Electrical Conduction Investigation of Pristine and swift heavy ion- irradiated Polyvinylidene fluoride Thin Film

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Abstract: In this paper, 100 MeV Silver and 75 MeV Oxygen Swift heavy ions (SHI) irradiation effects on the conduction behaviour of polyvinylidene fluoride (PVDF) have been investigated at different electric field in the temperature range 90 ^{0}C to 125^{0}C. PVDF samples of 20 μm thicknesswere irradiated with 100 MeV Ag-ion and 75 MeV Oxygen-ion at different fluences. The various mechanisms responsible for the charge transport phenomena were investigated by the studying the Current-voltage (I-V) characteristics at different temperature. The ionic jump distance "a" for pristine and SHI irradiated PVDF thin samples were estimated from I-V characteristics in the form of log I (Ln I) versus Voltage(E) at different temperature. The ionic jump distance estimated from the steady state conduction mechanism confirms the ionic hopping, Schottky and Poole-Frenkel conduction mechanism, which ultimately depends upon the fluence of irradiance. At higher electric fields, the non ohmic current is mainly governed by space charge limited (SCL) conduction and the conduction is mainly due to injected space charge.

Keywords: PVDF, SHI, SCL, Ionic jump distance, interfacial polarization

1. Introduction

The incarnation of microelectromechanical system (MEMS) & Nano-electromechanical system (NEMS) in last decade has produced rapid progress in the efforts of miniaturizing sensors and actuators. However the availability of the material with required characteristic has been one of the major constraints in accelerating these efforts. Polymers are the class of materials having great potential and promise for these applications. Multifunctional polymers are attractive class of material used for sensor and actuator applications [1-4]. Often the functionality of a single base material can be adapted to several applications by means of an appropriate modification. For instance, Polyvinylidene fluoride (used in present study) polymer have attracted attention in the last few decades because of its unique piezoelectric, pyroelectric, ferroelectric, and nonlinear optical properties, which promote its use after appropriate modification in many technological applications such as micro sensors and actuators, biomaterials and implantable medical devices, nonlinear optical components , ferroelectric memory etc.,[5, 6]. The suitability of polymeric materials for advanced technological applications including sensing and actuation can only be determined through clear

understanding of their exact molecular dynamics and micro structural - property relationship. Molecular dynamics directly linked with the understanding of various relaxation processes controlling physical, optical and chemical properties, charge-transport or charge-trapping mechanism of polymers [7-8].

The conduction mechanism in pristine PVDF has been discussed by many groups. They have contradicting opinion about the conduction mechanism in PVDF. Some research group claimed that the main conduction mechanism in a PVDF is hopping of ions [9]. This opinion was opposed by other groupswhich have the view that Schottky conduction of electrons is responsible mechanism of electrical transport in PVDF [10]. Thus the electrical transport mechanism in PVDF is not fully understood till date. An increase in conductivity in high fluence irradiated polymer samples has been reported by many other workers [11-12]. An apt understanding of electrical properties of pristine and swift heavy ion irradiated PVDF could provide a deep insight in the molecular origin of dipolar, space charge relaxation processes and charge transport mechanism. The charge transport mechanism in swift heavy ion irradiated (SHI) PVDF thin film samples is not fully explored yet.

2. 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 and 75 MeV Oxygen-ion at different fluences 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. The beam current was kept in range of 0.2-0.5 PnA to avoid any thermal decomposition. The electrical contacts were made by vacuum evaporation of silver on to both the surfaces of 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 fabricated furnace is 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.

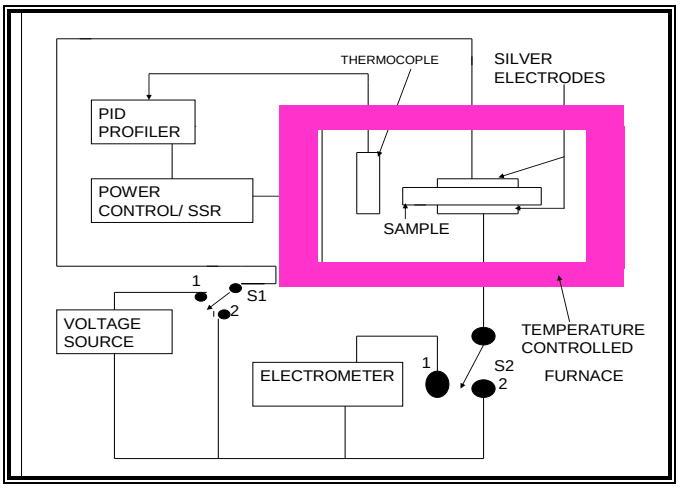

Fig. 1. Schematic for the I-V Measurements

3. Result and Discussion

The dependence of steady state dc conduction on electric field for pristine and ion irradiated (100 MeV Ag-ion and 75 MeV Oxygen-ion) PVDF thin film samples of thickness 20μm at different temperatures has been illustrated in figures 2- 5, plotted in the form of dc current (I) versus applied voltage(V) across the sample generally called I-V characteristic curves. The general nature of these curves is similar for both pristine as

well as SHI irradiated samples. The I-V characteristics for pristine and ion irradiated PVDF samples show an ohmic conduction behaviour at low electric fields region i.e., up to 60 volt and on other hand a deviation from the ohmic behaviour above this field is observed and nonlinearity increases with increases field. The nonlinear nature of I-V characteristics appears to be influenced by operating temperature. The thermal ionization of the trapping centers increases with an increase of temperature results to a lowering of the barrier across which the electrons/ions have to be transported and the conduction becomes ohmic. The ohmic behaviour can be explained by the fact that at lower electric fields, injection of carriers from the contact is very less and the initial current is constituted by the intrinsic free carriers present in the material.

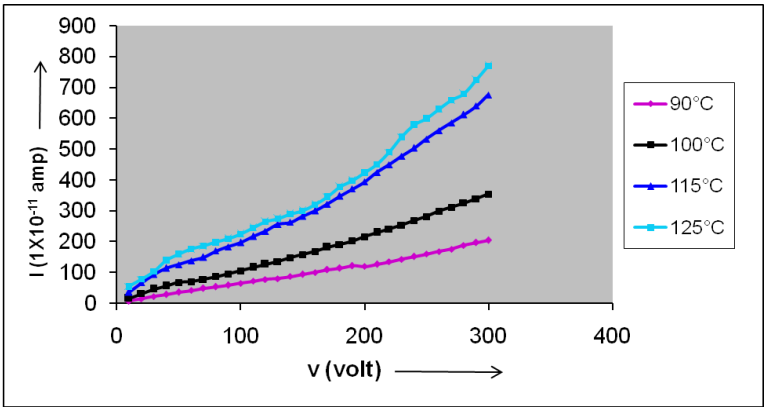

Fig. 2. I-V characteristic of 20 µm pristine PVDF thin film at different temperature

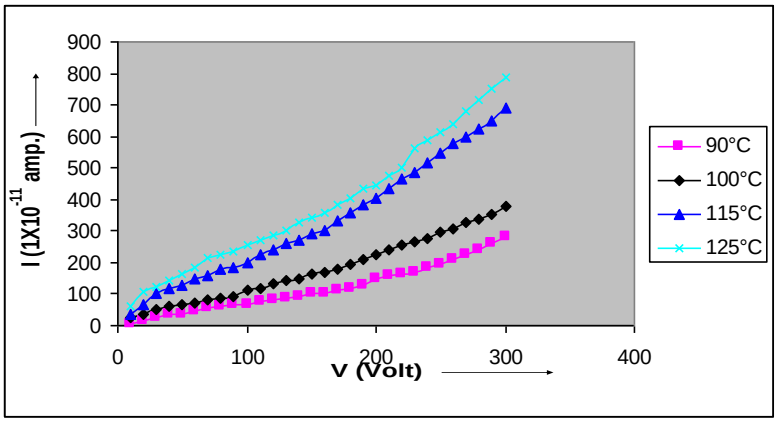

Fig. 3. I-V characteristic of 100 MeV Ag-ion (fluence; 1.875 X10^{11} ion/cm^2) irradiated PVDF thin film (20 µm) at different temperature

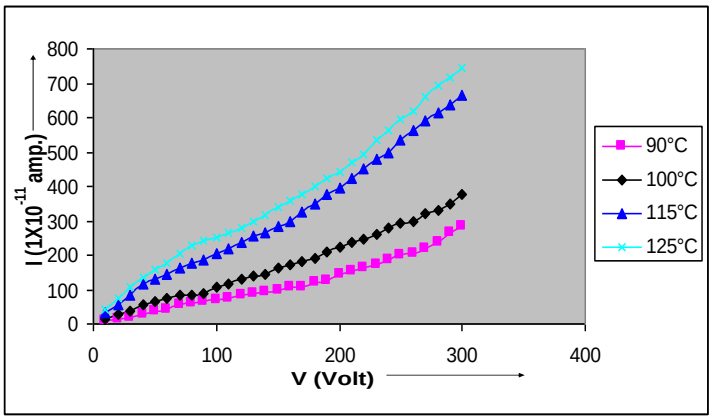

Fig. 4. I-V characteristic of 75 MeV Oxygen-ion (fluence; 5.625 X 10^{11}ion/cm^2) irradiated PVDF thin film (20 µm) at different temperature

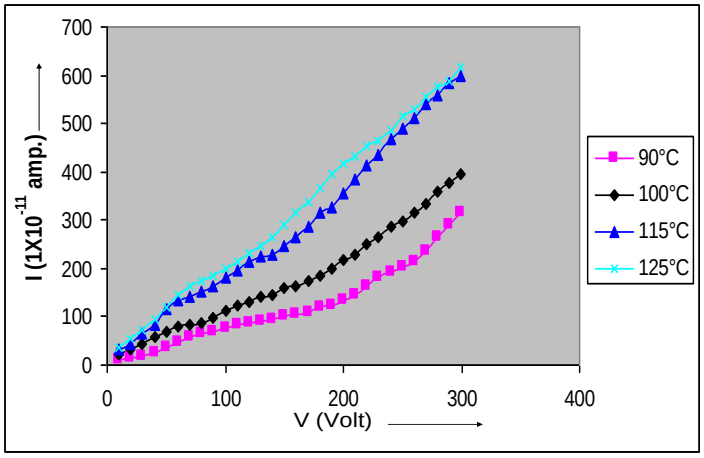

Fig. 5. I-V characteristic of 75 MeV Oxygen-ion (fluence; 5.675 X 10^{12} ion/cm^2) irradiated PVDF thin film (20 µm) at different temperature

The current will remains ohmic until the injected free carriers counterbalance the thermally created carriers. It is believed that at higher electric fields, the non ohmic current is mainly governed by space charge limited (SCL) conduction and the conduction is mainly due to injected space charge. The deviation from the ohmic behaviour can arise from many other processes for charge transport namely ionic hopping, Richardson-Schottky, Poole-Frenkel, and tunneling mechanisms etc. In the case of ionic hopping conduction current (I) is given as [13]

$$I = 2sqnav \exp\left(\frac{-U}{kT}\right)\sinh\left(\frac{qEa}{2kT}\right) \quad (1)$$

where q, n, a, U, k, ν, T and s respectively are the charge of ion, ionic concentration, ionic jump distance (in A^o), the barrier height, Boltzmann's constant, frequency of attempt for electron/ion to escape from trap, the absolute temperature (^0K) and the effective electrode area.

In the high electric field region where the non-linearity occurs ($qEa/2kT >> 1$), equation 1 can be written as

$$I = I_o \exp\left(\frac{qEa}{2kT}\right) \quad (2)$$

where $I_o = 2sqma\nu \exp\left(\frac{-U}{kT}\right)$

Table 1. Ionic jump distance 'a' obtained from the lnI versus E plots for Pristine, 100 MeV Ag-ion and 75 MeV Oxygen-ion irradiated PVDF (20 µm) samples

Ionic jump distance 'a' (Å)				
Temperature (^0C)	Pristine PVDF	Ag-ion (Fluence; 1.875X10^{11} ions/cm^2)	Oxygen-ion (Fluence; 5.62 5X10^{11} ions/cm^2)	Oxygen-ion(Fluence; 5.675X10^{12}ions/cm^2)
90	10.48	11.61	12.12	11.92
100	10.52	10.00	10.9	10.58
115	10.54	10.54	10.74	11.10
125	10.2	9.58	10.27	10.95

The slope of the straight line of the plot of log *I* versus *E* at constant temperature gives the ionic jump distance '*a'*. The *I - V* characteristics in the form of log *I (Ln I*) versus *E* curve for pristine and SHI (100 MeV Ag-ion and 75 MeV Oxygen-ion) irradiated PVDF samples of thickness 20 μm at different temperature have been illustrated in figures 6-9. The ionic jump distance '*a'* estimated from the slope of these curves is given in Table 1. The value of '*a'* varies with temperature over a range of 10.2 –10.54 A^0 for pristine PVDF samples. We find a systematic variation of '*a*' with temperature for pristine samples for the low and intermediate temperature range. At 125 ^{0}C temperature, a sudden decrease in ionic jump distance '*a*' is observed for pristine samples.

From the Table 1, it is observed that the ionic jump distance '*a*' values don't much differ in pristine and ion (100 MeV Ag-ion and 75 MeV Oxygen-ion) irradiated samples. For swift Ag-ion irradiated samples, the ionic jump distance '*a*' values show first decrease then increase in intermediate temperature range and further decrease at 125^{0}C.The ionic jump distance '*a*' values show decrease with temperature for low fluence(5.625X10^{11} ions/cm^2) Oxygen-ion irradiated samples. While for higher fluence(5.675X10^{11} ions/cm^2) Oxygen-ion irradiated samples, the ionic jump distance '*a*' values show first decrease then sudden increase at 115 ^{0}C and further decrease at 125^{0}C. The sudden increase in ionic jump distance '*a*' at higher temperature range for ion (100 MeV Ag-ion and 75 MeV Oxygen-ion) irradiated samples (Table 2) at 115 ^{0}C show an indication to some resonance type of phenomena in the interfacial polarization taking place at this temperatures. This behaviour is consistent with our dielectric constant/loss measurements in this temperature range [14, 15].

In case of 100 MeV (fluence; 1.875 X 10^{11} ion/cm^2) Ag-ion irradiated PVDF samples, the value of '*a*' is higher for temperature at 90 °C as compared to pristine samples and we find a increase in '*a*' at moderate and higher temperatures. In case of 75 MeV Oxygen-ion irradiated PVDF samples, we find a marginal decrease in '*a*' with increase in fluence in most of the cases at low and moderate temperatures. However at higher temperatures (115 and 125 ^{0}C) a significant increase in '*a*' with increase in fluence is observed. The variation of '*a*' with temperature in some other organic polymers has also been reported. The estimated ionic jump distance '*a*' values are within the range of few Å, implying the possible conduction mechanism in pristine and ion irradiated samples is due to the hopping of ions. This fact is further strengthening by the existence of a possibility of bulk ionization in ion irradiated PVDF samples resulting from the formation of free radicals. Thus is it will be reasonable to attribute the presence of ionic conductivity due to radiation induced free radicals and subsequent cross linking. The free radical formation mainly occurs due to the dissociation of the main side groups due to irradiation.

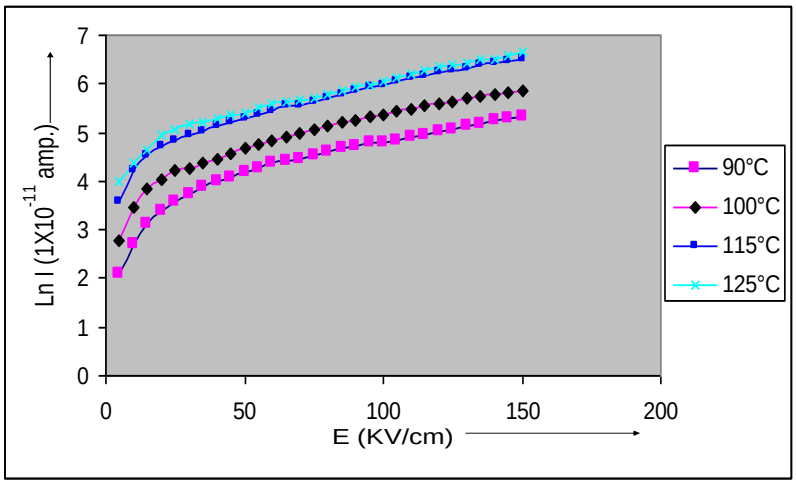

Fig. 6. Ionic hopping plots (log I - E) for pristine PVDF sample (20 μm) at different temperatures

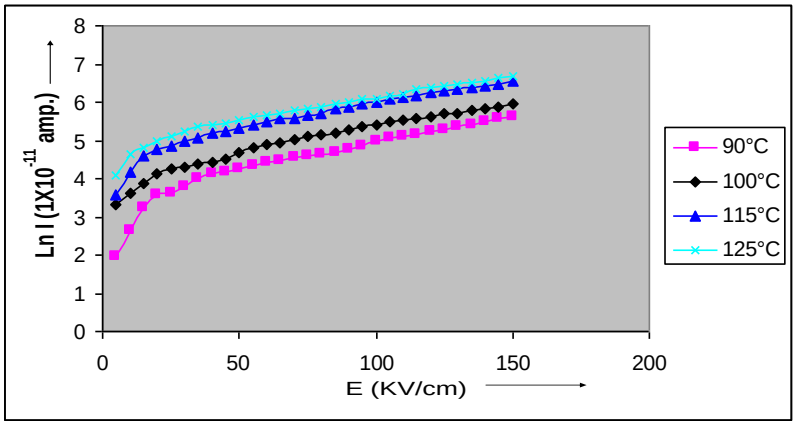

Fig. 7. Ionic hopping plots (log I - E) for100 MeV Ag-ion (fluence; 1.875 X10^{11} ion/cm^2) irradiated PVDF thin film (20 µm) at different temperature

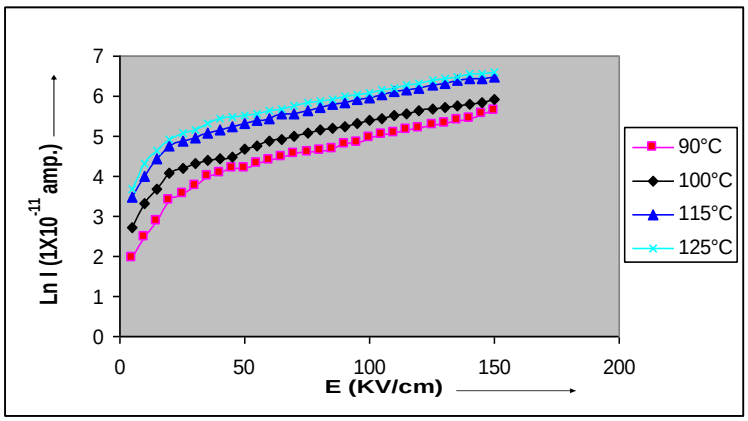

Fig. 8. Ionic hopping plots (log I - E) for75 MeV Oxygen-ion (fluence; 5.625X10^{11} ion/cm^2) irradiated PVDF thin film (20 µm) at different temperature

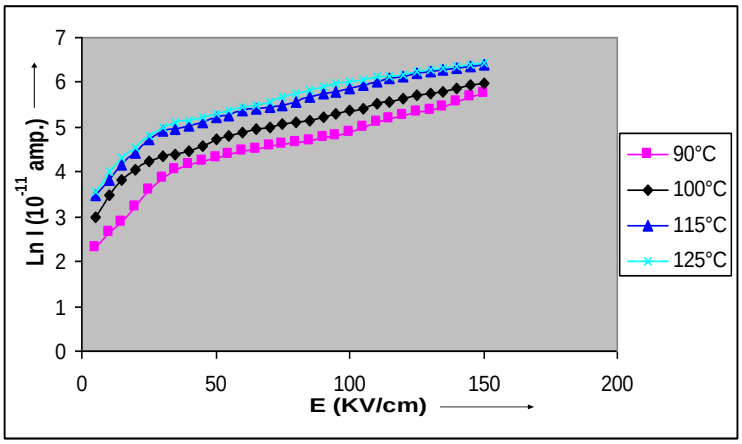

Fig. 9. Ionic hopping plots (log I - E) for75 MeV Oxygen-ion (fluence; 5.675X10^{12} ion/cm^2) irradiated PVDF thin film (20 µm) at different temperature

The fit of present results to other charge transport process mainly Richardson Schottky (RS) and Poole-Frenkel (PF) types of operating mechanism can also be examine. The current densities for these processes are expressed, respectively as [16];

$$I = AT^2 \exp\left(\frac{\beta_s E^{\frac{1}{2}} - \varphi}{kT}\right) \quad (3)$$

$$I = BE^{\frac{1}{2}} \exp\left(\frac{\beta_f E^{\frac{1}{2}} - \varphi}{kT}\right) \quad (4)$$

where A and B are constants, E the applied electric field, ϕ the effective work function, β_s &β_f are the Schottky and Pool-Frenkel coefficients respectively, given as

$$\beta_s = \left(\frac{e^3}{4\pi K \varepsilon_0}\right)^{\frac{1}{2}} \text{ and } \beta_f = 2\beta_s \quad (5)$$

where$e$, ε_0 and K are the electronic charge, vacuum permittivity and high frequency dielectric constant respectively. The Schottky mechanism involves the field assisted thermionic emission of charges from electrodes into the sample (resulting in a field dependent lowering of barrier potential) whereas in the Poole-Frenkel effect, the current is considered to be due to field assisted thermal excitation of electrons from traps into the conduction band.

The slopes of the Schottky plots (log I versus $E^{1/2}$ plots, figures 10- 13) give the experimental values of Schottky coefficient, β (β_{exp}). The theoretical values of β (β_{th}) are calculated using equation (4). Table 2 illustrates the β_{exp} and β_{th} values for pristine PVDF, 100 MeV Ag-ion irradiated PVDF (20 µm) samples at a fluence of 1.875 X10^{11} ions/cm^2 and for75 MeV Oxygen-ion irradiated PVDF (20 µm) samples at fluences; 5.625 X10^{11} and 5.675X10^{12} ions/cm^2. The β_{th} values have been estimated by taking the dielectric constant (K) of pristine and irradiated PVDF at higher frequency (10 KHz) measured using a precision LCR meter.

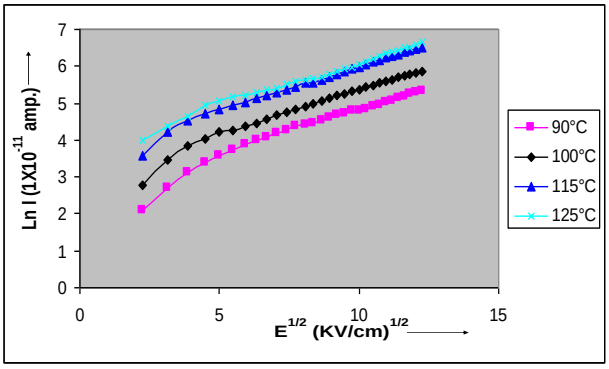

Fig. 10. Schottky plots (log I – $E^{1/2}$) for pristine PVDF sample (20 µm) at different temperatures

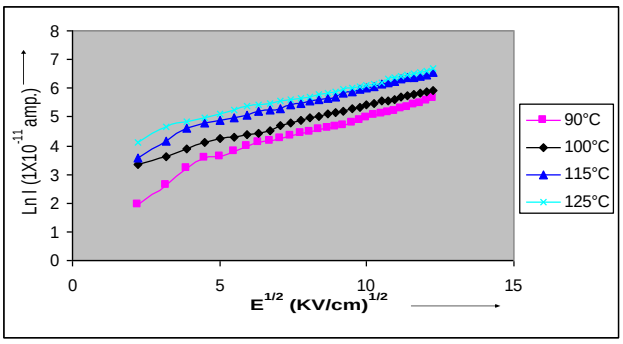

Fig. 11. Schottky plots (log I – $E^{1/2}$) for100 MeV Ag-ion (fluence; 1.875 X10^{11} ion/cm^2) irradiated PVDF thin film (20 µm) at different temperature

Table 2. Schottky Coefficient (β_s) for pristine and ion irradiated PVDF thin film samples at different temperature

Schottky Coefficient (β_s) (J m$^{1/2}$ V$^{-1/2}$) 10^{-24}								
Temperature / Samples	(90 ^{0}C)		(100 ^{0}C)		(115 ^{0}C)		(125 ^{0}C)	
	$\beta_{exp.}$	$\beta_{th.}$	$\beta_{exp.}$	$\beta_{th.}$	$\beta_{exp.}$	$\beta_{th.}$	$\beta_{exp.}$	$\beta_{th.}$
Pristine PVDF	1.37	2.93	1.36	2.91	1.35	2.87	1.3	2.86
Ag-ion (Fluence; 1.875X10^{11} ions/cm^2)	1.51	2.85	1.3	2.81	1.35	2.72	1.23	2.64
Oxygen-ion Fluence; 5.625X10^{11} ions/cm^2)	1.58	3.16	1.42	3.06	1.39	3.01	1.33	2.86
Oxygen-ion (Fluence; 5.675X10^{12} ions/cm^2)	1.54	3.09	1.35	3.04	1.43	3.00	1.42	3.16

It is observed from the Table 2 that β_{th} = 2 β_{exp}or slightly greater than 2 $\beta_{exp}$for pristine samples suggests that the electronic processes are favorable conduction processes in pristine PVDF over full experimental temperature range. we observe $\beta_{th}\approx 2\ \beta_{exp}$ for 100 MeV Ag-ion irradiated PVDF sample for operating temperature range except the temperature, 90 ^{0}C. This suggests the conduction mechanism in Ag-ion (fluence; 1.875X10^{11} ions/cm^2) irradiated PVDF samples is governed by Richardson-Schottky (RS) type and Poole-Frenkel (PF) type conduction mechanism in addition to ionic hopping conduction mechanism. For low fluence (5.625X10^{11}ions/cm^2) Oxygen-ion irradiated PVDF sample, we observed $\beta th \approx 2\ \beta_{exp}$for full experimental temperature rang which suggests that in ionic hopping conduction mechanism the Richardson-Schottky, Poole-Frenkel type (RS and PF) are also favorable conduction mechanism in low fluence Oxygen-ion irradiated PVDF samples over present experimental temperature range. While in higher fluence Oxygen-ion irradiated PVDF sample, we observe $\beta th = 2\ \beta_{exp}$at low temperature .i.e., 90 ^{0}C and $\beta_{th}>2\ \beta_{exp}$at higher temperature, which shows the evidence of the presenceof Richardson-Schottky and Poole-Frenkel type conduction mechanism. It can conclude that in ion irradiated samples, the charge transport is mainly governed by Poole-Frenkel type operating mechanism. While the estimation of ionic jump distance shows ionic hopping conduction process in both pristine as well as irradiated samples.

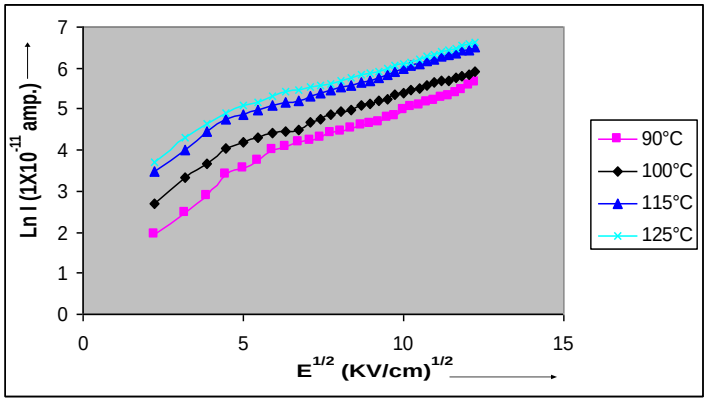

Fig. 12. Schottky plots (log I – $E^{1/2}$) for 75 MeV Oxygen-ion irradiated (fluence; 5.625X10^{11} ion/cm^2) PVDF thin film (20 μm) at different temperature

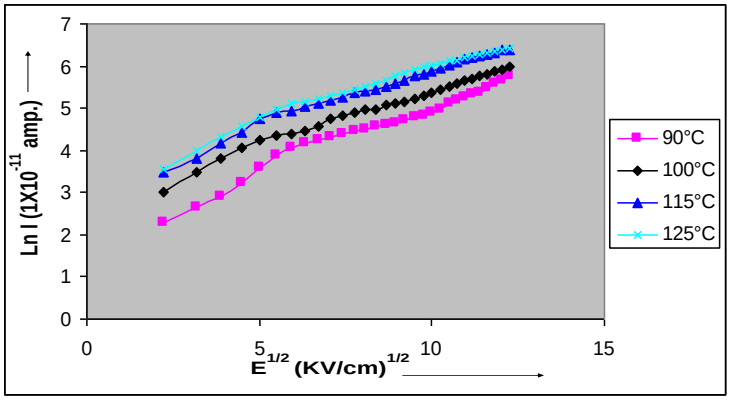

Figure 13: Schottky plots (log I – $E^{1/2}$) for 75 MeV Oxygen-ion irradiated (fluence; 5.675X10^{12} ion/cm^2) PVDF thin film (20 µm) at different temperature

4. Conclusions

The general nature of I-V characteristic is not affected due to ion irradiation, except an increase in steady state conduction. The ionic jump distance estimated from the steady state conduction mechanism confirms the ionic hopping, Schottky and Poole-Frenkel conduction mechanisms depending upon the fluence of irradiance. The major conclusions from I-V characteristics study are;

- Pristine and ion irradiated samples show small ohmic region where current varies linearly with increasing field (up to 30KV/cm)
- Ion irradiation samples, the charge transport are mainly governed by Poole- Frenkel conduction mechanism.
- The ionic jump distance estimation shows that the ionic hopping may also contribute in the conduction process in both pristine as well as irradiated samples.

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