



**HAL**  
open science

# Analysis of Charge Accumulation Phenomena by Physicochemical Analysis for fluorinated Polymer Films Irradiated by Proton

H Miyake, Virginie Griseri, U Chiba, K Enoki, Y Tanaka, G. Teysseire

► **To cite this version:**

H Miyake, Virginie Griseri, U Chiba, K Enoki, Y Tanaka, et al.. Analysis of Charge Accumulation Phenomena by Physicochemical Analysis for fluorinated Polymer Films Irradiated by Proton. 15th Spacecraft Charging Technology Conference (SCTC), Kobe, Japan, 25 - 29 June 2018, Jun 2018, Kobe, Japan. pp. 1-5. hal-03031116

**HAL Id: hal-03031116**

**<https://hal.science/hal-03031116>**

Submitted on 30 Nov 2020

**HAL** is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

# Analysis of Charge Accumulation Phenomena by Physicochemical Analysis for fluorinated Polymer Films Irradiated by Proton

H. Miyake<sup>(1)</sup>, V. Griseri<sup>(2)</sup>, U. Chiba<sup>(1)</sup>, K. Enoki<sup>(1)</sup>, Y. Tanaka<sup>(1)</sup>, and G. Teyssedre<sup>(2)</sup>

**Abstract**—In this paper, proton irradiated fluorinated polymer films are investigated by physicochemical analysis, such as PhotoLuminescence (PL), XPS and NMR. It has been observed that proton irradiated fluorinated films have a positive charge accumulation in the bulk under DC stress. The origin of this charge storage seems to be due to molecular chain scission. Therefore, this paper focused on physicochemical analysis results obtained on ETFE and FEP irradiated films. From the data, the scission, oxidization and crosslinking phenomena have been confirmed.

**Index Terms**—Proton irradiation, Physico-Chemical analysis, Fluorinated films, chain scission, oxidization.

## I. INTRODUCTION

Many dielectric materials are used for spacecraft as thermal control materials, such as MLI (Multi Layer Insulator), OSR (Optical Solar Refractor) and electrical insulation for wires harness. Those materials are charged up due to radioactive rays in space environment and discharges may occur. These discharging phenomena called ElectroStatic Discharges (ESD), are at the origin of some satellite fatal anomalies [1].

To understand the dielectric phenomena of thermal control materials on spacecraft irradiated by radio-active rays, such as electron, proton and  $\gamma$ -rays, an important experimental work has been performed in the last past thirty years [2-8].

In this paper, proton irradiated fluorinated polymer films are investigated. Until now, only space charge distribution on such materials has been studied. It was shown that pristine materials do not accumulate charges under DC voltage application. On the contrary, positive charges were observed in irradiated films. To go further in the understanding of such behavior it's necessary to establish the relationship between charge distribution and molecular structure. Therefore, in this study, we try to determine the molecular structure in irradiated fluorinated polymer using Photo-Luminescence (PL), FT-IR, XPS and NMR. We will then discuss the relationship between charge accumulation and molecular structure in proton irradiated fluorinated films.

This study was partly supported by the Inter-University Program for the Joint Use of QST (formerly JAEA and JAERI) Facilities and the Shared Use Program of QST Facilities. This work was also supported by JSPS/MEXT KAKENHI Grant Numbers JP18760242, JP23760292 and JP15KK0216.

## II. EXPERIMENTAL PROCEDURE

### A. Proton Irradiation Facility and Conditions

The proton beam irradiation was carried out in a vacuum atmosphere of approximately  $10^{-4}$  ~  $10^{-5}$  Pa using the 3 MeV tandem type ion accelerator facility in Takasaki Advanced Radiation Research Institute of National Institute for Quantum and Radiation Science and Technology (former name is JAEA) of figure 1.

The acceleration energy and the irradiation current density of the proton beam were set to 1.5 or 2 MeV and 30 nA/cm<sup>2</sup>, respectively, while the irradiation duration was fixed to 30 minutes.

### B. Samples

Commercially available ETFE (thickness : 100  $\mu$ m) and FEP (thickness : 100  $\mu$ m) films were selected for these measurements. Samples were irradiated by proton using the previously mentioned conditions.

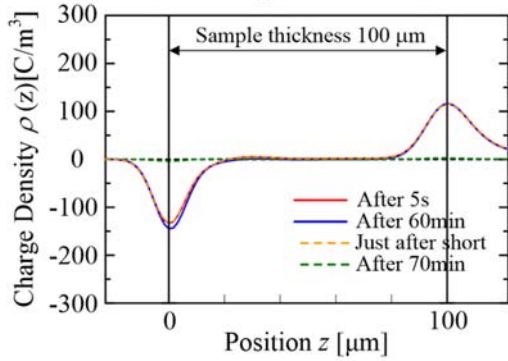
## III. SPACE CHARGE MEASUREMENTS RESULTS

### A. Space charge distribution in proton irradiated ETFE and FEP

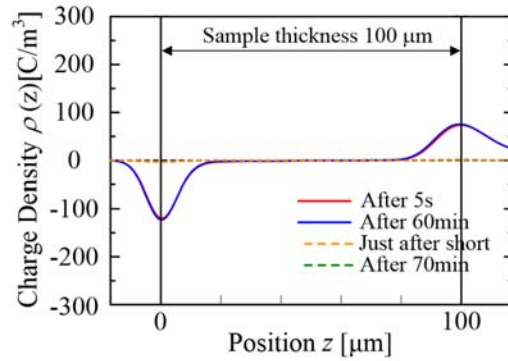
The Space Charge (SC) distribution in ETFE and FEP irradiated by protons are shown in Figure 2 and 3, respectively. These results were obtained by PEA method [8]. The measurements of proton beam sample were typically started one day after the end of the irradiation at atmospheric pressure. All the measurements were carried out at room temperature (approximately 25 °C). The charge distribution measurements were carried out under DC voltage, which corresponded to an average electric field of 100 kV/mm, for 120 min to observe the charge accumulation process. In these figures, the red line shows the SC distribution after 5 s starting voltage application, and the blue line shows the SC distribution after 120 min under voltage application. The orange and green broken lines shows the initial charge distribution and 20 min after short-circuit, respectively.

H. Miyake, U. Chiba, K. Enoki and Y. Tanaka are with the Tokyo City University, 1-28-1, Tamazutsumi, Setagaya-ku, 158-8557, Tokyo, Japan (e-mail: hmiyake@tcu.ac.jp)

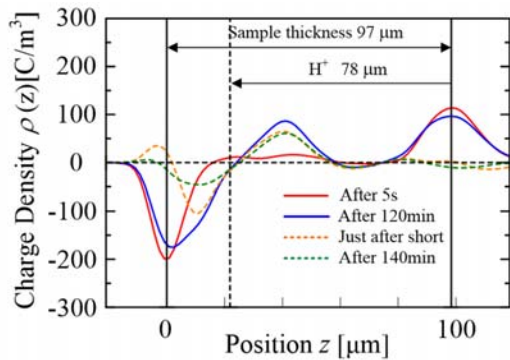
V. Griseri and G. teyssedre are with the Laplace, Université Toulouse III - Paul Sabatier 118, route de Narbonne - bât 3R3 - 31062 Toulouse cedex 9 France (e-mail: virginie.griseri@laplace.univ-tlse.fr)



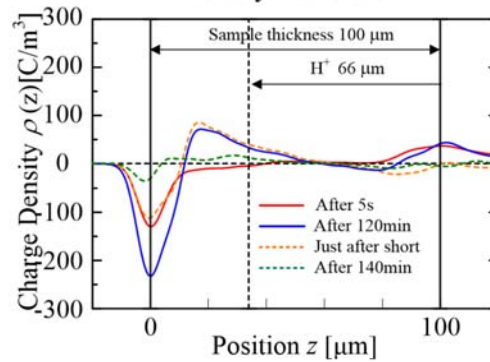
(a) Space charge distribution in pristine ETFE (non-irradiated).



(a) Space charge distribution in pristine FEP (non-irradiated).



(b) Space charge distribution in irradiated ETFE (2.0 MeV).



(b) Space charge distribution in irradiated FEP (2.0 MeV).

Fig. 2 Space charge distribution in pristine and proton irradiated ETFE under 100 kV/mm voltage application and subsequent short circuit.

Fig. 3 Space charge distribution in pristine and proton irradiated FEP under 100 kV/mm voltage application and subsequent short circuit.

Furthermore, the perpendicular black broken line appearing in the figures corresponds to the calculated maximum penetration depth determine from the Stopping and Range of Ions in Matter (SRIM) tables [9]. The energy of proton irradiation is 2.0 MeV.

From the figure 2 and 3 (a), we cannot observe any charges in the bulk of pristine ETFE and FEP films. However, on the proton irradiated samples, we can see positive charge accumulation near the proton maximum penetration depth in both cases. It is interesting to note that those accumulated positive charges still remain after short-circuit. It is expected that positive charges appeared due to proton irradiation however it is not obvious, at first sight, that they should remain stable. These results are explained in details in the paper [10].

From those results, we considered the origin of positive charge accumulation in those bulks by physicochemical analysis which is described in following sections.

#### IV. PHYSICOCHEMICAL ANALYSIS AND DISCUSSION

##### A. PhotoLuminescence measurements

The PL measurements have been carried out in the chamber available at the LAPLACE [11]. The figure 4 shows the PL

results of pristine and proton irradiated ETFE and FEP films. Although the excitation wavelength of this experiment was covering the range [200 – 300 nm], only the result at 285 nm which shows the big differential between pristine and irradiated samples are shown in this paper. From the figure 4, big peaks are observed at 300 at about 550 and just above 600 nm in pristine FEP and ETFE. Concerning the irradiated FEP and ETFE, a broad peak centered on 400 and 450 nm is observed. Furthermore, the peak at 300 nm of pristine ETFE has disappeared completely, whereas the peak above 600 nm is hidden by the presence of the broad peak mentioned just before. It is considered that the new big peak is generated by the creation of new local state in the forbidden band due to the scission of molecular bonds. And judging from the observed wave form, the level of local states might be created with the several energies, continually in forbidden band.

##### B. FT-IR measurement

VERTEX 70 (Buker Optics) was used to obtain FT-IR spectra. FI-IR spectra with ATR-mode of pristine and proton (1.5 MeV) irradiated ETFE is shown in figure 5. These results are normalized on the value at  $1040\text{ cm}^{-1}$ . The wavenumbers

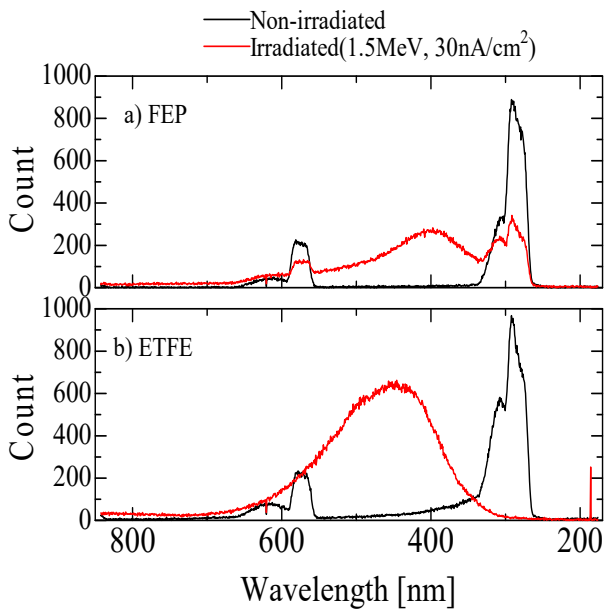


Fig. 4 PhotoLuminescence measurements results on 285 nm as an excitation light: (a) FEP and (b) ETFE.

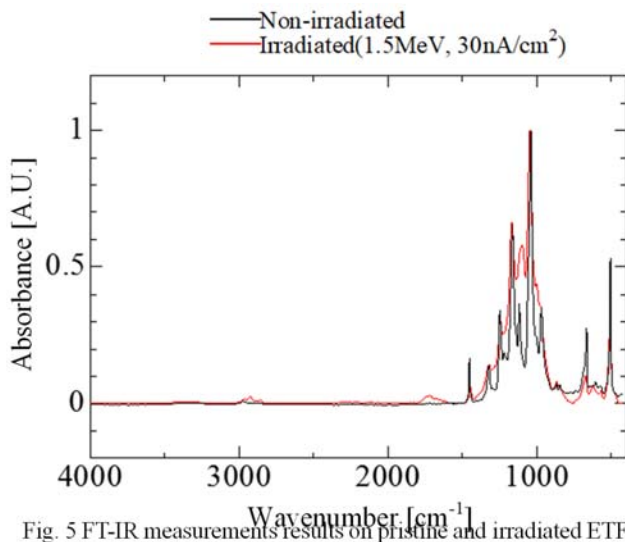


Fig. 5 FT-IR measurements results on pristine and irradiated ETFE.

which are related to molecular vibration mode are shown in Table 1 [12, 13]. After the ETFE irradiation new peaks were observed, between  $2831 - 2997 \text{ cm}^{-1}$  and  $1605 - 1807 \text{ cm}^{-1}$ . On the other hand, the peaks at  $669$  and  $509 \text{ cm}^{-1}$  are decreased, and the peaks between  $972 - 1425 \text{ cm}^{-1}$  related to  $\text{CF}_2$ , C-C and C-O molecular partly increased in amplitude and sprawled. From those results, it is considered that scissions of molecular chain were produced due to proton irradiation and unstable C molecular might be bonded with irradiated proton.

Table 1 Vibration mode of molecular on each wavenumber

Wavenumber [ $\text{cm}^{-1}$ ]	Molecular	Mode
2852	$\text{CH}_2$	symmetric stretching vibration
2921	$\text{CH}_2$	asymmetric stretching vibration
1740-1690	C=O	stretching vibration
1654	C=C	stretching vibration
1452	CH	deformation vibration
1146	$\text{CF}_2$	symmetric stretching vibration
1199	$\text{CF}_2$	symmetric stretching vibration
732	$\text{CF}_2$	symmetric stretching vibration
700-1200	C-C / C-O	stretching & scissoring vibration
650-1400	$\text{CF}_2$	stretching & scissoring vibration

It is assumed that such unstable C made new bonding with C double bond, C=O and C=C. At least, these results show the possibility of oxidization and crosslinking. Concerning  $\text{CF}_2$  mode, we could confirm both increase and decreasing phenomena.

Usually on PTFE films, formed by C and F atoms, scission type molecular species are observed after irradiation. On the contrary on PolyEthylene (PE) films, formed by C and H atoms, crosslinking type molecular species are identified after irradiation [14, 15]. As ETFE is elaborated by PE ( $\text{CH}_2$ ) and PTFE ( $\text{CF}_2$ ) parts, both scission and crosslinking phenomena might be produced due to proton irradiation, simultaneously.

Therefore, it is considered that  $669$  and  $509 \text{ cm}^{-1}$  was decreased due to scission. Furthermore, as ETFE is formed not only by  $\text{CF}_2$  but also by  $\text{CH}_2$ , it is assumed that the bonding state of  $\text{CF}_2$  was changed and shifted to dedicated states due to irradiation. This consideration may be related to the increasing and sprawled of peaks in the range  $972 - 1425 \text{ cm}^{-1}$ .

### C. XPS measurement

SSX-100 (SURFACE SCIENCE INSTRUMENTS) was used to obtain XPS spectra. The source of X-ray is Al  $K\alpha$  type anode ( $1487 \text{ eV}$ ) and the detecting energy range is  $0 - 1100 \text{ eV}$  with  $0.58 \text{ eV}$  of FWHM.

The results of XPS of FEP and ETFE are shown in Fig. 6 and 7, respectively. In those figures, the horizontal axis shows binding energy [eV] and the perpendicular axis shows measurement signal intensity [a. u.].

From Fig. 6 and 7, we can see the peak signal around  $300$  and  $700 \text{ eV}$  on the non-irradiated FEP and ETFE. Those peaks are related  $\text{C}_{1s}$  and  $\text{F}_{1s}$  signal, respectively.

Concerning proton irradiated materials, we could obtain the differential signal between non-irradiated and irradiated materials. The intensity of  $\text{F}_{1s}$  on FEP is decreased with irradiation energy progress. And  $\text{O}_{1s}$  peak was newly created at the surround  $500 \text{ eV}$ . Furthermore,  $\text{C}_{1s}$  signal was obtained precisely and shown in Fig. 6(b) – (d) and Fig. 7(b) – (c). From those figures,  $284.5$  and  $276.5 \text{ eV}$  show the origin of  $\text{CF}_2$  and CC or CH bonding, respectively.  $\text{CF}_2$  intensity decreased with

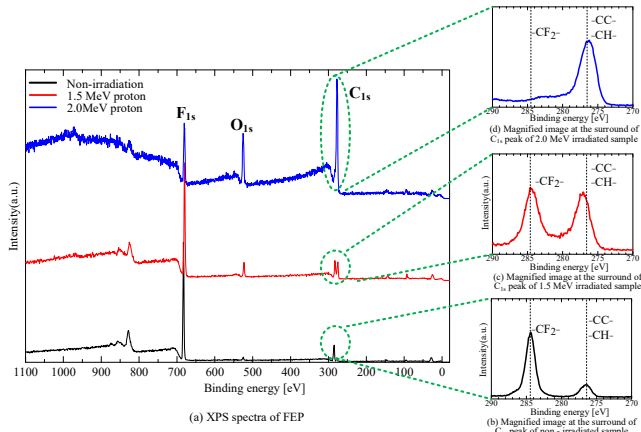


Fig. 6 XPS spectra of FEP irradiated by protons with the energy of 1.5 and 2.0 MeV

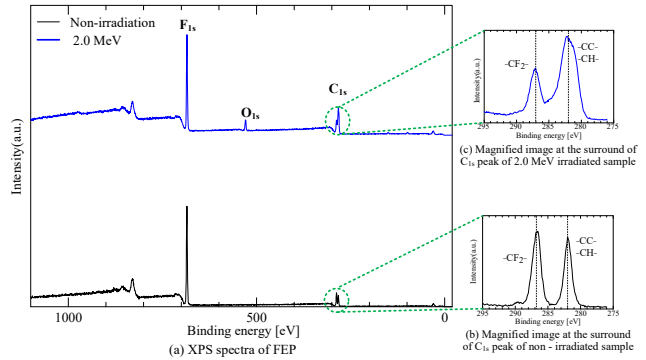


Fig. 7 XPS spectra of ETFE irradiated by protons with the energy of 1.5 and 2.0 MeV

irradiation proton energy progress and could not be observed on FEP irradiated by 2.0 MeV proton. CC or CH intensity increased with irradiation energy progress. Concerning the XPS spectra differential between irradiated and non – irradiated materials, although the intensities were different, we obtained same tendency on FEP and ETFE. On ETFE CF<sub>2</sub> does not vanish completely.

From the above results, we considered the bonding structure of irradiated sample. Concerning FEP, scission of CF<sub>2</sub> bonding was produced due to irradiation and disconnected F particle was swept out form the bulk of sample. Therefore, it is considered that the peak of F<sub>1s</sub> and CF<sub>2</sub> on C<sub>1s</sub> decreased. On the other hand, as the residual C chain create new binding with irradiated H<sup>+</sup> or cross linking, it was thought that the peak signal of CC or CH increased. Furthermore, from new peak creation of O<sub>1s</sub>, it seems that the irradiated samples were oxidized due to keep the sample under the air atmosphere after irradiation. And as the activated species were increased due to irradiation energy progress, we considered that the oxidation was proceeded.

Concerning of results of ETFE, the phenomena was little bit different from FEP results. CF molecule was also decreased. But the residual CF was still observed. And the oxidation was not proceeded to much compared with irradiated FEP.

From the above results, we thought that same tendency of XPS results was observed at the above FT-IR results. At least, it is considered that scission of CF<sub>2</sub> molecule might be produced from those results.

Next, when we compared between the SC accumulation phenomena and above XPS results, we should mention about the phenomena that the positive charges accumulated in the bulk near the cathode exceeding the proton penetration depth.

The scission and oxidation in FEP may be reduced the injection barrier between anode and sample and produced easy charge injection condition. And those might also produce the high mobility condition for hole.

Furthermore, normally, materials become radioactive due to proton irradiation with the energy of more than 2.0 MeV. Therefore, as the scission and oxidation area will be expanded

to non proton penetration area, it was considered that positive charge accumulation area was exceeded penetration depth.

#### D. NMR measurement

We tried to measure many spectra of irradiated sample. In this paper, we just introduce some big differential results between irradiated and non – irradiated sample.

Fig. 8 shows NMR spectra of ETFE focused on <sup>1</sup>H. From the figure, we can see some defect of CH<sub>2</sub> was observed at irradiated sample. It is considered that the irradiated H<sup>+</sup> (proton) may play to give some defect to original structure.

Fig. 9 shows NMR spectra on <sup>13</sup>C of ETFE and on <sup>19</sup>F of FEP. From the figure (a), although CH<sub>2</sub> peak intensity was same between irradiated and non – irradiated sample, the peak became broad. And CF<sub>2</sub> intensity peak of irradiated material was about 2.5 larger than the intensity of non – irradiated sample. On the contrary, from the figure (b), many CF<sub>3</sub> peaks in FEP were created. It is considered that CF<sub>2</sub> chain might be break due to irradiation and many terminations were produced as CF<sub>3</sub>.

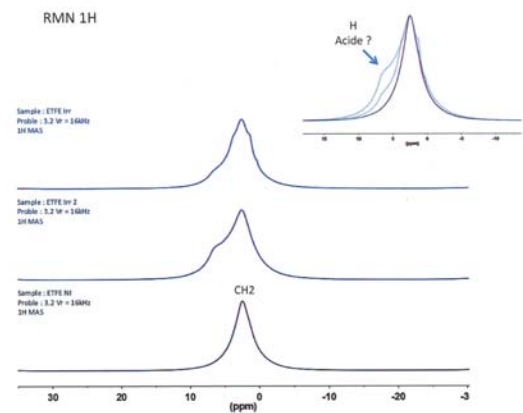


Fig. 8 Signal of <sup>1</sup>H of ETFE irradiated by protons with the energy of 2.0 MeV



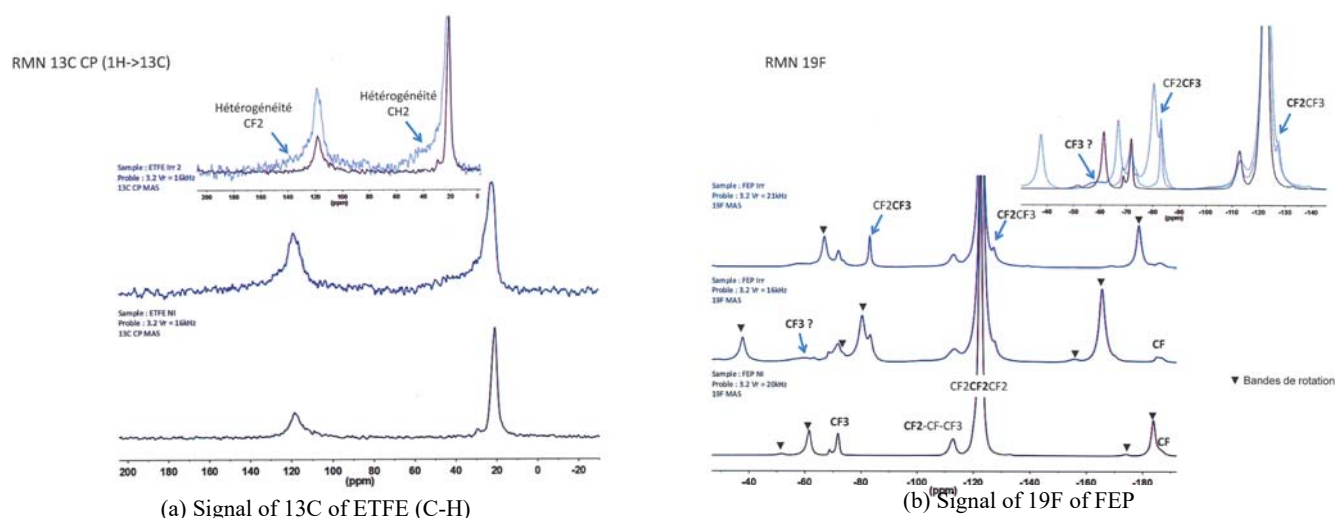


Fig. 9 XPS spectra of ETFE and FEP irradiated by protons with the energy of 2.0 MeV

However, we did not find the origin of the  $\text{CF}_2$  peak enhancement in Fig. 9(a), and many no-understandable peaks were observed in the irradiated sample in Fig. 9(b). Therefore, we should analyze more in detail. And we also try to make quantum chemical calculation from molecule modeling to producing NMR ideal signal for understanding the modification of molecule chain due to proton irradiation, in near future.

## V. CONCLUSIONS

Form the above results and discussion, concerning proton irradiated ETFE, we consider that morphology distortion, including scission and crosslinking, was produced due to irradiation. On the contrary, we also considered that the scission of molecule chain was dominant factor on FEP.

After irradiation, as unstable state still remained in the bulks, the oxidization could be continued during the sample storage in air atmosphere. These structural modifications are probably responsible for the positive charge accumulation observed in irradiated FEP and ETFE under high voltage application.

## REFERENCES

- [1] C. Koons, J. E. Mazur, R. S. Selesnick, J. B. Blake, J. F. Fennell, J. L. Roeder and P. C. Anderson, "The Impact of the Space Environment on Space Systems", Proceedings of the 6<sup>th</sup> Spacecraft Charging Technology Conference, Air Force Research Laboratory, Massachusetts (USA), pp.7-11, 26-29 October 1998.
- [2] D. Payan, R. Reulet, and B. Dirassen, "Electrostatic behavior of dielectrics under GEO-like charging space environment simulated in laboratory", 9<sup>th</sup> Spacecraft Charging Technology Conference, Proceeding, Tsukuba (Japan), pp. 65-74, 4-9 April 2005.
- [3] C. Perrin, V. Griseri, and C. Laurent, "Measurement of internal charge distribution in dielectrics using the pulsed electro-acoustic method in non contact mode", IEEE Trans. on Diel. E.I., Vol. 15, No. 4, pp. 958-964, 2008.
- [4] K. Nagasawa, M. Honjoh, T. Takada, H. Miyake, and Y. Yasuhiro, "Electric Charge Accumulation in Polar and Non-Polymers under Electron Beam Irradiation." IEEJ Trans. on F. M. (A), Vol. 130, No. 12, pp. 1105-1112, 2010.
- [5] J. E. West, H. J. Wintle, A. Berraisoul and G. M. Sessler, "Space-charge distributions in electron-beam charged Mylar and Kapton films", IEEE Trans. E.I., Vol. 24, No. 3, pp. 533-536, 1989.
- [6] M. Kojima, Y. Tanaka, T. Takada and Y. Ohki, "Measurement of Space Charge Accumulation in Gamma-irradiated Polyethylene with DC Voltage", IEE Japan Trans. on Fundamentals and Materials, Vol. 115, No. 2, 1995 [in Japanese].
- [7] H. Miyake and Y. Tanaka, "Space Charge Distribution in Polymethyl Methacrylate and Quartz Glass Irradiated by Protons", Sensor and Materials, Vol. 29, 2017 in press, <http://myukk.org/SM2017/>
- [8] T. Takada, H. Miyake, and Y. Tanaka: "Acoustic and optical methods for measuring electric charge distributions in dielectrics", IEEE Trans. Plasma Sci., Vol. 34, pp. 2176-2181, 2006.
- [9] J. F. Ziegler, J. P. Biersack and U. Littmark, "The Stopping and Range of Ions in Matter", Pergamon Press, ISBN 978-1-4615-8105-5, New York, 1985.
- [10] S? Yoishida, H. Miyake, T. Mori, U Chiba and Y. Tanaka, "Space charge accumulation behavior in fluorinated Polymer Films Irradiated by Proton under DC stress", IEEE International Conference Proceeding CEIDP, Fort Worth (USA-Alabama), Oct. 2017.
- [11] G. Teyssedre, J. Menegotto and C. Laurent, "Temperature dependence of the photoluminescence in poly (ethylene terephthalate) films", Polymer, Vol. 42, No. 19, pp. 8207-8216, 2001.
- [12] M. Nasef, H. Saidi, K. Zaman and M. Dahlan, "Electron beam irradiation effects on ethylene-tetrafluoroethylene copolymer films", Radiation Physics and Chemistry, Vol. 68, No. 5, pp. 875-883, 2003.
- [13] G. Calleja, A. Houdayer, S. Etienne-calas, D. Bourgogne, V. Flaud, G. Silly, S. Shibahara, A. Takahara, A. Jourdan, A. Hamwi, and B. Ameduri, "Conversion of poly(ethylene-alt-tetrafluoroethylene) copolymers into polytetrafluoroethylene by direct fluorination: A convenient approach to access new properties at the ETFE surface", J. Polym. Sci. Pol. Chem., Vol. 49, No. 7, pp. 1517-1527, 2011.
- [14] A. Charlesby, "Atomic Radiations and Polymers", Pergamon Press, Oxford, ISBN: 978-1-4831-9776-0, 1960.
- [15] JAEA database "JOPSS", [jopss.jaea.go.jp/](http://jopss.jaea.go.jp/)