Study of Trap Structure of Thermally Polarized Polyimide

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Received 10 February 2010; accepted 20 September 2011
DOI 10.1002/app.35679
Published online 22 December 2011 in Wiley Online Library (wileyonlinelibrary.com).

ABSTRACT: The trap structure of polyimide was studied using open-circuit thermally stimulated discharge current (TSDC). TSDC was observed in 25-μm thin film of polyimide at different condition of polarizing field and temperature. The one-sided vacuum-aluminized samples were used to record the open-circuit thermally stimulated current. The dipolar mechanism of relaxation is a possible mechanism to explain the behavior of TSDC peak at low temperature and field condition; however, hopping transport mechanism is prominent for the sample polarized with higher field and temperature. This is because deeper traps capture the charge carriers at high polarizing field and temperature and their subsequent trapping through hopping process. The influence of surface traps is caused by thermal polarization; it is evident due to lower value of activation energy, since activation energy of TSDC peak is corresponding to surface traps. The morphology of surface traps is verified by measuring the surface roughness using atomic force microscopy. The both type of charges (i.e., heterocharge and homocharge) are responsible for flow of current in presence of air gap. We report the role of surface and deep traps induced due to charging process. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 125: 520–526, 2012

Key words: activation energy; TSDC; atomic force microscopy

INTRODUCTION

Polymers generally have excellent physical and chemical properties. However, certain properties of polymers such as high electrical resistivity, wettability, and low surface energy are sometime compressed their applications. The buildup of static charge during processing and application of polymer films in packaging industries is often harmful to sensitive electronic components such as those used in the computer industry. Most of the polymers have very high surface and bulk resistivity, which causes static charge problems in many applications. As the polymer surfaces are nonreactive and surface modification involves the generation of high-energy species such as radicals, ions, and excited electronic state to promote the surface reaction. Surface modification of polymer film is quite often, if it is subjected to high-energy species such as flame, plasma, UV, laser, X-ray and γ-ray, electron beam, ion beam, high electric field, and temperature.[1–3] Therefore, the study of surface traps/defects is essential to understand complete electrical morphology of polymer through suitable technique.

The charge storage properties of insulating polymers are becoming widespread technological importance. The study of charge injection and carrier transport process in synthetic polymers is vital to the future utility of these polymers in almost any capacity.

The carrier mobility in insulating polymers is very small and the carriers are being predominantly located in traps. The carrier transport is described by several mechanisms but hopping mechanism is widely true for many polymers. Recently, Karl[4] reported that the crystallinity and molecular symmetry significantly (i.e., trapping of charge carriers) affect the charge transport and charge storage in organic solids.

The traps are formed by phenyl group or unsaturated groups in molecular structure or high-energy irradiation or high electric field and temperature. There are many methods to study the trap structure such as open- and short-circuit thermally stimulated current, frictional thermally stimulated current, transient currents in charging and discharging mode, and so on. However, atomic force microscopy (AFM) will record the surface morphology of polymer. The conjunction of open circuit thermally stimulated discharge current (TSDC) with AFM gives suitable justification of formation of surface traps due to application of electric field and temperature. The advantages of this technique are its ability to isolate the surface trap structure from complex structure of traps in polymeric material.[5–7]

The objective of this work is to understand the trapping of charge carriers either in surface and or in bulk traps; however, other techniques such as

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laser pulse technique are effectively measure the trap depth and distribution of charges at different depth. We have analyzed and identified the surface and bulk traps using open-circuit thermally stimulated current, and data was compared with surface roughness measured by AFM. The surface roughness in polymer samples is directly giving the information about the surface morphology. The information will be brought from these two techniques gives the role of trap structure in charge transport and charge storage capability of polyimide.

Theory of open circuit TSDC

The theoretical consideration for open-circuit TSDC is rarely reported. However, Turnout demonstrate the theory of open-circuit TSDC for one-sided metallized samples holding surface/space charges and having persistent dipole polarization can be expressed as:[5]

$$I(t) = \frac{\frac{d}{dt}[P(t) - \sigma(t)]}{1 + \varepsilon \frac{s_1}{s}} \quad (1)$$

where $P(t)$ is the dipole polarization, $\sigma(t)$ the planner charge density, ε dielectric constant for the material. s_1 and s are the thickness of air gap and sample.

The most relevant quantitative model for open-circuit TSDC was proposed by Van Seggern,[8] he suggested that current $I(t)$, measured in open-circuit TSDC, can be related to the equivalent surface voltage $V_o(t)$

$$I(t) = C_e.\beta \frac{d}{dt} V_0(t) \quad (2)$$

where β is the heating rate, t is the temperature; C_e is the sum of capacitance of air gap and capacitance of polymer sample.

where

$$\frac{1}{C_e} = \frac{1}{C_g} + \frac{1}{C_s} \quad (3)$$

The C_g and C_s are capacitances of air gap and polymer samples.

EXPERIMENTAL

Material

The 25-μm thin sheet of polyimide (kapton-H) was supplied by DuPont India. The circular samples of diameter 5 cm were cut from the rectangular sheet. The 99% pure aluminum (Sigma Aldrich) is used for preparation of electrode.

Procedure

The samples were thermally poled at different temperature (i.e., 303, 323, 373, 423, 473 K) with different polarizing field (i.e., 20, 50,100, 150, 200 kV/cm). The aluminum electrode was prepared by vacuum coating unit. The total time of polarization was taken to be 2.5 h including cooling of samples under electrical stress. During polarization, the free surface (unmetallized surface) of the sample was kept at positive potential. The air gap of 2 mm was introduced between the electrodes by thin mica sheet of 2 mm thickness in such a way that unmetallized samples face the upper electrode. The open-circuit TSDC was measured by means of Pico ammeter connected in external circuit with constant heating rate of 3 K. The AFM is carried out after thermal polarization of samples. The surface morphology was studied through AFM phase images. The phase images were recorded using an atomic force microscope (Model NTEGRA, NT-MDT) available at IIT Roorkee, India.

RESULT AND DISCUSSION

Three-dimensional topographical images of AFM (i.e., Figs. 1 and 2) are showing the surface morphology of polyimide (PI) films before and after thermal charging. As both physical and chemical degradation can introduce lots of defects and change the trap structure due to creation of new traps so that the trap energy level and quantity changes can be used as an indicator maker for determining the trap structure of polymer surface. This change is also reported by Fuqiang et al.[9] using corona ageing. The change in energy levels could be further verified by calculation of activation energy from open-circuit TSDC peak. It has also observed that the roughness

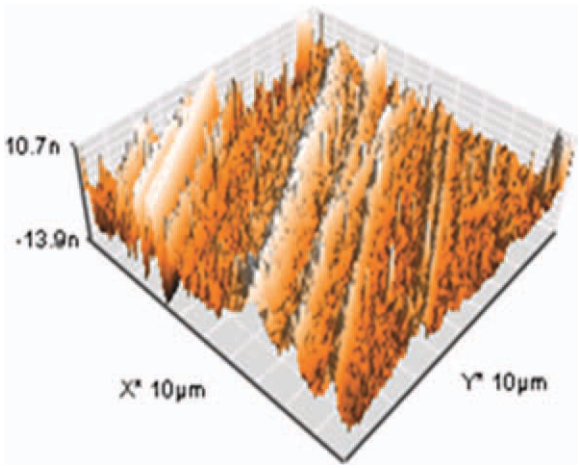

Figure 1 Topographical AFM image of PI samples before polarization. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

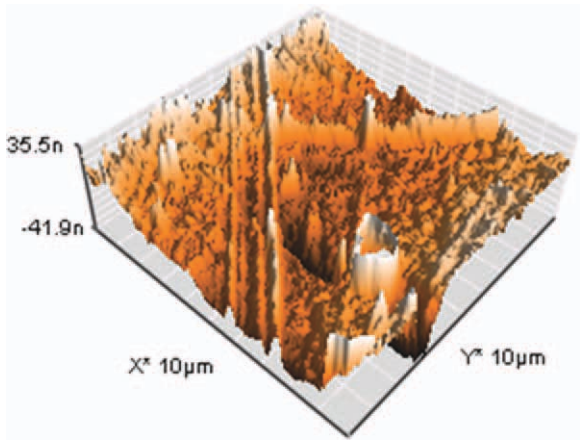

Figure 2 Topographical AFM image of PI samples polarized at 373 K with polarizing field of 100 kV/cm. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

of polymer surface increases with increase in polarizing field and temperature as shown in Figure 3. This is an agreement with open-circuit TSDC, because if the surface traps are prominent then activation energy for TSDC peaks will be small as observed in this study.

The open-circuit thermally stimulated current characteristics of polyimide samples polarized at different temperature with polarizing field of 20, 50, 100, 150, and 200 kV/cm are shown in Figures 4–8.

The magnitude of negative current (i.e., normal current) is found to be comparatively smaller than the current of positive polarity (i.e., anomalous current). If the polarity of current is same as charging current, it is known as anomalous current. However, if the polarity of current is opposite to the charging current is known as normal current. When the samples polarized with 20 kV/cm with polarizing temperature of 303 and 323 K, a single peak of negative polarity is appeared; however, generally the single peak of positive polarity is appeared when the sample was polarized with high field and temperature. When a thermally polarized PI sample is stored in an open circuit, the part of charge released is due to the thermal excitation. The released charge may either be compounded by conduction at their detrapping positions or pass through the sample thickness to the back electrode or then be compensated by image charge situated on the electrode, which brings about the loss of charge storage in the sample or retrapped by other traps during the transport in the bulk. We observe that the charge release increases with increasing polarizing temperature. This means that high polarization temperature allow the trapping of charge carriers in deeper traps; however, charge carriers trapped at surface traps at low polarizing temperature. The charge carriers could not cross the sample thickness when poled at low temperature and give the normal current as observed in

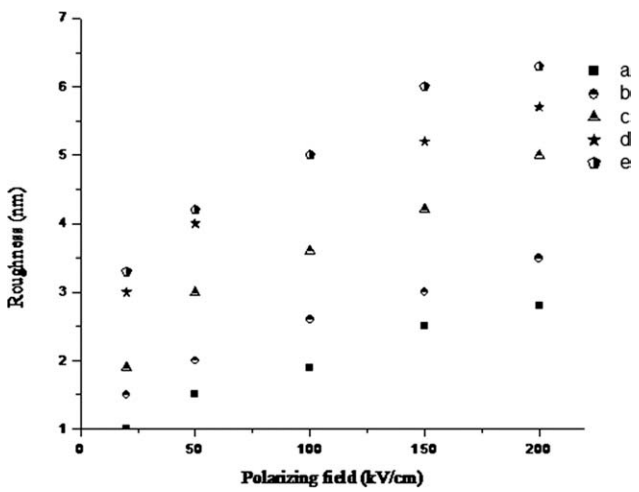

Figure 3 Roughness of PI samples polarized with different polarizing field at different polarizing temperature (i.e., a, 303 K; b, 323 K; c, 373 K; d, 423 K; e, 473 K).

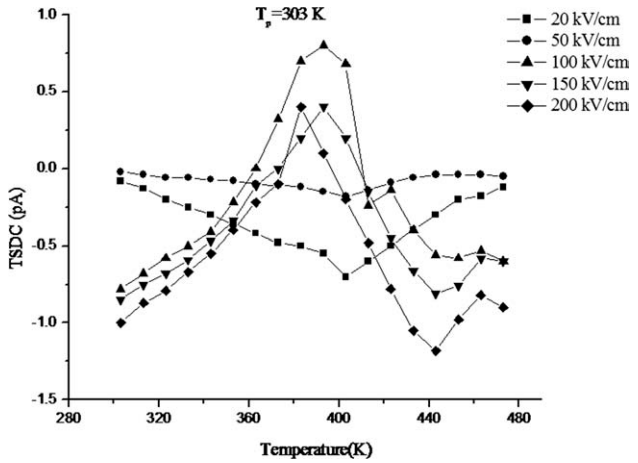

Figure 4 Open circuits TSDC in PI samples polarized at 303 K with different values of polarizing fields.

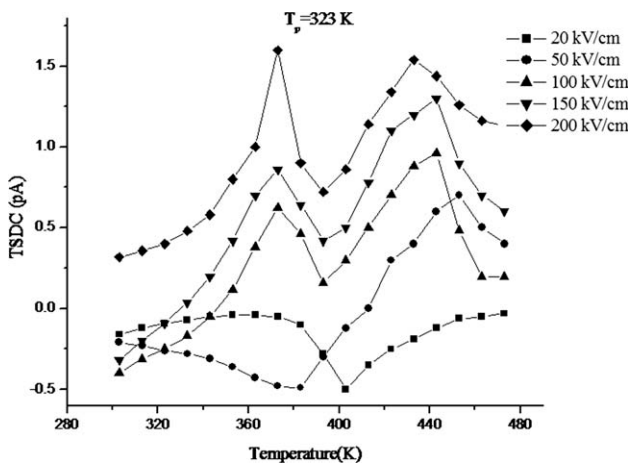

Figure 5 Open circuits TSDC in PI samples polarized at 323 K with different values of polarizing fields.

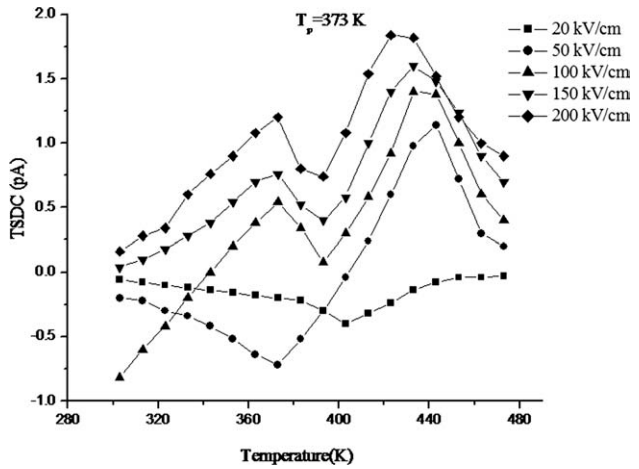

Figure 6 Open circuits TSDC in PI samples polarized at 373 K with different values of polarizing fields.

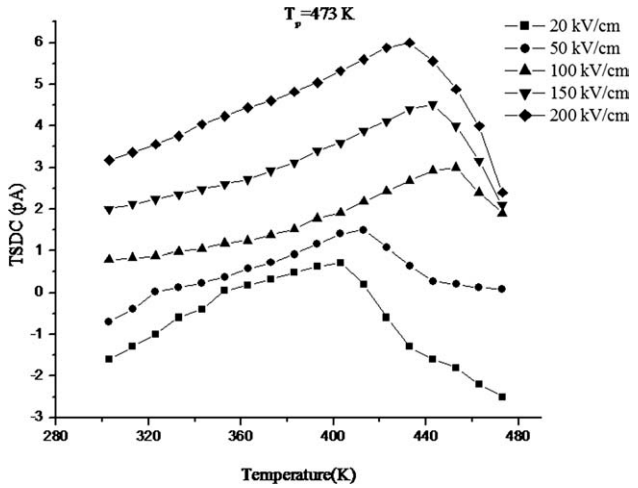

Figure 8 Open circuits TSDC in PI samples polarized at 473 K with different values of polarizing fields.

the present case. However, at high polarizing temperature, the charge carrier induces from deeper traps and compensated the image charges present in back electrode gives the anomalous current. The present investigation support the influence of surface traps is responsible for anomalous current. This process revealed the injection of charge carriers from deeper traps that may be captured by surface tarps present in other side of samples. Therefore, current measured in this case is due to the homocharge corresponding to positive sign of current. In another way, we can understand that the total current flows in external circuit are the sum of conduction current and displacement current. The sign of conduction current is negative but the sign of displacement current is positive. Thus, resultant current would flow in external circuit is due to the difference in magnitude of both the current.

The peak appearing in the open-circuit TSDC spectra of PI samples are representative of different relaxations or transitions. The low-temperature peak with negative current for sample poled with 20, 50 kV/cm and with positive current for sample poled with 100, 150, 200 kV/cm indicate that peak is contributed by dipole orientation as well as by space charge polarization. Subsequently, these polarization processes are corresponding to trapping of charge carriers in shallow and deep traps. These traps are supposed to be formed during polarization or present in polymer matrix.

In PI, two prominent transitions are characterized as a β- and α-peaks (also referred as β- and α-transitions) occurring in the increasing order of temperature are observed. The location and height of these peaks are usually governed by polarizing parameters. The β-peak which has been associated with dipolar orientation relaxation process usually occurs at low poling field and temperature, whereas α-peak which has been associated with space charge

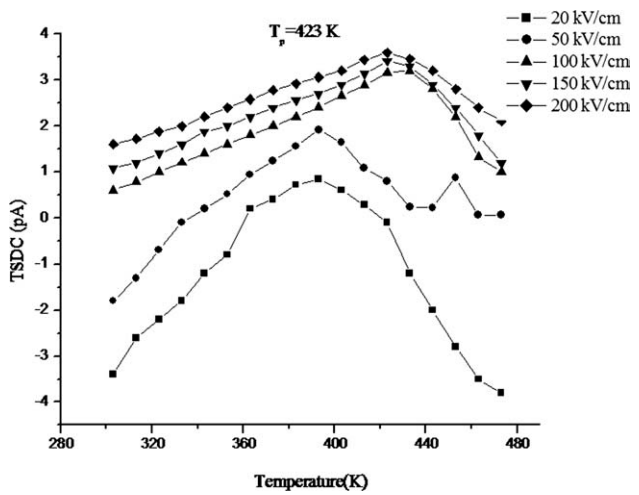

Figure 7 Open circuits TSDC in PI samples polarized at 423 K with different values of polarizing fields.

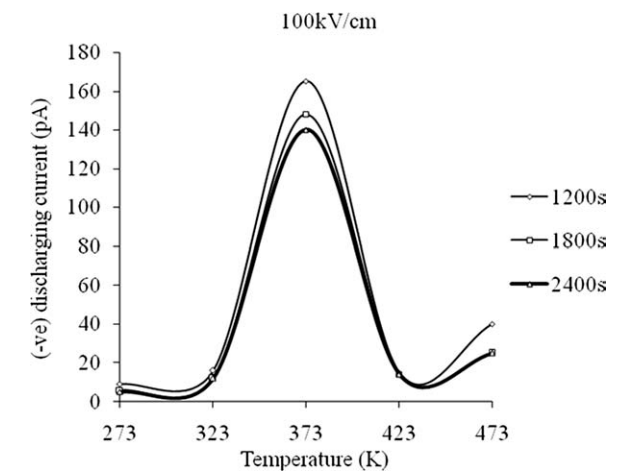

Figure 9 Isochronal of time dependent discharging current.

TABLE I
Open Circuit TSDC Parameters

Polarizing temperature (K)	Polarizing field (kV/cm)	Peak	Activation energy (eV)	Charge released ($\times 10^{-12}$ C)	Relaxation time ($\times 10^{-16}$ s)
303	20	I	0.69	1.15	2.04
		II	–	–	–
	50	I	0.01	2.85	1.01
		II	0.91	34.56	1.06
	100	I	0.92	1.03	1.06
		II	0.91	34.5	1.01
	150	I	0.99	21.50	1.10
		II	0.42	23.04	1.03
	200	I	0.88	11.52	1.10
		II	0.99	69.12	1.09
323	20	I	0.89	1.29	1.12
		II	–	–	–
	50	I	0.18	0.96	1.02
		II	0.57	16.47	1.07
	100	I	0.65	17.8	1.07
		II	0.39	18.8	1.02
	150	I	0.33	17.9	1.04
		II	0.42	25.9	1.03
	200	I	0.20	52.8	1.02
		II	0.33	70.04	1.02
373	20	I	0.32	2.76	1.02
		II	–	–	–
	50	I	0.10	2.95	1.02
		II	0.71	30.64	1.04
	100	I	0.76	17.97	1.09
		II	0.53	44.23	1.03
	150	I	0.22	31.44	1.02
		II	0.35	49.15	1.02
	200	I	0.14	43.77	1.01
		II	0.48	79.87	1.03
423	20	I	–	–	–
		II	0.24	34.6	1.02
	50	I	0.14	65.66	1.08
		II	0.37	64.51	1.02
	100	I	–	–	–
		II	0.10	120.57	1.00
	150	I	–	–	–
		II	0.17	103.46	1.01
	200	I	–	–	–
		II	0.15	137.47	3.01
473	20	I	–	–	–
		II	0.44	20.96	1.04
	50	I	–	–	–
		II	0.98	43.20	1.06
	100	I	–	–	–
		II	0.12	132.48	1.04
	150	I	–	–	–
		II	0.15	137.47	1.01
	200	I	–	–	–
		II	0.06	380.16	4.01

polarization is dominant at high polarizing field and temperature.[5,10,11] The position of β-peak is observed to be almost same for all polarizing field indicates the strong evidence for dipolar polarization. The activation energy for this peak has an agreement with dipolar polarization. The dipolar nature of this peak is further verified by isochronal of time dependent transient discharging current at different constant time as shown in Figure 9.

The appearance of two open-circuit TSDC peak indicates the charge carriers are trapped at trapping level of at least two different depths. The current releases for the second peak seem to be initiated by the macromolecular relaxation or more precisely the relaxation in the crystalline regions. Therefore, charge carriers are probably trapped as interfacial charges at the amorphous-crystalline boundaries. In our opinion, the detrapping of charge carriers is a

dual process arises from both the lowering of trap by molecular motions in the host polymer and thermal excitation of the charge carriers out of their traps. It is also revealed from open-circuit TSDC results that current is low for low penetration depth (i.e., low value of activation energy) for which the carriers moves only the short distance to the near electrode. It is evident from the open-circuit TSDC characteristics that at lower field and temperature, only few image charges are liberated from the electrodes, for which most of them are being neutralized by the attracted excess charges.

Generally, the open-circuit TSDC of PI samples reveal the existence of both homocharge and heterocharge. Stability of the charge storage in polymers depends on the interaction and the resulting mutual relaxation of the homocharge and heterocharge. As the heterocharge (i.e., polarization charges) is usually of the primary importance for polymers but the role of the homocharge was not given enough consideration so far; however, the stabilizing effect of the space charge on the residual polarization has already been reported.[12,13]

The sign of the discharge current is expected to be opposite to the charging current based on the theoretical background as reported by several researchers.[14,15] Sometimes, during charging, image charges are quite larger than the original charges indicate anomalous behavior of TSDC.

The open circuit TSDC is more sensitive for trap structure of material. We know that the change in voltage causes the movement of charge carriers in the bulk. The microscopic transport of charge carriers in the polymer is responsible for TSDC. This microscopic transport of charge carriers could be understood in terms of Mott Devis Model.[16] Recently, Deligoz et al. discussed and successfully applied the Mott Devis Model to understand the electron hopping in conventional polyimide based on pyromellitic dianhydride and benzophenonetetracarboxylicdianhydride.[17]

Actually, the insulating polymer is neither completely amorphous nor completely crystalline. Therefore, it is very difficult to interpretate the transport phenomenon in polymers. This model is an effort to discuss the transport of charge carries in insulating polymers. There are mainly the transports over extended states, band tail states (localized states), and states near the Fermi level (localized states). This model distinguished between all these kinds of transport. The transport over band tail state is hopping transport correspond to the activation energy lies from 0.4 to 0.6 eV. If value of activation energy is much more than that, this transport model is not operative by Phister and Scher.[18–22]

It has also been suggested by Phister and Scher that if the activation energy exceeded the suggested range then hopping of charge carriers will followed by energetic traps and the transport phenomenon is known as trap controlled hopping. This new model suggested the transport of carriers followed by hopping over energetic shallow band tail states and frequently captured by deeper traps because energy of deeper traps is higher than shallow trap. The Table I represents the activation energy of TSDC peak is higher in some cases and lower in some cases; therefore, we can conclude in our discussion that transport of charge carriers in polyimide is due to the trap controlled hopping. The open-circuit TSDC parameters are tabulated in Table I. It has been observed that the fluctuating value of activation energy, charge released, and relaxation time indicate that the traps are energetically distributed in polymer matrix including at the surface of polymer. As very low value of activation energy shows that surface tarps are originated during polarization or during film synthesis process. Thus, the surface properties of polymer could be modified in presence of electric field and temperature as shown by TSDC results; however, the modification of bulk properties could be possible by formation of blend or filling of inorganic particles in polymer. The relaxation time of the trapped charges for samples polarized at high field and temperature was found to be comparatively higher, explaining the good stability of trapped charge. Consequently, we believe that the surface traps are energetic and formed during the thermal polarization.

CONCLUSIONS

It is concluded that open-circuit TSDC measurements provide the useful information about the distribution of traps along with the existence of heterocharge and homocharge in PI samples. The increase in surface roughness with polarizing field and temperature is an agreement with increase in surface traps. Our results suggest that trap-controlled hopping is responsible for charge transport in thermally polarized polyimide. The correlation of open-circuit TSDC with surface roughness is reported first time.

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