

Thermally stimulated current spectra in nitrogen implanted fluorinated ethylene propylene

J P JOG, S B OGALE, S J WALZADE, A S OGALE,
S V BHORASKAR, M R BHIDAY and V N BHORASKAR
Department of Physics, University of Poona, Pune 411 007, India

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Abstract. Thermally stimulated current spectra of nitrogen implanted fluorinated ethylene propylene polymer foils have been studied. Two characteristic peaks have been obtained for samples implanted with nitrogen ions with energies ranging from 20 to 60 keV. The variations in the activation energies and relaxation times of charge carriers, as a function of implantation energy, have been attributed to the corresponding changes in the carrier distribution in the polymer. The carrier mobilities and mobility life-time products have also been estimated for the two characteristic peaks.

Keywords. Implantation; FEP; TSC; polymers; trapping; polarisation.

1. Introduction

In recent years considerable progress has been made in the field of ion implantation (Crowder 1973), particularly its application in semiconductors. However, studies on ion implantation in insulating materials and dynamics of injected charges are scanty although they are extremely important from the standpoint of device fabrication (Mayer *et al* 1970; Carter and Colligon 1968). These studies can throw much light on the basic charge transport phenomena in these materials.

Polymers, which have complex molecular chain structure with excellent insulating properties (Creswell 1969), are known to support charge distribution over very long periods of time. It is therefore useful in the fabrication of many devices based on the principles of static electricity. Charging of polymers is accomplished by several methods such as simultaneous application of heat and electric field (Sessler 1962, Perlman and Reedyk 1968 and Murphy and Frain 1968), Corona and Townsend discharge method (Tyler 1955; Reiser *et al* 1969 and Seiwatz and Brophy 1965, Monteith 1966, 1967) as well as non-penetrating beams. In most of these methods the charge distribution in the sample is not accurately known. It was therefore felt worthwhile to use implantation of selected ions of well-defined energies as a controlled method of doping the polymer foils. Thermally stimulated current (TSC) measurement technique was used to study excitation. Teflon-fluorinated ethylene propylene (FEP), a copolymer of polytetrafluoroethylene and hexafluoro propylene, was chosen as a substrate material because of its good charge storage characteristics (Bhiday and Rao 1975). Its TSC spectra were studied after implantation of N_2^+ ions for various values

of implantation energies. This paper reports the results of these experiments and their analysis using the method of Garlic and Gibson (1948).

2. Theoretical background

In TSC measurement one obtains the discharge current as a function of temperature, when the charges stored in the sample are released due to heating. The TSC spectrum thus obtained has several peaks, each one representing a typical charge release or depolarisation process in the solid as a result of the nitrogen implantation. The interaction of nitrogen with the lattice is assumed to result into charge sites which behave like dipoles (for simplifying the analysis). It is also assumed that nitrogen does not remain implanted in the lattice chains but helps in defect formation along its path of motion. Bucci and Fieschi (1966) developed a complete theory to account for TSC peaks, wherein they represented all the basic charge activation processes by equivalent dipole reorientation effects and obtained the following expression for TSC current.

$$J(T) = \frac{N\mu^2 E_p}{3kT_p \tau_0} \exp \left[-E/kT - (\beta\tau_0)^{-1} \int \exp\left(\frac{-E}{kT}\right) dT \right], \quad (1)$$

where N is the dipole concentration, μ is the dipole moment, k is the Boltzmann's constant, τ_0 a constant (having the dimensions of time), β the heating rate, E_p the polarising field, T_p the polarising temperature and E the activation energy.

The relaxation time τ for the dipoles at a temperature T is given by

$$\tau = \tau_0 \exp(E/kT). \quad (2a)$$

Here τ_0 is calculated from the relation

$$\tau_0 = \frac{kT_m^2}{\beta E \exp(E/kT)} \quad (2b)$$

Where T_m is the peak temperature. From the low temperature tail of equation (1) one can write

$$\log J(T) = \text{constant} - E/kT \quad (3)$$

The activation energy E is determined from the semilog plot of $J(T)$ versus $1/T$, as shown in figures 3(a) and 3(b).

3. Experimental

The FEP implantation was carried out using a 200 keV ion implantation system completely designed and fabricated in our institution. The implantation chamber, has a facility to hold four substrates in a single operation and the substrate orienta-

tion and its temperature can be externally controlled. In stable operation, substrate current of 15 to 20 μA can be obtained for various gaseous ionic species.

The main experimental arrangement consists of an oven, a linear temperature programmer and a current detector. The sample is mounted between two stainless steel electrodes inside the oven. The temperature is monitored by a chromel-alumel thermocouple. An electrometer amplifier is used as a current detector and a current-temperature plot is obtained with an X-Y recorder, at a heating rate of $6.4^\circ\text{C}/\text{min}$.

In the present experiment a 250 μm FEP foil was cut into pieces of $2.5\text{ cm} \times 2.5\text{ cm}$. These were implanted by N_2^+ ions for 45 sec keeping the current constant at $2\text{ }\mu\text{A}$ at three different energies 23, 43 and 54 keV. The TSC spectrum was recorded after 10 minutes.

4. Results and discussion

In order to obtain consistent results every experiment was carried out with a set of four identical samples subjecting them to ion bombardment under identical conditions. Before the bombardment, however, the TSC spectra of virgin FEP were recorded as shown in figure 1, and these were subtracted from the TSC spectra of corresponding implanted samples to obtain the net change in the TSC response due to ion implantation. The spectra shown in figure 2 correspond to FEP samples implanted with N_2^+ ions of 23, 43 and 54 keV energies. From figure 2 we observe that every implanted sample exhibits two distinct and well-defined peaks, the higher temperature peak being much weaker as compared to the low temperature one. Both the peaks were found to shift towards higher temperature with increase in the implantation energy. The distinct peaks with different activation energies (table 1) indicate the presence of two trapping levels—one ranging in energy from 0.5 to 0.7 eV and the other from 2.6 to 3.5 eV. The peak shift with the implantation energy is explained on the basis of the special distribution of charges in the sample.

The charge distribution in implantation is approximately Gaussian in shape and its maximum shifts deeper into the sample with increase of implantation energy. This known charge distribution allows us to interpret the small temperature shift in TSC

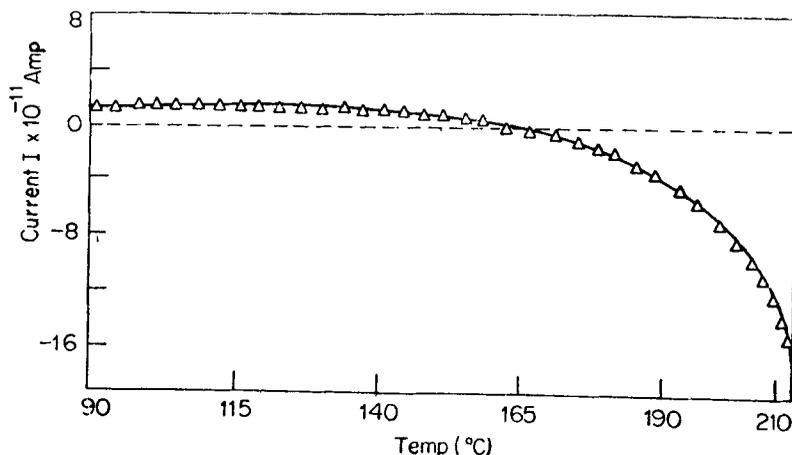


Figure 1. TSC spectrum of virgin FEP sample.

spectrum as a function of ion energy. However at this stage no definite conclusions can be drawn regarding the shift of the peak. Possibly the deeper trapped charges require larger amount of heat energy for them to diffuse to the surface. Though the sample is much thicker than the damaged region, the background (which is substantially weak) has been subtracted and hence the peaks correspond only to the changes due to implantation, and therefore the shift in TSC peaks can be related to the shift in the projected range of implanted ions.

The approximate constancy of peak shape and the range of temperature at which the maximum occurs lead us to infer that the basic nature of the defects formed does

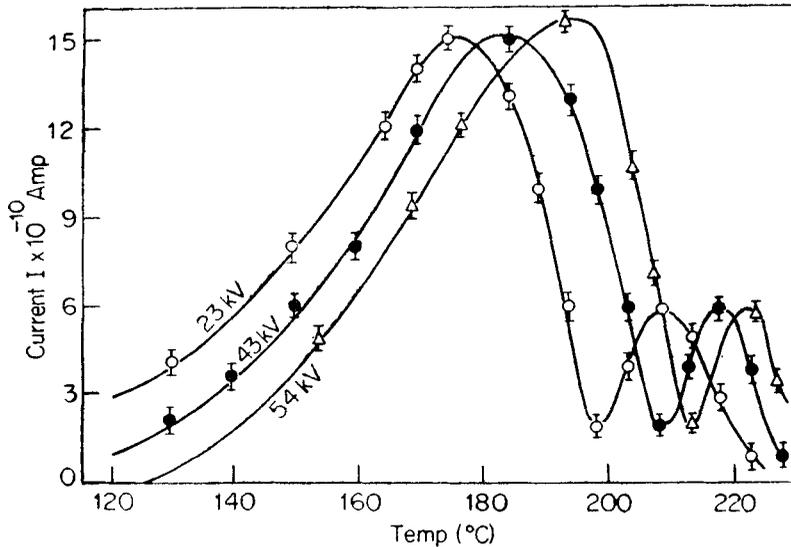


Figure 2. TSC spectra of ion implanted FEP.

Table 1. Values of parameters calculated from the experimental data

Ion Energy Peak No.	23 keV		43 keV		54 keV	
	I	II	I	II	I	II
Peak Temp. (°C)	175	210	182.5	220	195	223
Activation Energy (eV)	0.5074	2.698	0.6952	2.777	0.78	3.575
Total charge Q (coul) $\times 10^{-5}$	3.39	0.188	3.40	0.178	3.38	0.185
Relaxation time time (sec) $\times 10^3$	3.19	0.69	2.41	0.70	2.27	0.73
Relaxation time time (sec) at room temperature	2×10^5	9×10^{18}	2×10^6	8×10^{20}	1×10^7	3×10^{25}
Mobility (cm^2/Vsec) $\times 10^{-14}$	3.86	329	5.67	338	5.448	414.0
Mobility lifetime product (cm^2/V) $\times 10^{-12}$	12.37	230.85	12.17	239	12.37	230

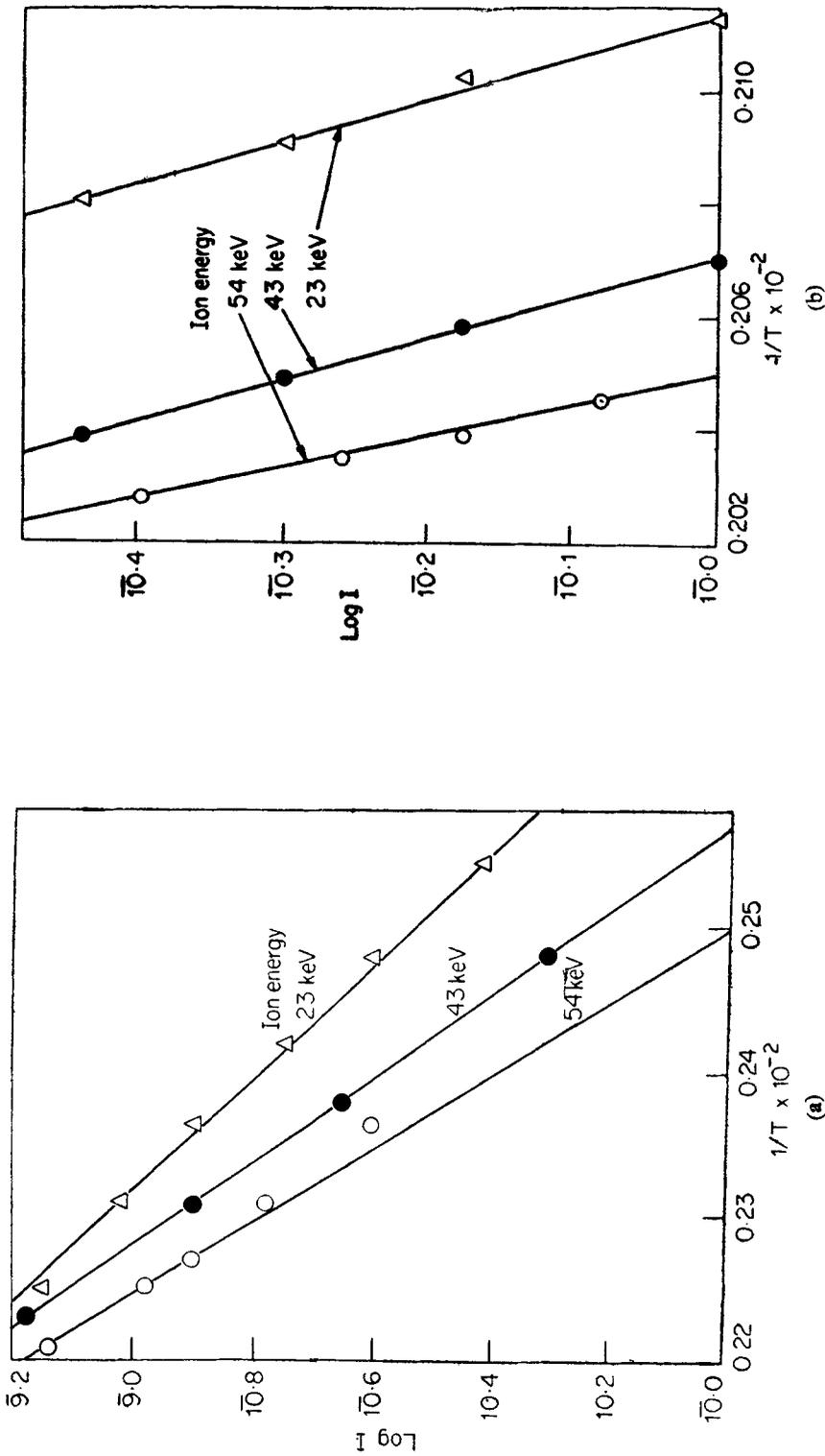


Figure 3. Semilog plot of current vs 1/T corresponding to (a) first peak in figure 2 and (b) second peak in figure 2.

not change drastically over the implantation energies used. The values of mobility of charge carriers, corresponding to the two distinct peaks, the relaxation time at the peak temperature, the activation energies of two trapping levels and the total charge under the peaks are reported in table 1. It is remarkable that the total charge under the peaks remains constant irrespective of the implantation energy. This is reasonable as the total dose of implanted ions in the three measurements is kept constant. Moreover the range distribution of ions in the bulk has a similar nature. The mobility of charge carriers and the mobility life-time product almost remain constant indicating that the basic nature of defects formed does not change drastically over the implantation energies used.

It is a good indication that the extrapolated relaxation time increases with increasing energy of ions and thus longer life of polarisation can be had at higher energy of implantation. It may also be pointed out that in our experiments significant peaks of TSC were obtained only beyond glass transition temperature of FEP. This result is consistent with our earlier observation (Walzade *et al* 1978). Implanting different heavy ions into the same polymer would provide additional information. The increase in the dose may result in increased damage inside the sample. The present experiment has revealed for the first time that implantation of polymers can be carried out to charge the polymer foil and study the charge dynamics. It is proposed to use higher energies of heavy ions to increase the degree of damage.

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