Surface Reaction on Polyvinylidenefluoride (PVDF) Irradiated by Low Energy Ion Beam in Reactive Gas Environment

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ABSTRACT: Polyvinylidenefluoride (PVDF) was irradiated by a keV Ar^+ ion in O₂ environment for improving adhesion between PVDF and Pt, and reaction between PVDF and the ion beam has been investigated by X-ray photoelectron spectroscopy (XPS). The adhesion test between Pt and the modified PVDF was carried out by boiling test, in which the specimens were kept in boiling water for 4 h. Two failure modes (buckling up due to weak adhesion and crack formation due to strong adhesion) of Pt films have been observed in the system. Contact angle of PVDF was reduced to 31 from 75° by the irradiation of $1 \times 10^{15} \text{ Ar}^+$ ions/cm² with oxygen flow rate of 8 sccm. The surface of the irradiated PVDF became more rough as ion dose increased. The improved adhesion mechanism and identification of newly formed chemical species have been confirmed by Carbon 1s and Fluorine 1s X-ray photoelectron core-level spectra. The main reaction occurred at the irradiated PVDF surface is an ion-beam-induced oxidation accompanied with preferential sputtering of fluorine. Newly formed chemical species at interface are regarded as ester and carboxyl groups. Adhesion of the Pt-PVDF interface was improved by ion irradiation in O_2 environment. This improvement is originated from the presence of carbon-oxygen bonds on the irradiated PVDF surface. Comparison of failure modes on the irradiated PVDF at various conditions after the boiling test shows that adhesion of Pt film is largely affected by the product of ion-assisted reaction. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 72: 41-47, 1999

Key words: PVDF; hydrophilic surface; ion beam irradiation; oxygen environment; X-ray photoelectron spectroscopy

INTRODUCTION

 CF_2 —) is one of the crystalline polymers and its phases are I(β), II(α), III(γ), and II_p(α''). I(β) and II_p(α'') phases of PVDF have a ferroelectric property and have spontaneous dipoles within their crystal structures. Cu or Al has been adopted as a metal electrode on PVDF due to fairly adhesive interface. However, demanding a high-quality ferroelectric property, chemically inert metals, such as Pt and Au with a large work function, are needed to minimize leakage current at the interface between metal and the polymer, but their

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poor adhesion to PVDF surface has to be solved as an electrode of PVDF thin film. The characteristics of fluorine-containing polymers have the low surface energy, hydrophobic property, and poor adhesion to other materials, and there is necessity to modify the hydrophobic surface into hydrophilic one without the degradation of electrical properties.

There are many physical and/or chemical methods in polymer modification, such as γ -ray, corona, direct current/radio frequency (DC/RF) sputter etching, arc discharge, plasma, and a few $\dot{M}eV \sim 100$'s keV ion beam.^{4,6-17} The surface modification of polymer has been applied for wetting to liquid, printing to dye, and enhancing adhesion to metals, ceramics, or polymers. However, the polymer surface is easily damaged by the irradiation of high energetic particles, resulting in crosslinking, bond scission, and carbonization, and the modified polymers with hydrophilic functional groups of low molecular weight are unstable in organic solvent so that functional groups could be solved into water. In previous articles,^{18–20} the modification by the ion-assisted reaction (IAR) could make the surface of specific polymer become hydrophilic one, in which poly-(ethylene terephthalate) (PET), polycarbonate (PC), and poly(methyl methacrylate) (PMMA) were modified into totally wettable hydrophilicsurface-bearing hydroxyl, carboxyl groups, and so on. Moreover, the adhesion of metal on the irradiated polyimide (PI), polytetrafluoroethylene (PTFE), and PC was significantly improved by the ion-assisted reaction.

In this article, chemical species on the irradiated PVDF were investigated by C1s and F1s X-ray photoelectron core-level spectra and wettability in terms of effects of ion energy, ion dose, and environment gas species. The relationship between ion irradiation and surface roughness was examined by atomic force microscope (AFM) and scanning electron microscope (SEM).

EXPERIMENTAL PROCEDURE

Commercial PVDF [(--CH₂---CF₂--)_n; Penn Walt Co.] was cut into $40 \times 20 \text{ mm}^2$ sheet, and the thickness of PVDF was 45 μ m. These specimens were rinsed by methanol and triple-distilled water for 5 min in the ultrasonic cleaner to remove the contamination on the surface. Drying was carried out for 4 h in the dry oven. The contact angle of the untreated specimen was measured, and they were introduced into the IAR system. The base pressure was 1 \times 10 $^{-5}$ Torr, and the working pressure was changed from 1.4 to 3.1 $imes 10^{-4}$ Torr as the O₂ gas flow rate increased. The Ar⁺ ion was generated by a cold hollow cathodetype ion gun equipped with a 5-cm convex grid. The current of the Ar⁺ ion beam was controlled by a discharge voltage and a discharge current. Amounts of ions were measured by a Faraday cup biased -24V to keep background electrons from entering it, and those were controlled by exposure time at a fixed ion beam current from 1×10^{14} to 1×10^{17} Ar⁺/cm². Acceleration potentials of Ar⁺ ion were fixed at 1.0 keV. Flowing rate of argon gas (99.9+%) was 1.5 sccm (mL/min) and the flowing rate of oxygen (99.99 + %) gas was fixed at 8 sccm by a mass flow controller. The oxygen gas was sprayed near the surface of PVDF during the ion beam irradiation. Schematic diagram of IAR system is shown in previous articles.^{18–20}

Contact angles (θ) of the specimens were measured by a contact angle meter (Tantec Co.; CAMmicro). In the measurement, 0.025 mL of tripledistilled water was dropped on six different places on the PVDF surface, and the average contact angle was calculated. The contact angle was measured just after dropping water. The deviation of contact angles was about 2-3°. AFM (Park's instrument) was used to examine the surface morphology for the Ar⁺ ion irradiated with and/or without the oxygen gas flow. Pt films on the irradiated PVDF were deposited up to 1000 Å by Ar⁺ ion beam ex situ sputter deposition. Base pressure is 5 \times 10⁻⁶ Torr, and working pressure is 8 $imes 10^{-5}$ Torr. The thickness of Pt film was uniform on the whole area of polymer surface. Adhesion of the Pt-PVDF system was compared using a boiling test, which was conducted by immersion in boiling water for 4 h. Observation of surface morphology was performed by an optical microscope with the magnitude of 100 times. Chemical reaction on the irradiated PVDF surface was investigated by X-ray photoelectron spectroscopy (XPS) (VG) using an Mg K_{α} line (hv = 1253.6 eV). Pass energy of the analyzer is fixed at 187.85 eV for acquiring the high-resolution core-level spectra. Base pressure was 1×10^{-10} Torr, and working pressure was 2×10^{-9} Torr in the process of acquiring XPS spectra.

RESULTS AND DISCUSSION

An adhesion test has been carried out by a scotch tape test, but the difference before and after



Figure 1 Microphotographs of Pt layers on PVDF modified by various Ar⁺ ion irradiation in an O₂ environment after a boiling test of 4 h: (a) pristine; (b) 5×10^{14} Ar⁺/cm²; (c) 1×10^{15} Ar⁺/cm²; (d) 1×10^{17} Ar⁺/cm².

treatments could not be found, except for the boiling test, one of the severe adhesion tests. The result of adhesion between Pt thin films and the PVDF after boiling test for 4 h was shown. Figure 1(a) shows the Pt on the pristine PVDF, and buckling phenomena of the Pt layer were observed on the whole area. The buckled area of Pt layer on PVDF irradiated by $5 \times 10^{14} \, \text{Ar}^+/\text{cm}^2$ with an O_2 flow rate of 8 sccm was reduced significantly, as shown in Figure 1(b). In the case of the Pt layer on the PVDF irradiated by $1 \times 10^{15} \text{ Ar}^+/\text{cm}^2$, there were no buckled layers, but there were many cracks in the Pt layer in Figure 1(c). Compared with above results, the stress-release mode of Pt-PVDF irradiated 1 \times 10^{15} $\rm Ar^+/cm^2$ with an $\rm O_2$ flow rate of 8 sccm was changed from the buckling mode of Pt film to the crack propagation mode in the Pt film. The crack propagation of the Pt film

on PVDF irradiated by $1 \times 10^{15} \, \mathrm{Ar^+/cm^2}$ with an O_2 flow rate of 8 sccm indicated that the adhesion of the Pt-PVDF system was remarkably improved to keep from infiltration of water into the Pt-PVDF interface, and the stress at the interface was released by the formation of crack due to strong adhesion. Within the Pt layers on the PVDF irradiated by 1×10^{16} and 1×10^{17} Ar⁺/ cm^2 with an O_2 flow rate of 8 sccm, a crack propagation mode still prevailed within Pt layer after boiling test. More irradiated than $1 \times 10^{15} \text{ Ar}^+/$ cm² with an O₂ flow rate of 8 sccm, the Pt-PVDF system kept a good adhesive interface. These trends suggest that Ar^+ ion irradiation in an O_2 environment should enhance the adhesion of Pt-PVDF system.

XPS analysis was conducted for identification of chemical states induced by the energetic ions



Figure 2 C1s photoelectron spectra of the pristine and the irradiated PVDF with increasing ion fluence: (a) pristine; (b) $5 \times 10^{14} \text{ Ar}^+/\text{cm}^2$; (c) $1 \times 10^{15} \text{ Ar}^+/\text{cm}^2$; (d) $1 \times 10^{16} \text{ Ar}^+/\text{cm}^2$; (e) $1 \times 10^{17} \text{ Ar}^+/\text{cm}^2$.

and the O_2 environment. Figure 2 shows the C1s spectra of pristine and irradiated PVDF. The C1s (a) spectra of pristine PVDF includes --CH₂--(286.2 eV) and —CF2— (290.8 eV) and shows a typical peak shape of pristine PVDF. Contrary to the result of the pristine, the C1s spectra of (b) and (c) irradiated by 5×10^{14} and 1×10^{15} Ar⁺/ cm^2 , respectively, showed that the peak intensity of --CF₂-- drastically decreased, and then new peaks related to oxygen and singly-fluorine bonded carbon appeared between -CH2- and $-CF_2$ peak positions. The peak of $-CH_2$ was shifted to a lower binding energy of about 285 eV, which means the neighboring of -CH2- was changed from highest electronegative fluorine atoms to other atoms, but not to C=C graphite carbon. More interesting results are the creation of new bonds at higher position over 286 eV, which indicates that C=O, C-O, and so on, were formed on the PVDF surface, as well as the remarkable reduction of -CF₂- peak intensity.

Adem et al.²¹ reported that the peak positions of carbonized, singly-oxygen-bonded, singly-fluorine-bonded carbon are located at -1.2, 0.7, and 3.1 eV higher than that of -CH₂-, respectively. Also, it was reported that there are singly fluorinated carbons and the peroxidation of radicals after the exposure of MeV ion beam irradiated PVDF to air.²¹ These newly formed bonds related to oxygen might be generated by a reaction between the remaining radicals and air. However, as shown in Figure 2, the complex spectrum (b) was observed in comparison of the reported spectra. It is considered that an artificial reaction of free radicals, produced by energetic ion and environment gas species, induced the generation of oxygen-doubly-bonded carbons. The newly formed bonds related to oxygen might be identified as -(C-O) and -(C=O) bonds. Generally, ion irradiation can only create bond scissions of C-C, C-H, and C-F bonds randomly, and ion irradiation could reduce $-CH_2$ — and $-CF_2$ — peak simultaneously.^{21–24} Formation of a C=C peak should appear at a lower position of -CH₂binding energy. In comparison to high-energy ion irradiation, $-CH_2$ and $-CF_2$ peak intensity showed a different reduction, and the artificial oxygen substitution in polymeric chain was wellnoticed instead of subsidiary oxidation resulting from the exposure to air in this experiment. C1s spectra of Figure 2(d) and (e) irradiated by 1 $imes 10^{16} ext{ and } 1 imes 10^{17} ext{ Ar}^+/ ext{cm}^2,$ respectively, represented the stiff increase of doubly bonded carbon (=C=), and their shapes were skewed to lower binding energy. Most fluorine atoms in polymeric chains on the irradiated PVDF surface were detached as shown in the $-CF_2$ peak of the (b)-(e) spectra in Figure 2. The carbonization of PVDF by high-dose low-energy ion irradiation is similar to the results reported by many researchers by whom high-energy ion and/or heavyweight ion irradiation has been investigated.²²⁻²⁴ In the PVDF irradiated by a high-energy ion beam, =C= lines were significantly increased, and -CH₂- and -CF₂- lines were remarkably decreased. The ==C== line was originated from the detachment of fluorine and/or hydrogen atoms. In comparison to the above XPS study and wetting property variation, the intended oxidation was attempted, and the polar groups, which were formed by IAR, could successfully change the surface properties of the irradiated PVDF.

In the case of other experiments, the creation of =C was explained in terms of electronic stopping power $(dE/dx)_e$. But in this experiment, the

energy of irradiating ions is 1 keV, and their distribution and induced damage should be investigated considering nuclear stopping power (dE/ $dx)_n$ and sputtering yield. The induced damage by 1 keV Ar⁺ irradiation and the reaction between the induced damage and the blown reactive O_2 gas have been considered. $(dE/dx)_{total}$ of PVDF calculated by Transport of Ions in Matter (TRIM) code is 17.60 eV/Å at 1 keV Ar⁺ ion irradiation and is a medium value between PE (9.30 eV/Å) and PTFE (22.00 eV/Å). The stopping power of the C—F bond (10.988 eV/Å) or the C—H bond (7.244 eV/Å) is larger than that of the C—C bond (3.938 eV/Å) at 1 keV. The surface binding energy (equivalent to heat of sublimation) of carbon (7.41 eV) is larger than that of fluorine or hydrogen. The detachment possibility of fluorine and hydrogen atoms might be higher than the carbon atoms at 1-keV ion irradiation. These simulation and XPS results may support preferential detachment of fluorine in terms of sputtering probability. From this simulation result, it might be concluded that Ar⁺ ion sputtered out fluorine or hydrogen atoms in PVDF polymer and resulted in the free radicals formation; thus, blown O_2 gas could react upon activated sites on PVDF. However, the PVDF surface irradiated by the Ar⁺ ions exceeding the optimum ion dose could be degraded and carbonized.

In order to confirm above results of C1s spectra, F1s photoelectron spectra are shown in Figure 3. With an increasing ion dose, the amount of the fluorine was reduced significantly. The preferential detachment of fluorine in PVDF occurred due to the energetic particles, as above mentioned. In the F1s spectra study, the small shift to low binding energy could be explained by reduction of molecular potential, which might be originated from preferential etching of high electronegative fluorine. The detachment of fluorine atoms resulted in carbonization and crosslinking. Compared with irradiated PTFE,^{25,26,27} preferential sputtering of fluorine can produce a cone-type fibrous surface and crosslinking after ion irradiation; however, the irradiated PVDF surface was relatively slightly affected.

Krupp²⁸ reported that functional groups on the polymer surface, such as ester or carboxyl groups, could enhance the adhesion between the metal and polymer. In the case of PVDF exposed to ozone, newly formed oxygen-bonded carbon was identified as radicals produced by -(C-O) of oxygen atom.²⁹ Similar to results of exposure to ozone, carbon atoms in polymeric chains were



Figure 3 F1s photoelectron spectra of the pristine and the irradiated PVDF with increasing ion fluence: (a) pristine; (b) $5 \times 10^{14} \text{ Ar}^+/\text{cm}^2$; (c) $1 \times 10^{15} \text{ Ar}^+/\text{cm}^2$; (d) $1 \times 10^{16} \text{ Ar}^+/\text{cm}^2$; (e) $1 \times 10^{17} \text{ Ar}^+/\text{cm}^2$.

activated by detachment of fluorine atoms and could react upon the oxygen species. These radicals play an important role on contact electrification for thin layer adhesion. This result can strongly support the fact that the enhanced adhesion strength of Pt layer on the PVDF results from the generation of polar groups after IAR treatment.

In order to investigate the surface of PVDF irradiated in the O_2 environment, contact angles to water were measured and are shown in Figure 4. At most, only Ar^+ ion irradiation enabled the contact angle to water to be lowered from 75 to 50°. The contact angle of water on the irradiated PVDF was reduced from 75 to 31°. But, when the PVDF surface was irradiated by Ar^+ ion in the O_2 environment, the contact angle of PVDF irradiated by the Ar^+ amount exceeding 1×10^{15} ions/ cm², reincreased to 65°. Contact angle variation of Ar^+ ion irradiation only showed higher values than those in the O_2 environment. This difference of contact angle can support the fact that the role



Figure 4 Contact angle variation of irradiated PVDF with increasing ion fluence.

of blown O_2 gas is a reactant with the irradiated PVDF and the formation of polar groups on PVDF. Also, from the result of the irradiated PVDF in the O_2 environment, the contact angle variation could suggest that the 1-keV Ar⁺ ion effectively participates in generating free radicals. The contact angle measurement indicated that, by the IAR treatment, the surface of PVDF is hydrophilic, and the contact angle might increase due to the formation of =C at the high ion dose. From XPS and the contact angle result, the concentration of hydrophilic functional groups on the modified PVDF decreased by the degradation of the PVDF surface irradiated at a high ion dose, resulting in a carbonization phase. As mentioned above in the XPS study, the =C = phase increased with the increment of the Ar^+ ion dose. Surface degradation of PVDF could be also explained by the shape change of the C1s photoelectron spectra. Also, the new peaks appeared between the --CF₂-- and --CH₂-- peak positions in Figure 2(b) and (c), which are related to oxygen environment.

The surface roughness of substrate has a strong relationship to adhesion of the overlayer. The rough surface enables the overlayer to be interlocked and/or could suggest more adsorption sites. In the case of PTFE, adhesion of Cu on a cone-type fibrous PTFE surface was enhanced by crosslinking and interlocking.^{26,27} In order to be compared with the result of PTFE, the surface roughness of the irradiated PVDF was investigated by AFM, and root-mean square $(R_{\rm rms})$ roughness values of the irradiated PVDF are shown in Figure 5. The $R_{\rm rms}$ roughness values were changed from 88 Å of the pristine PVDF to 55.8, 77.4, 90.0, and 106.0 Å of the PVDF irradiated by $5\times10^{14},$ $1\times10^{15},$ $1\times10^{16},$ and 1×10^{17} Ar^+/cm^2 , respectively. The 10s Å order of R_{rms} roughness change irradiated by 5×10^{14} and 1 $\times 10^{15} \text{ Ar}^+/\text{cm}^2$ could not explain the dramatically enhanced adhesion between Pt and PVDF. The smooth surface of PVDF irradiated by a low ion dose can be induced by ion erosion. As the Ar⁺ ion dose increased, the surface of irradiated PVDF became slightly rough. From this roughness variation, it could be inferred that the increase of the $R_{\rm rms}$ roughness might be originated from preferentially detachment of fluorine atoms and amorphous phase of PVDF by Ar⁺ ions, but more study is needed to understand the roughness change of PVDF at keV ion irradiation. Consequently, it is considered that the surface roughness variation could not play a role in improving adhesion of the Pt-PVDF system.



Figure 5 $R_{\rm rms}$ surface roughness of the pristine and the irradiated PVDF with increasing ion fluence.

CONCLUSIONS

The surface chemical states of the PVDF specimens irradiated by an Ar^+ ion with an O_2 environment were investigated. The oxygen environment played an important role on reaction upon the activated surfaces of the irradiated PVDF. This oxidation induced by the Ar⁺ ion resulted in ester and/or carboxyl groups on the irradiated PVDF surface. Fluorine atoms in the chains of the irradiated PVDF were preferentially sputtered. Detachment of fluorine and the surface oxidation promoted wettability on the irradiated PVDF, and the PVDF surface irradiated by the 1-keV ion beam is successfully changed to a hydrophilic one. The compositional change in fluorine-polymer suggests many possibilities in the fields of metallization on polymers, printing on polymers, and polymer blending, such as vinylidenefluoride-trifluoroethylene (VDF-TrFE). The above results indicate that the activated sites, which are originated from the detachment of hydrogen and fluorine atoms by energetic ions, reacted upon the O_2 environment.

REFERENCES

- Phelan, Jr., R. J.; Mahler, R. J.; Cook, A. R. Appl Phys Lett 1971, 19, 337.
- Korn, U.; Rav-Noy, Z.; Shtrikman, S. Appl Opt 1981, 20, 1980.
- 3. Toda, M. Ferroelectrics 1979, 22, 911.
- Sussner, H.; Michas, D.; Assfalg, A.; Hunklinger, S.; Dransfeld, K. Phys Lett 1973, 45A, 475.
- Lang, S. B.; Sollish, B. D.; Moshitzhy, M.; Frei, E. H. Ferroelectrics 1980, 24, 289.
- 6. Wintersgill, M. C. Nucl Instrum Methods 1984, B1, 595.
- Puglisi, O.; Licciardello, A.; Calcagno, L.; Foti, G. Nucl Instrum Methods 1987, B19/20, 865.
- 8. Livi, R. P. Nucl Instrum Methods 1985, B10/11, 545.

- Jacobson, S.; Johnson, B.; Sundqvist, B. Thin Solid Films 1983, 107, 89.
- Griffith, J. E.; Qiu, Y.; Tombrello, T. A. Nucl Instrum Methods 1982, 198, 607.
- 11. Tombrello, T. A. Nucl Instrum Methods 1983, 218, 679.
- Flitsch, R.; Shi, D. Y. J Vac Sci Technol 1990, A8, 2376.
- Wie, C. R.; Shi, C. R.; Mendenshall, M. H.; Livi, R. P.; Vreeland, Jr., T.; Tombrello, T. A. Nucl Instrum Methods 1985, B9, 20.
- Mitchell, I. V.; Williams, J. S.; Smith, P.; Elliman, R. G. Appl Phys Lett 1984, 44, 193.
- Mitchell, I. V.; Nyberg, G.; Elliman, R. G. Appl Phys Lett 1984, 45, 137.
- Suzuki, Y.; Kusakabe, M.; Iwaki, M.; Suzuki, M. Nucl Instrum Methods 1988, B32, 120.
- Torrisi, L.; Calcagno, L.; Foti, A. M. Nucl Instrum Methods 1983, B32, 142.
- Choi, W. K.; Koh, S. K.; Jung, H. J. J Vac Sci Technol 1996, A14, 2366.
- Koh, S. K.; Choi, W. K.; Cho, J. S.; Song, S. K.; Jung, H. J. Mater Res Soc Proc 1995, 354, 345.
- Koh, S. K.; Song, S. K.; Choi, W. K.; Han, S. N.; Jung, H. J. J Mater Res 1995, 10, 2390.
- Adem, E. H.; Bean, S. J.; Demanet, C. M.; Le Moel, A.; Duraud, C. M. Nucl Instrum Methods 1988, B32, 182.
- Torrisi, L.; Percolla, R. Nucl Instrum Methods 1996, B117, 387.
- Torrisi, L.; Ciavola, G.; Percolla, R.; Benyaich, F. Nucl Instrum Methods 1996, B116, 473.
- Torrisi, L.; Ciavola, G.; Foti, G.; Percolla, R. Nucl Instrum Methods 1996, A382, 361.
- Koh, S. K.; Park, S. C.; Kim, S. R.; Choi, W. K.; Jung, H. J.; Pae, K. D. J Appl Polym Sci 1997, 64, 1913.
- Chang, C.; Baglin, J. E. E.; Schrott, A. G.; Lin, K. C. Appl Phys Lett 1987, 51, 103.
- 27. Chang, C. Appl Phys Lett 1987, 51, 1236.
- 28. Krupp, H. Inst Phys Conf Ser 1971, 1, 1.
- Golub, M. A.; Cormia, R. D. Polymer 1989, 30, 1576.