.

The UV–vis measurements were performed in the wavelength range from 190 to 900 nm, using the UV–vis spectrophotometer model JASCO V560, Japan. During the measurements, the UHMWPE films were held in a metal holder after cleaning with bi-distilled water, keeping air as a reference.

3. Results and discussion

3.1. Photoluminescence (PL) studies

Fig. 2 shows the PL spectra of UHMWPE bombarded with 130 keV He ions for fluences in the range 10^{12}–10^{16} ions/cm^2. PL band with peak at ~706 nm is recorded. It is observed that the PL intensity is found to be reduced with increase of ion fluence. For most ion energy range of interest, nuclear stopping by small atoms such as He is negligible because the Rutherford cross-section and momentum transfer by the low mass is small [22]. Therefore, the decrease in intensity with increase the ion fluencies might be attributed to the formation of defects (cf. Fig. 1) and destruction of surface chemical species due to increase the energy deposited through electronic energy loss ($S_e \gg S_n$). This decrease in the luminescence intensity with increase ion fluence prove the formation of new radiative recombination levels [17], which can be related to He ion beam, induced compositional transformation to the surface layer. In order to study the destruction or compositional transformation due to He ion bombardment UHMWPE, we have performed UV–vis studies of pristine and ion bombarded UHMWPE.

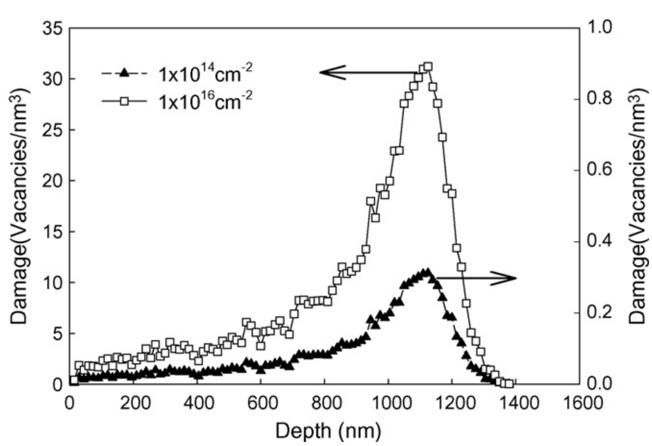

Fig. 1. SRIM calculated the depth distribution of damage for 130 keV He ions in UHMWPE.

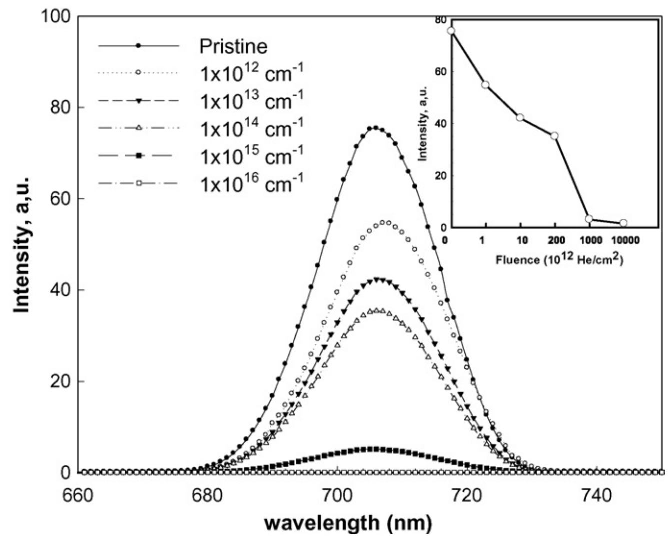

Fig. 2. Photoluminescence spectra (λexc 350 nm) of 130 keV He ions bombarded UHMWPE as a function of He ion fluence.

3.2. Optical studies

3.2.1. UV–vis absorption spectroscopy

The optical absorption method can be used for studying of the optically induced transition and can supply information about the energy gap and the bond structure in crystalline and amorphous materials [23]. Fig. 3 shows the UV–VIS spectra of the UHMWPE bombarded with different fluences of 130 keV He ions in the range of (200–850 nm). A considerable increase in the optical absorption can be observed for each treated sample, when compared to that of the untreated one. This increase in the optical absorption due to He ion beam is in a good agreement with the creation of new electronic level in the forbidden gap [17]. These electronic levels are located in the forbidden gap and increase the optical absorption. The decrease in PL intensity with increase the ion fluence as observed previously can be attributed to the dominant increase in the optical absorption of

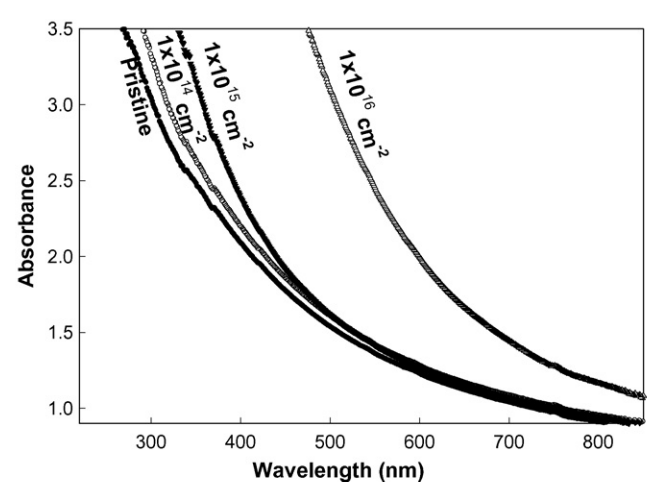

Fig. 3. UV/vis absorption spectra of pristine UHMWPE bombarded with 130 keV He ions of fluences range (1×10^{14}–1×10^{16} cm^{-2}).