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# TSDC measurements and analysis of pristine and 100 MeV Ag- swift heavy ion irradiated Polyvinylidene fluoride (PVDF) thin film

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Thermally stimulated depolarization current (TSDC) measurements have been used to investigate the various dielectric relaxation processes in pristine and 100 MeV Ag swift heavy ion (SHI) irradiated Polyvinylidene fluoride. The films of 20 µm thickness were irradiated with 100 MeV Ag-ion at fluence; 1.8 X$10^{11}$ ions/cm$^2$. Thermally stimulated depolarization (TSD) current measurements were carried out in the temperature range $30^0$ –165 $^0$C at different polarization temperature ($T_p$) and polarization field ($E_p$). The heating rate (2 ºC/min) and polarization time (1 hrs.) have been kept constant in all TSDC measurements. TSDC characteristics of pristine show a well defined current maxima (termed as β-peak) around the polarization temperature ($T_p$) in the temperature region $70^0$-120 $^0$C, another current maxima around 162 $^0$C (termed as δ-peak) and in certain cases a kink is also observed around 135 $^0$C. The β-peak is attributed to the dipolar relaxation process and δ-peak is associated with the premelting of the sample. The number of peaks actually appearing in these spectra and their location, height and sharpness are governed by depolarization parameters ($T_{p,}$ $E_p$)**.** The TSDC characteristics of 100 MeV Ag-ion irradiated PVDF samples (fluence: 1.8×$10^{11}$ ions/cm$^2$) in the temperature range $30^0$-165 $^0$C almost follow the similar pattern as in case of pristine samples except one more TSD current maxima around 120 $^0$C, termed as α-peak (α relaxation) ascribed to the space charge polarization process owing to the formation of new deep traps and in some cases notably those corresponding to low values of $E_p$ and $T_p$, an additional shoulder designated as γ has also been observed around 55 $^0$C. The activation energy and pre-exponential factors corresponding to β-peak and α-peak were also estimated at different polarization temperature ($T_p$) and polarization field ($E_p$).

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*Keywords:* PVDF, TSDC, SHI, Activation energy (U), Pre-exponential factors($\tau_0$)

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## 1. Introduction

Polyvinylidene fluoride has acquired immense importance in development of micro sensors and actuators because of its excellent mechanical, pyroelectric, ferroelectric, piezoelectric properties and exceptional biocompatibility. The exceptional biocompatibility of PVDF film is used in the development of skin transducer, implantable medical devices and micro actuators [1]. However, the performance of sensors and actuators based on PVDF may be affected due to the strong interaction of various kinds of radiations such as ultraviolet, γ-rays, X-rays, low energetic ions and swift heavy ion with the sensor material. The interaction of these radiations with medium may change the various dielectric relaxation processes in PVDF. The behavior of PVDF under exposure of different kinds of radiation [2-7] has been reported before. These studies reveal the enhancement in electrical conductivity and change in crystallinity of PVDF [2]. The crystallinity plays a crucial role in piezoelectric, mechanical, optical, electrical and even thermal properties of polymers [2]. However, little has been reported on the swift heavy ion (SHI) radiation on the dielectric relaxation behaviour of PVDF. In a polymer, the charge-storage and charge decay processes are mainly governed by the various dielectric relaxation processes such as orientation of permanent dipoles (orientation polarization), interfacial polarization and space charge polarization. In this paper, we are investigating the dielectric relaxation behavior of pristine and 100 MeV Ag- swift heavy ion irradiated Polyvinylidene fluoride (PVDF) thin film samples of 20 µm thickness using TSDC technique.

The Thermally stimulated depolarization current spectra are capable to provide significant analysis of dielectric relaxation processes [8-12]. The TSDC spectra obtained from heating an electret consist of various current peaks characterizing different operative mechanisms through which a thermoelectret stores its charge. The number, location and shape of these current peaks are the characteristics of the polymeric sample under investigation. Further the relative contributions of the individual constituent processes such as orientation of permanent dipoles (orientation polarization), interfacial polarization and space charge polarization are strongly governed by the electret forming conditions viz. polarizing field ($E_p$), polarizing temperature ($T_p$) and storage time ($t_s$) etc. The detailed investigation of these peaks reveals information regarding trapping/trapping parameters (activation energy, relaxation time, capture cross-section and charge density).

## 2. Theoretical considerations of TSDC

When a polarized polymer heated at constant heating rate, decay of polarization $P$ may be described as [12]:

$$P(t) = P_e\left[\exp\left(-\int_0^t \frac{dt}{\tau}\right)\right] \tag{1}$$

where $\tau$ is the dipolar relaxation time and $P_e$ is the equilibrium or steady-state polarization which has been shown by Langevin to be

$$P_e = \frac{SN_d\, p_\mu^2 E_p}{kT_p} \tag{2}$$

In this expression $S$ is a geometrical factor depending on possible dipolar orientation (for free rotating dipoles, $S = 1/3$), $N_d$ is the concentration of dipoles, $k$ is Boltzmann's constant, $p_\mu$ is the electrical dipole moment and $E_p$ is applied electrical field operating on the dipoles. The temperature variation of $\tau$ is given by Arrhenius type equation [12] as:

$$\tau(T) = \tau_0 \exp\left(\frac{U}{kT}\right) \tag{3}$$

where $\tau_0$ is the relaxation time at infinite temperature (the inverse of which is known as the characteristic frequency factor and usually related to the vibrational frequency of the material ) and $U$ is the activation energy needed to orient or disorient molecular dipoles. The TSD current density is the rate of change of polarization given as;

$$J_D(t) = \frac{-dP(t)}{dt} = \frac{P(t)}{\tau} \tag{4}$$

In order to obtain the current density produced by the progressive decrease in polarization in the course of a TSDC experiment, where time and temperature are simultaneously varied, the differentiation must be performed in terms of the new variable $T$. This parameter can be introduced by assuming a simple temperature program, most generally a linearly increasing temperature from a temperature $T_0$ (initial), so that

$$T = T_0 + qt \tag{5}$$

where $q = \frac{dT}{dt}$ is the heating rate.

Using equation (1), (2), (4) and (5), the current density $J_D$ during a TSDC experiment can be written as;

$$J_D(T) = \frac{P_e(T_p)}{\tau_0}\exp\left(-\frac{U}{kT}\right)\exp\left[-\frac{1}{q\tau_0}\int_{T_0}^{T}\exp\left(-\frac{U}{kT'}\right)dT'\right] \tag{6}$$

The first exponential which dominates in the low temperature range, is responsible for the initial increase of the current with temperature (increase of mobility of the rotating dipoles), while the second exponential which dominates at high temperature, gradually slows down the current rise and then depresses it very rapidly, especially for high activation energies (progressive exhaustion of the induced polarization). Differentiation of equation 6 leads to an expression for peak temperature ($T_m$)

$$T_m = \left[\frac{U}{k}\, q\,\tau_0 \exp\left(\frac{U}{kT_m}\right)\right]^{1/2} \tag{7}$$

It is clear from the above equation that the position of a dipolar TSDC peak is a function of the parameters $q$, $\tau_0$ and $U$. In the low temperature tail region *(T<<Tm)* of the TSDC spectrum since the integral term in the $J_D(T)$ function [equation (6)] is negligible, the first exponential dominates the temperature rise of the initial current so that

$$J_D(T) = A\exp\left(-\frac{U}{kT}\right)$$

or (8)

$$\ln J_D(T) = \ln A - \left(\frac{U}{kT}\right)$$

where $A$ is a constant.

The activation energy can be determined from $\ln J_D$ *vs* $1/T$ curves. In first approximation, a straight line is obtained, the slope of which gives $-U/k$. Once the activation energy is known, the characteristic time constant can be calculated using equation 7, as

$$\tau_0 = \frac{kT_m^2}{qU\exp\left(\frac{U}{kT_m}\right)} \tag{9}$$

## 3. Experimental details

The PVDF polymer was procured from the firm DuPont (USA) in flat film forms of 20 µm thickness. The samples of size 1 sq. cm were mounted on a ladder for the irradiation in a vacuum chamber. The ladder was loaded in a chamber kept in a high vacuum of the order of $10^{-6}$ Torr. The films were then irradiated with 100 MeV Ag- ion at fluence rate $1.8 \times 10^{11}$ ions/cm$^2$ using the PELLETRON facility at Inter University Accelerator Centre (IUAC), New Delhi. The ion beam fluence was measured by integrating the ion charge on the sample ladder with time. Ion energies were selected in such a manner that they can easily pass through the PVDF films. In present investigation, beam current was kept low {0.2 and 0.5 PnA **(**particle nanoampere**)**} to avoid any thermal decomposition. The electrical contacts were made by vacuum evaporation of silver onto both the surfaces of the samples using vacuum coating unit manufactured by

Vacuum Instruments Company Limited, New Delhi (India). This Coating unit can provide a vacuum of the order of $10^{-6}$ Torr. A special design metal mask of desire size and circular in shape was used to restrict the coating within the required periphery on the samples.

The sample holder design for this purpose was suspended in a specially designed temperature controlled furnace (for thermo-electret formation), shielded against stray pickups. The furnace could be capable of heating the sample at some arbitrary uniform rate, from room temperature to 170 $^0$C. The designed experimental setup is shown schematically in Fig. 1.

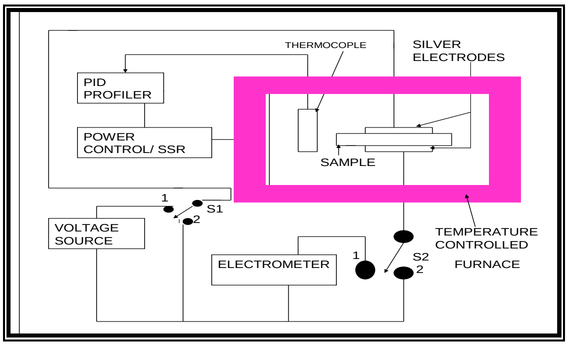

*Fig. 1. Schematic diagram of the experimental setup for the TSDC measurements.*

The samples were polarized (Electret formation) by subjecting them to the desire dc bias field ($E_p$) at constant temperature ($T_p$) for 1hour. The sample was then rapidly cooled to the room temperature within fixed time (1/2h) in the presence of Ep. After cooling process the applied electric field Ep was terminated/ switch off and electrodes were short-circuited for about 10 minutes in order to eliminate the frictional stray surface charges accumulated during polarization. The Fig. 2 shows the TSDC procedure as a plot of temperature versus time. The TSD current obtained by heating the polarized samples at constant heating rate ($2^0$C/minute) from room temperature to $170^0$C were measured with the help of Keithley electrometer (Model 6517A). The corresponding activation energy has been calculated through the initial rise method.

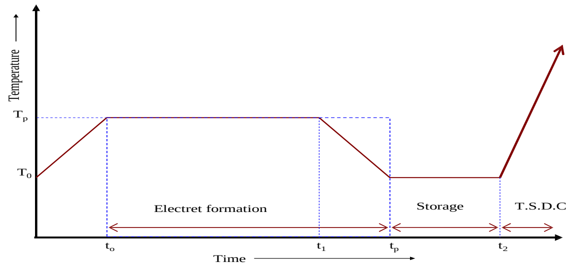

*Fig. 2. Experimental schematic representation of TSDC procedure: $T_0$, initial temperature; $T_{p,}$ polarization temperature; $t_0$ , start of polarization; $t_1$ , start of cooling; $t_p$ , switching off the field $E_p$; $t_2$ , start of heating the sample and recording the current as the function of temperature.*

The depth profiles were estimated using SRIM (Stopping range of ions in matter) calculations. The projected range of 100 MeV Ag-ion beams in the PVDF was calculated to be 25.55 µm using the SRIM-08 code (Ziegler 2008), which are larger than the thickness of PVDF samples

### 4.1 Results: TSDC spectra of Pristine PVDF samples

Figs. 3 and 4 illustrate the TSD current spectra of 20 µm pristine poly phase-PVDF samples in the temperature range $30^0$ –165 $^0$C. The heating rate (2 ºC/min) and polarization time (1 hrs.) have been kept constant in all TSDC measurement. The number of peaks actually appearing in these spectra and their location, height and sharpness are governed by depolarization parameters.

#### (i) Polarization temperature ($T_p$) dependence

The effect of polarization temperature ($T_p$) on TSDC spectra of pristine PVDF samples (Ep = 125 KV/cm) has been shown in Figs. 3. All TSDC characteristics show a well defined peak (termed as β-peak) in the temperature region $70^0$-120 $^0$C. Another peak is observed around 162 $^0$C termed as δ-peak. In certain cases a kink is also observed around 135 $^0$C. The β-peak shifts toward higher temperature with increasing $T_{p.}$ An increase in β- peak intensity is also observed with $T_p$. The activation energies associated with β-peak were calculated using initial rise method. These energies can be calculated from the TSD current spectra illustrated in Figs. 3 and 4. The activation energy and pre exponential factor for β- peak were also estimated and shown in Table 1.

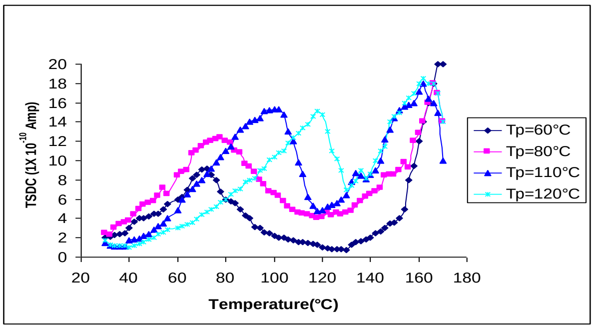

*Fig. 3. TSD current spectra of 20 µm Pristine PVDF at polarization field $E_p$ = 125 kV/cm for different polarization temperature ($T_p$).*

#### (ii) Polarization field ($E_p$) dependence

The TSD current spectra of PVDF samples polarized at different fields ($E_p$) at constant Tp = 80 $^0$C have been illustrated in Fig. 4. All TSDC characteristics spectra show the occurrence of β-peak around temperature 80 $^0$C. Inset of the Fig. 4 shows the variation of peak current ($I_m$) with $E_p$ (kV/cm) for β-peak. Though the peak location is unaffected by $E_p$, the peak magnitude increases with increase $E_p$. The δ- peak is also observed around 164 $^0$C. The peak magnitude also observed increases with $E_p$. A small kink were around 122 $^0$C. The kink intensity increases but shifted towards lower temperature side with increase in $E_p$.

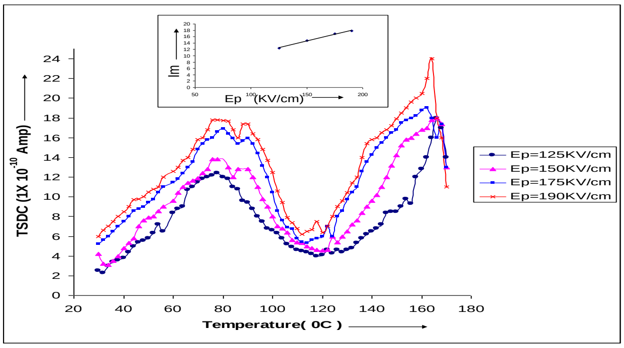

*Fig. 4. TSD current spectra of Pristine PVDF (20 μm) at polarization temperature Tp = 80°C for different polarization fields, and Inset of the figure 4 shows the variation of peak current ($I_m$) with $E_p$ (kV/cm) for β-peak.*

*Table 1. The activation energy and pre exponential factor for β- peak at different polarization temperature and field $E_p$ for pristine PVDF (20 μm) samples.*

| Polarization Field $E_p$ | Polarization temperature $T_p$ (°C) | β-relaxation | | |
|---|---|---|---|---|
| | | Peak temperature $T_m$ (°C) | U(eV) | $\tau_o$ (1 × $10^{-5}$) S |
| 125 kV/cm | 60 | 72 | 0.33 | 7.75 |
| 125 kV/cm | 80 | 80 | 0.36 | 3.9 |
| 125 kV/cm | 110 | 102 | 0.51 | 0.062 |
| 125 kV/cm | 120 | 118 | 0.33 | 39 |
| 150 kV/cm | 80 | 80, 88 | 0.55 | 0.006 |
| 175 kV/cm | 80 | 80,90 | 0.29 | 0.5 |
| 190 kV/cm | 80 | 80,88 | 0.21 | 1121 |

### 4.2 TSDC spectra of Ag- Ion Irradiated samples

The representative TSDC spectra of 100 MeV Ag-ion irradiated PVDF samples (fluence: 1.8×$10^{11}$ ions/cm$^2$) in the temperature range 30$^0$-165 $^0$C have been illustrated in Figs. 5 and 6. These characteristics spectra almost follow the same pattern as in case of pristine samples. Though there is a loss in the smoothness of β-peak. In some cases notably those corresponding to low values of $E_p$ and $T_p$, an additional shoulder designated as γ has also been observed around 55 $^0$C.

#### (i) *Poling Temperature ($T_p$) Dependence*

The effect of $T_p$ on TSD current spectrum of 100 MeV Ag-ion irradiated PVDF samples (at $E_p$ =125 **kV/cm**) is illustrated in Fig. 5. The β-peak (β-relaxation) appears in temperature region 75$^0$ -118 $^0$C dependent on the polarization temperature $T_p$. The magnitude also increases with increasing $T_p$. The δ- peak is also observed around 164 $^0$C.

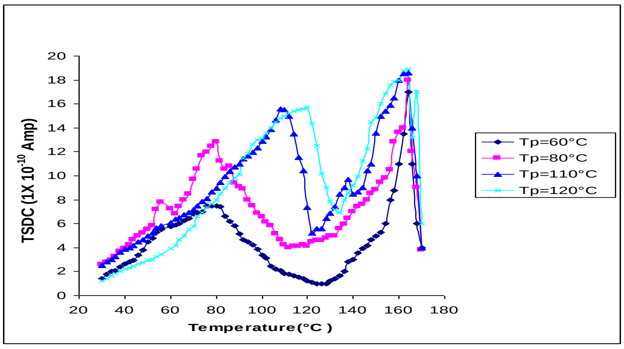

*Fig. 5. TSD current spectra of 100 MeV Ag-ion irradiated 20μm PVDF thin film at polarization field $E_p$ = 125KV/cm for different polarization temperature ($T_p$).*

#### *(ii) Polarization field (Ep) dependence*

The effect of polarization field *(Ep)* on the TSDC spectra of 100 MeV Ag-ion irradiated PVDF samples ($T_p$=80 $^0$C) has been illustrated in Fig. 6. The TSDC spectra, in addition to β-peak (at 80 $^0$C) and δ- peak (at162 $^0$C) consist of one more TSD current maxima around 120 $^0$C, termed as α-peak (α relaxation). The peak intensity for all the peaks increases with $E_p$. The variation of β-peak intensity with $E_p$, the variation of α-peak intensity with $E_p^{1/2}$ has been shown in Fig. 7 (a) and (b) respectively. The activation energies associated with β-peak and α – peak were calculated using initial rise method. These energies can be calculated from the TSD current spectra illustrated in Figs. 5 and 6. The activation energy and pre-exponential factors corresponding to β-peak and α-peak are given in Table 2.

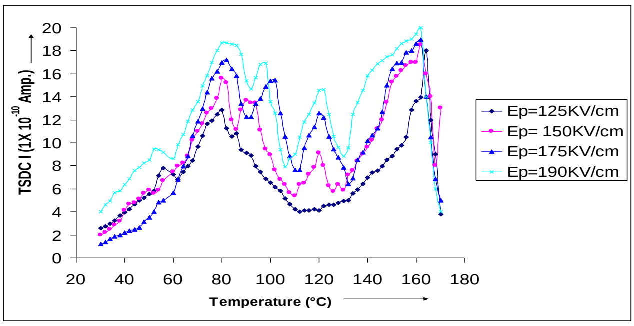

*Fig. 6. TSD current spectra of 100 MeV Ag-ion irradiated PVDF (20 μm) at plarization temperature $T_p$ = 80°C for different polarization fields, $E_p$.*

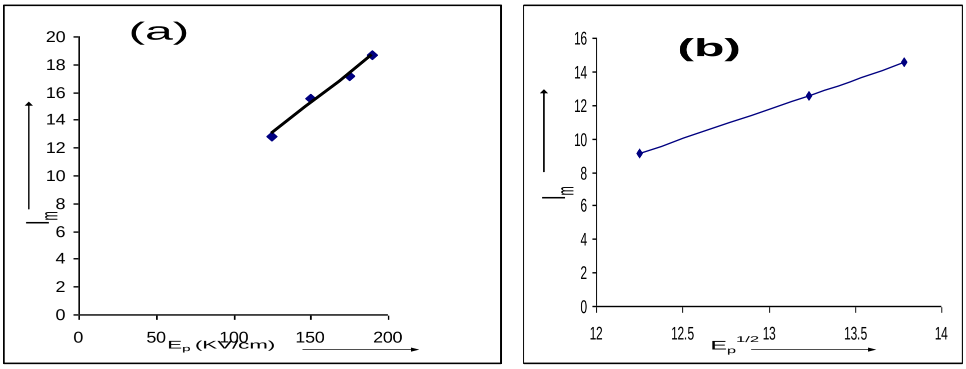

*Fig. 7. Variation of peak current ($I_m$) with (a) $E_p$ (kV/cm) for β-peak (b) $E_p^{1/2}$ for α-peak in 100 MeV Ag-ion irradiated PVDF (20 μm) samples at $T_p$ = 80 °C.*

*Table 2. The activation energy and pre exponential factor for β- and α- relaxation at different polarization temperatures and fields Ep for Ag-ion irradiated PVDF (20 μm) samples.*

| Poling Field $E_p$ (kV/cm) | Poling Temp. $T_p$ (°C) | β-relaxation | | | α-relaxation | | |
|---|---|---|---|---|---|---|---|
| | | Peak Temp. $T_m$ (°C) | U(eV) | $\tau_o$ $(1\times10^{-5})$ s | Peak Temp. $T_m$ (°C) | U(eV) | $\tau_o$ $(1\times10^{-5})$ s |
| 125 | 60 | 78 | 0.41 | 0.6 | - | - | - |
| 125 | 80 | 80 | 0.29 | 50 | - | - | - |
| 125 | 110 | 108 | 0.21 | 0.002 | 138 | 0.61 | 0.01 |
| 125 | 120 | 120 | 0.26 | 410 | - | - | - |
| 150 | 80 | 80, 90 | 0.28 | 84 | 120 | 0.48 | 0.29 |
| 175 | 80 | 80, 100 | 0.44 | 0.27 | 120 | 0.57 | 0.01 |
| 190 | 80 | 80, 96 | 0.28 | 84 | 122 | 0.7 | 0.0004 |

## 5. Discussions

In the present TSDC spectra, the β-peak can be associated to the dipolar relaxation process. The dipolar origin of β-relaxation arises from $CF_2$ linkage which is strongly polar in nature. The dipolar origin of β-relaxation can be observed from certain characteristics of β-peak such as (i) peak current varies linearly with the polarization field (inset Fig. 4) indicating an uniform bulk polarization (ii) a shift in the β-peak temperature towards higher temperature with increasing polarization, $T_p$ and (iii) the activation energy, U (Table 1) by Neagu etal for dipolar relaxation process in PVDF polymer [13]. In certain cases we observed an additional current peak (~90°C) in the vicinity of β-peak (Fig. 4) particularly at higher $E_p$. We term this as β'-peak. We associate the β' relaxation process to the dipolar nature of $CH_2$.

The distribution of activation energies for β-relaxation process (Tables 1) suggests that the relaxation process originates from within the crystalline phase as also observed by Neagu etal for dipolar relaxation process in PVDF polymer [13]. A small kink which appears around 122 $^0$C in pristine PVDF show an indication of α-relaxation (space-charge relaxation) discusses later on.

The effect of 100 MeV Ag-ion irradiation on β-relaxation can be analyzed from the TSDC behaviour of ion irradiated PVDF samples (Figs. 5-7). Owing to the fact that the β-peak originate from the orientation of $CF_2$ linkage, the interaction of energetic ion with $CF_2$ group will determine the changes occurring in β relaxation. The linear variation of β-peak intensity with $E_p$ for both Ag-ion irradiated samples show that the β-relaxation does not change significantly as compared to pristine PVDF upon ion irradiation (Fig. 7(a)). The values of β-peak current ($I_{\beta)}$ for irradiated samples are more than those of pristine samples for all $E_p$. though we expected a decrease in β-peak intensity in ion irradiated samples owing to the loss of polar groups (demerization of polar groups), the increase in $I_\beta$ indicates the formation of some dipolar groups in PVDF upon irradiation enhancing β relaxation process. FTIR spectra of irradiated PVDF samples also reveals the presence of carbonyl groups (C=O) [14]. The formations of new sub polar groups due to ion irradiation have been reported in Kapton-H polyimide polymer [11].

The high temperature peak (α-peak) in ion irradiated samples is ascribed to the space charge polarization process. The α-peak is pronounced at high temperature and fields are an agreement to the fact that this relaxation is favorable to high Ep/Tp values [12]. The space charge character of α-peak is confirmed from the fact that its peak current varies linearly with $(E_p)^{1/2}$ [Fig. 7 (b)]. Further the space charge nature of α- relaxation is confirmed from the high values of its activation energies (Tables 2). The origin of α- relaxation is governed by several factors. One of the major causes for this relaxation is interfacial polarization which owing to Maxwell Wagner Sillars (MWS) effect [8, 12]. The other cause for α- relaxation is the injection of charge carriers from the electrodes at the metal polymer interface. An enhancement in the interfacial polarization and hence α-relaxation is expected in irradiated samples owing to the production of large number of free radicals arising from the scission process of polar groups[15].

The α-relaxation in ion irradiated samples significantly depends on the charge trapping mechanism through shallow/deep trapping centers In PVDF the free radical formation resulting from the demerization of polar $CF_2$ and $CH_2$ groups, becomes the source of these energy traps. This is also confirmed from the FTIR spectra of irradiated PVDF samples [14]. The presence of $CF_2$ and $CH_2$ in this polymer is revealed by the absorption bands, appearing around 1181 $cm^{-1}$ and 974 $cm^{-1}$ respectively [14]. The decrease in the intensity of these absorption bands in irradiated samples confirms the demerization of $CF_2$ and $CH_2$ groups.

## 6. Conclusions

I have investigated SHI irradiation induced changes in PVDF thin films using TSDC technique. TSD current spectra are also used to estimate activation energy and pre-exponential factors corresponding to β-relaxation and α-relaxation processes. The α-relaxation processes show higher activation energy to β-relaxation processes. The significant conclusions drawn from our present TSD current investigations are;

- The β-peak in TSDC spectra has been associated to the dipolar nature of $CF_2$ group.
- The ion irradiations not only affects the β-relaxation process but also results in the formation of shallow/deep energy trap centers in form of conjugate bonds.
- The ion irradiation significantly affects the α-relaxation process and also creates new sub polar group.
- The irradiation induced scission process causes formation of free radicals, providing large number of deep energy centre enhancing α-relaxation.

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