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Space charge analysis in polyimide (kapton–H) samples

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Abstract The space charge trapping/detrapping in thermally charged polyimide (PI) samples have been studied by means of "Final Thermally Stimulated Discharge Current" (FTSDC). We investigate the effects associated with space charge behavior in PI near glass transition region. The FTSDC spectra consist of space charge peak attributed trapping of charges at different trapping levels. The peak positions are found to be very sensitive with poling time, discharging time, and heating rate. The apparent activation energy distributed in the range from 0.51 to 1.12 eV, and the charge released has been found to be varying with poling temperature (T_p) and poling time (t_c)/discharging time (t_d). The decay of space charge (Q) resembled an agreement with interfacial polarization.

Keywords FTSDC · Space charge · Apparent activation energy · Glass transition temperature · Charge transport

Introduction

Polyimides (PIs) are a class of amorphous organic material that has proven promising as a possible replacement for SiO_2 as an insulator in microelectronics. The average molecular mass, dielectric constant, and glass transition temperature are 40×10^3 g mole^{-1}, 3.4, 360–410 K, respectively, as reported in data sheet provided by Dupont (USA). There are a number of different commercially available PI films used in the semiconductor industry, and their properties vary significantly. The main reason for the investigation of PI films is that they offer a new generation of low permittivity dielectrics, some of which have been reported to have a permittivity of less than $2\varepsilon_o$. Since lower dielectric constant insulators dissipate less power in FETs (field effect transistors), these materials may begin to find their way into the Microelectromechanical System (MEMS) community. Polyimides are material of low dielectric constant. Their main function in MEMS has been in circuits and as a layer of chemically active sensor materials on membranes and cantilevers. As such, PIs are generally not considered for structural applications. The main impetus for developing PIs was that they could have a lower dielectric constant than SiO_2, which could represent a major reduction in power consumption on integrated circuits. Thus, much like copper, PIs are likely to find introduction into the MEMS market through their inclusion in the consumer electronics market [1].

During the last two decades, a lot of experimental data on space charge accumulation in insulating polymers have been published. These data, or at least those for commercially important polymers such as polytetrafluoroethylene (PTFE), the copolymer fluorinated ethylene–propylene (FEP), PI, and polypropylene have been reviewed recently [2, 3].

The appearance of space charge inside insulating polymer is known to favor aging and electrical breakdown. Therefore, space charge appears to be an important challenge to the insulating polymer industry. The space charges are electrical charges (electron, ions etc.) which are trapped in certain trapping levels of insulators, especially when applying an electric field. The question arose whether the charge trapping occurs randomly or specifically in the

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structure of polymeric material. So far as the dipolar mechanism is concerned, space charge mechanism, charge transport process, and conduction mechanism of PI have been explained on the basis of thermally stimulated discharge current, transient current, and dielectric constant measurement experiments [4–7]. This technique enables us to clearly isolate the space charge in insulating polymer.

In recent years, several techniques such as isothermal charging current (ICC), isothermal discharging current (IDC), thermally stimulated discharge current (TSDC), fractional polarization of thermally stimulated current (FPTSDC), and final thermally stimulated discharge current (FTSDC) have been developed to understand the nature of charge transport and trapping in insulating polymeric materials. The space charge study in polyamide (PA), low density polyethylene and polyethylene terephthalate (PET) using FTSDC is reported earlier. The results of these polymers show that FTSDC has high sensibility and reproducibility [8–12]. The FTSDC technique allows for a quick characterization of space charge relaxation process contributing to the dielectric response of the sample under investigation. In this method, the sample is isothermally poled for a time $t_{c,}$ and then discharge for a time t_d to allow the depolarization in lowest activation mode. During poling and discharging, the ratio t_c/t_d controls the energy distribution and spatial distribution of trapped charge. The trapping of charge carriers in polymers depends upon several parameters such as charging condition, and chemical and electronic structure. The time required for trapping of charge carriers depends upon discharging and poling time (t_p). If trapping time is large enough, the discharging time is very large and discharging current is very low; however, there is still space charge trapped in the sample. If the material is stable at high temperature and heating rate is high as compared to trapping time, then the FTSDC will have the significant meaning that there is still space charge in the sample.

The aim of this article is to show how space charge analysis in PI near glass transition region can be investigated, particularly in kapton–H samples, using FTSDC measurement.

Experimental

The new technique for combining isothermal charging and discharging with non-isothermal measurements has been recently reported by Neagu group of researchers in careful study of space charge dynamics in insulating material [13, 14]. This technique is superior to thermally stimulated discharge current because it does not take into account the long time needed for trapping and detrapping of charge. In this technique, the selection of charge and discharge conditions (field, temperature, and ratio of charging and discharge times) allows the distinct features of space charge traps to appear as peaks in the final thermally stimulated discharge current (FTSDC). In this study, samples were charged and discharged at different times, and temperatures; however, applied DC electric field was kept constant in all the cases. The DC field was applied for time t_c at constant temperature, followed by a discharge at the different temperature during time t_d. This process allows the storage of charge in certain trapping levels under selective charging. During FTSDC measurement, the sample was heated at a low constant rate (i.e., *b*). This process allows the analysis of the space charge stored in the sample during selective charging.

In order to know the glass transition temperature of PI, the DSC was recorded many times with the heating rate of 5 K min^{-1}. The glass transition temperature was found to be 370 K.

The 25-μm thick samples were supplied by Dupont (USA) under trade name Kapton-H. The circular samples of diameter 5 cm were cut from rectangular sheet. The sample was conditioned before measurement (i.e., kept at 100 K in short-circuited condition for 12 h) to allow for drying, and to remove eventual volatile contents. This step was essential for achieving good reproducibility of results. The samples were vacuum aluminized on both side and polarized by thermal charging at elevated temperature and field. The FTSDC is recorded by means of Keithley electrometer 610 °C. In order to avoid the effect of ground loop and extraneous electrical noise, the electrometer was properly shielded and grounded. The FTSDC means that the experimental conditions are chosen in such a way that it can be assumed the current is mainly determined by charge relaxation at higher temperature. On the other hand, the experimental conditions can be chosen such that current is assumed to be due to movement of detrapped charges (i.e., space charges). The FTSDC was recorded in short-circuit mode at different values of poling temperature, poling field, poling time, discharging time, and heating rate. All observations were carried out at higher temperature; therefore, the temperature shown in Kelvin means that 273 should be added to read it in Kelvin.

Results and discussion

Figure 1 shows the FTSDC thermograms of PI samples poled at 200, 240, 280, and 320 K with poling field of 200 kV cm^{-1}. These thermograms are characterized by single broad peak. This peak is assumed to be associated with a structural transition. The FTSDC was found to be increasing with increasing poling temperature. The position of peak is observed to get shifted toward higher temperature side with increasing poling temperature. At higher value of discharging temperature, there is a significant increase in the current, and peak progressively shifts to higher temperature as T_p increases. There is no well-accepted reason for temperature shift between poling temperature and maximum intensity of peak temperature(T_m). The peak current was found to increase at a temperature above the poling temperature; probably current is determined by space charge detrapping. The FTSDC is generated by the charge detrapped from deeper traps. Space charge detrapping should be very closely related to the local electrode poling process which induces space charge in the polymer [13].

Thus, we can associate FTSDC peak with the release of the space charge induced by the poling process. It is consistent with the general behavior of the space charge induced by external electric field, as the calculated apparent activation energy of the trapping of space charge varies according to trap depth. The relative penetration depth was calculated using the relation reported in literature [14, 15]. It is evident from the calculated value of relative penetration depth, which increases with increasing poling temperature (i.e., 0.04–0.09). This feature indicates the trapping of space charges in the traps of different depth [16]. The measured current implies the release of the charge carriers from traps and the subsequent transport of these carriers from their place to electrodes.

The FTSDC peak position changes significantly with poling temperature (T_p). The peak position and magnitude primarily reflect the field-assisted charge trapping/detrapping mechanisms, and secondarily reflect the local molecular dynamics. This behavior of peak is well discussed by Neagu et al. [11].

It is suggested that the TSDC of PI originated at a low temperature is due to the depolarization of dipoles and at the high temperature region it comes from trapped ions/electron space charges. Since FTSDC was started above 200 K and low temperature peak is masked. Therefore, in principle, dipolar effect is assumed to be negligible. The FTSDC peak is related to the glass transition in the constrained amorphous phase.

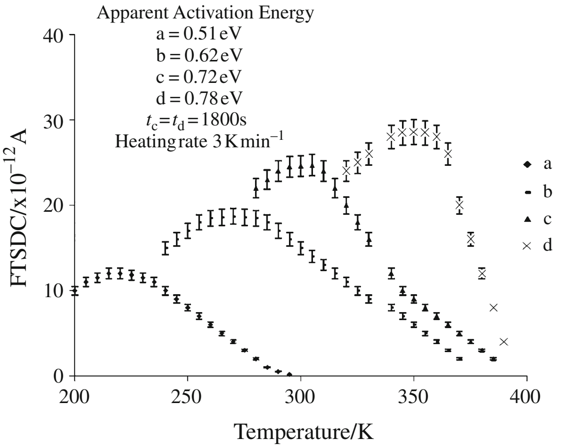

Fig. 1 FTSDC thermograms obtained at different temperatures (i.e., $a = 200$ K, $b = 240$ K, $c = 280$ K, $d = 320$ K) with poling field of 200 kV cm^{-1}

The relaxation at temperature $T > T_m$ increases significantly as T_p approaches near glass transition temperature (T_g) region. This relaxation is related to T_g. It is associated with intermolecular motion corresponding to motion of side groups and large-scale segmental motion. The previously mentioned thermomechanical study in PI [17] has found that the peak in glass transition region is due to the motion of rigid dianhydride moiety and a nonrigid (either flexible or semirigid) diamine moiety. The semirigid diamine moiety allows only rotational motion of aromatic rings below T_g, while a flexible moiety permits torsional motions above T_g. Similar peaks are reported for polyamides (PAs), polyurethanes, and bisphenol A polycarbonate nanocomposite indicating the onset of glass transition [18, 19].

Thus, FTSDC peak appears to be in glass transition region and affected by thermally induced paracrystalline ordering. The paracrystalline ordering could change with heating rate and affect the position of FTSDC peak as observed in this study. The study of polymer conductivity is important to understand the dipolar current, if the conductivity of amorphous polymer like PI increases with increase of poling temperature, which suggests that current is due to motion of charge carriers [20, 21]. We have observed that conductivity of PI increases with increase in poling temperature, which confirms that the FTSDC is mainly due to motion of charge carriers and dipolar current does not allow to flow in FTSDC system.

In general, the thermally stimulated current peaks in polymer samples appeared to be mainly due to (i) the motion of side group, (ii) dipolar polarization or polarization by trapped charge carriers, and (iii) space charge polarization or polarization by the injection of charge carriers in the bulk [22, 23]. In view of the above considerations and experimental evidences, we believe that the FTSDC peak occurred due to the injection of charge carriers (i.e., space charge) and their trapping in different trapping levels. This is further supported by calculated apparent activation energy of FTSDC peak which varies from 0.5 1 to 1.12 eV, which is in very good agreement with the value reported in literature [24].

Figure 2 shows the dependence of peak current in the poling field (V_p) for $T_p = 200$ K and $t_c = t_d = 1800$ s. The peak current shows the linear relationship with poling field. We conclude from this result that the peaks determined by ion movement and/or charge trapping in different trapping levels [21]. In order to investigate whether activation energy of a system is unique or not, one requires additional information, for example: what will be the behavior of FTSDC, if we vary the time scale of experiment? Figure 3 represents the FTSDC thermograms obtained at T_p = 320 K, $V_p = 200$ kV cm^{-1}, and different values of $t_c = t_d$. It has been observed that peak appears around 360° ± 5 K. The shape and position of the peaks change, when $t_c = t_d$ increases. The activation energy increases from 0.78 to 0.92 eV, when $t_c = t_d$ increases from 600 to 1800 s. We found an interesting result that peak shifts toward lower temperature as $t_c = t_d$ increases. In this experiment, we have maintained the equilibrium between poling and discharging time and determined the apparent activation energy. It is evident that charge is stored in the sample during the poling time, and charge is released during the discharging time. It gives the information about energetic and spatial distribution of surface/bulk traps at different values of $t_c = t_d$. The apparent activation energy is calculated using Bucci and Fieschi method [25]. The apparent activation energy increases with increasing t_p and t_d, which indicates that charge is released from deeper and deeper traps.

Figure 4 shows the FTSDC thermograms at T_p = 320 K, $V_p = 200$ kV cm^{-1}, $t_c = 1800$ s, and for different discharging times ranging from 600 to 2400 s. The shape of peak is found to change as t_d increases. The decreasing behavior of all the thermograms is almost same. It indicates that same traps are charged during the poling time. It is observe that as t_d increases, the charge from shallow traps decreases, and consequently, the charge is released from deeper and deeper traps located inside the bulk. The charge released from sample is absolutely related to discharging time. The charge released is calculated using the relation

$$Q = S/b \int_{T0}^{T} I(T)dT \tag{1}$$

where S is the sample area, and b is the heating rate. FTSDC is the function of temperature and discharging time, which provide the direct information about decay of stored charges.

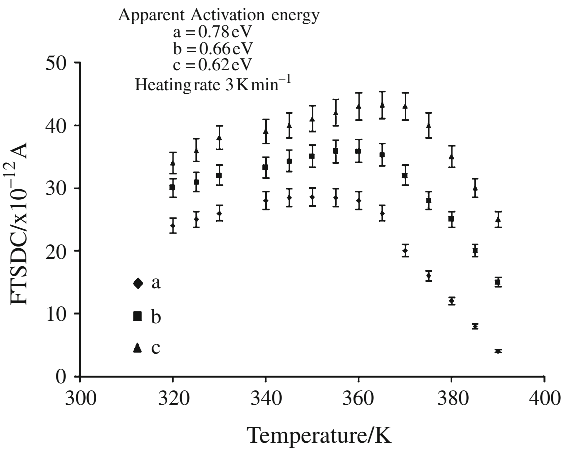

Fig. 3 FTSDC thermograms obtained at 320 K with poling field of 200 kV cm^{-1} at different values of poling time and discharging time (i. e., $t_c = t_d$: a = 1800 s, b = 1200 s, c = 600 s)

Figure 5 shows that the charge released decreases with increasing value of t_d. It has been found that total charge released is proportional to log t_d, and discharging current is proportional to $1/t_d$. This behavior supported the injection of charge carrier from metal-to-polymeric surface [26, 27]; it should be the result of interfacial polarization. This result is in agreement with Curie–Von Schweider law. In order to investigate charge detrapping and transport mechanism, the heating rate dependence of FTSDC is recorded (Fig. 6). Figure 6 shows the thermograms obtained at 320 K with poling field of 200 kV cm^{-1} and $t_c = t_d = 1800$ s for different heating rates from 3 to 5 K min^{-1}. We have observed that as heating rate varies from 3 to 5 K min^{-1}, the peak shifts continuously to higher temperature side. The apparent activation energy for this peak varies from 0.78 to 1.12 eV when heating rate increases from 3 to 5 K min^{-1}. The shift in peak with heating rate means that there is maximum charge stored at 350 K and, that is why,

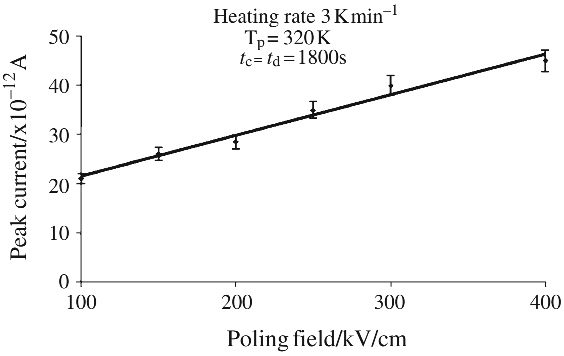

Fig. 2 Poling field-dependent peak current of FTSDC thermogram

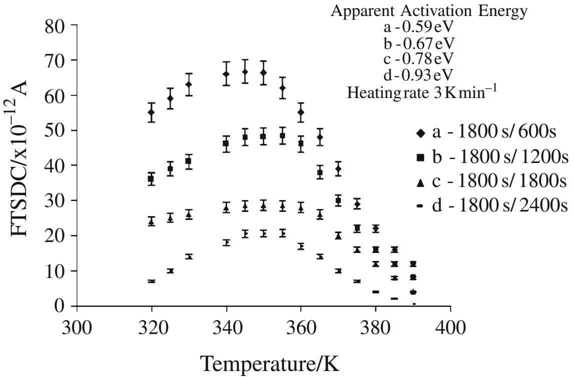

Fig. 4 FTSDC thermograms obtained at T_p = 320 K with poling field of 200 kV cm^{-1} under different discharging times (i. e., t_c/t_d)

peak slowly shifts to higher temperature with increasing heating rate. This peak is related to the glass transition in the constrained amorphous phase. This shift suggests that detrapping process needs a time scale that can be modified by using various heating rates. The higher value of apparent activation energy in all cases represents that traps are induced during polarization and having ionic nature. The relaxation process in PI is reported earlier [28, 29] using TSDC experiment. TSDC shows two peaks mainly: first peak is assigned to dipolar relaxation and second peak is assigned to space charge relaxation. The observed apparent activation energy for space charge peak indicates that space charge is not alone responsible, but partial effect of dipolar relaxation also has been observed. Therefore, TSDC technique is not significant to clearly separate the dipolar and space charge relaxation; however, FTSDC technique can clearly separate the space charge relaxation. The shift in FTSDC peak with heating rate indicates that ionic charge carriers are trapped in deeper and deeper traps. Therefore, traps are supposed to be ionic in glass transition region.

The FTSDC experiment was undertaken with different electrode materials such as Cu, Al, and Ag. The differences in FTSDC with different electrode systems were not significant and are in good agreement with the results as reported by Sessler et al. [30] who reported the dependence of current densities in PI upon electrode material such as Al, Au, and Ag, and the difference in charge injection between electrode material and space charge was not so remarkable.

The charge associated into the sample at T_g level is mainly trapped in thermally connected traps. The increase of current is mainly due to the increase of free charge and mobility; however, the current decay is controlled by collapse of the trapped charge and decrease of the relaxation time with increasing temperature. It has been observed that the FTSDC is due to space charge detrapping when $t_d > t_c$ (Fig. 4). The similar behavior is observed at $t_c = t_d$ is in agreement with current being originated due to space charge detrapping.

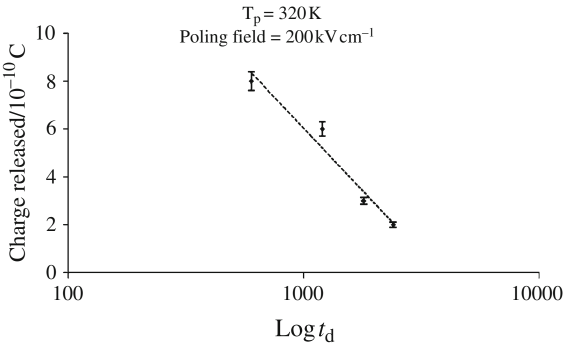

Fig. 5 Charge released obtained from FTSDC peak of Fig. 4 versus log t_d curve

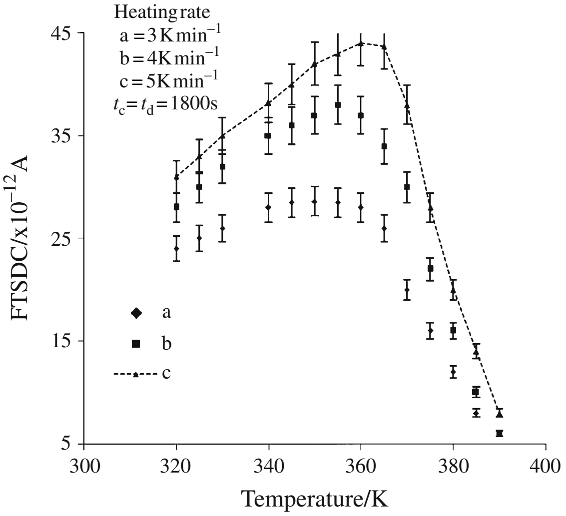

Fig. 6 FTSDC thermograms at different heating rates

Conclusions

It is concluded that the FTSDC technique can be used to analyze the study of space charge dynamics in polymers. The activation energy associated with trapping sites varies in a broad range, which indicates the energetic distribution of trapping site in PI structure and subsequent trapping of charge carriers. The peak current increases with poling temperature and heating rate revealed the mechanism of space charge dynamics near glass transition region. Finally, different characteristics of FTSDC peak favor the formation of space charge near glass transition region and their subsequent trapping in energetic traps.

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