Density of Bulk Trap States in Polymeric Films

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***Abstract*— Fundamental understanding of carrier mobility related prebreakdown phenomena in dielectrics provides insights into high field transport phenomena as well as associated aging and onset of charge injection induced instability. A system for measuring resistive current through a dielectric film during a ramp voltage to breakdown has been developed to address the limits of conventional steady-state approaches in which the sample typically fails prior to achieving steady state current at around sixty percent of breakdown field. Prebreakdown conduction in polypropylene, polystyrene, and polyethylene-terephthalate thin films with varying molecular structure, crystallinity, and chain orientation were studied under room temperature as well as elevated temperature. Space-charge-limited current spectroscopy is used in the data analysis to extract more information from the experimental data. Critical transport parameters, such as prebreakdown density of bulk trap states, were extracted to provide a quantitative basis for comparative study and material engineering for improved high field performance.**

Keywords—prebreakdown, space-charge-limited current, density of states

I. INTRODUCTION

Dielectric films with high capacitive energy storage density are the most pervasive and least reliable devices, used in the DC-link of power conversion systems, filtering, power factor correction, and pulsed power systems [1]. In a broader sense, fundamental research on dielectric materials could lead to the discovery of critical enabler for payload efficiency and affordable high power density of various integrated electric propulsion and drive systems [2]. Through intensive research, candidate material families have been explored which include relaxor ferroelectric polymer based blends, copolymers, nanocomposites and nanolaminates, as well as modified glassy polymers through the addition of cyanoethyl, thiol, or sulfonyl polar side groups [3-5]. In addition to all-organic polymers, polymer chemical space searches have led to new promising organometallic polymer dielectric families [6]. These recent discoveries indicate the untapped opportunities within the vast polymer chemical space.

While rational design through hierarchical chemical space searches shall be continued [7], fundamental questions related to the degradation and breakdown of polymer dielectrics when subjected to large electric fields should be addressed [8-10]. The behavior of a material experiencing ultra-high fields has long defied a fundamental understanding due to the fact that dielectric degradation and breakdown process in engineering materials is extremely complex as a result of the interplay between the magnitude of the electric field, the time span of imposition of the field, the temperature, and the state and morphology of the material. Dielectric degradation which eventually culminates in breakdown is essentially the progressive creation and accumulation of atomic and nanoscale defects, assisted by electric field, time and temperature. Conduction and defect accumulation provide positive feedback to each other, culminating in eventual catastrophic breakdown. The highest possible electric field that a defect-free material can tolerate has a special significance which corresponds to the intrinsic breakdown strength, determined solely by the material's chemistry and crystal structure [11]. The dielectric degradation and breakdown phenomena thus need much more understanding to guide ultimately the development of new electric field tolerant insulators with high breakdown strength. As a result, pre-breakdown study is essential in revealing the nature and onset of the injection and transport of charge carriers with high mobility, and the carrier mobility induced instabilities under extremely high electric fields.

Carrier mobility-related prebreakdown phenomena can only be studied within microscopic dimensions or under transient conditions, as power dissipation would cause thermal runaway for a macroscopic geometry [12,13]. Numerous past efforts to characterize and study conduction and aging of dielectrics under quasi steady-state condition could only reach around two thirds of the breakdown field as a result of failure of rapid aging [14,15]. A system for measuring resistive current through a planar dielectric film during a linear ramp voltage to breakdown has been developed to address the limits of conventional quasi steady-state approaches. During voltage ramp, the current through the sample is a combination of the resistive current, the capacitive current, as well as, for the case of nonlinear polar dielectric, the polarization current, i.e., $j(t) = \varepsilon_0 \varepsilon \frac{\partial E(x,t)}{\partial t} + \frac{\partial P(x,t)}{\partial t} + j_c(x,t)$. The capacitive current is much greater than the resistive current even near the breakdown field. Thus to measure the resistive current through polymeric films up to breakdown, the capacitive current must be cancelled dynamically during a ramp voltage.

The system uses a small sinusoidal modulation signal on top of the voltage ramp to track the capacitive current. With the negative feedback loop formed by a voltage controlled amplifier and a dual-phase lock-in amplifier, the capacitive current can be actively canceled during the measurement. The remaining signal at the output represents the residual resistive current through the sample. The use of the VCA represents a substantial improvement over a previous system, as it provides much greater dynamic range [16]. It shall be noted that prior to the introduction of this method of active capacitive current cancellation, measurement of high field conduction during a voltage ramp has been limited to heat resistant polyimides which can be subjected to extremely high temperature such that the conduction current dominants the total measured current [17].

II. Experiment

Metalized film was used as sample electrodes with an active area of about 1 cm by 1 cm to form a metal-insulator-metal structure (MIMS) with the unmetalized test film sandwiched in between the electrodes. Four types of capacitor grade films were included in this study, 7.6 um bi-axially oriented polypropylene (BOPP) film manufactured by the sequential draft-tenter process, 12.5 um BOPP film manufactured by the simultaneous-stretching process (bubble/blow-molding), 11.5 um polyethylene terephthalate (PET) film manufactured by the sequential draft-tenter process, and 10 um polystyrene (PS) film. All the materials under study possess stereoregularity. Capacitor grade films based on PP and PET are isotactic with varying polymorphorphism, while atactic PS is completely amorphous. Before the measurement, each sample was conditioned to approximately 100 MV/m to ensure good electrode contact and to eliminate any air bubbles trapped between the electrodes and the sample.

In the actual measurement, a 300 V/s DC ramp voltage superimposed with 10 V modulation was applied to the maximum voltage permitted right below breakdown, for three consecutive times. This is intended to separate and minimize the absorption current. The integrated resistive current as a function of electric field was measured. The integral of resistive current (charge) as a function of field for tenter BOPP is shown in Fig.1 as an example. All the measured conduction charge vs. electric field data are "noisy", which could be related to current oscillations from energetic modes of transport. Further probing of such energetic modes of transport is under study by using pressure wave based charge profiling technique(s) with high spatiotemporal resolution. the integrated resistive current during the first run is always greater than the subsequent runs. The difference between the first run and subsequent runs is mainly due to filling of traps at the interface between crystalline and amorphous regions. The third run data were taken for analysis as they represent mostly the conduction current. A comparison of the integrated resistive current as a function of electric field for the four polymeric films based on data taken from the third run was presented in a previous paper [18].

The resistive current was also measured at elevated temperatures. A large heating stage was used to matain a uniform temperature across the sample throughout the whole measurement period. A cover was placed over the heating stage to prevent the air circulation in the chamber. Each sample was placed on the heated stage for 5 minutes before any measurement to ensure the sample well reached the pre-set temperature. Thermocouples were attached to the surface of the heating stage and the electrode to monitor the sample temperature. Besides room temperature measurement, each type of sample wss tested also under 323K and 348K, respectively. Current density was calculated by taking derivitive of charge data with respect to time. In order to take derivitive of the experimental data, a soomthing function in MATLAB was carefully used. Fig.2 shows the temperature dependent space-charge-limited current (TDSCLC) results for all the material

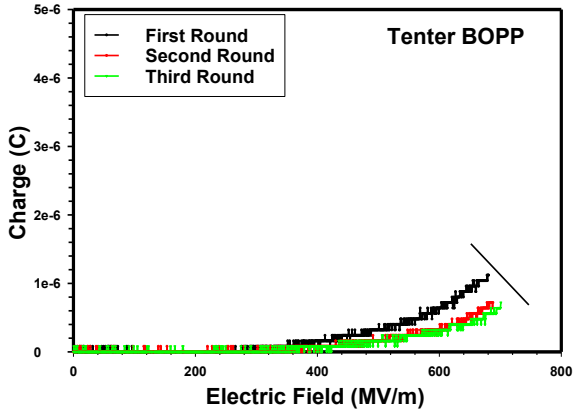

Fig. 1 Comparison of the currents for the four capacitor grade films under study based on the third run data in (a) linear scale plot (b) log-log plot.

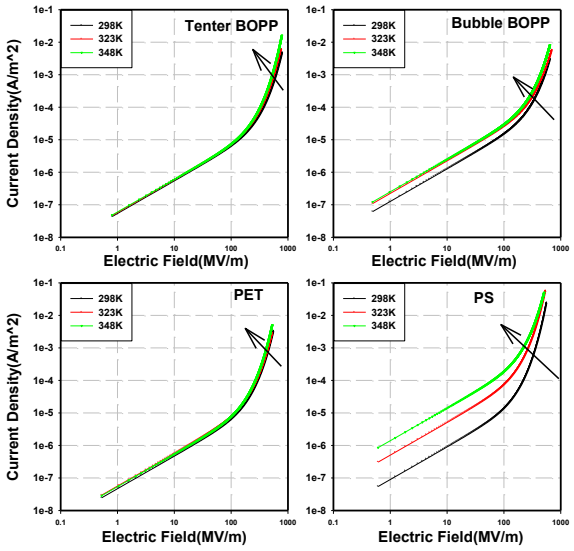

Fig. 2 Current density vs electric field result under log scale based on TDSCLC measurement.

under study. A trap free Space-Charge-Limited-Current (SCLC) model will yield a straight line with a slope of 2 in the log-log current density vs field plot. [19] Under low field, the ohmic conduction region has a slope of 1 and the transition point to the space charge limited region for all the materials is around 100MV/m. Under high field, all the materials exhibit slopes higher than 2, indicating the presence of traps. Among the samples studied, polystyrene has the highest slope and the highest current density. All materials show the trap limited conduction region and they fail breakdown before reaching trap filled conduction region. The current densities for all material increase with applied temperature. For all three semi-crystalline materials, the slope of current density is also increasing with temperature while for the case of polystyrene, the slope actually decrese with temperature. Experimental results were further analyzed next.

III. DATA ANALYSIS

SCLC spectra were further analyzed to extract characteristic parameters for transport. In SCLC theory, it is assumed that the current is dominated by the charges thermally activated from localized traps into delocalized band. The starting point is by solving the transport Ohm's law equation together with Poisson equation. The shape of these experimentally determined SCLC curves reflects the increment of the space charge with respect to the shift of Fermi energy during the transient application of high field [20,21]. The first and higher order derivatives of the temperature modulated current density plots as a function of electric field can be employed to yield transport parameters such as the density of trap states [22]. As shown in Fig.3, the room temperature result is projected to the current density-electric field plane for the room temperature density of states calculation. For a simplified transport model with unipolar carrier injection from an ideal ohmic contact free from thermal equalization, the following bulk density of trap states, measured in reference to the mobility edge of the conduction band can be calculated from the temperature dependent SCLC (TDSCLC) spectra [20-22]

$$\frac{dn_s}{dE_f} = \frac{1}{k_B T}\frac{\varepsilon\varepsilon_0}{eL^2}\frac{2m-1}{m^2}(1+C) \tag{1}$$

with

$$C = \frac{B(2m-1)+B^2(3m-2)+d[\ln(1+B)]/d\ln U}{1+B(m-1)} \tag{2}$$

and

$$B = \frac{\mathrm{d}\,m}{\mathrm{d}\ln(U)}\frac{1}{m(m-1)(2m-1)} \tag{3}$$

where L is the sample thickness, U is the applied voltage, m = d(ln$j$)/d(ln$U$), the slope of the log-log j-U plot. For the reconstruction of DOS, the applied voltage must be correlated to the activation energy. Arrhenius analysis of the TDSCLC spectra was conducted (as shown on the temperature-current density plane in Fig.4) to extract the activation energy for any given U according to E_a= -d (ln$j$)/d(k_bT)$^{-1}$ to correlate the electric

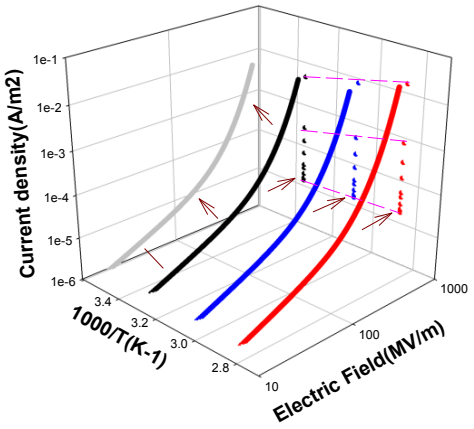

Fig.3 TDSCLC Data analysis process. The data projected to the left plane were used to extract DOS information as a fuction of applied field. The projection on the right was used to correlated the applied field to activation energy.

field to the energy level of the traps which are being filled at. The slope of the fitted straight line will yield the activation energy under each given applied field. These experimental results suggest deep traps can only be sampled under field prebreakdown.

With the methodology mentioned above, the bulk trap density of states with respect to conduction band edge for the four capacitor films were constructed, as shown in Fig.4. An exponential distribution of bulk trap DOS was observed for all three crystalline materials, while the amorphous polystyrene exhibited a distinctive DOS with much greater bulk trap depth of 2.0-2.5eV. The bulk trap depth for PS prebreakdown is greater than the space charge trap depth determined by thermally stimulated depolarization current (1.4eV), but very close to the reported activation energy of 2.0eV which was thought to be associated with the movement of entire molecular chain [23]. As noted above, the resistive current measured for amorphous/atactic polystyrene increased from run-to-run, possibly because the electrical properties of amorphous/atactic

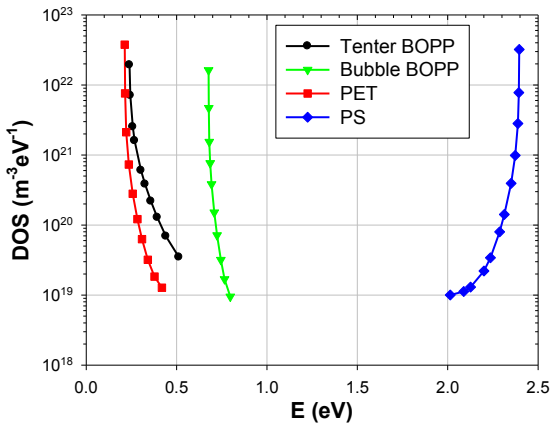

Fig.4 Density of bulk trap states for all the four polymer materials under study.

polystyrene changed gradually from field-induced change in its polymer structures. The analysis gives differing trap DOS for the two types of BOPP, i.e, 0.3 to 0.5eV for tenter BOPP and 0.6 to 0.7eV for bubble BOPP. They can be separated by their different processing condition, i.e. sequentially stretching vs. simultaneously stretching. PET has a low breakdown field hence have a shallow trap distribution. This density of trap state distribution stays well in line with respect to their dielectric performance.

IV. Discussion and Summary

In summary, an active capacitive current cancellation system has been developed to extract pre-breakdown conduction parameters for polymeric thin films under extreme fields to provide a quantitative basis for the study of charge injection and transport, which correlate apparently to the crystallinity, size, distribution and orientation of crystalline domains, as well as steric configuration and imperfections. Such a system allows the reconstruction of density of bulk trap states related to prebreakdown conduction in wide band gap polymeric dielectric films by employing the TDSCLC analysis. Next this technique will be employed to probe the extreme field transport in model dielectric films with controlled chemical and physical imperfections as well as varying structures as the result of high field aging.

It shall be noted that both the hopping conduction model and SCLC model emphasis the physical transport through localized states. As shown in Ref.18, hopping model fits the experimental data better in low field region while SCLC naturally couples the transport equation with Poisson field. By large, hopping model is a bulk limited conduction model while SCLC is established based on charge injection through the electrodes. The mobility is modulated by trapping for both models with the availability of carriers for transport partitioned based on band theory. Implementation of the hopping conduction model relies experimentally on the establishment of so called quasi-steady-state [24] and is more sensitive to the characteristic trap depth towards which the energy distribution of carriers approaches slowly under a fixed external bias. In principle, SCLC samples the entire energy distribution (DOS) of defect states dynamically, although care must be taken during the measurement and analysis as in a typical engineering material there are concurrent processes in multiple length and time scales such as interfacial polarization and interfacial trapping.

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