

# Effects of Ultraviolet Photon Irradiation on the Dielectric Properties of Polyimide

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Ultraviolet photons were irradiated to the surface of all-aromatic polyimide films using a KrF excimer laser or a KrCl excimer lamp, and electrical properties such as permittivity, dielectric loss factor, conductivity, and space charge distribution were measured. In the case of the intense laser irradiation, the photo-induced change is drastic. The irradiated side of the sample is carbonized and becomes conductive. The apparent thickness of the remaining insulating region estimated by the space charge distribution measurements agrees with that observed by an optical microscope. The permittivity of the remaining apparently insulating region decreases as the irradiation proceeds, which is due to a decrease in the number of carbonyl groups. The dielectric loss factor and conductivity in this region increase since the leakage current increases even in this apparently insulating region. The activation energy of conduction also increases. In the case of the weak lamp irradiation, the permittivity decreases and the conductivity increases, although clear surface change is hardly observable. It is indicated from space charge distribution measurements that carrier traps are formed by the irradiation.

**Keywords :** polyimide, ultraviolet rays, space charge, conductivity, permittivity

## 1. Introduction

Owing to the recent development of space technologies, many artificial satellites and space shuttles have soared into orbits. Organic insulating polymers used in such spacecrafts must have superior performance under severe adverse environments in space. Among many such polymers, polyimide is used as thermal protective covering on the surface of spacecrafts, since it has a superior heat resistance and high durability under space environments. It is also used as an insulating material for coils in rotating machines for high-temperature use.

There could be many possible factors such as atomic oxygen, temperature cycle, radioactive rays, and ultraviolet (UV) photons that induce degradation of organic polymers. In order to specify the most influential factor, individual effects must be separated. For example, the reaction of atomic oxygen on the surface of polyimide has been studied<sup>(1)(2)</sup>. Effects of irradiation of UV photons have also been studied<sup>(3)</sup>, since UV irradiation is used as a measure to improve the surface property of polyimide or as a precise processing tool to fabricate a micro-structure in polyimide. As for the latter fabrication process by an intensive laser, presence of threshold in the absorbed energy density has been reported for UV photons with a wavelength in the region from 248 nm to 351 nm<sup>(3)</sup>. Namely, assuming that the photon energy absorbed by the sample is defined by the product of the energy density per unit surface area of a single laser pulse and the optical absorption coefficient at the wavelength, the polyimide surface is etched only when it is higher than  $5 \times 10^3$  J/cm<sup>3</sup>.

In the present paper, effects of UV photon irradiation on the dielectric properties of polyimide are examined in both cases that the energy absorbed is above or below the threshold.

## 2. Experimental Procedures

The samples used are all-aromatic polyimide Kapton-H<sup>®</sup> films supplied from DuPont-Toray Co., Ltd. Those with a nominal thickness of 50  $\mu$ m were used for measurements of conduction current and infrared attenuated total reflection (IR-ATR) spectroscopy, while those of 125- $\mu$ m thick were used to measure the permittivity, dielectric loss factor, and space charge distribution. For the permittivity and dielectric loss factor measurements, a gold upper electrode with a diameter of 25 mm and a gold guard electrode with an inner diameter of 36 mm and an outer diameter of 80 mm were evaporated on the sample surface, while gold electrodes with a diameter of 20 mm were evaporated on the two surfaces to measure the conduction current.

The sample surface was irradiated in air at room temperature either by a KrF excimer laser (Lambda Physik, Compex 205) at a wavelength of 248 nm, or by a barrier-discharge type KrCl excimer lamp (Usio, UER 20-222) at 222 nm. With a thermosensitive power meter and an UV-luminous material, the energy density of the laser was estimated to be about 300 mJ/cm<sup>2</sup>/pulse at a frequency of 1 Hz, and that of the lamp to be 5.5 mW/cm<sup>2</sup>. In the case of the laser, the product of the energy density per unit area by a single pulse and the optical absorption coefficient at 248 nm is  $6.6 \times 10^4$  J/cm<sup>3</sup> and is higher than the threshold. In the case of the lamp, its comparison with the threshold is impossible, since the lamp is a continuous light source. However, it is quite reasonable to assume that the etching cannot occur by the lamp since its power density is only about  $5 \times 10^{-10}$  times of that of the laser.

The permittivity and dielectric loss factor were measured by a dielectric analyzer (Ando TR-10C) using its standard measurement electrodes (SE-70) in a frequency range between  $6 \times 10^1$  to  $10^5$  Hz. Conduction current was measured by applying a dc voltage of 3 kV to the sample. Space charge distribution

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was measured by the pulsed electroacoustic method. The voltage applied was 3 kV for the samples irradiated by the KrF excimer laser, while it was 5 kV for those irradiated by the KrCl excimer lamp. The space charge distribution was measured during the voltage application period of 30 min and the following short-circuit period of 90 min. Silicone oil was applied at the interface between the sample and electrodes to facilitate the acoustic transmission.

The IR-ATR measurement was done with a Fourier-transform IR spectrometer (Jasco, Winspec 50) using an attached ATR unit

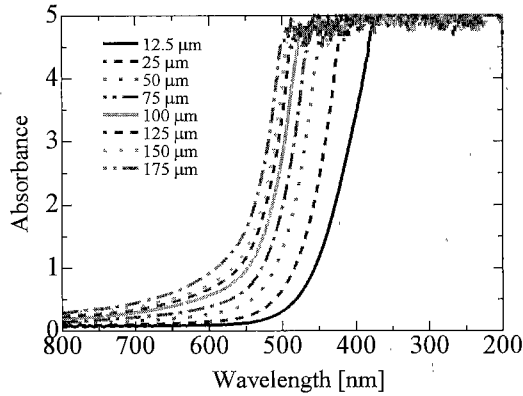
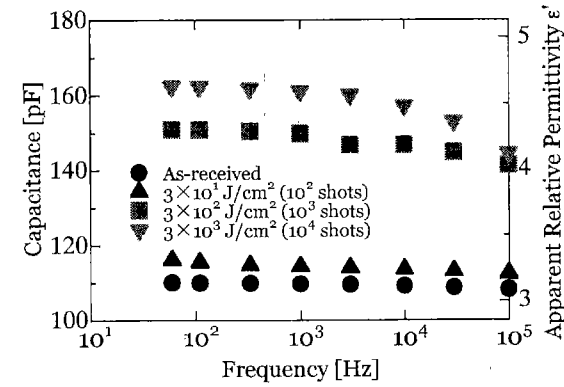
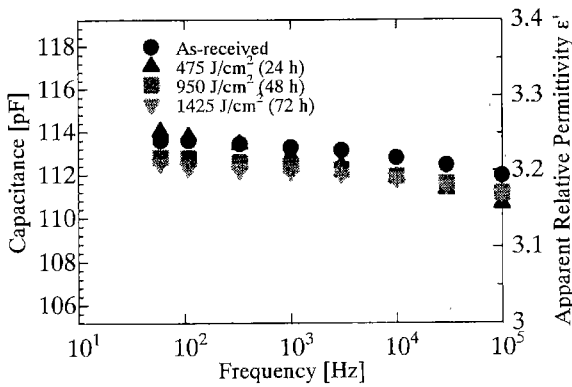


Fig. 1. UV absorption spectra of all-aromatic polyimide with different thicknesses



(a) Irradiated by the laser



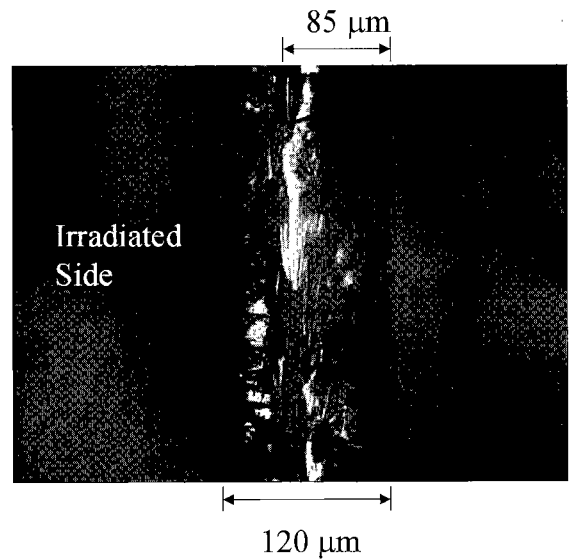
(b) Irradiated by the lamp

Fig. 2. Capacitance and apparent relative permittivity of the irradiated samples

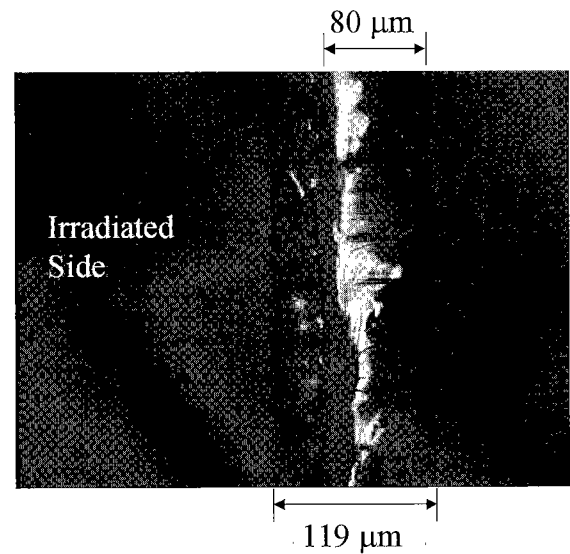
and a Ge prism. The resolution and scan number were set to be  $4 \text{ cm}^{-1}$  and 16, respectively. Assuming that the refractive index is 1.78 for polyimide and 4.0 for Ge, the optical penetration depth is shorter than  $1 \mu\text{m}$  at the measurement wavelengths. Therefore, only the surface was examined by the IR-ATR.

### 3. Results and Discussion

Figure 1 shows UV spectra as a function of wavelength measured using eight samples with different thicknesses. The ordinate represents the absorbance, which is defined by  $-\log_{10}(I_2/I_1)$ , where  $I_1$  and  $I_2$  are intensities of the incident and transmitted light, respectively. Even in the thinnest sample, the absorbance exceeds 5 around 400 nm. This indicates that all the photons irradiated are absorbed in the vicinity of the incident surface and that no effect is induced beyond that region.



(a) The sample irradiated to  $300 \text{ J/cm}^2$  ( $10^3$  shots)



(b) The sample irradiated to  $3 \text{ kJ/cm}^2$  ( $10^4$  shots)

Fig. 3. Optical microscopic photographs of samples irradiated by the laser

Figure 2 shows the change in electrostatic capacitance as a function of frequency measured with the non-irradiated sample and those irradiated by UV photons. When the sample was irradiated by the excimer laser, the capacitance clearly increases with an increase in the irradiated energy density as shown in Fig. 2(a), while no such clear increase is seen for the samples irradiated by the excimer lamp as shown in Fig. 2(b). Apparent values of permittivity calculated using the measured capacitance values under the assumption that the sample thickness did not change by the UV irradiation are also shown in Fig. 2.

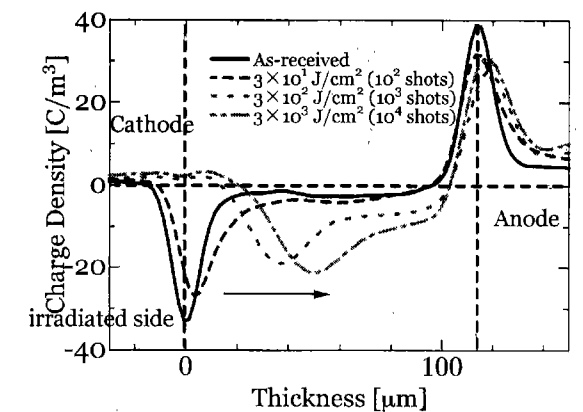
Figure 3 shows cross-sectional views observed by an optical microscope for the samples irradiated by the laser. Note that the thickness is reduced by the irradiation. It becomes 122  $\mu\text{m}$  after the irradiation of  $10^2$  shots ( $= 30 \text{ J/cm}^2$ ), 120  $\mu\text{m}$  after  $10^3$  shots ( $= 300 \text{ J/cm}^2$ ), or 119  $\mu\text{m}$  after  $10^4$  shots ( $= 3 \text{ kJ/cm}^2$ ) from the original thickness of 125  $\mu\text{m}$ . This thickness reduction was observed with a high reproducibility throughout the whole irradiated area. Furthermore, the irradiated side becomes black in color to a certain depth, which is considered to have been carbonized by irradiation<sup>(4)(5)</sup>. The remaining thickness, presumably holding a good electrical insulating property, can be read from Fig. 3 as 85  $\mu\text{m}$  and 80  $\mu\text{m}$  for the samples irradiated to  $10^3$  and  $10^4$  shots, respectively.

Figure 4(a) shows the space charge distributions in the samples irradiated with the laser, and Fig. 4(b) shows those irradiated with

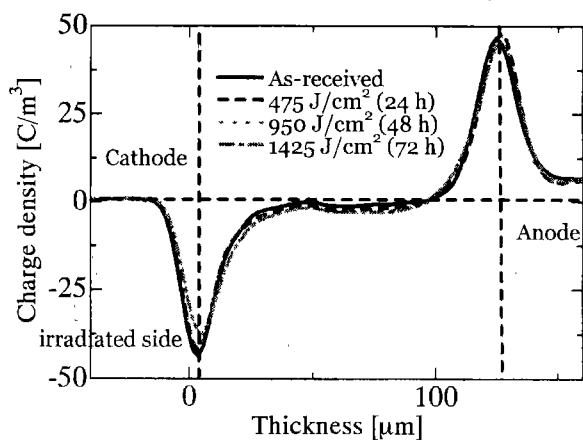
the lamp. All the distributions were observed under the application of a dc voltage for 30 min. The voltage applied was 5 kV for Fig. 4(b), while it was determined to be 3 kV for Fig. 4(a) by taking the reduction in the effective insulating thickness into consideration. Figure 4(a) clearly shows that the negative charge peak had moved to the inside of the sample as if the cathode irradiated by the photons had been moved to that position. This strongly indicates that the irradiated part of the sample was carbonized and became conductive. The apparent remaining thicknesses are estimated to be 122  $\mu\text{m}$ , 90  $\mu\text{m}$ , and 75  $\mu\text{m}$  for  $10^2$ ,  $10^3$ , and  $10^4$  shots, respectively. The latter two values are fairly in good agreement with the values estimated from Fig. 3. As for the samples irradiated by the lamp, neither reduction in thickness nor the appearance of a distinct carbonized region was observed by the microscope, consistently with the result shown in Fig. 4(b).

The carbonization of the laser-irradiated samples should have influenced the calculation of their permittivity or conductivity values. Figure 5(a) shows their relative permittivity values re-estimated from the results shown in Fig. 2(a) by assuming that the carbonized region and the rest are perfectly conductive and insulating, respectively. Figure 5(b) shows similarly re-estimated values of the dielectric loss factor.

The change in the re-estimated permittivity with the photon energy density in the laser-irradiated polyimide shown in Fig. 5(a) is somewhat similar to that observed in the lamp-irradiated

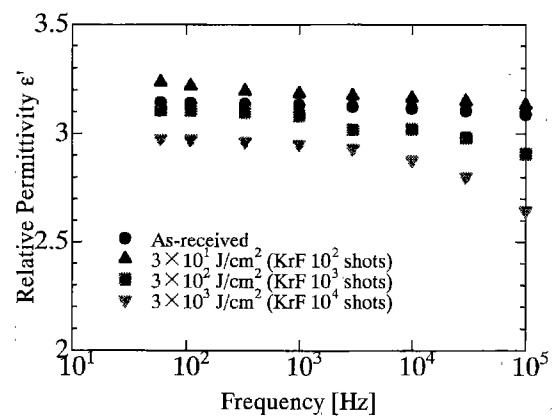


(a) Irradiated by the laser.

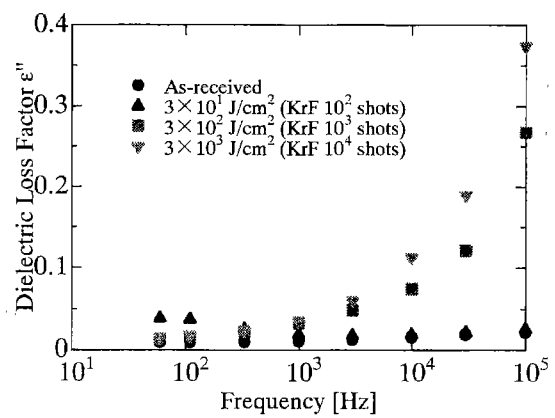


(b) Irradiated by the lamp

Fig. 4. Space charge distributions during the application of dc voltage



(a)



(b)

Fig. 5. Relative permittivity (a) and dielectric loss factor (b) of the remaining apparently insulating region of the laser-irradiated samples

polyimide shown in Fig. 2(b). The permittivity seems to decrease as the photon irradiation proceeds. In order to examine the reason for this, IR-ATR spectra were obtained. Those observed in the laser-irradiated samples and in the lamp-irradiated samples are shown in Figs. 6(a) and 6(b), respectively. Distinct peaks at  $1720\text{ cm}^{-1}$  due to carbonyl groups, at  $1500\text{ cm}^{-1}$  due to the imide vibration, at  $1380\text{ cm}^{-1}$  due to bonds between benzene ring and nitrogen, and at  $1249\text{ cm}^{-1}$  due to bonds between benzene ring and oxygen<sup>(6)</sup> are seen in the non-irradiated samples. It is clearly shown that these peaks decrease as the irradiation proceeds. The photon energy of the laser is 5.0 eV, while that of the lamp is 5.6 eV. If these values are compared with energies of the bonds characteristic to polyimide, the photon energies are larger than the bond energies of C-N (3.0 eV), C-O (3.7 eV), and C-C (3.6 eV), while they are smaller than the bond energy of carbonyl (7.1 eV). However, in the case of the laser, two-photon absorption is quite plausible. Furthermore, it has been reported that the number of carbonyl groups decreases and that carbon monoxide gas desorbs when polyimide is irradiated by photons with a wavelength of 193 nm ( $= 6.4\text{ eV}$ ) from an ArF excimer laser<sup>(7)</sup>. A possible reason for this is that C-N bonds in the imide rings and C-C bonds connecting the benzene rings and carbonyl groups were broken to desorb carbon monoxide<sup>(7)</sup>. Since these reactions can be induced by the photons from the lamp, similar bond scission should have

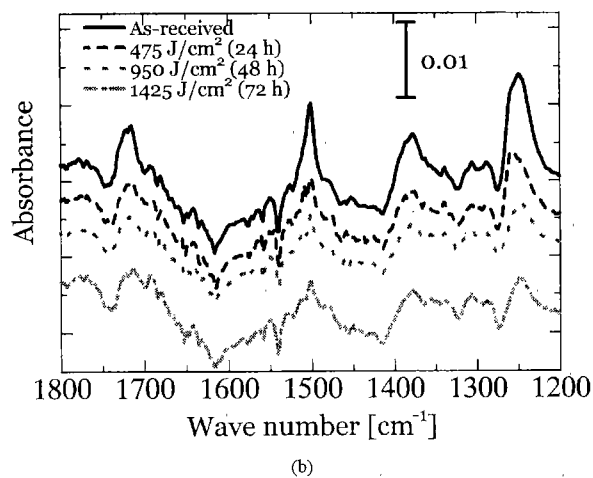
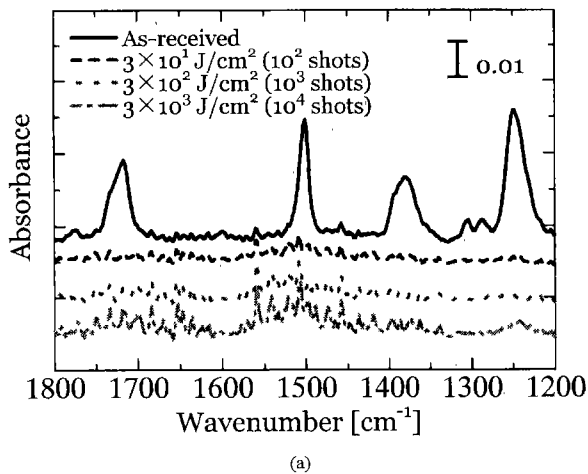


Fig. 6. IR-ATR spectra of the laser-irradiated (a) and lamp-irradiated samples (b)

occurred in the present experiment, which decreased or extinguished the above absorption peaks even in the case of the lamp-irradiated sample. Since the carbonyl group is polar, it can surely contribute to permittivity. Therefore, the reduction in the number of carbonyl groups by irradiation is considered to be the reason for the decrease in permittivity shown in Figs. 2(b) and 5(a).

As shown in Fig. 5(b), the re-estimated dielectric loss factor in the laser-irradiated sample increases by the photon irradiation of  $3 \times 10^2$  or  $3 \times 10^3\text{ J/cm}^2$ , especially at frequencies higher than  $10^3\text{ Hz}$ . The dielectric loss factor is an indicator of imperfect leaky dielectric property and becomes larger if the leakage current in the sample increases. Figure 7 shows the conductivity values of the remaining apparently insulating region calculated from the current values observed 90 minutes after the initiation of the voltage application. In both cases that the sample was irradiated by the laser [Fig. 7(a)] or by the lamp [Fig. 7(b)], the current density increases with an increase in the irradiated energy density. It is reasonable to assume that part of the remaining dielectric region in the laser-irradiated sample is slightly conductive even though the part still holds the color apparently the same as the original.

The activation energy of conduction is higher at temperatures higher than  $120\text{ }^\circ\text{C}$  than at lower temperatures, regardless of the sample having not been irradiated or having been irradiated by the lamp or laser as shown in Fig. 7. This is probably due to an increase in mobility of ions and/or due to an increase in free

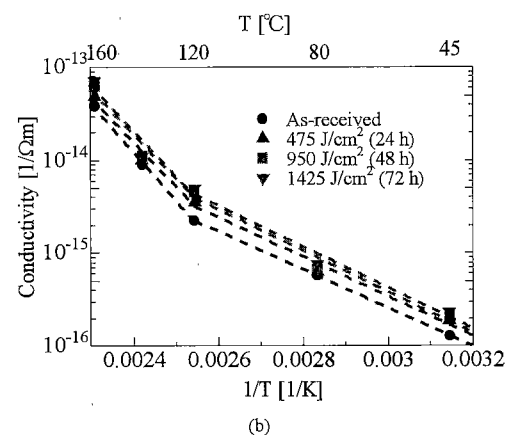
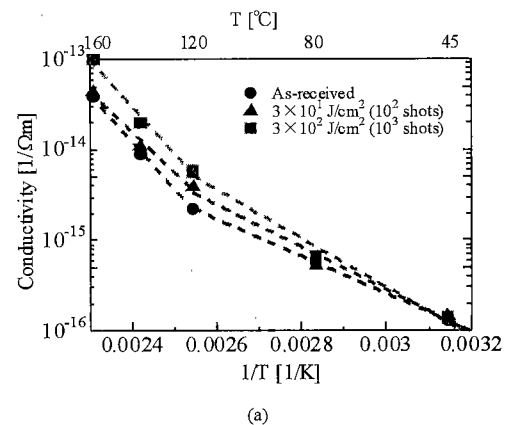


Fig. 7. Temperature dependence of the conductivity in the remaining apparently insulating region of the laser-irradiated (a) and lamp-irradiated samples (b)

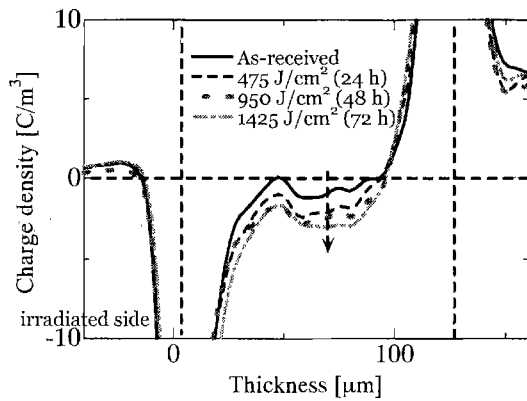
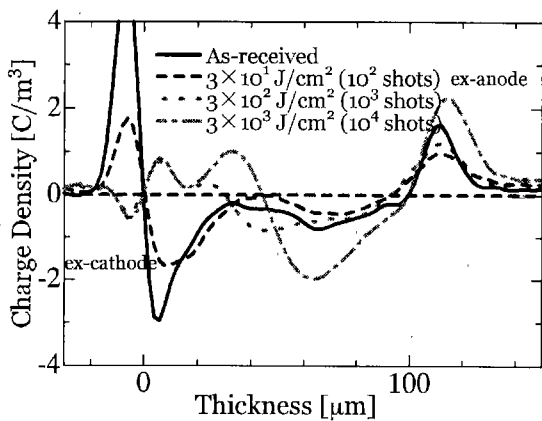
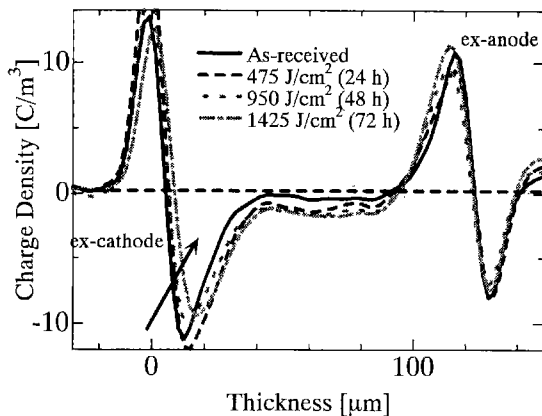


Fig. 8. Space charge distributions during the application of dc voltage in the lamp-irradiated samples



(a)



(b)

Fig. 9. Space charge distributions 5 minutes after the short-circuit following the application of dc voltage in the laser-irradiated (a) and lamp-irradiated samples (b)

volume<sup>(8)(9)</sup>. Furthermore, the activation energy at temperatures lower than 120 °C increases with the advance in the photon irradiation by the laser as shown in Fig. 7(a). A similar increase in the activation energy of conduction was reported in polyethylene irradiated by an electron beam<sup>(10)</sup>. On the other hand, the activation energy does not change in the case of the lamp irradiation as shown in Fig. 7(b).

As shown in Fig. 4(a), plenty of negative charge is seen inside

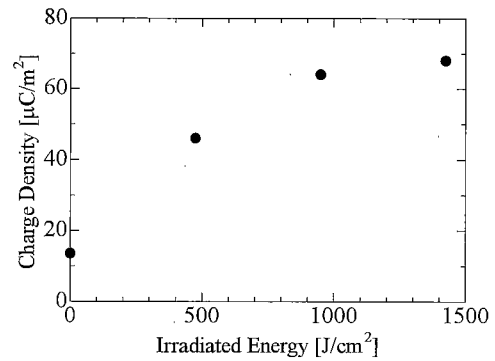


Fig. 10. Total amount of the space charge remaining inside the lamp-irradiated samples 5 minutes after the short-circuit

the polyimide irradiated by the laser. Since the appearance of such charge in the lamp-irradiated sample is unclear in Fig. 4(b), a magnified distribution is shown in Fig. 8. Although the amount is small, similar charge accumulation is also seen in the lamp-irradiated sample, and the charge amount increases as the number of irradiated photons increases. Figure 9 shows the space charge distributions measured five minutes after the laser-irradiated or lamp-irradiated sample had been short-circuited following the dc voltage application for 30 min. The positions at which the space charge is seen in Fig. 9 are the same as the ones seen in Figs. 4 and 8. This means that part of the space charge is immobile and is trapped inside the sample. Figure 10 shows the total amount of space charge remaining inside the sample as a function of the total photon energy irradiated by the lamp, obtained by integrating the charge distribution shown in Fig. 9(b). It is shown that the trapped charge amount increases as the irradiation proceeds. This is consistent with a report that carrier traps are formed in a polymer film by the irradiation of UV photons<sup>(10)</sup>.

#### 4. Conclusions

Ultraviolet photons were irradiated to all-aromatic polyimide using a KrF excimer laser or a KrCl excimer lamp. In the case of the intense laser irradiation, the photo-induced change is drastic. The irradiated side of the sample is carbonized and becomes conductive. The apparent thickness of the remaining insulating region estimated by the space charge distribution measurements agrees with that observed by an optical microscope. The permittivity of the remaining apparently insulating region decreases as the irradiation proceeds, which is due to a decrease in the number of carbonyl groups. The dielectric loss factor and conductivity in this region increase since the leakage current increases even in this apparently insulating region. The activation energy of conduction also increases.

In the case of the weak lamp irradiation, the permittivity decreases and the conductivity increases, although clear surface change is hardly observable. It is indicated from space charge distribution measurements that carrier traps are formed by the irradiation.

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