



Time of flight-secondary ion mass spectrometry analysis of protein adsorption on a polyvinylidene difluoride surface modified by ion irradiation



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ABSTRACT

We investigated the effects of nanoscopic surface modification of polyvinylidene difluoride (PVDF) and low-density polyethylene (LDPE) by plasma-based ion implantation on protein adsorption with time of flight-secondary ion mass spectrometry (ToF-SIMS) analysis. The chemical composition of the LDPE and PVDF surfaces was changed by ion irradiation. In particular, irradiation substantially decreased the number of C–H and C–F bonds on the PVDF surface, but only slightly decreased that of C–H bonds for LDPE. These decreases may reflect a higher hydrogen recombination rate of the LDPE than the PVDF surface. An increase in oxygen was observed on both the LDPE and PVDF surfaces following ion irradiation, but was saturated after irradiation of $1 \times 10^{15} \text{ cm}^{-2}$ on the PVDF surface. The hydrophilicity of the ion-irradiated LDPE surface was promoted with an increase of the total ion fluence. Ion irradiation also changed the surface properties of PVDF to become more hydrophilic, but the variation did not correlate with the total ion fluence presumably due to the presence of fluorine atoms and the saturation of oxidation. Both bovine serum albumin (BSA) and collagen adsorption were suppressed on the LDPE surface by ion irradiation, which may have resulted from a decrease of the hydrophobic interaction. By contrast, ion irradiation increased protein adsorption on the PVDF surface, and BSA was adsorbed more than collagen, whereas there was no difference in the adsorption between BSA and collagen on the ion-irradiated LDPE surface. Moreover, the adsorption of BSA decreased on the oxygen- and fluorine-rich PVDF surface. These results indicate that the nanoscopic composition changes on the PVDF surface affect the adsorption behavior of BSA. Specifically, ferroelectric property on the PVDF surface was changed by ion irradiation and the nanoscopic change in polarity presumably affected the protein adsorption. Our findings suggest that selective adsorption control of protein can be achieved by ion irradiation to PVDF surface.

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1. Introduction

Achieving adhesion control of proteins has been investigated for various applications, such as in anti-fouling systems [1] and for the design of biocompatible interfaces [2–4]. In particular, the selective adhesion control of proteins is one of key technologies and is expected for the evolution of regenerative medicine and tissue engineering [5,6]. Polymer materials have been widely employed as base materials to develop a biocompatible interface owing to their chemical stability. However, most of polymer surfaces induce

non-specific protein adsorption, which leads to undesired consequences, such as a platelet thrombus in the blood vessels following plasma protein adsorption. Various chemical approaches for the modification of polymer surfaces have been developed to control protein adsorption, including a phospholipid polymer coating [7], graft of a hydrophilic polymer brush [8–11], and conjugation of a self-assembled monolayer [12,13]. These processes have been in practical use but are limited only to the anti-nonspecific adsorption of proteins. Exploitation of physical processes using energetic charged particles, such as ion implantation techniques, is also effective to modify the polymer surface [14–19]. Plasma-based ion implantation (PBII) is one of the ion-irradiation techniques and has widely studied for surface modification [20,21]. The applied pulsed-plasma in PBII prevents thermal impact and charge-up on insulated surfaces [22]. The process is better suited for modifications of polymer materials.

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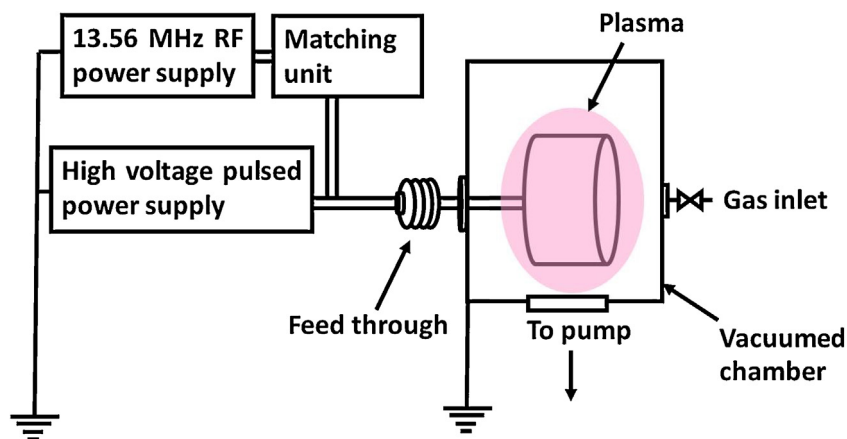


Fig. 1. Experimental setup for plasma-based ion implantation.

Polyvinylidene difluoride (PVDF) film has a high mechanical strength and hydrophobicity, and has been widely adopted in biomedical and bio-separation applications, such as for immunoblotting assays and in a bio-filtration system [23–25]. Low-density polyethylene (LDPE) has a similar molecular structure to PVDF with a C–C main chain and substitutes hydrogen atoms for fluorine atoms. In this study, we evaluated the surface modification of LDPE and PVDF with the PBI method utilizing time of flight-secondary ion mass spectrometry (ToF-SIMS) analysis. We also investigated the adsorption of bovine serum albumin (BSA) and collagen on the modified surfaces and discussed the controllability of the adsorption properties.

2. Experimental

The PBI technique was used for the surface modification of polymer films [20]. The experimental setup is illustrated in Fig. 1. Pulsed plasma was generated by an RF (13.56 MHz) power of 1000 W with an Ar pressure of 8×10^{-2} Pa. During the plasma generation step, a negative pulsed-DC voltage of 20 kV was applied to the electrode. The pulse width was 50 μ s for the RF plasma and 5 μ s for the negative-DC voltage, respectively. These pulses were synchronized with a repetition frequency of 1000 Hz. A total ion fluence was set from 1×10^{14} to 1×10^{17} ions/cm², corresponding to 1–1000 ions/nm², respectively. The total ion fluence was controlled by the integrated time of the applied DC pulse current. The implantation process was calculated with a Monte Carlo simulation program, Stopping and Range of Ions in Matter (SRIM2008) [26]. The estimated cross section on PVDF surface is approximately 6×10^3 nm² for implantations of 1×10^4 ions into an identical point, that is, 0.6 nm²/ion. The deposited energy is 27.1 eV on the surface within a thickness of 0.1 nm. Polyvinylidene difluoride (PVDF) film with a thickness of 200 μ m was purchased from Bio-Rad Lab. (Immun-Blot PVDF Membrane). Low density polyethylene (LDPE) film with a thickness of 110 μ m was purchased from Gunze Limited. (FUN-CRARE). These polymers have the –C–C– main chain with different bonds; C–H in LDPE, and alternate C–H and C–F in PVDF. The non-irradiated PVDF surface was stable and showed no chemical changes over the long term. In addition to the as-irradiated PVDF samples, oxidized PVDF surfaces retained for a longer term (approximately 2 years) after ion irradiation were also evaluated. Contact angle measurement with diluted water was conducted on the ion-irradiated surfaces to evaluate the changes in hydrophilicity induced by ion irradiation. Seven data points were acquired for each contact angle measurement and were averaged excluding the maximum and minimum values.

Protein adsorption was examined with two kinds of proteins, BSA (SIGMA-ALDRICH Corp., Mw: 66 kDa) and collagen (I-PC, KOKEN Co., Mw: 300 kDa). Each protein was dissolved in phosphate buffered saline (PBS) at a concentration of 0.1 μ mol/L (pH: 7.2). First, the ion-irradiated film was dipped in methanol for 30 s and soaked in distilled water for 30 min. Then, 10 μ L of BSA or collagen solution was dropped onto the ion-irradiated film surface. After holding the protein on the surface for 5 min, the film was rinsed in 2 mL of distilled water for 5 min 3 times; thus, the total rinse process took 15 min.

The ion-irradiated polymer surface and the protein adsorption were analyzed with a ToF-SIMS system (PHI TRIFT V nanoTOF by ULVAC-PHI Inc.) with liquid-metal-ion guns of Au. The primary ion was Au₃⁺, which was accelerated at 30 kV with a pulse width of 20 ns. A raster size of the primary ion beam was 100 μ m \times 100 μ m with a resolution of 256 \times 256 measuring points. The detailed conditions are described elsewhere [27].

The adsorption of BSA and collagen was evaluated with a secondary ion count at $m/z = 70$ (proline, C₄H₈N⁺) normalized by CF⁺ ($m/z = 31$) for PVDF and by C₂H₃⁺ ($m/z = 27$) for LDPE, assigned from the polymer films, respectively.

3. Results and discussion

3.1. Surface modification of LDPE and PVDF by plasma-based ion implantation

The negatively charged secondary ions from the ion-irradiated surface were acquired with ToF-SIMS. The ion count is normalized to that of CH⁻. In our previous in situ measurement [27], the count ratio of CH⁻ between ion-irradiated and non-irradiated areas was almost constant within about a 20% variation up to a total ion fluence of 1×10^{16} cm⁻². Here, we adapted CH⁻ count for the normalization.

Fig. 2(a) shows the dependence of the total ion fluence on the normalized ion count ratios for LDPE. Contrary to an increase of O⁻/CH⁻ and C₂⁻/CH⁻, H⁻/CH⁻ slightly decreased following ion irradiation. Fig. 2(b) shows the dependence of the total ion fluence for PVDF. H⁻/CH⁻ decreased during the course of ion irradiation, reaching a constant level beyond the total ion fluence of 1×10^{15} cm⁻². F⁻/CH⁻ and C₂⁻/CH⁻ decreased with an increase in the total ion fluence. O⁻/CH⁻ increased but saturated at around 1×10^{15} cm⁻². As reported in our previous in situ measurement in the high vacuum chamber [27], the ion-irradiated surfaces of LDPE and PVDF have exhibited recombination with ambient gas molecules after dissociation of the hydrogen and/or fluorine atoms and the PVDF surface has shown a lower recombination rate than

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