Study of localized states in FEP by space charge limited current measurements

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The measurement of ohmic and space charge limited current at different temperatures in fluorinated ethylene propylene (FEP) of 250 μm thickness is reported. The current–voltage characteristics follow the theoretically proposed models for the mechanism of conduction in the thin insulating films. The experimental results have been analysed on the basis of the existing knowledge and a few important parameters related with the transport mechanism in FEP have been evaluated. Two temperature-induced changes in the activation energy E for conduction have been observed. For $T<413$K, $E\simeq 0.2$ eV; for $413<T<458$K, $E\simeq 0.5$ eV and for $T>458$K, $E\simeq 0.99$ eV. It is observed that the specimen is extrinsic over all the temperature ranges. From these findings the density of states in the conduction band, the depth of Fermi level from the conduction band, the statistically important energy levels and their densities of states have been determined. The presence of discrete electron levels at depths 0.2 eV, 0.5 eV and 0.99 eV below the conduction band having densities of states 2.8×10^{22}, 1×10^{19} and 4.6×10^{12} respectively have been determined which are dominant over the three temperature regions. Energy band diagram for FEP is plotted.

Keywords

INTRODUCTION

The study of ohmic and space charge limited currents in semiconductors and dielectrics is capable of providing considerable insight into the mechanism of charge transport and carrier trapping in these materials. Although the concepts of solid state physics cannot be directly applied to the polymers as they are amorphous molecular materials, a phenomenological analogy may be drawn between polymers and inorganic insulators.

The problem of applying band theory to amorphous polymers is discussed by Ioffe and Regel[1]. They have inferred that the periodic electric field of lattice is not essential for the occurrence of typical semiconducting properties and band model can be applied in case where there is a loss of periodicity in lattice.

As polymers are wide gap insulators, intrinsic carrier generation is not probable. The study of electrical conductivity in these materials must therefore include the investigation of the following two points: (1) generation and (2) transport of charge carriers; moreover as the purification of these polymers is not attempted before the electrical measurements, impurities may provide free carriers[2-4]. The injection from the electrodes is the main source of charge carriers in high polymers[5,6]. Although electronic nature of conduction is more probable in case of high polymers, and more so when they are injected. Ionic conduction has also been proposed by Seanor[7] and Konsaki *et al.*[8] in polymers at high temperatures. It is known that ionic conduction in polymers occurs when ionizable groups are present either intrinsically or as impurities. Alternatively Fleming and Ranicar[9] have suggested electronic type of conduction within the framework of the energy band model. An important argument for the electronic mechanism of conductivity in polymers includes trapping phenomena.

Although the charge storage mechanism in the copolymer fluorinated ethylene propylene (FEP) has been extensively studied[10-12], the study of electrical conduction has received considerably less attention. The measurement of ohmic and space charge limited conduction in FEP is reported in this paper.

An attempt has been made to locate the most probable localized levels (trapping levels) on the basis of existing theoretical models for conduction in thin insulating films[13,14].

THEORETICAL BACKGROUND

The mechanism of electrical conduction in thin insulating films has been discussed by Lamb[13] and few important theoretical models have been put forward. Dielectric materials which are basically insulators are capable of carrying electric currents by virtue of carriers injected at one or both the electrodes. According to the basic assumptions, if an ohmic contact is made at the surface of an insulator, electrons flow from the metal to the conduction band of the insulator. Due to the injected charges near the electrodes there is a generation of space charge near the electrodes which affect the conduction mechanism. As an effect, ohmic conduction changes into space charge limited (SCL) conduction as the applied electric field is increased.

Moreover, in practice, the character and the magnitude of the SCL conduction is modified due to the presence of the localized trapping centres which try to immobilize the injected charge carriers. The space charge limited current thus contains a factor due to trapping, and is given by

$$J_{\mathrm{SCL}}=\frac{9}{8}\theta\mu\varepsilon\frac{V^2}{s^3} \qquad (1)$$

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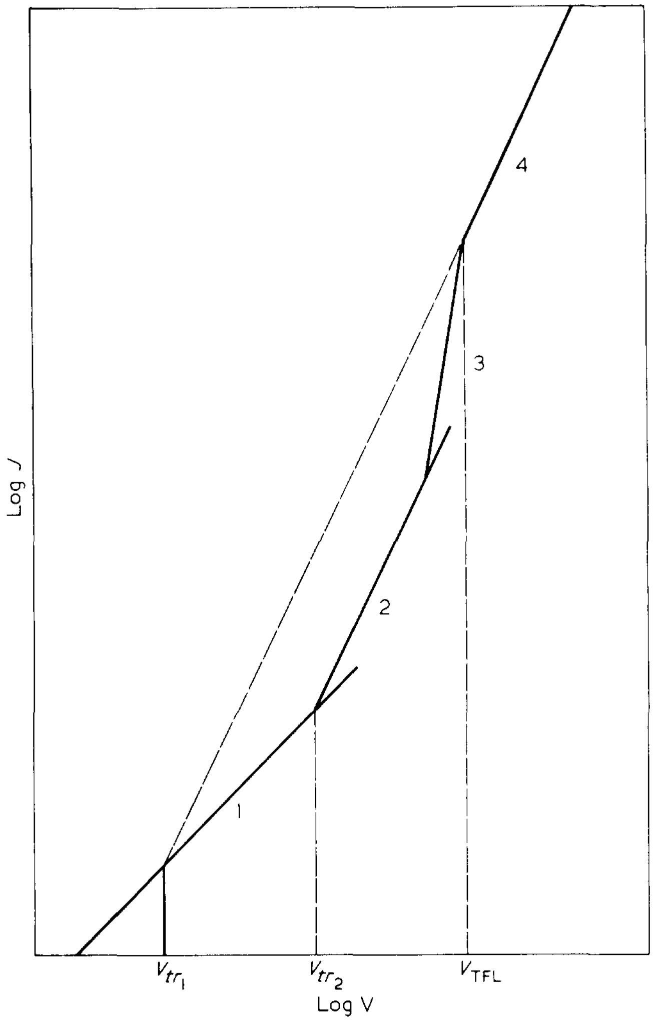

Figure 1 One carrier space charge limited current–voltage characteristics for an insulator

where μ is the microscopic mobility, V is the voltage across the sample, ε the dielectric constant, s the sample thickness and θ is the ratio of the free carriers to the trapped charge carriers and is given by

$$\theta=\frac{N_c}{N_t}\exp[-(E_c-E_t)/kT] \qquad (2)$$

where N_t is the trap density, N_c is the density of states in the conduction band and E_t the statistically dominant trapping level.

It is clear, therefore, that both the ohmic and SCL currents are thermally activated and their corresponding activation energies are contained in n and θ.

The general behaviour of current–voltage characteristics in case of carrier space charge limited currents for an insulator is shown in *Figure 1*, where V_{tr1} is the voltage corresponding to the transition from ohmic to the space charge limited current in absence of traps given by

$$V_{tr1}=\frac{8}{9}\frac{ns^2e}{\varepsilon} \qquad (3)$$

Similarly, the transition voltage V_{tr2} at which the current converts from ohmic to the space charge limited behaviour in presence of traps is given by

$$V_{tr2}=\frac{8}{9}\frac{ens^2}{\varepsilon\theta} \qquad (4)$$

Evidently, V_{tr2}, which is dependent on both n and θ, has a thermal activation energy equal to the difference between the activation energies for the ohmic and space charge limited regions. It has been shown by Roberts and Schmidlin[14] that the two activation energies are equal to (E_c-E_t) if the material is extrinsic in nature. The extrinsic condition corresponds to common usage to the extent that the location of the Fermi level depends on the excess donor concentration (N_d-N_a) where N_d is the number of donors in the system and N_a the number of acceptors.

With this definition, Roberts and Schmidlin have calculated the different characteristics of extrinsic and intrinsic materials where a single trapping level dominates the statistics over the corresponding temperature region. The thermally generated carriers n_m in the extrinsic case are given by

$$n_m=\frac{N_d-N_a}{N_t}N_c\exp[-(E_c-E_t)/kT] \qquad (5)$$

Consequently the activation energies associated with either ohmic or SCL conduction will yield the depth of dominant trapping levels if the material is extrinsic. In non-extrinsic case energies for ohmic and space charge limited conduction are different. Thus we have an experimental way to determine uniquely the nature of the sample. Simple straight line segments of log J *versus* $1/T$ in the ohmic and space charge limited regions unambiguously determine this fact.

The donor excess is given by:

$$(N_d-N_a)=\frac{9}{8}\frac{V_{tr2}}{es^2}\varepsilon \qquad (6)$$

The density of states for the dominant energy levels which may also be obtained from the *J–V* curves is given by:

$$N_{ti}=N_c\frac{V^2}{J_{SCL}}\frac{9}{8}\frac{\mu\varepsilon}{s^3}\exp[(E_c-E_t)/kT] \qquad (7)$$

where i stands for the number of dominant trapping levels corresponding to a specific temperature region. The energy and density of statistically dominant levels in the sample can thus be calculated from the experimental observations.

Here we have tried to analyse the conduction mechanism in the copolymer FEP, based on the above theoretical models of Roberts and Schmidlin.

EXPERIMENTAL

The copolymer FEP type A (Du-Pont De Nemours) 250 μm thick consisting of 11–18 mole% hexafluoropropylene in tetrafluoroethylene was used in the experiments. The measurements were taken on samples of size 2 cm × 2 cm provided with vacuum evaporated electrodes of copper on both the surfaces. The current–voltage characteristics at different constant temperatures were recorded with the help of previously described experimental set up[15]. The temperature of the sample was controlled with an accuracy of 0.4% using a temperature programmer throughout the measurements

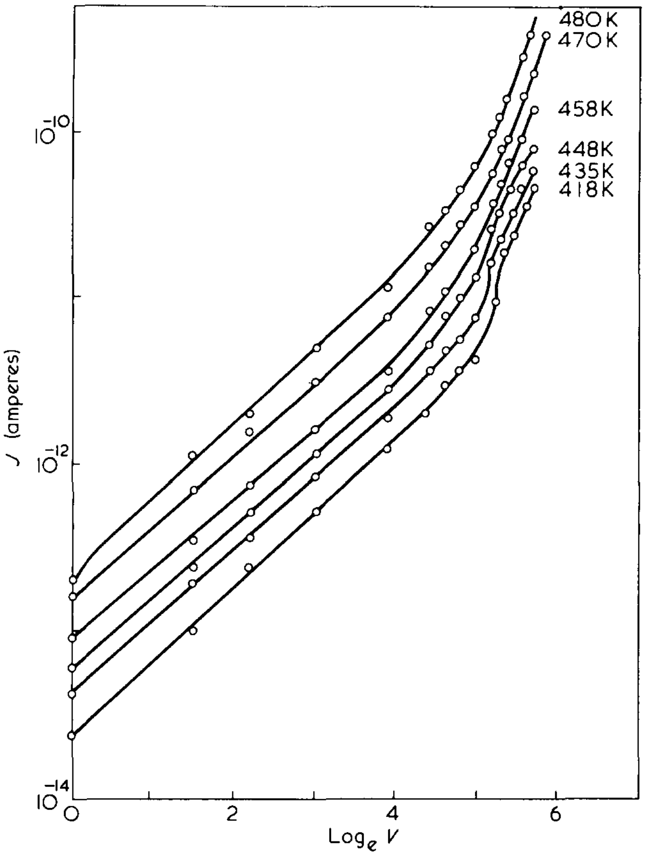

Figure 2 *J–V* characteristics of FEP at different temperatures

and the current was recorded in thermal equilibrium. The current voltage characteristics were established up to a maximum temperature of 483K.

RESULTS AND DISCUSSION

From the current, recorded in the thermal equilibrium, the *J–V* characteristics for the specimen were plotted corresponding to temperatures ranging from 418K to 480K. The specimen was heated up to 480K after each measurement, prior to taking further readings, in order to release the residual space charge. *Figure 2* shows a typical set of *J–V* characteristics at different temperatures. The characteristics consist of ohmic region with a slope of approximately unity for field strengths below 2 kV cm^{-1}, converting into an almost quadratic region of slope 2 for field strength in excess of these values. It is also observed that the current increases sharply at a field strength of 6 kV cm^{-1} to a trap free quadratic region at low temperatures. With increasing temperature the knee in the SCL region (in region 3, *Figure 1*) disappears. This may be quite likely due to the increased molecular motions in the sample above the glass transition temperature. The glass transition temperature of this sample has been determined[16] to be equal to 453K. *Figure 2* shows a finite variation in the nature of *J–V* characteristics above this temperature. In the glass transition region, micro-Brownian motion is liberated gradually and the high potential barrier (which restricts the migration of ions at low temperatures) may disappear or change their position temporally or spatially. It is likely that the average barrier height against ionic transport is sensitive to temperature in the glass transition region.

The thermally generated carrier density 'n' has been calculated from equation (3) for different temperatures using the values of transition voltages, V_{trl} as shown in *Figure 1*.

From these data the hypothetical distance of the Fermi level from the bottom of the conduction hand, had the sample remained trap-free, has been determined to be equal to 0.5 eV by semi-log plot of log n *versus* $1/T$ as shown in *Figure 3*.

The ratio of free to trapped charge carriers is obtained by comparing the 'trap free SCL current' in the region 4 with 'SCL current in presence of trapping', i.e. in region 2. A semi-log plot of θ *versus* $1/T$ (*Figure 4*) gives an activation energy of 0.208 eV which is equal to the depth of the most dominant trapping level, below the conduction band.

The trap density in the material N_t can be found from the voltage V_{TFL} at the end of region 2, at which all the traps are filled and as a result the SCL current rises sharply entering into a trap-free SCL region. This is given by

$$V_{\mathrm{TFL}} = \frac{2N_t e s^2}{3\varepsilon} \tag{8}$$

where N_t = trap density; e = electronic charge; s = thickness of the sample; and ε = dielectric constant. The value of N_t has been calculated using the experimental data and is found to be 5.7×10^{21} cm^{-3}. Using equation (2) N_c is calculated to be equal to 1.4×10^{24} cm^{-3}.

The mobility of charge carriers has been determined in the trap free (θ free) SCL region with the help of equation (1). It may be assumed that the only temperature dependent term in the current expression is the mobility μ. The value of μ has been found to vary from 4.8×10^{-7} cm^{-2} V^{-1} s^{-1} to 4.8×10^{-8} cm^{-2} V^{-1} s^{-1} in the temperature range 300K to 423K. The values of mobility

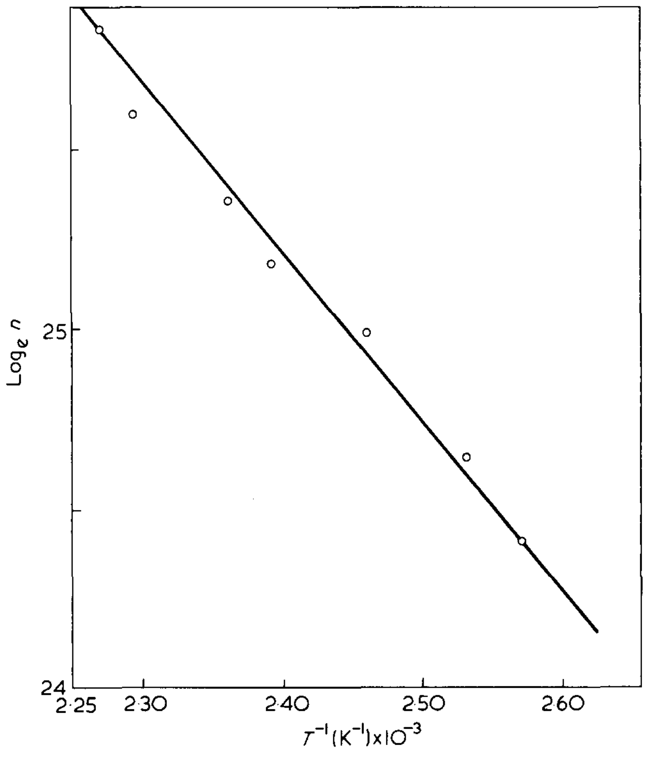

Figure 3 Plot of log *n versus* 1/*T*

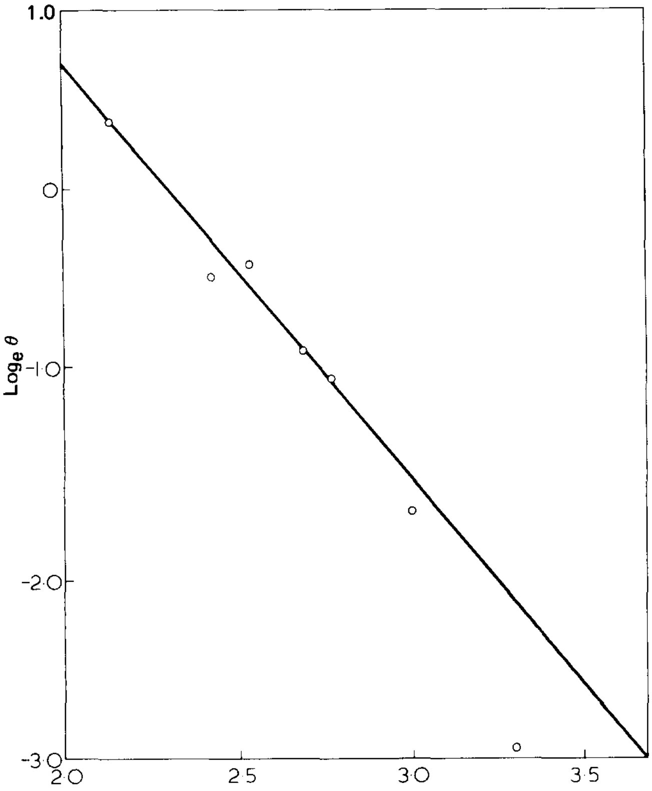

Figure 4 Plot of log θ *versus* 1/*T*

in FEP which have been reported[10,11,17] are also in the range of 10^{-5} to 10^{-17}. Considering this wide variation in the values of mobility found in the literature, the values obtained in the present experiment appear to be acceptable.

Location of dominant trapping levels

Following the arguments of Roberts and Schmidlin for the current–voltage characteristics of wide band gap semiconductors, comparison of activation energies in the ohmic and SCL regions over different temperature ranges uniquely determine the dominant energy levels for each type of carrier as mentioned and discussed earlier. *Figure 5* shows the semi-log plot of current *versus* reciprocal of temperature corresponding to the voltages in the ohmic and SCL (with trap) regions. Two prominent transitions are clearly observed occurring at about 413K and 458K; these temperatures divide the whole spectrum into the three prominent regions. The thermal activation energies for ohmic and SCL conduction are identical within the experimental error in all the three temperature regions. This clearly indicates that the sample behaves like an intrinsic material over the entire temperature range. The dominant energy levels which are determined in the extrinsic sample simply by the activation energies of conduction, are calculated for three temperature regions and are tabulated in *Table 1*.

The donor excess can be determined from equation (6). The value of V_{tr2} is 50±5 V and using $\varepsilon = 1.9 \times 10^{-13}$ farads cm^{-1}, equation (6) gives a donor excess of $1.6 \times 10^{+11}$ cm^{-3}. The densities of states for the three dominant trapping levels in the three temperature regions can be readily determined from equation (7) by substituting the appropriate value of $(E_c - E_t)$ corresponding to that temperature region. Substituting the effective density of states in the conduction band, $N_c = 1.4 \times 10^{24}$ cm^{-3}, as determined earlier, the densities of states for three different energy levels have been calculated and presented in *Table 1*.

These dominant energy levels can be compared with the trapping levels we obtained from the results of t.s.c. experiments of electron irradiated FEP[18]. These are 0.25, 0.57, 1.07, 1.3 and 2.3 eV. Out of these the former three levels are in close agreement with the values obtained in the present study. The trapping level of 0.99 eV is also in close agreement with the reported value of 1.0 eV

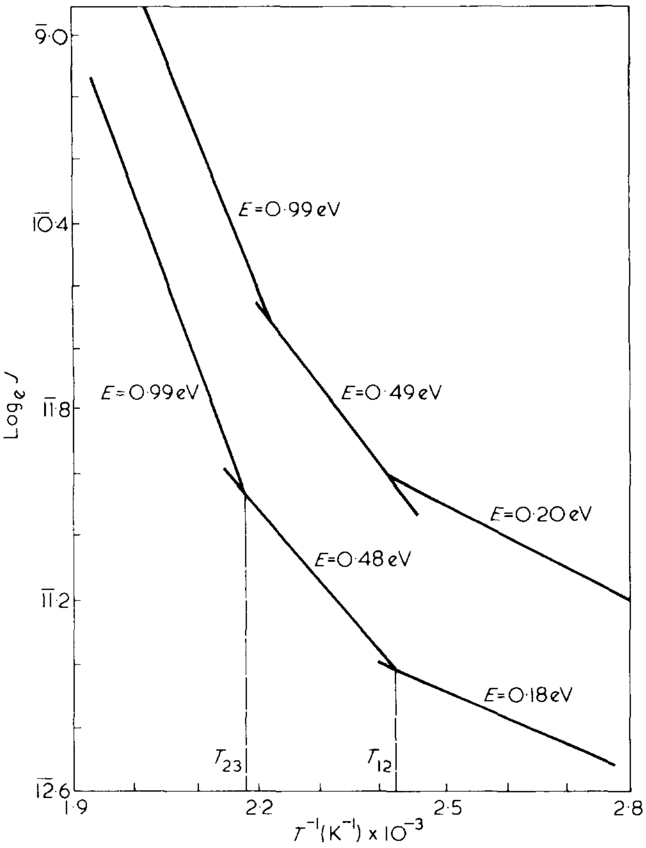

Figure 5 Log *J versus* 1/*T* for ohmic and SCL regions

Table 1 FEP parameters

(1) Hypothetical Fermi level Trap density	E_F N_t	0.5 eV 5.7×10^{21} cm^{-3}
(2) Density of states in conduction band	N_c	1.4×10^{24} cm^{-3}
(3) Mobility	μ	4.8×10^{-7} cm^2 V^{-1} s^{-1} at 300K 4.8×10^{-7} cm^2 V^{-1} s^{-1} (at 423K)
(4) Donor excess	$(N_d - N_a)$	1.6×10^{11} cm^{-3} V^{-1}
(5) Trapping levels	E_{t1} E_{t2} E_{t3}	0.20 eV 0.49 eV 0.99 eV
(6) Densities of dominant trapping levels	N_{t1} N_{t2} N_{t3}	2.8×10^{22} cm^{-3} 1×10^{19} cm^{-3} 4.6×10^{12} cm^{-3}
(7) Capture cross-section	S_1 S_2 S_3	1.6×10^{-30} cm^2 4.3×10^{-22} cm^2 3.0×10^{-12} cm^2

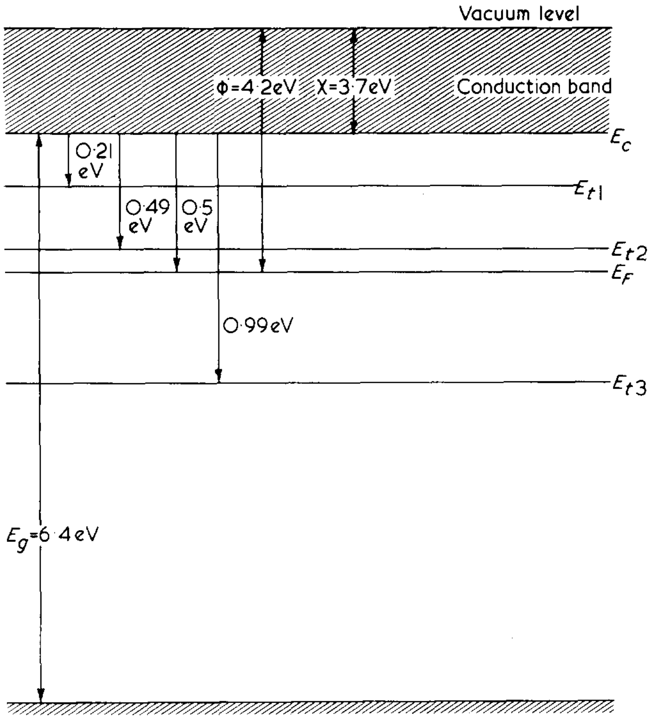

Figure 6 Band picture of FEP as expected from the experimental data

obtained by Seggern from the t.s.c. of the electron irradiated FEP[12].

The capture cross-sections for these trapping levels are calculated from the expression[19]

$$\frac{v}{S}=10^{26}\left(\frac{T}{300}\right)^2 \qquad (9)$$

where v is the attempt-to-escape frequency, S is the capture cross-section, and T is the absolute temperature. The escape frequency is calculated from the t.s.c. data[18] corresponding to the energies 0.2, 0.5 and 1.0 eV. The cross-sections are tabulated in *Table 1*.

A band picture of FEP can be projected from the data obtained from the foregoing measurements. The Fermi level (hypothetical) is determined to be at 0.5 eV from the bottom of the conduction band. Assuming the work function of FEP to be 4.2 eV[20], the electron affinity is calculated to be equal to 3.7 eV. The average value of electron affinity in polymers has been reported to be equal to 3 eV[21], which roughly agrees with our results. *Figure 6* shows the expected band picture where the band gap is assumed to be 6.4 eV[22] from the reported data.

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