

Investigation of the Stability of Organic Gate Dielectrics by the Isothermal Transient Current Method

T.S. Böske^{1,2}, G.H. Gelinck³

Philips Research, Integrated Device Technologies, Prof. Holstlaan 4, 5656 AA Eindhoven, Netherlands

W. Krautschneider

Technische Universität Hamburg-Harburg, Arbeitsbereich Mikroelektronik, Eissendorfer Str. 38, 21073 Hamburg, Germany

Abstract— We characterized bias induced instabilities of organic gate insulators in MIM structures by measuring the transient current response upon application of a bias. The observed effect is believed to be caused by mobile charges, most probably ions, whose mobility is moderated by the moisture content of the dielectric. Based on this we estimated initial distribution, mobility and amount of charges.

Keywords— Organic Gate Dielectric; Mobile Ions; Transient Current; ITC; Organic Insulator

I. INTRODUCTION

Polymer electronics holds the promise of low cost large area electronics. Even though significant progress towards the manufacturability of entire circuits has been done [1], [2], the operational and lifetime stability of organic field effect transistors is still an open subject. A significant issue in the stability of organic thin film transistors, OTFTs, is the shift of the threshold voltage upon applying a gate bias. This effect has previously been researched in hybrid OTFT which comprised an inorganic gate dielectric and an organic semiconductor. The shift of the threshold voltage in hybrid TFTs is related to the buildup of charges at the semiconductor/insulator interface [3], [4], [5], [6].

To simplify the production of circuits with OTFTs it is desirable to adopt organic materials for the gate insulator. Organic gate dielectrics introduce additional drift mechanisms. In these materials, apart from charge build-up, an additional contribution of mobile ions within the gate insulator is observed [7].

This work investigates the stability of the gate dielectric used in OTFTs, but now measured in capacitor metal-insulator-metal (MIM) structures. In the MIM structure a thin (200-350nm) polymer insulator is sandwiched between two metal electrodes. The structures were manufactured using the same process as OTFTs - the electrodes of the MIM structures are the source/drain and gate layer in a bottom gate OTFT process. We used the isothermal

transient current method, where a constant bias is applied to the electrodes and the evolution of current with time is measured at a constant temperature.

II. EXPERIMENTAL

The Isothermal Transient Current (ITC) method probes mobile charges by their displacement current. A constant bias is applied to the electrodes and the variation of current over time is recorded. The temperature is held constant. If mobile charges are present in the insulator, they will rearrange under the field and give rise to a displacement current which is proportional to the amount and mobility of the charges. If initial charging of the capacitor and leakage is neglected, and ion-blocking electrodes are assumed, this process can be described by:

$$J(t) = Q_m \frac{\gamma(t)}{dt} \quad (1)$$

Here Q_m refers to the mobile charge per area and $\gamma(t)$ describes the normalized charge distribution, the charge centroid, in dependence of time. The evolution of $\gamma(t)$ over time depends on many factors such as type and mobility of mobile species and internal field distribution. When a bias is applied, the charges will rearrange starting from an initial distribution $\gamma(0)$ until they are blocked at an electrode with a new distribution $\gamma(t_{tr})$. The transit time t_{tr} is observed as a discontinuity in the transient current. The initial distribution $\gamma(0)$ can either be enforced by driving the ions to one electrode, or be calculated by comparing measurements for both positive and negative bias. Ideally, the amount of mobile charges can then be determined by integrating eq. 1:

$$\int_0^{t_{tr}} J(t) dt = (\gamma(t_{tr}) - \gamma(0)) Q_m = \Delta Q_m \quad (2)$$

ΔQ_m is a fraction of the total mobile charge depending on redistribution. If more than one species of charges is present in the dielectric, the contributions of all species will be superimposed on the measured current. Assuming that $\gamma(t)$ is approximately a linear function of t , the ion

¹Now at Infineon Technologies MDC, Dresden

²Electronic mail: boescke.external@infineon.com

³Electronic mail: gerwin.gelinck@philips.com

mobility μ can be estimated as:

$$\mu \approx (\gamma(t_{tr}) - \gamma(0)) \frac{d^2}{V_{bias} t_{tr}} \quad (3)$$

where d is the thickness of the insulator.

The ITC method has been successfully applied to determine the mobility of sodium ions in silicon dioxide [8] and for the characterization of ion conductors [9]. In these systems little influence of leakage currents could be observed. The ion transient time is associated with a sudden drop of the current. This behavior is well explained and can be modeled analytically [10], [11].

Few reports exist on the application of the ITC method to the characterization of ions in polymers. Here no clear drop of current is observed. Instead, one or more characteristic peaks in the transient current were found [12], [13], [14], [15]. The peak is usually associated with the time at which the species of ion arrives at the electrode [12], [13].

A. Device preparation

The devices, which were investigated in this work, were manufactured in a process developed for organic integrated circuits [16], [1]. The structures were fabricated on a polyethylenephthalate foil laminated to a silicon support wafer. Bottom electrodes were formed by photolithographical patterning of a physical vapor deposited gold or aluminum film. The gate dielectric, a photoimageable polymer, was deposited by spin coating to a thickness between $d=200\text{nm}$ and 350nm and structured to form contact holes. Top electrodes were formed by the subsequent deposition of gold and a patterning step. The electrode area of the devices was $355\mu\text{m} \cdot 345\mu\text{m}$. The final step, the deposition of an organic semiconductor to form transistors, was omitted.

B. Measurements

All measurements were performed with an Agilent 4155C parameter analyzer. The samples were contacted by means of a guarded micro probe, either in air (40% and 60% r.h.) or in a moisture free nitrogen atmosphere. Samples were held at room temperature ($18 - 20^\circ\text{C}$). The transient current measurements were taken in the "sampling" mode of the analyzer. Usually one or two samples per second were taken in "long" integration time setting. The bias was applied to the top electrode of the structure, while the bottom electrode was grounded. Every measurement was carried out on a virgin device. Unless noted otherwise all measurement refer to Gold-Polymer-Gold (Au-polymer-Au) structures.

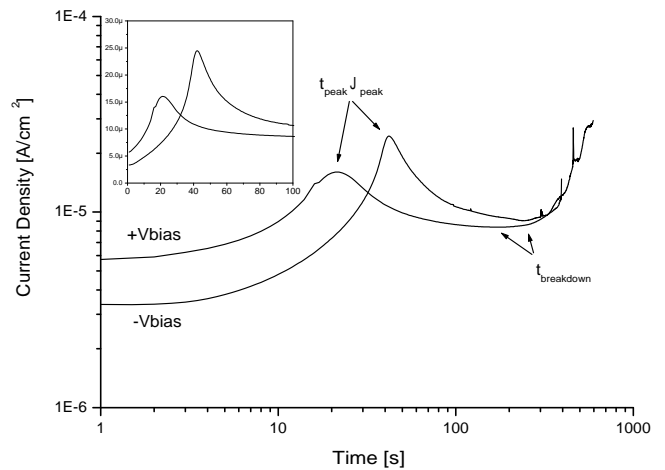


Fig. 1. ITC measurement for a MIM structure with $d = 205\text{nm}$. The applied bias was $\pm 60\text{V}$, which corresponds to a field of $E = 2.44\text{MV/cm}$. The inset shows a lin-lin plot of the peaks.

III. RESULTS AND DISCUSSION

Figure 1 shows two transient current measurements of an Au-polymer-Au structure in air with 40% r.h., one for a bias of $+60\text{V}$ and one for a bias of -60V . Most apparent is a peculiar feature, a local maximum after a certain time. The time and current density associated with this feature will be denoted as t_{peak} and J_{peak} . The feature itself will be referred to as "peak". A significant finding is the electrical asymmetry of the device. Both t_{peak} and J_{peak} are smaller for positive bias than for negative bias. This was observed in all examined Au-polymer-Au structures. At longer timescales the current starts to rise again. When the current reaches a certain level, the device breaks down and is physically destroyed.

Repeated measurements at different positions on the wafer yielded nearly identical measurements, indicating good reproducibility of the measurements. These findings also suggest that the observed current variation is a consistent feature of the dielectric film and not a function of localized variations such as weak spots within the MIM structure. Further experiments showed that the occurrence of the peak depends on the history of the sample. When the measurement was interrupted for a few seconds, the evolution of the current continued approximately at the state where the bias was removed. This behavior ceased when the device was allowed to relax for more than approximately one hour. Total reversibility of ITC measurements in polymers has been reported in the literature after prolonged relaxation and annealing of the devices [17], [14]. However, for practical purposes we decided to use virgin devices for each measurement.

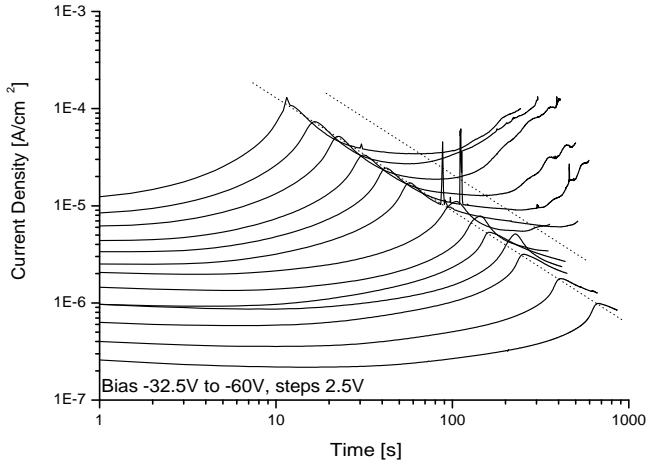


Fig. 2. Series of transient responses for a structure with $d = 205\text{nm}$ and varied bias.

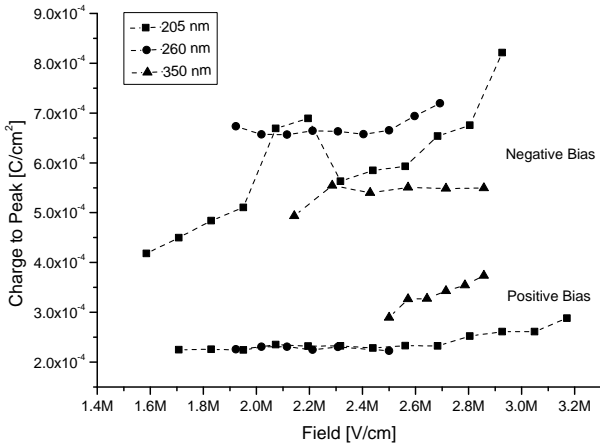


Fig. 3. Integrated charge until t_{peak} in dependence of bias and polarity.

A. Influence of Bias

Figure 2 shows a group of current transients for different negative bias at a relative humidity of 40%. A general observation is that the peak formation depends on the applied bias; increasing in speed with higher field strength. The current peaks align to a straight line (dotted) with a slope close to -1 in the log-log plot. Thus the product of J_{peak} and t_{peak} is independent of bias, suggesting that the observed current is the result of the motion of a fixed amount of charges. When the peak time is interpreted as the advent of a species of ions at an electrode we can set $t_{tr} = t_{peak}$ and use eq. 2 to calculate ΔQ_m in figure 3.

It is not possible to derive the polarity and species of the charges that give rise to the peak, perhaps the peak originates only from a highly mobile dominant fraction of positive ions. Slower charges may still be in transit lead-

ing to an additional current contribution. ΔQ_m shows a weak dependence on bias, but a strong dependence on polarity. This can be explained by a non uniform initial ion distribution, where the ions in the virgin devices are more concentrated close to one of the electrodes. The charge to peak can be used to estimate a lower bound for the total mobile charge and the initial distribution as:

$$N_m = \frac{\Delta Q_m^+ + \Delta Q_m^-}{q} \quad (4)$$

$$\gamma(0) = \frac{\Delta Q_m^-}{\Delta Q_m^+ + \Delta Q_m^-} \quad (5)$$

Here q is the electron charge, N_m the density of mobile charges per area and ΔQ_m^- and ΔQ_m^+ the charge to peak for positive and negative bias polarity respectively. The initial distribution was 0.6 for the 350nm sample and 0.7 for the thinner samples. Assuming that the peak is based on the motion of positive ions this means that the ions are distributed closer to the bottom electrode. The estimated total density of charges was $\approx 5 \cdot 10^{15} \text{cm}^{-2}$ for all samples. This would then indicate that up to 0.5% of the bulk material is dissociated and mobile, depending on ion valence. We consider this value unrealistically high.

B. Influence of Water Content

From literature it is known that the moisture content has a significant influence on the conductivity of polymers[18]. To investigate the influence of water sorption, additional experiments were performed in dry nitrogen atmosphere. After the samples were subjected to moisture free environment, the water slowly diffused out of the polymer. Since the metal electrodes act as barrier, the water has to diffuse laterally within the MIM structure until it can desorb. This leads to extremely high time constants, until equilibrium with the atmosphere is reached. The timescale of this process is in the order of days, so that measurements could be made at different stages of water removal.

Figure 4 shows a series of ITC experiments for a sample that had been stored in dry nitrogen atmosphere for one day and still contained residual water. Compared to the measurements at 40% r.h. the current decreased and the time to peak increased significantly. In addition the shape of the curve changed and a clear minimum was introduced before the appearance of the peak.

After the sample had been subjected to the nitrogen atmosphere for two weeks, no peak could be measured within 10^5s of stressing (inset of figure 4). Instead of a peak only a decaying current was observed. This behavior is believed to be an underlying relaxation process that is

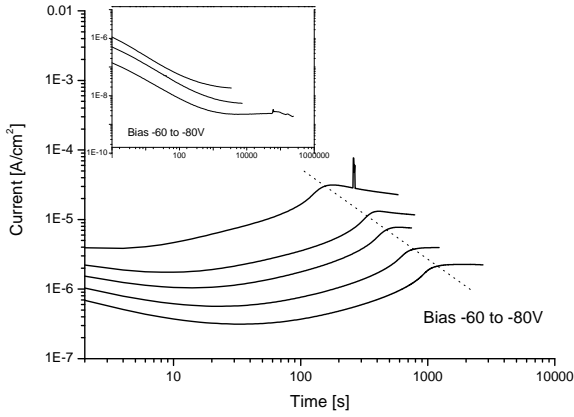


Fig. 4. ITC measurement for a MIM structure with $d = 205nm$ after 1 day in a moisture free atmosphere. The inset shows a measurement on a structure with $d = 260nm$ after 2 weeks dehydration.

independent of moisture - it was concealed by the higher current of the process taking place at increased water content. The transient follows a power law as $J(t) \propto t^{-n}$ with n close to 1, the Curie - von Schweidler law, which is usually observed in disordered insulators and related to dielectric relaxation processes with distributed time constants [19]. The physical origin of this effect can not be determined easily and has to be considered an open topic. Models have been proposed based on dipole response [20] or protons in double wells [21]. However at fields above $2MV/cm$, as applied here, an additional injection of electrons from the electrodes into traps with widely distributed trapping times cannot be ruled out.

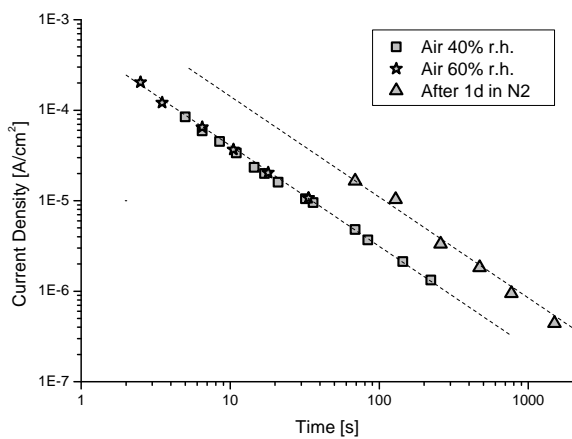


Fig. 5. J_{peak} vs. t_{peak} for a device with $d = 205nm$ at different moisture levels.

Figure 5 shows values of J_{peak} vs. t_{peak} at different

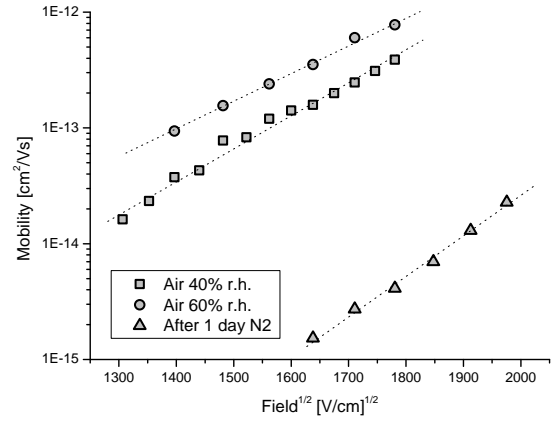


Fig. 6. Ion mobility for a dielectric with $d = 205nm$ at different moisture levels. The dotted lines show fits to eq. 6.

moisture levels for the same sample and polarity. Apart from the series at extremely low moisture levels, all points follow the same line. The deviation for the dry sample could stem from an increased influence of the underlying relaxation current. This scaling rule indicates that the amount of transported charge is independent of moisture content, and the water does not provide additional charges. In fact, the water only appears to moderate the transport of ions. This behavior was also reported for the transport of sodium ions in polyimide[17].

C. Ion Mobility

We extracted the ion mobility using eq. 3 for a series of positive polarity measurements in dependence of bias and moisture content. The field dependence of the obtained values within the examined bias range follows a straight line in a Poole-Frenkel plot (figure 6), which means that it follows a function as:

$$\mu(E) = \mu'_0 \cdot \exp\left(\frac{q}{2k_b T} \sqrt{\frac{qE}{\pi\epsilon_0\epsilon_r}}\right) \quad (6)$$

With ϵ_0 being the permittivity of vacuum, ϵ_r the relative permittivity, k_b and T the Boltzmann constant and temperature respectively. Parameters for fits to this equation are listed in table I. The Poole-Frenkel mechanism describes

Ambient moisture level	$\mu'_0 [cm^2/Vs]$	ϵ_r
r.h. 60%	$3.4 \cdot 10^{-17}$	46
r.h. 40%	$5.5 \cdot 10^{-18}$	34
1 day in N2	$2.3 \cdot 10^{-20}$	23

TABLE I

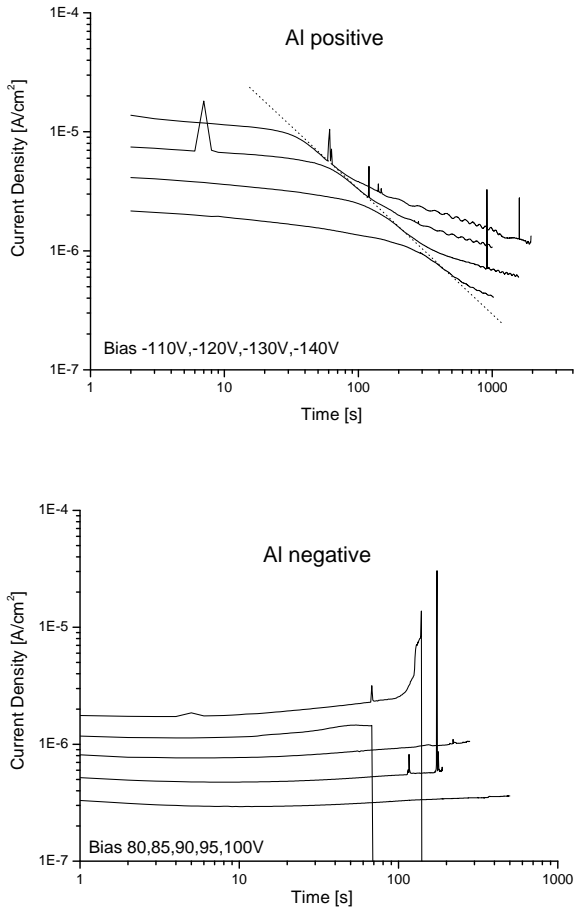


Fig. 7. Transient current response of a gold-polymer-aluminum structure with $d = 350nm$ for different bias and polarity.

the transport between adjacent potential wells by field assisted thermionic emission [22].

A general trend is the increase of the pre factor μ'_0 with higher moisture content, while ϵ_r decreases. The relative permittivity exceeds the electronically determined value ($\epsilon_{r,el} \approx 4.5$) by an order of magnitude. Similar exponential factors have been reported by others for polyimide [23] and epoxy [19]. The ramifications of this observation are not clear at this point, but it implies that the Poole-Frenkel mechanism is inadequate to describe the conduction of ions in this material.

D. Influence of Contact Metal

To investigate the influence of the contact material, additional structures were manufactured where the gold bottom electrode was replaced by aluminum. Figure 7 shows the results of a series of ITC measurements with different bias for both polarities. In contrast to the Au-polymer-Au structures, different mechanisms were observed with respect to polarity. When the Al electrode was biased neg-

atively, a relatively constant current was observed and the devices broke down quickly. No peak was noticed. When the Al electrode was biased positively, the current leveled off slowly until a clearly defined drop was visible after a certain time. Similar to the peaks in Au-polymer-Au structures, the inflexion points align on a straight line with a slope of -1, again indicating that this effect is related to a fixed amount of charges. Despite the high bias the current is lower as compared to the Au-polymer-Au structure and no breakdown was observed within 2000s.

E. Discussion

The strong dependence of the characteristics on the contact metal indicates that the current transients cannot be explained by the motion of charges in the bulk alone. One possibility is the occurrence of both electronic and ionic currents in the bulk. Once a bias is applied ions accumulate at the electrodes and enhance the field locally. This would in turn facilitate the injection of electronic charges. In that case a dependence of the work function of the electrode would be observed, which would explain the dependence on the contact metal. This model has been used to describe transient currents in polyimide [14], where the peak was attributed to transient electronic currents. However, the scaling of the peak position, indicating the transport of a fixed amount of charges, can not be explained convincingly with this model.

An alternative explanation is based on electrochemical reactions at the electrodes [18]. In this model ions drift from the bulk to an electrode and are neutralized by the exchange of electrons. No electronic current is required in the bulk. The measured transients would be directly equivalent to the ionic current, which corresponds to the motion of a fixed amount of contaminants and explains the peak scaling. If electrochemical reactions are dominant, their nature depends on the type of contact metal. Gold is relatively inert and would rarely react with ions. In contrast the aluminum electrode is very reactive. When it is biased negatively it seems to degrade quickly, leading to early breakdown of the devices. For positive bias the aluminum forms a self passivating oxide layer which inhibits further reaction and would explain high resistance to breakdown. This model implicitly assumes all mobile charges to be ionic, and that the electronic contribution to the current is negligible. Hence, in this model ca. 0.5% of the bulk material is ionogenic.

IV. CONCLUSIONS

In conclusion, we performed isothermal transient current measurements on MIM structures with thin organic insulators. A peak in the transient current was found, which

was attributed to the advent of charges at one electrode. The product of peak time and current, and thus the charge associated with the peak, varies only weakly with bias and moisture content. Therefore it is assumed that a fixed amount of mobile ions dominates the process. Based on this it was possible to estimate density, initial distribution and the mobility of the ions. It was shown that the water content of the polymer moderates the mobility of charge carriers, but is not a source of charges itself. The interpretation of the results is still ambiguous due to the difficulty in explaining the mechanism of interaction between, and the relative contribution of, ionic and electronic currents.

We note that a similar discussion plays a role in describing the operating mechanisms in so-called polymeric light-emitting electrochemical cells [24].

V. ACKNOWLEDGEMENTS

The authors would like to thank the entire Polymer Vision technology team for manufacturing the devices.

REFERENCES

- [1] G. Gelinck, H. Huitema, E. van Veenendaal, E. Cantatore, L. Schrijnemakers, J. van der Putten, T. Geuns, M. Beenhakkers, J. Giesbers, B.-H. Huisman, E. Meijer, E. Mena Benito, F. Touwslager, A. Marsman, B. van Rens, and D.M. de Leeuw. Flexible active-matrix displays and shift registers based on solution-processed organic transistors. *Nature Materials*, 3:106–110, 2004.
- [2] W. Clemens, W. Fix, J. Ficker, A. Knobloch, and A. Ullmann. From polymer transistors towards printed electronics. *J. Mater. Res.*, 19:1963, 2004.
- [3] W.A. Schoonveld, J.B. Oostinga J. Vrijmoeth, and T.M. Klapwijk. Charge trapping instabilities of sexithiophene thin film transistors. *Synth. Met.*, 101:608–609, 1999.
- [4] H.L. Gomes, P. Stallinga, F. Dinelli, M. Murgia, F. Biscarini, D.M. de Leeuw, T. Muck, J. Geurts, L.W. Molenkamp, and V. Wagner. Bias-induced threshold voltages shifts in thin-film organic transistors. *Appl. Phys. Lett.*, 84(16):3184–3186, 2004.
- [5] M. Matters, D.M. de Leeuw, P.T. Herwing, and A.R. Brown. Bias-stress induced instability of organic thin film transistors. *Synth. Met.*, 110:998–999, 1999.
- [6] D. Knipp, R.A. Street, A. Volkel, and J. Ho. Pentacene thin film transistors on inorganic dielectrics: Morphology structure property, and electronic transport. *J. Appl. Phys.*, 93(1):347–355, 2003.
- [7] S.J. Zilker, C. Detcheverry, E. Cantatore, and D.M. de Leeuw. Bias stress in organic thin-film transistors and logic gates. *Appl. Phys. Lett.*, 70(8):1124–1126, 2001.
- [8] J.P. Stagg. Drift mobilities of Na⁺ and K⁺ ions in SiO₂ films. *Appl. Phys. Lett.*, 31(8):532–533, 1977.
- [9] M.-H. Lee, S.-I. Pyun, and H.-C. Shin. The kinetics of lithium transport through LiNiO₂ by current transient analysis. *Solid State Ionics*, 140:35–43, 2001.
- [10] G. Frenning and M. Stromme. Theoretical derivation of the isothermal transient ionic current in an ion conductor: Migration, diffusion, and space-charge effects. *J. Appl. Phys.*, 90(11):5570–5575, 2001.
- [11] G. Frenning. *Charged Particle Transport: As Information Source about Ion Conductors, Dielectric Materials and Drug Delivery Systems*. PhD thesis, University of Uppsala, Sweden, 2002.
- [12] M. Watanabe, M. Rikukawa, K. Sanui, and N. Ogata. Evaluation of ionic mobility and transference number in a polymeric solid electrolyte by isothermal transient ionic current method. *J. Appl. Phys.*, 58(2):736–740, 1985.
- [13] K. Friedrich, J. Ulanski, G. Boiteux, and G. Seytre. Time-Of-Flight Ion Mobility Measurements in Epoxy-Amine Systems during Curing. *IEEE Transactions on Dielectrics and Electrical Insulation*, 8(3):572–576, 2001.
- [14] H.J. Neuhaus, G.B. Hershkowitz, and S.D. Senturia. Conduction transients in polyimide: Effect of sodium ions and water. *Third International Conference on Polyimides*, pages 527–535, November 1988.
- [15] H.J. Neuhaus and S.D. Senturia. Conduction transients in polyimide. *ACS Symposium Polymeric Materials for Electronics Packaging and Interconnection*, pages 176–189, September 1988.
- [16] G. H. Gelinck, T. C. T. Geuns, and D. M. de Leeuw. High-performance all-polymer integrated circuits. *Appl. Phys. Lett.*, 77:1487–1489, 2000.
- [17] H. Neuhaus. *Electrical Conduction in Polyimide*. PhD thesis, Mass. Inst. Tech, Cambridge, 1989.
- [18] G. Leclerc and A. Yelon. Electrochemical effects and charge-transport phenomena in metal-polymer-metal systems under vacuum and water-vapor atmosphere. *J. Appl. Phys.*, 64(7):3713–3717, 1988.
- [19] R. Lovell. Decaying and steady current in an epoxy polymer at high electric fields. *J. Phys. D*, 7:1518–1530, 1974.
- [20] R. Coelho. *Physics of Dielectrics*. Elsevier, 1979.
- [21] H. Kliem. Dielectric Small-signal Response by Protons in Amorphous Insulators. *IEEE Transactions on Electrical Insulation*, 24:185–197, 1989.
- [22] G. Barbottin and A. Vapaille. *Instabilities in silicon devices*. Elsevier science publishing, 1986.
- [23] G.M. Sessler, B. Hahn, and D.Y. Yoon. Electrical conduction in polyimide films. *J. Appl. Phys.*, 60(1):318–326, 1985.
- [24] J.C. deMello, N. Tessler, S.C. Graham, and R.H. Friend. Ionic space-charge effects in polymer light-emitting diodes. *Phys. Rev. B*, 57:12951–12963, 1998.