

Charge- Storage Capability of Fluorocarbon Polymer Films

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Fluorocarbon polymer films were irradiated with accelerated electrons. In order to examine the stability of injected electrons, thermally stimulated discharge current was measured. The TSD curve gave a broad peak at around 200°C. At room temperature, the amount of TSD current was small. As the mechanism of charge storage, carrier trap is important. Such traps are mainly present at $\begin{array}{c} \text{F} \quad \text{F} \\ | \quad | \\ -\text{C}-\text{C}- \\ | \quad | \\ \text{F} \quad \text{F} \end{array}$ chain and the interfaces between two adjacent crystal parts, and between crystal part and amorphous part. The stored charge is also stable against water.

KEY WORDS Electron-bombarded FEP/ EPE/ PFA films/ Stability of injected charge/

I. INTRODUCTION

Permanently electrified materials "Electrets" have gained much importance in the fields of acoustic transducers, switches, electrophotography, electrostatic recording, air filters, motors, generators, dosimeters and biophysics.¹⁾ The prosperity of electrets is mainly due to the development of polymer films which have good electrical, mechanical, thermal and chemically stable properties. In many polymers, fluorocarbon polymers are most excellent both in resistivity and in charge storage capability. As the crystallographic structure of the polymers is the mixture of crystal part and amorphous part, it is expected that there are many carrier trap levels stemming from the imperfection of the crystal part, the amorphous part and the interface between them. Such trap levels have been considered to play an important role in the charge storage. According to this assumption, the charge stored in electrets is thermally unstable. But the stability is most important in the case of application. In this paper, the examination of the thermal and moist stabilities of the FEP foil-electret formed by bombardment of electrons and the comparison of its result with that of other fluorocarbon polymers are reported.

II. EXPERIMENT

1) Electrification

Before irradiation, Nickel was evaporated on one side of 12.5 μm fluorocarbon foils. The thickness of the Nickel foil was 400 Å. A brass ring of 10 ϕ was stucked on the evaporated surface. Monopolar electrets were prepared by irradiating such foils from the opposite side of the evaporated surface with accelerated electrons which had the range smaller

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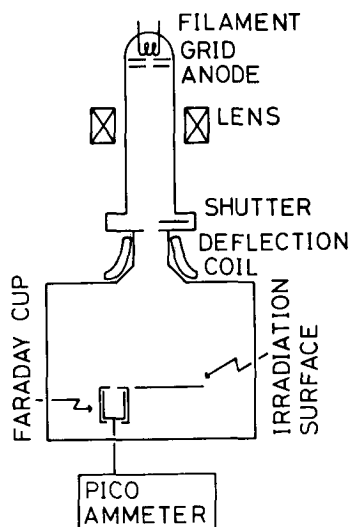


Fig. 1 Electron irradiation apparatus.

than the thickness of the foils. Electron irradiation apparatus is shown in Fig. 1. Electrons emitted thermally from the filament were accelerated by the anode, and then focused on the irradiation surface by the lens. When passing through deflection coil, electrons were deflected so as to sweep uniformly the irradiation surface. The intensity of the beam was monitored by a Faraday cup during irradiation, and was several tens nA. The vacuum in the apparatus was kept below 1×10^{-5} Torr. Surface potential of the foil electret after electron irradiation was measured by a universal electrometer.

2) Thermally stimulated discharge (TSD)

The foil electret prepared by the electron irradiation was heated at a constant rising rate. At the same time, discharge current was measured with a pico-ammeter. The setup of the measuring system is shown in Fig. 2. The foil was inserted between the upper and lower electrode with the evaporated surface contacting to the lower electrode.

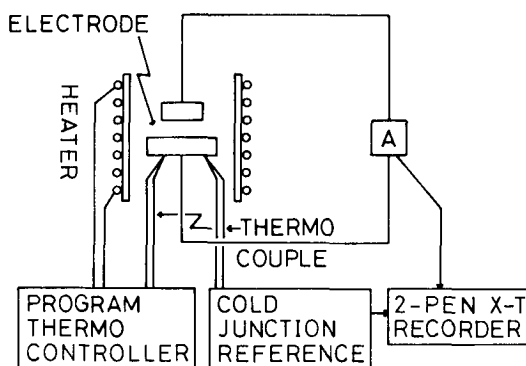


Fig. 2 Setup for measuring thermally stimulated discharge current.

The separation of the two electrodes was 1 mm. The rise rate of the temperature was controlled by the thermocontroller and was set to be 5°C per minute. The temperature of the lower electrode was monitored by using the thermocoupler, and was recorded on the 2-pen X-T recorder together with the discharge current.

III. RESULTS AND DISCUSSION

1) Formation of electrets

The surface potential of the FEP foil-electret electrified by electron injection with the surface density of σ_0 is described as

$$V = \sigma_0 x / 2.2 \epsilon_0 \quad (1)$$

where ϵ_0 denotes vacuum dielectric constant, and x denotes the mean depth measured from the metalized surface. The factor 2.2 in the denominator means the specific dielectric constant of FEP foil. When an accelerated electron bombards a material, several secondary electrons leave it. In taking account of this effect, Eq. (1) is rewritten as

$$V = (1-s) \sigma_0 x / 2.2 \epsilon_0 \quad (1')$$

where s denotes secondary electron emission factor. Figure 3 shows the relations between surface potential and total charge which was injected by using 20 keV electrons into

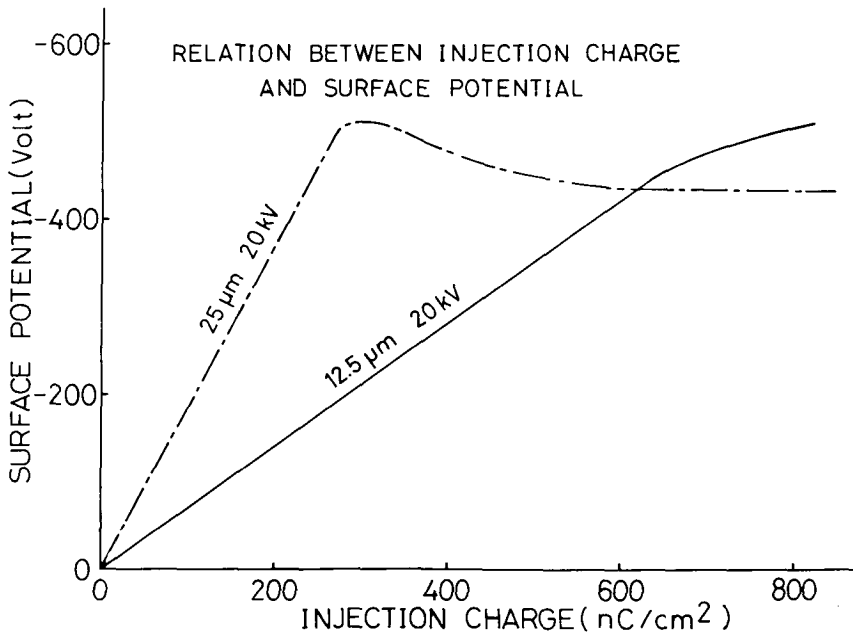


Fig. 3 Relation between injected charge and surface potential of the electret formed. Solid line shows the relation in the case of 12.5 μm film and 20 keV electrons, dot-dashed line in the case of 25 μm film and 20 keV electrons.

12.5 μm and 25 μm FEP foils. From the two curves in Fig. 3, we can get the values for the mean depth x (we assume x to be the mean depth for 12.5 μm foil, and $x+12.5$ to be that for 25 μm foil) and the secondary electron emission factor s ; $x=7.7$ and $s=0.82$. The mean range for 20 keV electrons penetrating into the FEP foil is obtained to be 4.8 μm , which is similar to the value in Ref. 1. As shown in Fig. 3, surface potential exhibits saturation at about -500 V. As the saturation takes place at the same surface potential for both 12.5 μm and 25 μm foils, it is not due to the breakdown of the electric insulator in the foil. Rather, it is a surface phenomenon originating from the radiation induced conductivity.

2) Examination of the thermal stability of electrets

The electrons stored in the electret are activated thermally from the trapped states. When electrons move toward the lower(upper) electrode, the pico-ammeter detects positive (negative) current. Figure 4 shows thermally stimulated discharge current for three electrets, which were electrified with the density 200 nC/cm² of 18 keV electrons, the density 100 nC/cm² of 18 keV electrons and the density 200 nC/cm² of 24 keV electrons. As seen from the figure, electrons activated thermally at low temperature move as a whole toward the upper electrode. With the increase of the temperature, the number of electrons moving toward the lower electrode prevails over the electrons moving toward the opposite direction. And then, the curve shows a positive peak at around 200°C. The curve for the density 200 nC/cm² of 24 keV electrons shows another positive peak at around 75°C, just above the temperature at which a negative peak arises. This peak

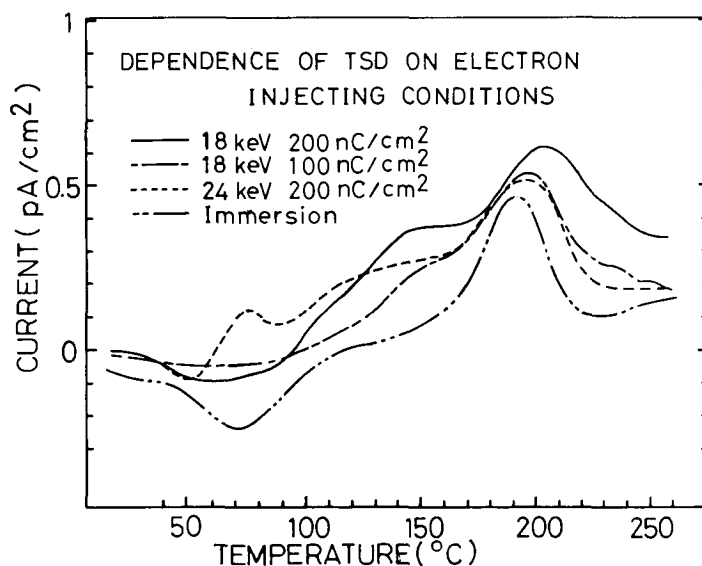


Fig. 4 Thermally stimulated current measured for the 12.5 μm FEP foil-electrets which were electrified with 18 keV 200 nC/cm², 18 keV 100 nC/cm² and 24 keV 200 nC/cm² electron irradiation. TSD current measured after immersion in the water is also shown.

indicates that the electrons which moved initially toward the upper electrode turned soon to the opposite direction. The negative peak is also seen in other curves. It is considered that the negative peak is caused by the space charge effect and the radiation induced conductivity. If only one carrier trap level is assumed to be present at the energy E_t , the temperature T_m where TSD curve gives a peak is related to E_t as follows,²⁾

$$\frac{\beta}{B} = \frac{kT_m^2}{E_t \exp(E_t/kT_m)} \quad (2)$$

where β , B and k denote the rise rate of the temperature, the constant (which depends on the density of the states in the conduction band, the thermal velocity and so on), and Boltzmann's constant respectively. It is natural to consider that there are many trap levels in the FEP foil so that superposition of Eq. (2) over various values of E_t is necessary for the quantitative discussion. One proof of the above prediction is given in Fig. 5. Two electrets were prepared under the same irradiation condition. One of them was heated at 150°C for one hour before measuring TSD current. As for the other one, TSD current was measured without preheating. The difference between two curves is shown in Fig. 5. This curve represents all the detrapped electrons which were initially trapped at trap levels below $E = k \times (150 + 273)$. There is a peak at around 150°C.

It is interesting to consider the origin of the peak appearing at around 200°C in the TSD current curve. Three kinds of fluorocarbon polymer films, Teflon FEP, Toyoflon EPE and Toyoflon PFA were electrified with the density 100 nC/cm² of 18 keV electrons. The comparison of the TSD current curves for three electrets is shown in Fig. 6. Each curve has a broad peak at around 200°C. This fact suggests that the peak stems from the common structure present in the three polymer films. It is conjectured that the common structure of polytetrafluoroethylene-like chain may play an important role for

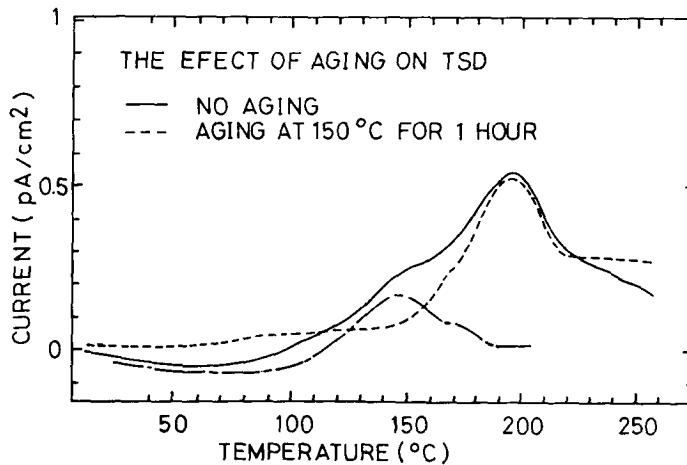


Fig. 5 The effect of aging at 150°C for one hour on TSD current. TSD currents for the electrets with and without aging were compared.

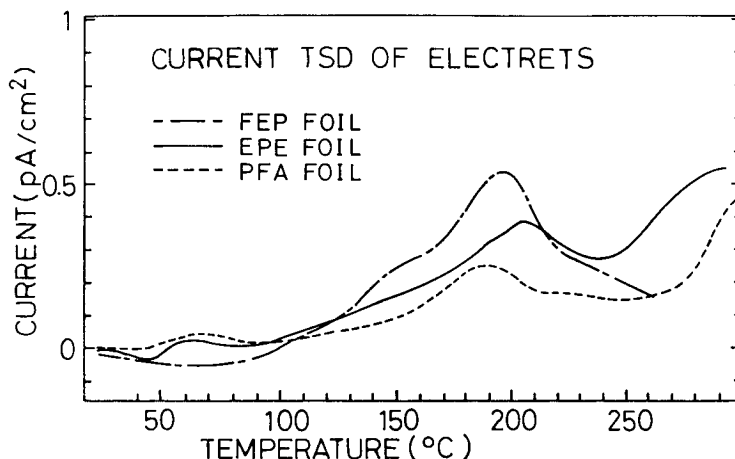


Fig. 6 Comparison of TSD Current for Teflon FEP, Toyoflon EPE and Toyoflon PFA foil-electrets which were electrified on the same condition. 12.5 μm films were used.

the origin of the peak. The TSD currents for EPE and PFA films increase rapidly at around melting temperatures (EPE: 290~300°C, PFA: 302~310°C). This fact means that some of injected electrons are trapped at interfaces between two adjacent crystal parts in the film, and between crystal part and amorphous part.

3) Examination of the moist stability of FEP foil electret

The application of electrets to the biological and medical fields has been promoted recently. Consequently, the examination of the moist stability of electrets has become important. When an electret is immersed in the water, the surface potential decreases considerably, because the electret attracts positive ions in the water. Figure 4 shows a TSD current measured for the electret after immersion in the water for one minute. By immersion, the surface potential decreased from -258 V to -12 V. However, the TSD current is comparable to that for the electret without immersion. This fact indicates that the charge-storage capability is scarcely degraded by water. This is consistent with the low water-absorption rate of the FEP film.

In conclusion, fluorocarbon polymer foil electrets are stable at room temperature. It seems that Toyoflon EPE has most excellent stability. The internal charge storage in electrets is scarcely affected by water. Most stable carrier trap levels seem to

be present in the structure $\begin{matrix} \text{F} & \text{F} \\ | & | \\ -\text{C}- & \text{C}- \\ | & | \\ \text{F} & \text{F} \end{matrix}$ and the interfaces between two adjacent crystal parts, and between crystal part and amorphous part.

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