

Low Dielectric Constant of MeV Ion-Implanted Poly(vinylidene fluoride)

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Abstract: Poly (vinylidene fluoride) (PVDF) samples were implanted by using high energy (MeV) F^{2+} and Cl^{2+} ions. We observed that AC dielectric constant of the ion-implanted PVDF samples decreased from 10.5 to 2.5 at 1 kHz as the ion dosage increased from 10^{11} to 3×10^{14} ions/cm². From differential scanning calorimetry experiments, we observed that PVDF samples become more disordered state through the ion implantation. The decrease of the number of bonding of C-H and C-F and the increase of unsaturated bonding were observed from X-ray photoelectron spectroscopy experiments. The emission of HF and H₂ molecules during the ion implantation was detected by residual gas analyzer spectrum. Based upon the results, we analyzed that the low AC dielectric constant of the MeV ion-implanted PVDF samples originated from the reduction of polarization due to the structural change of the CF₂ molecules in the MeV ion-implanted PVDF samples.

Keywords: poly(vinylidene fluoride), ion implantation, AC dielectric constant, interlayer dielectric.

Introduction

Ion implantation on polymers induces the chain scission, cross-linking,¹⁻³ and carbonization,^{2,4,5} resulting in the modification of mechanical,¹ electrical,^{4,7} and optical⁸⁻¹⁰ properties. Many efforts have been made for the modification of polymers by using keV ion implantation. Though the modified properties of ion-implanted polymer have been reported recently, the relation between the structure and the electrical properties of ion-implanted polymers and the reaction mechanism between implanted ions and polymers have not been thoroughly studied, because of complicated morphology of polymers.^{1,2,11} In this study, we used high energy (MeV) ion implantation for the change of surface and bulk properties of poly(vinylidene fluoride) (PVDF) with relatively simple chemical structure, and studied the variation of electrical properties such as dielectric constant, because insulating polymers with low dielectric constant have been used for interlayer dielectric (ILD) materials for electrical devices.¹²

The rate of energy transfer from implanted ions to target atoms plays an important role for the modification of materials.¹⁻³ The total energy transfer is the sum of the nuclear stopping power and the electronic stopping power. The

stopping power (eV/nm) is equivalent to the linear energy transfer (LET, eV/nm/ion).^{13,14} Electronic stopping is the interaction between implanted ions and electron clouds of the target atoms, which induces the unsaturated bonding and cross-linking between chains.^{1,2,13} Nuclear stopping is the interaction between implanted ions and nuclei of target atoms, which induces the chain scission.^{1,13,15} The structural change of polymers depends on the energy, the dosage, the charge of implanted ions, and the structure of target material. For polystyrene (PS) sample, through 300 keV He⁺ ion implantation, the cross-linkings between polymer chains had been observed.² In the case of poly(methyl methacrylate) (PMMA) sample, the steric hindrance of the large methyl-ester groups induced the chain scission.¹

In this paper, PVDF films were implanted by using MeV energy ions (F^{2+} and Cl^{2+}). The PVDF has a relatively simple chemical structure with repeated units such as $-CH_2-CF_2-$, and has been studied for fundamental research¹⁶⁻²⁰ and applications.²¹ Therefore, it is expected that the interaction between ions and polymer backbone can be easily understood. We report the structural and electrical properties of the MeV energy ion-implanted PVDF films, based on the results of Scanning Electron Microscope (SEM), Differential Scanning Calorimetry (DSC), X-ray Photoelectron Spectroscopy (XPS), Residual Gas Analyzer (RGA), and AC dielectric constant experiments. We observe that the MeV

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ion implantation on PVDF samples reduces the electric dipole moment due to the break of C-F bonding, resulting in the decrease of AC dielectric constant with increasing ion dosage.

Experimental

The PVDF has a repeat unit such as $-\text{CH}_2-\text{CF}_2-$, which exhibits a vacuum electronic dipole moment of 7×10^{-30} Cm associated with positively charged H atoms and negatively charged F atoms.¹⁶ When these dipole moments are aligned in one direction, the PVDF has a spontaneous polarization. The resulting crystalline structure is β phase, and is responsible with ferroelectricity¹⁶ and pyroelectricity²² of the PVDF. When the crystalline structure has *trans-gauche*⁺-*trans-gauche*⁻ (TG^+TG^-) conformation, it is α phase without the spontaneous polarization.¹⁶⁻¹⁹

The α -PVDF films were purchased from Good-Fellow company, and the thickness of the film was $80 \mu\text{m}$. The ion implantation was performed by using the 5SDH-2 tandem Van de Graff accelerator at Korea Institute of Geology, Mining, and Materials (KIGAM). During ion implantation, the chamber had been kept under vacuum below 10^{-6} Torr. The ions used were 3 MeV F^{2+} , and 3.9 MeV Cl^{2+} . AC dielectric constant was measured by using ASTM D150-81 method at room temperature, in which the edge effect is eliminated by the use of guard ring. The AC dielectric constant of the pristine PVDF samples at 1 kHz was measured to be ~ 10.5 . The residual gas analysis (RGA) was performed by using Balzer QMS200M2 residual gas analyzer, which was placed on the chamber to detect the molecular emission during ion implantation. Because this analyzer was not located at the front of the target holder, heavy molecules emitted from the target material would not be detected. The transport of ions in matter (TRIM) code,²³ which can analyze the collisions between the implanted ions and atoms in target material with statistical dynamics, was utilized to simulate the stopping power and the implanted thickness. The DSC measurements were performed by using DSC 2010 (TA instruments). The XPS spectra were obtained from ESCALAB MK-II spectrometer.

Results and Discussion

The stopping power and the projected range of ions are estimated by the simulation of TRIM code. For both 3 MeV F^{2+} and 3.9 MeV Cl^{2+} ion-implanted PVDF samples, the projected range was calculated to be $\sim 3 \mu\text{m}$, and the electronic stopping power ($(dE/dx)_e$) is dominant compared to the nuclear stopping power ($(dE/dx)_N$) as listed in Table I. This high electronic stopping causes the production of radicals and excited electrons, which induces the cross-linking and bond breaking.^{1,13} Figure 1 shows the SEM images of the cross section of F^{2+} and Cl^{2+} ion-implanted PVDF films.

Table I. Trim Code Simulation: The $(dE/dx)_e$ and $(dE/dx)_N$ Represent the Electronic Stopping Power and the Nuclear Stopping Power, Respectively

Ion	Ion Energy	$(dE/dx)_e + (dE/dx)_N$ (keV/ μm)	$(dE/dx)_e$ (keV/ μm)	Projected Range (μm)
F^{2+}	3 MeV	1682	1672	3.12
Cl^{2+}	3.9 MeV	2414	2372	2.79

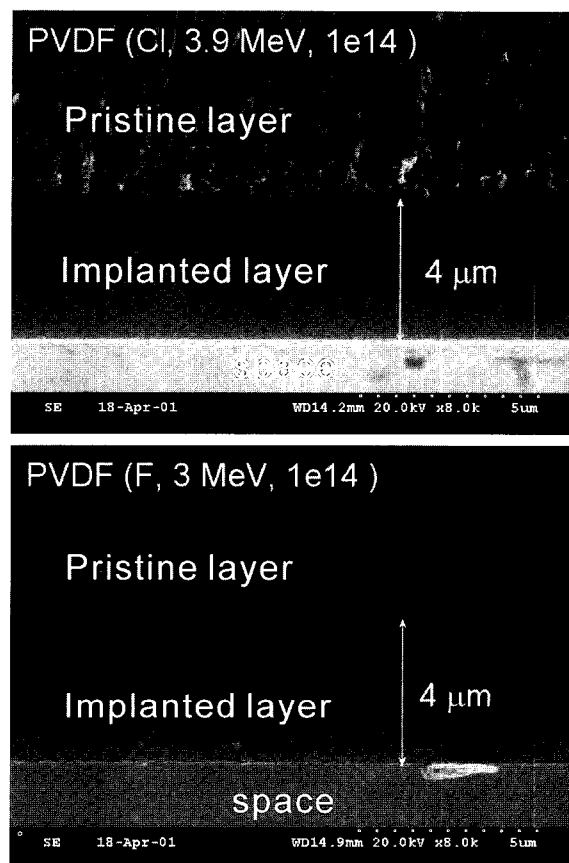


Figure 1. The SEM images of the cross section of the MeV ion-implanted PVDF films.

The thickness of the ion-implanted layer for both samples is $\sim 4 \mu\text{m}$, which is approximately accordance with the theoretical results, as listed in Table I. The thickness of the ion-implanted layer has been used for the measurements of AC dielectric constant.

Figure 2 presents the AC dielectric constant (κ') at 1 kHz of the pristine and ion-implanted PVDF samples as a function of ion dosage. Because the implanted and pristine layers in the ion-implanted PVDF sample are in the serial connection between top and bottom electrodes for the measurement of κ' , those layers are considered as the series circuit of two capacitors. The measured κ' at 1 kHz decreases as ion dosage increases. The κ' of the 3 MeV F^{2+} (3.9 MeV Cl^{2+}) ion-im-

planted PVDF samples with 10^{14} ions/cm² dose is measured to be 2.5 (3.5), while the κ' of the pristine PVDF samples is 10.5. The decrease of κ' of the ion-implanted PVDF samples originates from the reduction of polarization due to the structural change.

Figure 3 presents the DSC curves of the pristine and 3.9 MeV Cl²⁺ ion-implanted PVDF samples. The endothermic peak from 140 to 170 °C is observed for the pristine and ion-implanted samples. The melting temperature (T_m) and the line-shape of curves of the ion-implanted samples are similar with those of the pristine sample. We observe the decrease of the melting enthalpy (ΔH_m), i.e., the relatively small area of heat flow, for the ion-implanted PVDF samples, implying more disordered state of the ion-implanted PVDF samples.^{24,25} For 3 MeV F²⁺ ion-implanted PVDF samples, we observe the

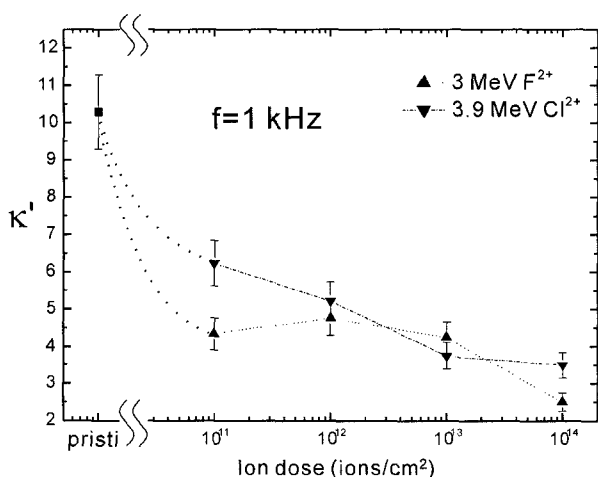


Figure 2. AC dielectric constants at 1 kHz of the pristine and ion-implanted PVDF samples.

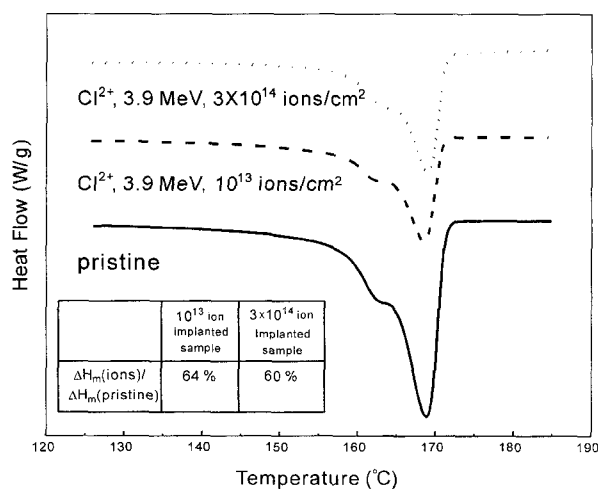


Figure 3. DSC curves of the 3.9 MeV Cl²⁺ ion-implanted PVDF samples.

same results.

Figure 4 shows the FT-IR spectra for the PVDF samples implanted by using 3.9 MeV Cl²⁺ ions. Two absorbance peaks at 1713 and 1620 cm⁻¹ are assigned to the stretching vibrations of -CF=CH- and of -(CF=CH)₂, respectively.²⁶ The peak at 1754 cm⁻¹ is due to the stretching vibrations of -CF₂-CH=CF₂. The intensity of absorbance peaks increases with an increasing Cl²⁺ ion dosage. The absorption peak due to oxidation is observed at 1850 cm⁻¹.²⁶ The radicals induced by the interaction between ions and the medium introduce chemical bondings with oxygen in the air. The FT-IR spectrum of the 3 MeV F²⁺ ions implanted sample is similar with that of the 3.9 MeV Cl²⁺ ions implanted one. These structural change is confirmed by XPS experiments.

Figure 5(a) and (b) compare XPS carbon 1s (C1s) spectra

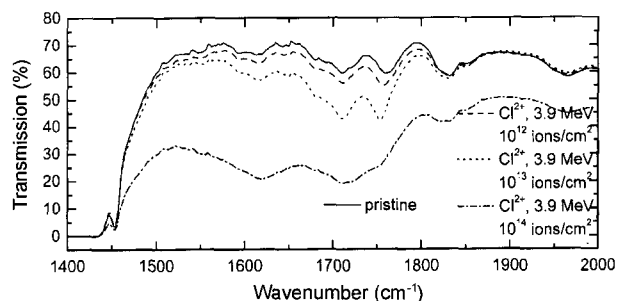


Figure 4. FT-IR spectra of the PVDF samples implanted by 3.9 MeV Cl²⁺ ion.

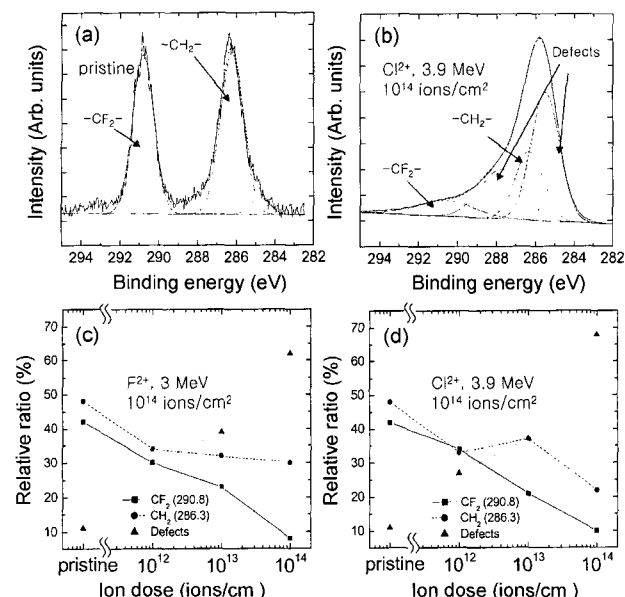


Figure 5. XPS results of the PVDF films. (a) Carbon 1s spectrum of the pristine PVDF films; (b) carbon 1s spectrum of 3.9 MeV Cl²⁺ ion-implanted PVDF films. The variation of the area ratio of chemical bonds as a function of ion dosage of (c) 3 MeV F²⁺ ion-implanted and (d) 3.9 MeV Cl²⁺ ion-implanted PVDF samples.

of the pristine and 3.9 MeV Cl^{2+} ion-implanted PVDF films (10^{14} ions/cm² dose), respectively. The peaks of CH_2 and CF_2 bonds are appeared at 286.3 and 290.8 eV, respectively, in the pristine film, as shown in Figure 5(a).²⁷ The peak of CF_2 bonding at 290.8 eV dramatically decreases due to the Cl^{2+} ion implantation as shown in Figure 5(b). The increase of the intensity of peaks at 287.7 and 285.5 eV, which are assigned to the defects such as singly fluorine bonded, oxygen bonded, and carbonized carbons are also observed. The broad peak at 287.7 eV originates from the singly fluorine bonded carbon and oxygen bonded carbon, and the peak at 285.5 eV originates from the carbonized carbon.^{28,29} Figure 5(c) and (d) show the area ratio of decomposed peaks obtained from XPS C1s spectra of the 3 MeV F^{2+} and 3.9 MeV Cl^{2+} ion-implanted PVDF films. The results indicate that the CH_2 and CF_2 bonds decrease and the defects increase with increasing ion dosage.

Figure 6(a) and (b) show the atomic ratio of C and F atoms as a function of ion dosage in the ion-implanted PVDF samples obtained from XPS wide spectra. As the ion dosage increases, the ratio of C atoms increases, while that of F atoms decreases, indicating the carbonization.³⁰ This result

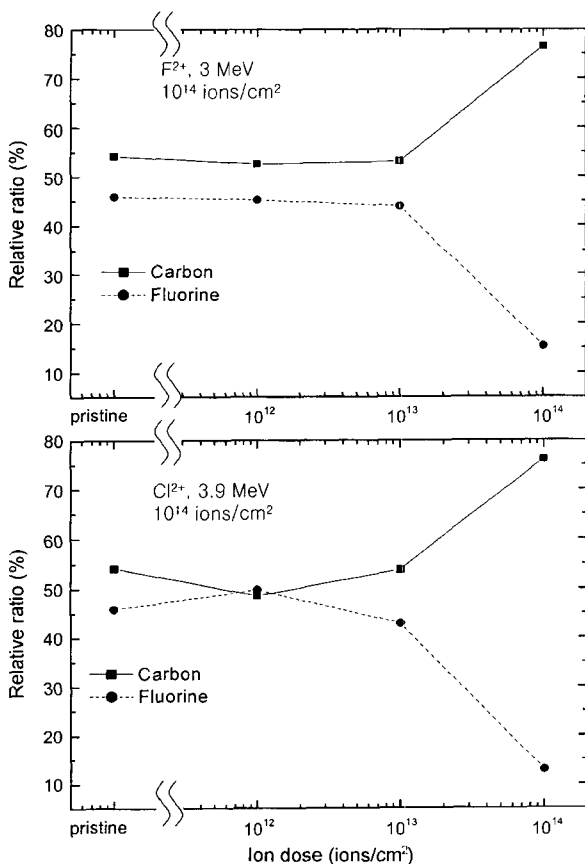


Figure 6. The variation of the atomic ratio on the surface of the PVDF films implanted by (a) 3 MeV F^{2+} and (b) 3.9 MeV Cl^{2+} ions.

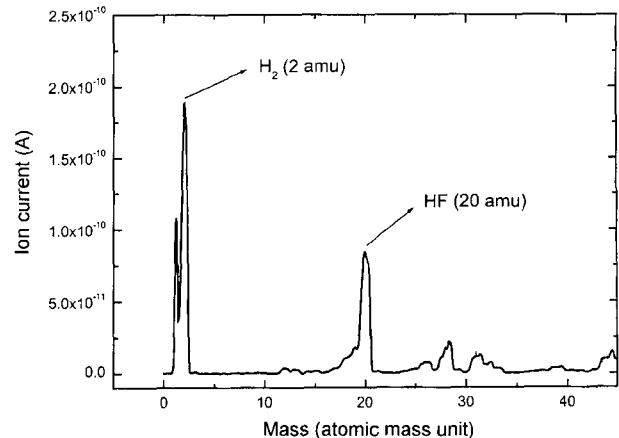


Figure 7. RGA spectrum of the PVDF samples through 3.9 MeV Cl^{2+} ion implantation.

qualitatively agrees with the results of XPS experiments as shown in Figure 5.

Based on the results studied here, the interaction between high energy (MeV) ions and constituent atoms in the PVDF backbone induces the disordered morphology. We observe the carbonization, the disorder, the increase of defects, and the decrease of CF_2 bonds after the MeV ion-implantation on the PVDF samples. With increasing ion dosage, CF_2 bonds are broken, and some of F atoms are separated from polymer backbone. Then, they are combined with other excited atoms, such as F and H atoms.³⁰⁻³² The emission of the HF and H_2 molecules was detected from RGA spectra as shown in Figure 7. The difference of ion current between the on and off states of the ion beam was measured in ampere unit. In the ionized process of polymer backbone, the ionized carbon atoms interact with the adjacent excited carbon atoms. As a result, the π -bonds are formed, and the double bonding structure is formed in PVDF polymer backbone,^{1,26,30,31} resulting in the increase of XPS C1s peaks at 285.5 and 287.7 eV in Figure 5(b).^{30,31,33,34} The bonds generated from the oxidation contribute to the increase of the peak intensity at 287.7 eV as shown in Figure 5(b).^{26,33} Because of the increase of the singly fluorine bonded carbon structure in polymer main chain, the decrease of the CF_2 molecules, and the disordered morphology in the ion-implanted PVDF samples, the polarization due to electric dipole moments between CF_2 and CH_2 molecules in the polymer backbone relatively decreases compared to the pristine PVDF sample, which contributes to the decrease of AC dielectric constant with increasing ion dosage.

Conclusions

PVDF films were implanted by using high (MeV) energy F^{2+} and Cl^{2+} ions. The ion dosage varied from 10^{11} to 3×10^{14} ions/cm². We observe that AC dielectric constant of the 3

MeV F^{2+} ion-implanted PVDF sample at 1 kHz is measured to be 2.5, while that of the pristine sample is 10.5. This result suggests that the MeV ion-implanted PVDF sample can be used for low dielectric interlayer material for electrical devices. The decrease of the melting enthalpy of the MeV ion-implanted PVDF samples is observed through DSC measurements, which implies that the system becomes more disordered state with the MeV ion implantation. Based on the results and the analyses of XPS experiments, as the stopping power and the ion dosage increase, the carbonization, the increase of structural defects, and the decrease of CF_2 bonds are occurred, which reduces the polarization between CH_2 and CF_2 molecules. This results in the decrease of AC dielectric constant with increasing ion dosage in the MeV ion-implanted PVDF systems.

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