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Loss of carbonate ester bonds along Fe ion tracks in thin CR-39 films

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In order to identify the chemical modification along nuclear tracks in CR-39 detectors, we have made a series of FT-IR measurements for thin CR-39 plastic films irradiated by Fe ions. The films were reduced in the thickness by long time chemical etchings down to 5 μm from as-received CR-39 sheets of 100 μm thick. It enabled us to obtain unsaturated IR spectra. The samples were exposed to 147 MeV Fe ions at HIMAC in air. Amount of loss of carbonated ester bonds due to the exposure was assessed from the changes in the absorbance of C=O and C-O-C bonds with Fe fluence. The assessed G-value for destroy of carbonate ester bonds was found to be about 10 (scission/100eV).

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1. Introduction

In our last study on 130 MeV carbon ion tracks in CR-39, we had found that the parts between two carbonate ester bonds in each repeat unit of the polymer networks were segmented into small molecules, including two CO_2 for each, along ion trajectory (Yamauchi et al., 2005a). We think such relatively long part segmentation promises CR-39 to be a prominent track detector. This finding was based on in situ FT-IR measurements for the film of 15 μm thick at the medium energy line facility of the GANIL, Caen, France. We had confirmed the decrease of ether bonds, 1099 and 1141 cm^{-1}, and attained successfully two important parameters of the G-value of 5.5 (scissions/100eV) and the corresponding track core radius of 1.1 nm. We observed an obvious formation of CO_2, 2338 cm^{-1}, and assessed the G-value of 3.6 and track core size of 0.63 nm. Unfortunately we had failed to take into account the escape of CO_2 during the irradiation and the measurements. In addition, we had simply applied a specific mole absorption coefficient of gaseous CO_2 to this case where the revolution of the molecule was suppressed. It was easy to observe the absorption band of CO_2, but quantitative treatments for this gas were still difficult.

FT-IR measurements for thin CR-39 films have been tried by several authors, which were prepared by chemical etchings. For examples, Lounis-Mokrani et al. studied the chemical and optical modifications of CR-39 films induced by 22.5 MeV proton beams, as well as giving a well summarized assignments for the peaks on IR spectra (2003). Tse et al. examined photo-degradation process in CR-39 films by UV radiation at various wavelength (2006). Recently, UV-cured CR-39 films on PET were developed for the purpose of radiobiological experiments (Gaillard et al., 2005). These are, however, too thick to obtain an un-saturated IR spectrum for the carbonate ester bonds, from which CO_2 gases are produced by the radiological scission.

In the present study, we obtained the thin CR-39 films below 5 μm by chemical etchings. We found the G-values of the loss of carbonate ester bonds and assessed the corresponding track core radius. The obtained result supports our previously proposed view that the part between two carbonate ester bonds are segmented along ion tracks in CR-39.

2. Experiments

Thin CR-39 films with two different thicknesses of 15 and 5 μm were

prepared by chemical etching from commercially obtainable pure CR-39 sheets with a nominal thickness of 100 μm (BARYOTRAK, Fukuvi chemical Industry Co., Ltd., Japan). Sheets were cut in a size of 20x20 mm^2. The etchings were made in 6M KOH solution kept at 70 ˚C without stirring. It took about 40 hours to reduce the thickness down to 15 μm. Handlings of thin films with a normal forceps became difficult when their thickness is below 15 μm. For the further etching down to 5 μm, we utilized a sieve of stainless steel as a sample holder (see Fig. 1). Succeeding to the etchings the samples were rinsed in distilled water carefully and then dried in clean and dark space after blew-out the excess water on the surface. Fe ion exposure was performed in air at the medium energy irradiation system of Heavy Ion Medical Accelerator in Chiba (HIMAC), NIRS, Japan (Yasuda et al., 2005). The incident energies of Fe ions on the films were 147 MeV for 15 μm samples and 140 MeV for 5 μm ones. The fluences were ranging from $7x10^{10}$ to $2x10^{11}$ ions/cm^2. At these fluences, overlapping of latent tracks was negligible. FT-IR measurements were performed for every films examined both before and after the irradiation, using a conventional spectrometer FTIR-8400S (SHIMADZU, Japan).

3. Results and discussion

3.1. Reduction of CR-39 thickness by etching

Figure 2 shows FT-IR spectra of as-received and etched CR-39 films with indicating thickness, plotting absorbance as a function of the wavenumber. For films less than or equal to 5 μm thickness, we obtained the totally unsaturated spectrum, including peaks for carbonate ester bonds. As shown here, the absorbance decreases generally with the reduction of the thickness.

In applying the Beer-Lambert law to evaluate the density of considering bonds in polymer network, we must determine the film thickness precisely. As shown in Fig. 3, the net-absorbance for typical bands is proportional to the film thickness measured by a micrometer. This kind of correlation between the thickness and absorbance give a calibration line, from which we are able to assess the film thickness by only measuring IR spectra. The band assignments for major ones were given in the literatures (Darraud et al., 1994; Gagnardre et al., 1993; Lounis-Mokrani et al., 2003; Malek and Chong., 2002; Saad et al., 2005) and we also confirmed them by a semi-empirical quantum chemical calculations using CAChe program (Fujitsu, Japan).

3.2. Loss of carbonate ester bonds

Figure 4 shows IR spectra of CR-39 films with 5 μm thick before and after the 147 MeV Fe ion irradiation at a fluence of 1.5×10^{11} ions/cm^2. It is obvious that the absorption bands at 1260 cm^{-1}, C-O-C, and at 1745 cm^{-1}, C=O, decreases in height by the exposure, which compose the carbonate ester bond. The relative absorbance, A/A_0, was attained at examined fluences, where A_0 is the original net absorbace of the considering bonds. Here, A/A_0 is equal to the survival fraction, N/N_0, that is the ratio of the number density of the considering bond, N, to that of original, N_0. The results are shown in Fig. 5, plotting A/A_0 against the fluence for the both bands. They give the almost identical trend. Based on these observations, we are able to derive the following experimental formula,

$$N / N_0 = 1 - \sigma_i \cdot F, \tag{1}$$

where F is in ions/cm^2 and σ_i is a constant for the bond i in cm^{-2}. The constant σ_i means the effective track area where the considering bonds were lost, from which we can derive the track core radius of 5.4 nm as summarized in Table 1. It also enables us to calculate the G-value par 100 eV, using the fundamental relation as,

$$G = 7.89 \times 10^{15} \frac{\sigma_i N_0}{LET}, \tag{2}$$

where N_0 is in mol/kg and LET is in keV/μm. In this case, the mean LET of Fe ion in the films were 5200 keV/μm. Then, G-values for loss of carbonate ester bond was calculated to be about 10 (scission/100eV).

3.3. Decrease of ether bonds

To estimate the G-value for the loss of ether bonds, we utilized CR-39 films with 15 μm thick. Figure 6 indicates IR spectra of the films before and after the exposure to 140 MeV Fe ions with a fluence of 2.0×10^{11} ions/cm^2. The peaks at 1027, 1094 and 1140 cm^{-1} are assigned to the ether bonds. At a glance, they seem to increase with the exposure, but the net absorbance for each peak certainly decreases. This is a result of the general increment of absorbance at the examining region of wavenumber, which can be caused by the formation of small molecules inside the film (Lounis-Mokrani et al., 2003).

Figure 7 indicates the changes in the relative absorbance, A/A_0, for ether bonds

as a function of the fluence. The two peaks of 1027 and 1140 cm^{-1} have the same trend on the ion fluence, showing almost linear reduction that can be expressed by Eq. 1. The other peak has different behavior from them. It was really difficult to assess the net absorbance for this peak located between other two peaks. So we attain the constant σ_i for the ether bonds from 1027 and 1140 cm^{-1}, and they gave 5.9 nm for track core radius. Since the mean *LET* of Fe ion in the films were 5400 keV/μm, Eq. 2 tells us the G-value for loss of ether bond was 6 (scission/100eV) .

3.4. Track core radius

The present authors have already evaluated the track core size in CR-39 for various ions using the UV and the AFM methods (Yamauchi et al., 2003, 2005b). These have been carried out for ions with energies corresponding to Bragg peaks, and the result was summarized as a function of the averaged *LET* as shown in Fig. 8. We compared carefully the present results for Fe ions and also the previous one for C ions by means of IR method with the previous ones those obtained by UV method. The track core sizes of Fe ion estimated from both loss of carbonate ester bonds and ether bonds agree well to the previously estimated trend.

Now we can say that all of the ether bonds and almost of carbonate ester bonds will break along the Fe ion track core. This fact insists that the parts of polymer chain of CR-39 between two carbonate ester bonds were segmented into small molecules composed by one or two carbon atoms including CO_2.

4. Conclusions

We have successfully obtained thin CR-39 films with thickness less than 5 μm, which made it possible for us to attain unsaturated IR spectra of the films with an ordinary spectrometer. Amount of loss of carbonated ester bonds due to the irradiation by 147 MeV Fe in air has been determined from the changes in the absorbance of C=O and C-O-C bonds as a function of Fe ion fluence. The assessed G-value for destroy of carbonate ester bonds was about 10 (scission/100eV) and the corresponding track core radius was 5.4 nm. Similar analyses have been made for the ether bonds using 15 μm films. The G-value for the loss of it was about 6.0 and the track core radius was 5.9 nm. These experimental results support the track segmentation model, which says the part

between two carbonate ester bonds in each repeat unit of CR-39 polymer network segmented into small molecules along the nuclear track.

Acknowledgements

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Figure Captions

Fig. 1 A CR-39 film with 3 μm thickness on a sieve as a holder.

Fig. 2 FT-IR spectra of CR-39 films with various thickness.

Fig. 3 Changes in absorbance for some bands of CR-39 with film thickness.

Fig. 4 Spectral changes observed in 5 μm CR-39 exposed to 147 MeV Fe ions.

Fig. 5 Decrease of carbonate ester bonds with Fe ion fluence.

Fig. 6 Spectral changes observed in 15 μm CR-39 exposed to 140 MeV Fe ions..

Fig. 7 Decrease of ether bonds with Fe ion fluence.

Fig. 8 Track core radius against stopping power.

Table 1

Summary of radio-sensitivity of carbonate ester and ether bonds in CR-39.

bonds			Fe ion	
			G-value	Track Core radius (nm)
carbonate ester	C-O-C	1260 cm^{-1}	10	5.4
	C=O	1745 cm^{-1}	10	5.4
ether	C-O-C	1027 cm^{-1}	6	5.9
		1140 cm^{-1}	6	5.9

Fig. 1

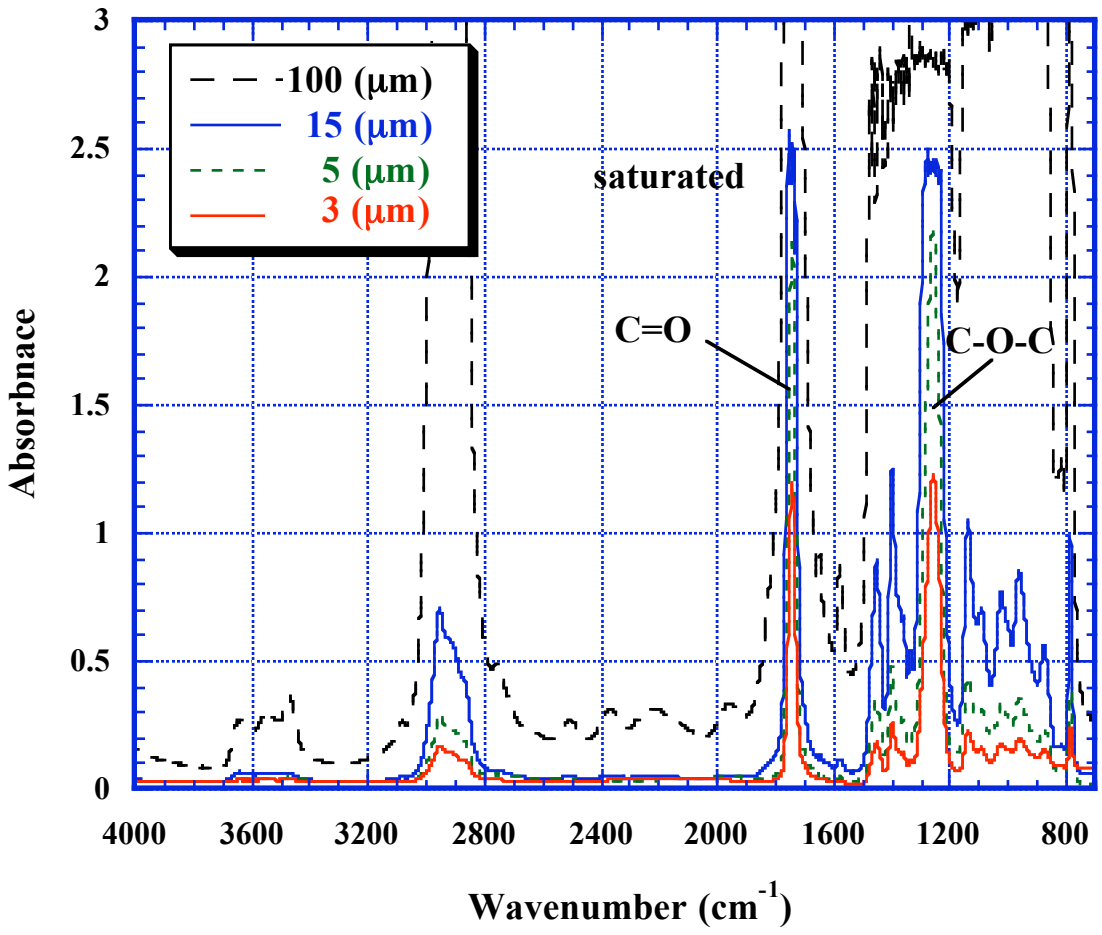
100 (μm)
15 (μm)
5 (μm)
3 (μm)
saturated
C=O
C-O-C
Absorbnace
Wavenumber (cm-1)
3
2.5
2
1.5
1
0.5
0
4000
3600
3200
2800
2400
2000
1600
1200
800

Fig. 2

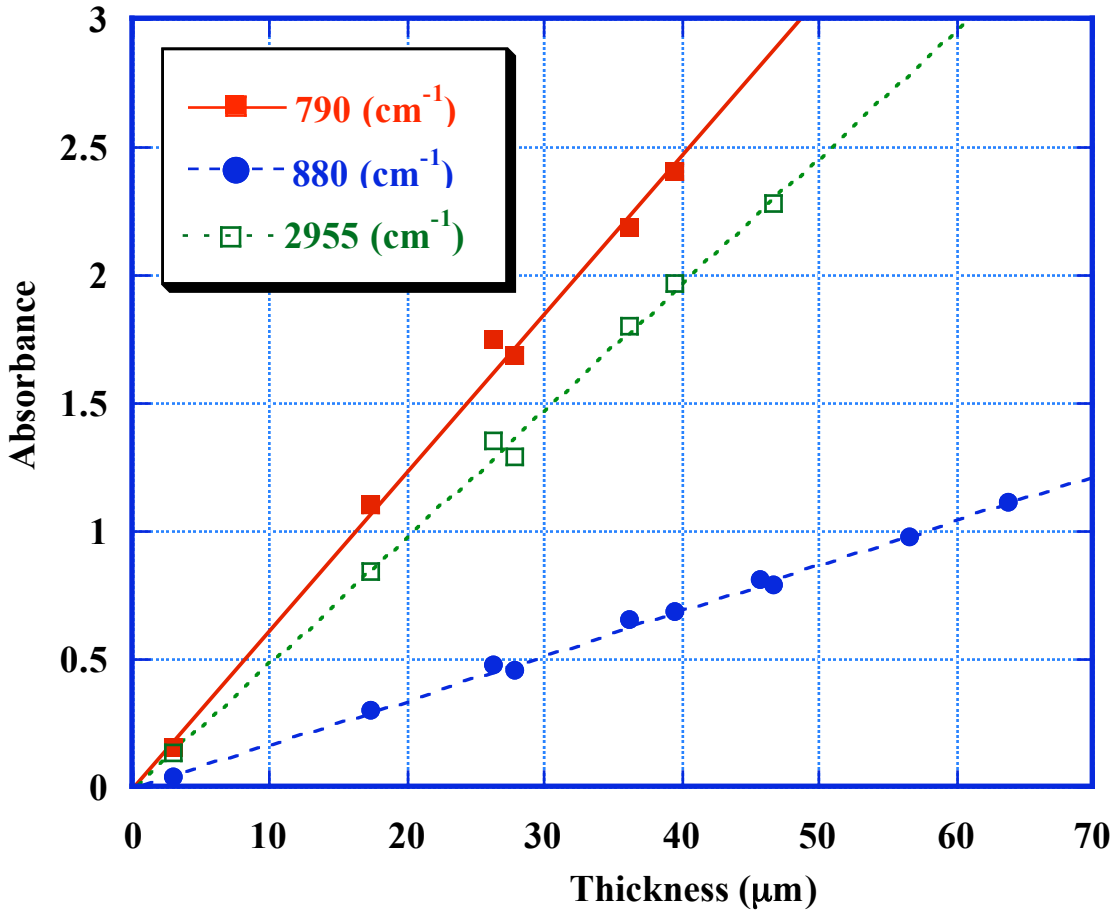
790 (cm-1)
880 (cm-1)
2955 (cm-1)
Absorbance
Thickness (μm)
0
0.5
1
1.5
2
2.5
3
0
10
20
30
40
50
60
70

Fig. 3

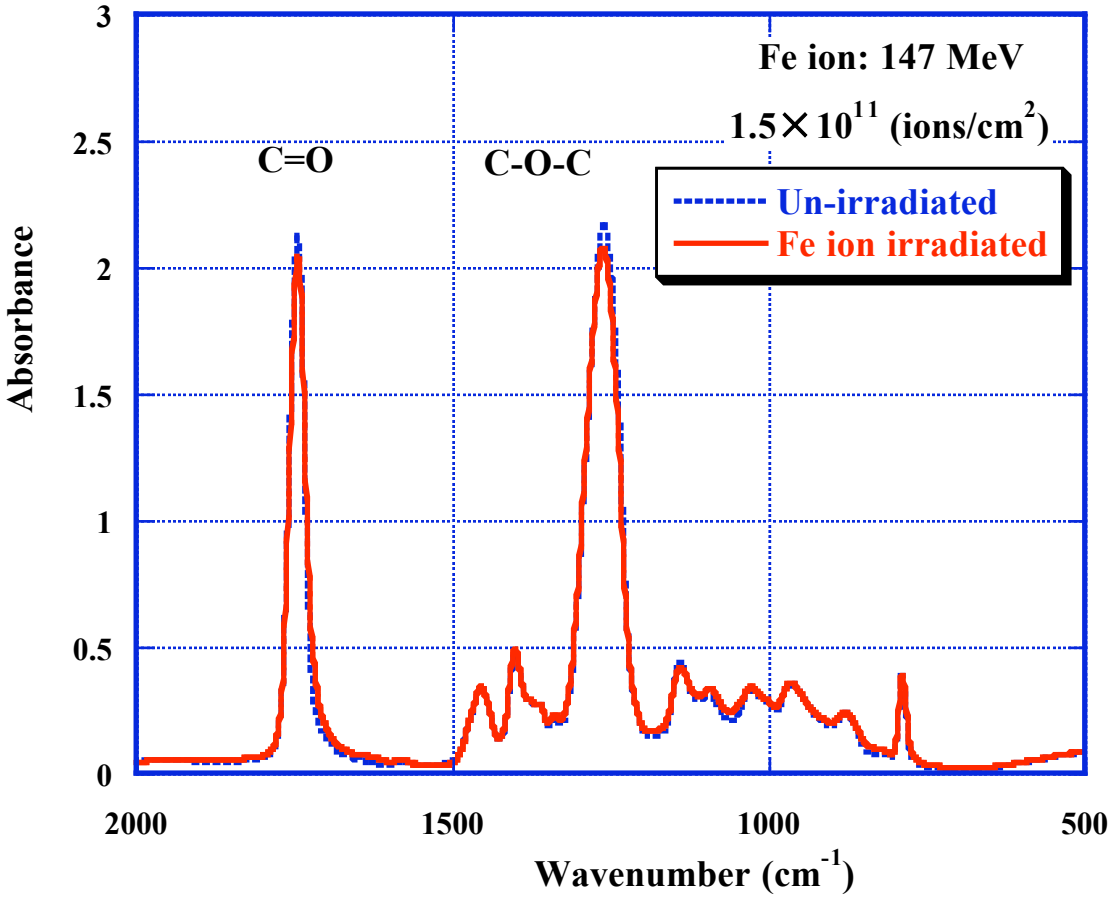
Fe ion: 147 MeV
1.5×10^11 (ions/cm^2)
C=O
C-O-C
Un-irradiated
Fe ion irradiated
Absorbance
Wavenumber (cm^-1)
3
2.5
2
1.5
1
0.5
0
2000
1500
1000
500

Fig. 4

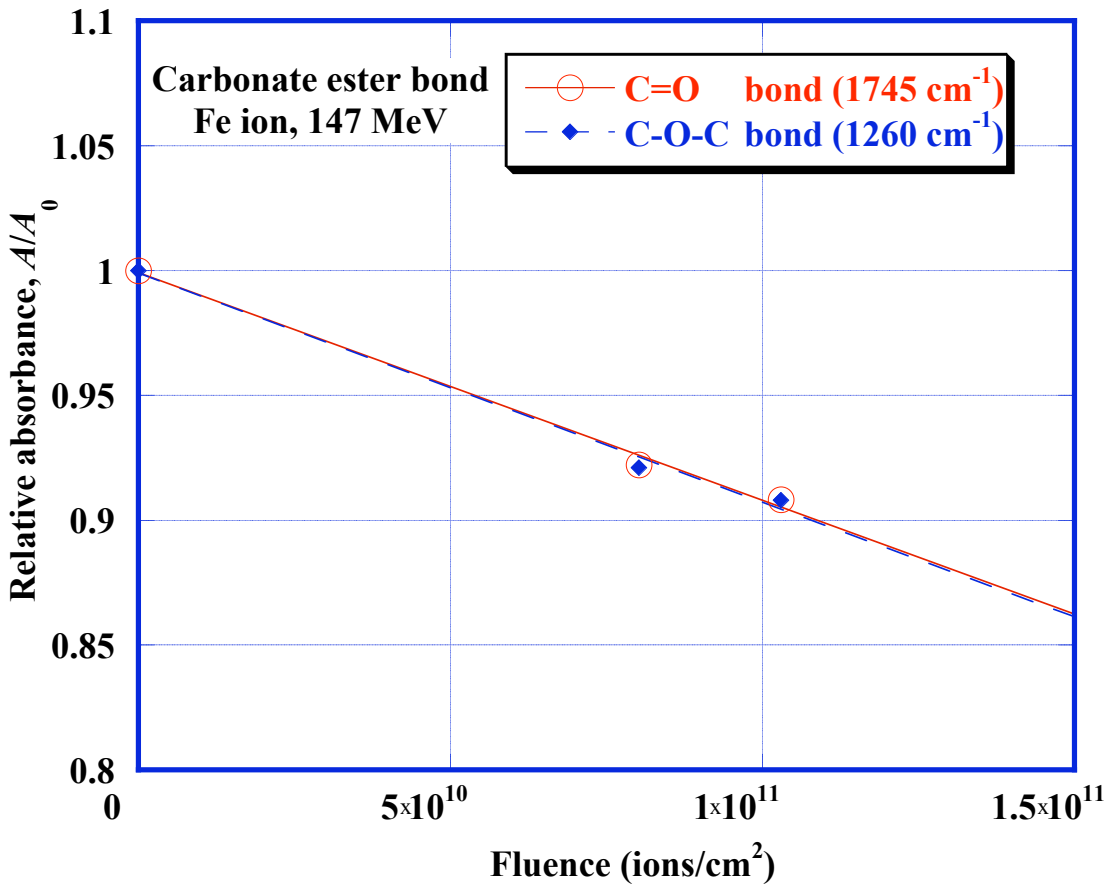
Carbonate ester bond
Fe ion, 147 MeV
C=O bond (1745 cm-1)
C-O-C bond (1260 cm-1)
Relative absorbance, A/A0
1.1
1.05
1
0.95
0.9
0.85
0.8
0
5x10^10
1x10^11
1.5x10^11
Fluence (ions/cm2)

Fig. 5

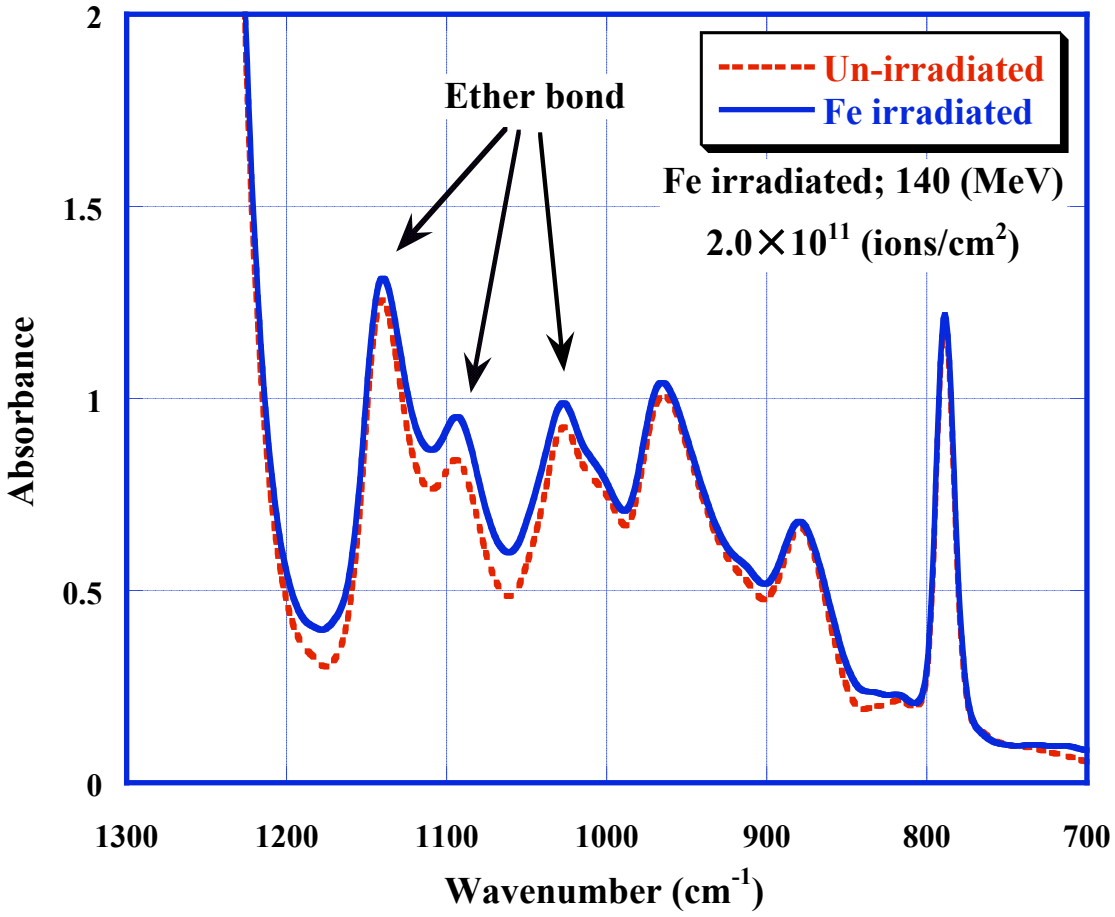
Un-irradiated
Fe irradiated
Ether bond
Fe irradiated; 140 (MeV)
2.0×10^11 (ions/cm^2)
Absorbance
Wavenumber (cm^-1)
2
1.5
1
0.5
0
1300
1200
1100
1000
900
800
700

Fig. 6

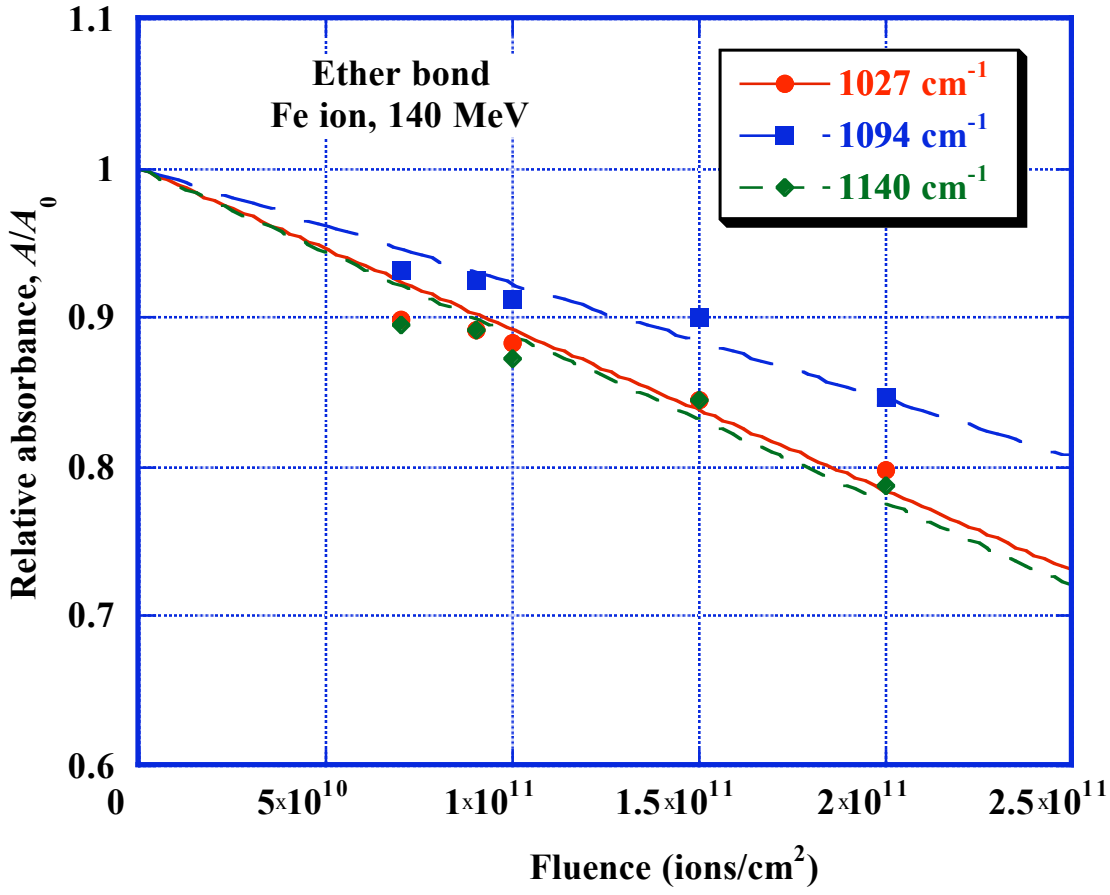
Ether bond
Fe ion, 140 MeV
1027 cm-1
1094 cm-1
1140 cm-1
Relative absorbance, A/A0
Fluence (ions/cm2)
1.1
1
0.9
0.8
0.7
0.6
0
5x10^10
1x10^11
1.5x10^11
2x10^11
2.5x10^11

Fig. 7

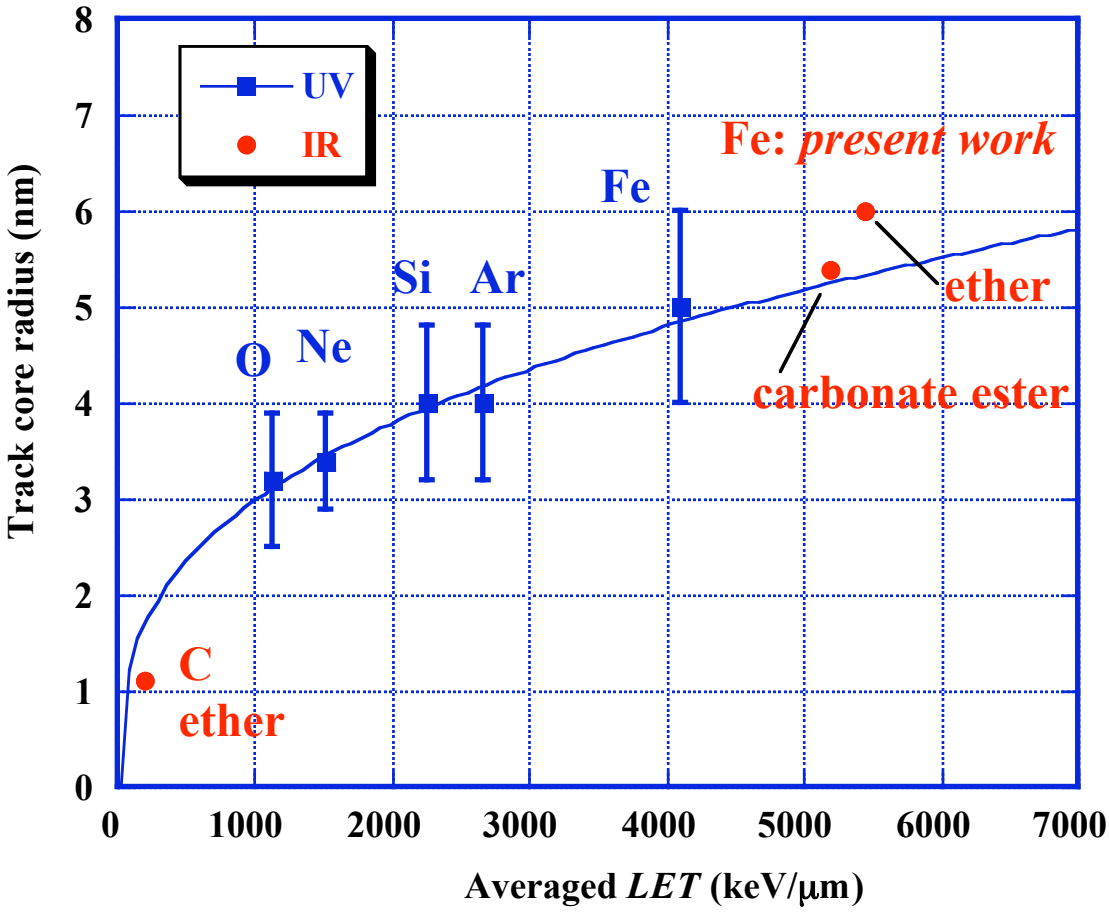
Track core radius (nm)
Averaged LET (keV/μm)
UV
IR
Fe: present work
Fe
Si
Ar
O
Ne
ether
carbonate ester
C
ether
0
1
2
3
4
5
6
7
8
0
1000
2000
3000
4000
5000
6000
7000

Fig. 8