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Effect of Complex Ion Beam/Plasma Treatment of the Surface Functionalization and Crystal Phase Transition of Piezoelectric Poly(vinylidene fluoride)

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We scrutinized the effect of complex ion beam and plasma treatment on the surface functionalization and crystal phase change of poly(vinylidene fluoride) films. The stretched and poled PVDF films were used for this investigation. Ion-beam and plasma treatment were employed for the surface modification of PVDF. The surface treatments induced some changes of chemical composition as well as changed the morphology of PVDF surface. It had a large influence on the interfacial adhesion with thermally deposited metal electrodes on the PVDF. Surface modifications such as ion beam irradiation and plasma treatment played a pivotal role in the determination of interfacial strength between PVDF and electrodes as well as the change of crystal structure in electromechanical PVDF film. While the amount of β-phase crystal in PVDF decreased with treatment time, the interfacial adhesion increased with the modification time. In this research, we were able to find optimum treatment conditions for enhancing the adhesion and retaining piezoelectric structure.

Keywords: ion beam irradiation; piezoelectric properties; plasma treatment; poly(vinylidene fluoride); surface modification

INTRODUCTION

Poly(vinylidene fluoride) has been widely investigated for nonvolatile memory device, infra red sensor, and actuator applications due

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to its piezoelectric, pyroelectric, and ferroelectric properties [1,2]. Especially, for electric applications, the interfacial adhesion between PVDF and metal electrodes is required. For enhancing the interfacial strength, a lot of research has been performed using various methods; alkaline treatment [3]; UV-induced graft copolymerization with glycidyl methacylate and 1-vinyl imidazole [4]; plasma treatment [5]. However, its poor adhesion properties and poor wettability have presented severe problems in many applications because fluoropolymers have very low surface energy, which causes negligible adhesion to metals [6,7]. On the other hand, some studies reported that such various surface treatments for enhancing surface energy could have a severe influence on the decrease of piezoelectric and ferroelectric properties of PVDF [8]. Therefore, not only enhancing the surface tension but also retaining the piezoelectric/ferroelectric properties should be considered. However, there is no research about both of those factors so far.

In this study, to improve the interfacial adhesion between a PVDF film and a thermally deposited aluminum metal-layer, we employed a complex surface treatment of Ar^+ ion beam irradiation and/or RF oxygen plasma treatment. As well, through an investigation of the effect of surface modification on the piezoelectric/ferroelectric structure and properties, we attempted to make clear the reasons for degrading the electromechanical properties. In addition, we suggested an optimum treatment time with consideration of the two factors mentioned above.

EXPERIMENTALS

Materials employed in this study were commercial piezoelectric PVDF films and copper sheets with a thickness of 40 μm. The piezoelectric PVDF film was purchased from Kureha Inc. (Japan). The density, piezoelectric constant, and dielectric constant were $1.78 \times 10^3\,kg/m^2$, 30 pC/N, and 13, respectively. The surface modification system was composed of a conventional plasma treatment system and a low energy ion beam irradiation system with reactive gas feeding system. For the first process Ar^+ ion beam was irradiated on the PVDF surface with a reactive O_2 gas (IBOG). The flow rate of Ar gas was 2 sccm, and the oxygen gas was fed with the flow rate of 5 sccm. The working pressure was kept under 10^{-4} Torr. In the case of the second process, we only treated O_2 plasma on the specimens (OPla). The third process was O_2 plasma treatment after low-energy Ar^+ ion beam irradiation (IBOPla). A radio frequency (13.56 MHz) plasma was generated by RF power source (RF5S-PF power products Inc.), and the plasma power

was fixed at 100 W. The gas used in this system was O_2 with the fixed flow rate of 10 sccm. Above all, Ar^+ ion beam was irradiated, and then O_2 plasma was treated on the surface of the samples for the predetermined time, respectively. The AFM images in this article were obtained from Multimode Scanning Probe Microscope (Park System, Inc.). The chemical components on the surfaces of modified PVDF films were analyzed by using XPS and the spectra were recorded with a Surface Science 2803-S spectrometer ($hv = 1.5$ keV). An aluminum layer of about 200 nm in thickness was thermally evaporated onto the surface modified PVDF films. Then, the deposited aluminum surface was adhered to a copper sheet using an epoxy adhesive. The assembly was cured at 50 for 5 h and then was subjected to T-peel test using a universal testing machine (Instron. Inc.) at a room temperature. The crosshead speed was 10 mm/min and all the reported results are averages of 20 measurements. XPS studies were employed for cleaved surface characterization. In addition, the chemical components on the surfaces of PVDF and aluminum were analyzed by using X-ray photoelectron spectroscopy (XPS). The crystal structures of PVDF films modified by ion beam and plasma treatment were studied by wide angle X-ray diffraction (WAXD) experiment. The piezoelectric constant at the drawn direction, d_{33} was measured by the laser reflection system including high voltage power supply and high voltage interface.

RESULTS AND DISCUSSIONS

Surface Characterization

Figure 1 shows the AFM images of PVDF surface with treatment time in various surface modification processes. Especially, the Figure 1(a) indicates that the surface of neat PVDF was not relatively smooth and flat. Therefore, as shown in Table 1, we were able to observe the roughness decreased at the beginning, and then, continuously increased. In general, the surface morphology of PVDF was largely

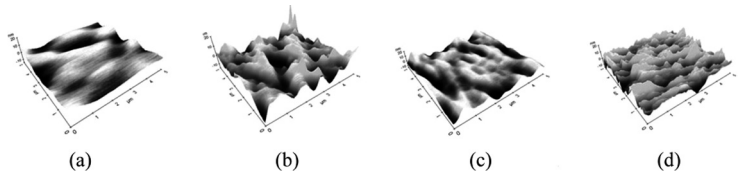

FIGURE 1 AFM images of surface modified PVDF films with three different processes. (a) Neat PVDF; (b) IBOG-2 min; (c) OPla-5 min; and (d) IBOPla-5 min.

TABLE 1 Surface Roughness of Surface Modified PVDF

Treatment time (min)	IB (Ar^+ ion beam)	IBOG (Ar^+ ion beam + O_2 gas)	(O_2 plasma)	IBOPla (Ar^+ ion beam + O_2 plasma)
0 (Neat)	7.366	7.366	7.366	7.366
0.1	9.278	7.914		
0.2	11.52	9.22		
1	14.398	9.468	6.17	8.62
2	14.948	10.773	4.612	7.43
3			6.3	8.504
5			7.402	9.556

changed by various processes of surface treatment with treatment time. The surface modification occurs first through the collision between Ar^+ ion and PVDF molecules on the surface in case of ion beam irradiation. And then, reactive oxygen gas or oxygen plasma was incorporated on the surface. The etching pits, which were seen at short irradiation times, evolved to grass-like structures, which became deeper and wider with the increasing irradiation time as a result of the physical bombardment. Figure 1(d) exhibits the fully developed and roughened surface. In Figure 2(a), the XPS analysis shows that the two C1s peaks of neat PVDF were symmetric and they have a narrow full width at half-maximum (FWHM). However, in Figure 2(b), the C1s peaks of Ar^+ ion beam treated and O_2 plasma (IBOPla) treated PVDF sample were merged, lowered, and asymmetric. It is attributed to the fact that oxygen containing groups were incorporated to the surface as well as a lot of defluorination was occurred. It means the surface functionalization occurred due to the surface modification. The peak can be decomposed into five peaks by using Gaussian and Lorentzian peak fitting code: C−H or C−C peak at 285.0 eV, C−O peak at 286.5 eV, C=O peak at 287.9 eV, COO peak at 289.0 eV, and C−F peak at 289.6 eV appeared. Table 2 shows the O/C atomic ratio of surface modified PVDF with treatment time. In all of the three processes, O/C atomic ratio increased with the increase of treatment time. However, at more than 5 min of plasma treatment and 2 min of ion beam treatment time, the O/C atomic ratio decreased. It can be explained by carbonization of PVDF surface and re-etching effect: much more bombardment with the atoms on the PVDF surface could not only make cross-linking between polymer chains but also etch the funtionalized surface again [10]. Especially, IBOPla-5 min shows the highest ratio of oxygen to carbon while IBOG has the lowest one. It is ascribed to the fact that the effect of plasma treatment

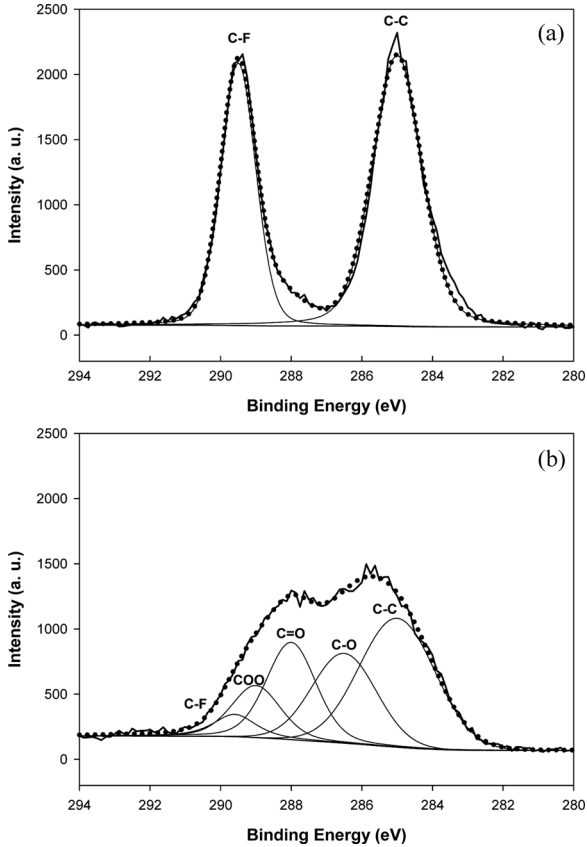

FIGURE 2 XPS spectra of neat PVDF (a) and surface modified PVDF (b).

TABLE 2 O/C Atomic Ratio of Surface Modified PVDF

Treatment type	Treatment time (min)	Atomic ratio of O/C
Neat PVDF		0
IBOG (Ar^+ ion beam + O_2 gas)	1	0.173
	2	0.199
OPla (O_2 plasma)	1	0.489
	3	0.503
	5	0.543
IBOPla (Ar^+ ion beam + O_2 plasma)	1	0.335
	3	0.533
	5	0.612

becomes larger due to the increased surface area and radical generation by ion beam irradiation. On the other hand, in plasma treatment only process (Opla), the roughness change was small while the effect of surface functionalization was good due to its relatively low kinetic energy and electrically high potential to bond with the polymer chains on surface.

Interfacial Adhesion between Surface Modified PVDF and Aluminum

Krupp *et al.* presented functional groups on the polymer surface, such as ester or carboxyl groups, could enhance the adhesion between the metal and polymer [11]. Also, Goloub *et al.* reported carbon atoms in polymer chains were activated by defluorination and could react with oxygen species [12]. These radicals play an important role in contact electrification for thin layer adhesion. This result can strongly support the fact that the enhanced adhesion between aluminum and PVDF films from the generation of polar groups after ion beam/plasma treatments. In the case of PTFE, adhesion of several metals on a roughened and fibrous PTFE surface was enhanced by crosslinking and interlocking [13]. However, PVDF has not the same behavior. Figure 3 shows

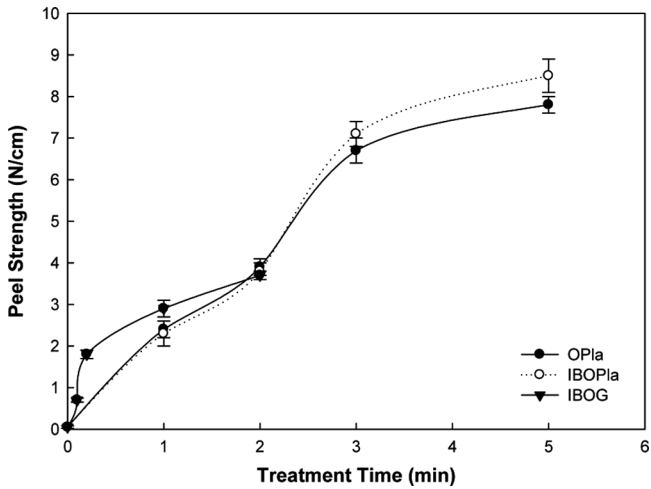

FIGURE 3 Peel strength of surface modified PVDF/aluminum interface with treatment time. The used surface modification methods were IBOG (Ion Beam irradiation with a reactive Oxygen Gas (●)), OPla (Oxygen Plasma treatment (○)), and IBOPla (Ion Beam irradiation and then Oxygen Plasma treatment (▼)).

the adhesive strength for the adhesive joint between the PVDF films and the aluminum layer as a function of the treatment time. Several facts are interesting to note: First, untreated PVDF shows a very low interfacial strength under 1.0 N/cm although the surface roughness was not low, relatively. Second, the peel strength is significantly affected by the functional groups and the topology on the modified surface. Especially, in case of oxygen plasma treatment, although the surface roughness slightly decreased up to 2 min at the beginning of surface treatment, the peel strength increased. It was suspected to be the reason for the large effect of chemical interaction on the bonding between PVDF and aluminum. Lastly, the interfacial strength continuously increased with the treatment time regardless types of surface modification in this study.

Piezoelectric Structure and Properties of Surface Modified PVDF

We carried out the wide angle X-ray diffraction experiments for the investigation of internal structure change due to the surface modifications. Figure 4 exhibits the change of crystal structure with treatment

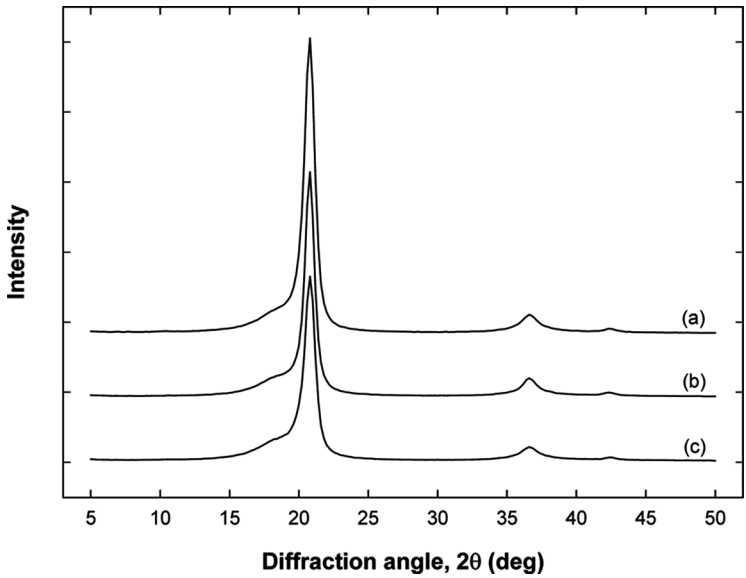

FIGURE 4 X-ray diffraction spectroscopy of ion beam/plasma treated PVDF films. (a) Neat PVDF; (b) IBOPla-3 min; and (c) IBOPla-5 min.

time in the case of IBOPla-treated samples. With the increase of oxygen plasma treatment time, the crystallinity generally decreased. Furthermore, in particular, the amount of polar β-phase crystal at 20.6° (110) of 2θ significantly decreased. This result agrees with that of Virk *et al*. [9]. The decrease in intensity can be explained by a decrease in lattice spacing. The peaks suggest an evolution of the crystalline structure of PVDF toward a more disordered state which means amorphous structure due to oxygen plasma treatment. The decrease of β-crystal was revealed much more obviously although the α-phase crystal also decreased. It is attributed to the fact that our samples were a fully stretched and poled piezoelectric PVDF film, so that the crystal of Form-I (β-phase) was well developed. As well, the reason for the severe decrease of β-phase crystal can be explained by the fact that Form-I is relatively more unstable than Form-II (α-phase). In addition, the samples treated ion beam only (IB) was severely decreased. It can be ascribed to the fact that higher temperature was generated and the ion beam can easily make chain scission when accelerated ions collided with PVDF polymer chains.

The piezoelectric constant, d_{33} which is normal to plain of the film was measured for scrutinizing the effect of surface modification on the change of piezoelectric properties of drawn and poled PVDF film. The results in Figure 5 are calculated using laser detecting system.

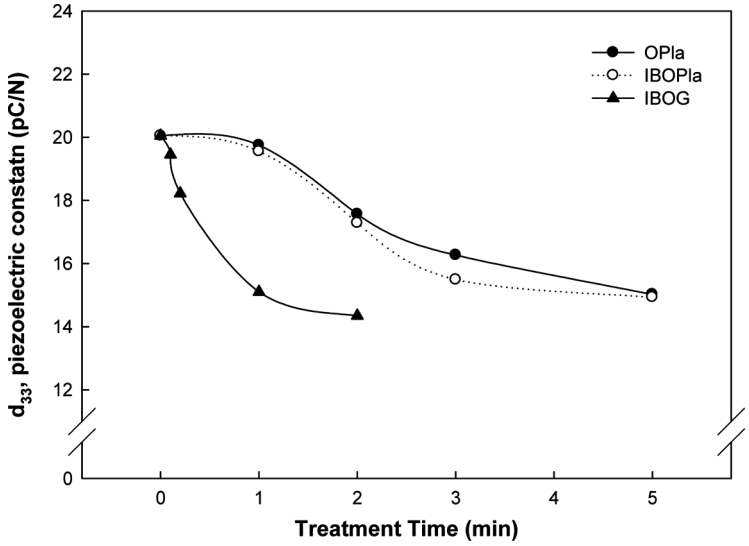

FIGURE 5 Variation of the piezoelectric constant of surface modified PVDF with treatment time.

The piezoelectric constant at the 33-direction mode which is normal to plain of the film decreased with treatment time. In fact, d_{33} of IBOG-treated PVDF samples decreased more rapidly than that of other samples. It is because relatively long ion-beam irradiation onto the PVDF surface can make the β-phase decrease and the polarization lose due to the occurred temperature as well as generated functional groups on the PVDF surface, as already mentioned. Thus, it is necessary to consider both of the adhesion strength between PVDF and aluminum and the piezoelectricity at the same time. Therefore, we suggest optimum range of treatment time to satisfy the above two conditions: the interfacial adhesion strength increased with treatment time while the piezoelectric constant decreased. Thus, if considered the proper processing conditions of surface treatment, not only enhanced adhesion between piezoelectric PVDF film and aluminum layer but also retained high piezoelectricity can be achieved.

CONCLUSIONS

We investigated the effect of complex ion beam and plasma treatment on the surface functionalization and crystal phase change of poly(vinylidene fluoride) films. Surface modifications such as ion beam irradiation and plasma treatment played an important role in the determination of interfacial strength between PVDF and electrodes as well as the change of crystal structure in electromechanical PVDF film. Ion beam irradiation and Oxygen Plasma treatment was the most excellent method for improving the interfacial strength. According to the treatment time on the PVDF surface, the T-peel strength increased. However, relatively long treatment time made the piezo/ferroelectric properties weak. Therefore, we can suggest an optimum condition for increasing great adhesion and retaining electrical piezo/ferroelectric properties.

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