High-dose boron and silver ion implantation into PMMA probed by slow positrons: Effects of carbonization and formation of metal nanoparticles

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Abstract. The Doppler broadening slow positron beam spectroscopy (SPBS) data for the previously observed effect of carbonization in high-dose (>10¹⁶ ion/cm²) 40 keV boron-ion-implanted polymethylmethacrylate (B:PMMA) and another one obtained for the effect of formation of metal nanoparticles in high-dose 30 keV silver-ion-implanted polymer (Ag:PMMA) are compared. Following to the Doppler broadening SPBS results, a difference in the high-dose ion-irradiation-induced processes in B:PMMA and Ag:PMMA is detected.

1. Introduction

Ion implantation is well-known as a powerful experimental tool for altering and significant modification of surface structure of materials. Two main features, important for practical use, such as carbonization and formation of metal nanoparticles are expected for polymer materials subjected to high-dose (>10¹⁶ ion/cm²) low-to-medium energy ion implantation (for reviews, see [1,2]).

High-dose ion-irradiation-induced processes in polymers are accompanied by substantial improvements in hardness, wear resistance, oxidation resistance, resistance to chemicals, and electrical conductivity due to carbonization [3-7].

Recently, carbonization or formation of carbon nanostructures has experimentally been verified [8] for 40 keV boron-ion-implanted polymethylmethacrylate (B:PMMA) by using slow positron beam spectroscopy (SPBS) based on Doppler broadening of positron annihilation γ-rays as a function of incident positron energy and positron annihilation lifetime at an positron energy of 2.15 keV. The SPBS results have also been found in consistent with Raman spectroscopy results for same structures B:PMMA [9,10].

The present work is aimed to compare the Doppler broadening SPBS data for the previously observed effect of carbonization in high-dose B:PMMA [8] with the Doppler broadening SPBS data for high-dose 30 keV silver-ion-implanted in same polymer (Ag:PMMA) with metal nanoparticles (NPs).
2. Experimental
Low-energy ion implantation of the polymer was performed under a pressure of $10^{-5}$ Torr at room temperature with an ILU-3 ion accelerator (KPTI, Russia) [2,11,12]. As substrates, 1.2-mm-thick PMMA plates with a high optical quality and transparency in a wide spectral range 400-1000 nm were used. Ag:PMMA samples were fabricated with an energy of 30 keV, an ion current density of 1 μA/cm$^2$ and doses of $2.5 \times 10^{16}$ and $1.0 \times 10^{17}$ ion/cm$^2$ (both doses are enough for the formation of Ag NPs in the surface region of polymer [2,11-16]) and were tested using Doppler broadening technique (TUS, Japan). The experimental system used was a magnetically guided slow positron beam apparatus with a trochoidal $E \times B$ filter [17]. The beam diameter was about 6 mm and the energy of the incident positrons ranged from 0.1 to 30 keV. The 511 keV $\gamma$-rays from the samples were detected using a Ge detector in coincidence with a NaI(Tl) detector.

3. Results and discussion
Figure 1 shows positron annihilation Doppler broadening $S$-parameter dependences for the virgin (non-irradiated) PMMA and B:PMMA [8] and Ag:PMMA samples formed with a dose of $2.5 \times 10^{16}$ ion/cm$^2$ as a function of incident positron energy in the range 0-30 keV. Apart from the surface effect below 0.4 keV, the $S$-parameter for the pristine sample is practically constant, while that for the irradiated sample showed remarkable reduction below an incident positron energy $E_p \approx 4$ keV for B:PMMA and $E_p \approx 2$ keV for Ag:PMMA. Similar behavior of the $S$-$E_p$ dependence for ion-irradiated polymeric materials has been observed for 150 keV He$^+$-implanted poly-L-lactic acid (PLLA) polymer [18,19]. The decrease in the $S$-parameter shows that the low momentum component of the Doppler broadened photon peak is decreased for implanted sample. This fact could be interpreted by a reduction of the positronium formation fraction as it has been mentioned for He:PLLA [19] and experimentally verified using positron annihilation lifetime measurements at incident positron energy of 2.15 keV for B:PMMA [8]. According to the analysis of $S$-$E_p$ dependence performed in the work of Saito et al. [19] and recovery of the $S$-parameter for $E_p$ larger than 8 keV for B:PMMA and 4 keV for Ag:PMMA as seen in Fig. 1, it is suggested that $E_p \approx 4$ keV for B:PMMA and $E_p \approx 2$ keV for Ag:PMMA, which correspond to the middle value of the $S$-parameter, could be explained as that the positrons implanted with such energy annihilate around the Bragg peak of the ion implantation.

![Figure 1](image-url)  
Figure 1. Positron annihilation Doppler broadening $S$-parameter for the pristine PMMA and irradiated B:PMMA (left, the error bars are within the size of the symbol) [8] and Ag:PMMA (right) formed with a dose of $2.5 \times 10^{16}$ ion/cm$^2$ as a function of incident positron energy in the range 0-30 keV. Vertical arrows indicate incident positron energy, $E_p$, for the middle point of the $S$-parameter. The $S$-parameters for B:PMMA and Ag:PMMA are different from each other because the experiments were conducted with different measuring systems.
Figure 2 shows positron annihilation Doppler broadening $S$-parameter for the irradiated B:PMMA samples with doses of $2.5 \times 10^{16}$, $3.75 \times 10^{16}$, and $5.0 \times 10^{16}$ ion/cm$^2$ [8] and Ag:PMMA samples with doses of $2.5 \times 10^{16}$ and $1.0 \times 10^{17}$ ion/cm$^2$ as a function of incident positron energy in the range 0-5 keV. It is seen that a rather stable behavior of $S(E_p)$ parameter in the near-surface range 0-1 keV for the high-dose B:PMMA samples is observed. At the same time, in the case of the higher dose Ag:PMMA the increase of $S(E_p)$ parameter in the near-surface range 0-1 keV is seen. It is suggested that the detected difference in the $S(E_p)$ dependences is probably due to formation of Ag nanoparticles for high-dose Ag:PMMA [2,16] and changes of density in the near-surface region of polymer. Besides, the surface sputtering effect for Ag:PMMA, which was first observed and published in the work [20], should be also taken into account as additional surface modification factor as shown in Fig. 3. In order to make more reliable conclusions the further Doppler broadening SPBS study of Ag:PMMA with higher ion doses and positron annihilation lifetime measurements are needed.

Figure 2. Positron annihilation Doppler broadening $S$-parameter for the irradiated B:PMMA samples with doses of $2.5 \times 10^{16}$, $3.75 \times 10^{16}$, and $5.0 \times 10^{16}$ ion/cm$^2$ (left) [8] and Ag:PMMA samples with doses of $2.5 \times 10^{16}$ and $1.0 \times 10^{17}$ ion/cm$^2$ (right) as a function of incident positron energy in the range 0-5 keV. The $S$-parameters for B:PMMA and Ag:PMMA are different from each other because the experiments were conducted with different measuring systems.

Figure 3. 3D image of surface sputtering for 30 keV Ag:PMMA with a dose of $2.5 \times 10^{16}$ ion/cm$^2$ [20].
4. Conclusions
The Doppler broadening SPBS data for the previously observed effect of carbonization in 40 keV B:PMMA (2.5×10^{16}, 3.75×10^{16}, and 5.0×10^{16} ion/cm^2) [8] and for 30 keV Ag:PMMA (2.5×10^{16} and 1.0×10^{17} ion/cm^2) with metal nanoparticles have been compared. It has been established that a rather stable behavior of $S(E_p)$ parameter in the near-surface range 0-1 keV for the high-dose B:PMMA samples is seen; whereas in the case of the higher dose Ag:PMMA the increase of $S(E_p)$ parameter in the near-surface range 0-1 keV is detected.

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