Time-resolved Kelvin probe microscopy to study population and depopulation of traps in electron or hole majority organic semiconductors

Jason P. Moscatello^a, Chloe V. Castaneda^a, Alyina Zaidi^a, Minxuan Cao^a,
Ozlem Usluer^b, Alejandro L. Briseno^b, Katherine E. Aidala^{☆a}

^a*Department of Physics, Mount Holyoke College, 50 College Street, South Hadley, MA, USA*

^b*Department of Polymer Science and Engineering, Conte Research Center, University of Massachusetts, 120 Governors Drive, Amherst, MA 01003*

Abstract

We present a time-resolved Kelvin Probe Force Microscopy (KPFM) technique that can record carrier motion on the scale of milliseconds, appropriate for polycrystalline materials like organic semiconductors. The organic semiconductors are studied in a transistor geometry to which we apply a step voltage to the back-gate. We record the change in potential at a specific location and observe the times associated with filling and emptying majority carrier traps, observed in hole majority carrier poly(3-hexylthiophene-2,5-diyl) (P3HT) and a perylene diimide electron majority carrier, PDI-CN2. We see signs of bias stress with repeated measurements in P3HT.

Keywords: scanning probe microscopy, organic semiconductors, organic photovoltaics, charge motion, P3HT, PDI-CN2

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1. Introduction

Non-traditional semiconductors like organic materials[1, 2], arrays of colloidal quantum dots[3, 4], metal oxides[5, 6], metal dichalcogenides[7], and perovskites[8, 9] are now employed in flexible electronics and next-generation
5 photovoltaics; however, they suffer from low mobilities compared to traditional

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[☆]Corresponding author. E-mail address: kaidala@mtholyoke.edu (K. Aidala)

crystalline inorganic materials, and their transport properties are heavily influenced by trap states[2, 3, 4, 5, 6, 7, 8, 9]. Substantial work goes into characterizing these trap states for individual materials with techniques that range from illumination-free transient current[10] to (thermal) admittance spectroscopy[11],
10 Fourier transform photocurrent spectroscopy[12], deep level transient spectroscopy[13], and capacitance-voltage or capacitance-frequency[14] measurements, for example. Depending on the characterization method and the model that is used to interpret the results, these techniques do not always agree, nor are they all sensitive to the same trap states[13]. Kelvin Probe Force Microscopy (KPFM) is
15 typically used to create spatial maps of surface potential, to determine variations in workfunction or map potential across a device [15]. KPFM has been used to perform surface potential-gate bias spectroscopy [16, 17], and to resolve time dependent phenomenon like photovoltage in response to illumination [18] and the injection of charges in an oligothiophene derivative [17] and PbS nanocrystal
20 films [19].

Here we introduce a technique that measures both the injection and extraction of carriers in devices occurring on the millisecond to second time scale in organic field effect transistors (OFETs). By applying a sudden voltage to the back-gate of an OFET, we can watch the time-resolved screening of this applied
25 potential. The technique is sensitive to the population and depopulation of trap states that directly contribute to observed hysteresis and bias stress in OFETs, complementary to other techniques that measure trap states. We investigate a hole majority carrier, poly(3-hexylthiophene-2,5-diyl) (P3HT), and an electron majority carrier, a perylene diimide, PDI-CN2 (ActivInk N1400, from Polyera),
30 to demonstrate the viability of this technique.

2. Methods and Materials

2.1. Sample Fabrication

Devices were fabricated in a back-gate, bottom contact configuration in order to be compatible with SPM techniques; a schematic of the device is shown in Fig-

ure 1(a). Substrates were n-type (Sb-doped) low resistivity (0.008-0.020 Ω -cm) silicon with a 200 nm thermally grown oxide layer (University Wafer). Source and drain electrodes were photolithographically patterned using a dual-layer of Shipley 1313 photoresist over Futurrex LOR5A. The deposited electrodes were 50 nm thick gold with a 3 nm titanium adhesion underlayer, deposited by e-beam evaporation. Before depositing the organic material, the device substrates were ultrasonically cleaned in a bath sequence beginning with 3:1 deionized water:Micro-90, followed by deionized water, then acetone, and finally ethanol before a final five minute oxygen plasma clean.

For the P3HT devices, the substrates were silanized by immersion in a solution of 5 μ L of octadecyltrichlorosilane (Acros Organics) per mL of toluene (anhydrous 99.9%, Sigma Aldrich) for 1.5 hours in a PTFE dish. After immersion the substrates were rinsed in clean toluene and dried. P3HT (96+% regioregular, >32k Mw, Rieke Metals) was added to chloroform (anhydrous, Sigma Aldrich) in a ratio of 12 mg/mL and mixed with a magnetic stirrer. For PDI-CN2, the substrates were not silanized. The PDI-CN2 solution was made by adding chloroform dropwise to the vial containing the PDI-CN2 and a magnetic stirrer, until all the material dissolved at a concentration of about 5 mg/mL.

The substrate was pre-wetted by dispensing chloroform (through a 0.2 μ m PTFE filter) and spinning at 3000 rpm for 30s. The P3HT solution was then dispensed (through a 0.2 μ m filter) onto the substrate and spun at 3000 rpm for 60 s (1000 rpm for PDI-CN2). The sample was then annealed at 150°C for 30 minutes resulting in a 30 nm film. Finally, the organic film from the outer 2-3 mm of the sample surface was mechanically removed to prevent shorting to the back-gate. In order to make a consistent electrical connection to the back gate in our measurement cell, the samples are mounted on steel chucks by mechanically removing the native oxide on the underside of the substrate with a diamond-tip scribe and placing a small amount of conductive paint (PELCO Conductive Colloidal Silver Paint) on the chuck before positioning the substrate; the device is cured for at least 16 hours in vacuum before testing. This method

of contacting the backgate results in ohmic contacts of about $30\ \Omega$.

2.2. Current-Voltage Measurements

Characteristic current-voltage curves were obtained using a Keithley 2400 source-meter and a 6517b electrometer/high resistance meter; these data were
70 taken in a nitrogen environment before the samples were exposed to ambient conditions.

To take three-terminal measurements on the AFM, the samples were placed in a custom cell (based on the Asylum Research polymer heater stage[20]) that can be closed to protect the samples from ambient conditions (the bottom half
75 of the cell is shown in Figure 1(b)); nitrogen is run through the cell at a rate of 382 mL/min. Samples were exposed to air for approximately ten minutes while transferred from the glove box to the closed cell. Current-voltage measurements were taken in the closed cell using the Asylum Research AFM controller box, Kepco high voltage power supplies, and a FEMTO current-to-voltage amplifier.

2.3. Scanning Probe Microscopy

Topographical and KPFM measurements were performed on an Asylum Research MFP-3D AFM; Pt-coated tips were used in order to make electronic measurements (Olympus AC240TM) with a resonant frequency of 70 kHz and a spring constant of 2 N/m. During KPFM measurements, a small amplitude AC
85 voltage is applied to the tip, causing the tip to oscillate if the tip and sample surface are not at the same potential. To record the potential at the surface, a feedback loop applies a DC voltage (V_{DC}) to the tip that minimizes the oscillation; the minimal force occurs when the tip and surface are at the same potential, allowing us to record the surface potential relative to the tip. KPFM
90 is typically used to scan across an area to map the local potential difference between the tip and sample surface [15]. Fast time resolution can be achieved by positioning the tip at a single point over the organic semiconductor and recording changes in potential. We position the tip some distance from our grounded electrodes and record the potential below the tip as the back-gate is switched

95 on and off in the device. In this way, we observe charges moving into and out of
the film. The maximum voltage of our KPFM feedback loop is approximately
6 V.

3. Results and discussion

3.1. Control

100 To introduce the time-resolved KPFM we start with a control sample. The
geometry is identical to the finished samples but lacks the organic film. The
geometry of the wafer and electrodes yields an estimated capacitance of 5 nF.
The source and drain electrodes are grounded. We take a topographic scan near
the electrodes and position the tip 40 μm from the electrode gap edge. We then
105 turn on the KPFM feedback to record the potential of the surface.

Figure 2 (solid black line) shows the applied gate voltage. When the AFM
tip is placed over the gold electrode, there is no change in measured potential
as the gate is turned on and off. In this case (blue dashed line), the electrons in
the gold move too quickly for the KPFM feedback loop to register a change, and
110 the potential remains at zero. If the tip is placed over the bare SiO_2 layer (red
dotted line), the measured surface potential follows the potential applied to the
back gate. Charges cannot move into or through the oxide, so the unscreened
gate potential is measured by the tip. By fitting an exponential to this rise in
measured KPFM potential, we find a time constant of 3ms, which sets the time
115 resolution of our system. We can measure charge motion in materials on the
scale of milliseconds. This time resolution is set in our system by the mechanical
bandwidth of the cantilever in amplitude modulation mode, corresponding to a
time constant $\tau = \frac{2Q}{f_0}$ [21]. Typical values for our cantilevers are $f_0 \approx 75 \text{ kHz}$
and $Q \approx 50$, giving a time constant $\approx 4 \text{ ms}$. There is an inherent tradeoff
120 in amplitude modulation mode between sensitivity and response time. Active
damping, or different cantilevers, can improve response time when sensitivity is
not required.

Figure 1: (a) Schematic of the FET device architecture. (b) The bottom of the closed cell. Conductive clips hold the sample in place and make the source and drain contacts; the clips are connected to wires which feed through to the outside of the cell. The gate connection is made through the steel chuck. Two additional ports permit tubes that serve as the gas inlet and outlet.

Figure 2: Characterization of the time-resolved KPFM using a control wafer with no organic film and applying a voltage to the back-gate (black solid line). When the tip is positioned above the grounded gold electrodes (blue dashed line), the measured potential is constant because the screening from the gold occurs faster than the KPFM loop can respond. When the tip is positioned over the silicon oxide surface (red dotted line), the local surface potential follows the gate voltage. The time constant describing the response time of the KPFM loop is approximately 3ms.

Figure 3: Typical I_{DS} vs. V_{DS} curves for a P3HT OFET.

3.2. P3HT Devices, hole majority carrier

As shown in the output curves (Figure 3), the P3HT has p-type character;
125 the hole mobility in these devices was $\approx 2 \times 10^{-3} \text{ cm}^2/(\text{Vs})$ using the saturated
current calculation[22], consistent with other reports[23]. Figure 4 shows the
time-resolved KPFM of a P3HT OFET. The solid black line indicates the voltage
applied to the back-gate of the device, and the tip was positioned over the P3HT
40 μm from the edge of the device gap at a height of 1 μm . The dotted red line
130 shows the measured local surface potential as the gate voltage is turned on and
off.

As the gate is switched from zero to its negative value of -6 V, there is a sharp
potential peak in the negative direction that decays back to the original neutral
potential (Figure 4). The negative potential applied to the back gate is not
135 immediately screened, and holes are injected from the grounded Au electrodes
into the film under the influence of the back gate, screening it over time. Next,
when the gate is switched back to zero bias, there is a similar peak and decay
with the opposite sign. As the negative potential is turned off, there are initially
excess holes in the film which must return through the grounded electrode. A
140 similar situation occurs for a positive gate voltage. Applying a positive gate
gate voltage pushes holes out of the film, revealing an initial positive potential
peak which decays to neutral as holes leave the film. Finally, when the gate is
switched back to zero, there are fewer holes in the film, leading to a net negative
surface potential which decays back to neutral as holes are injected back into
145 the film.

The decay of the potential fits poorly to a single exponential or a single
stretched exponential, both of which have been shown to fit some transients
that are dependent on traps, and double exponentials and double stretched
exponentials are often used when single exponentials are insufficient[24, 17].
150 For simplicity and a good fit to the decay of the potential, we use the sum of
two exponentials, given by Equation (1).

$$f(t) = A_1 e^{-t/\tau_1} + A_2 e^{-t/\tau_2} \quad (1)$$

While the double exponential suggests there are two dominant physical mechanisms, meaningful quantitative physical interpretation of a four parameter fit is challenging. The weighted average time constant helps us to accurately capture
155 the difference among the curves, given by [25]:

$$\bar{\tau} = \frac{A_1\tau_1^2 + A_2\tau_2^2}{A_1\tau_1 + A_2\tau_2}. \quad (2)$$

Figure 4 includes the weighted average time constants for each peak. For the negative back-gate potential, the time constant for holes entering the film ($\bar{\tau} = 0.5$ s) is faster than the time constant for the holes exiting the film ($\bar{\tau} = 0.6$ s). This finding is consistent across devices regardless of age of device
160 and air exposure, though the magnitude of the time constants may vary. The same trend is seen for the positive gate voltage. The time constant for holes exiting the film as the positive gate voltage is applied ($\bar{\tau} = 2.9$ s) is longer than holes entering the film as the gate voltage returns to zero ($\bar{\tau} = 0.9$ s). We see no evidence of minority carrier transport in the current-voltage curves.
165 The longer time constants associated with holes exiting the film could be due to either an extraction barrier (larger than any injection barrier) or to the need to empty traps in order to push the necessary number of holes out of the film. We performed spatial KPFM scans across the channel while applying a range of source-drain voltages, none of which showed any potential drops at either
170 electrode, suggesting an ohmic contact between the Au electrodes and P3HT.

The fact that it is faster to inject holes than to extract holes can be explained by considering the prominent role that traps play in charge motion in devices like these. Given the 5 nF capacitance of the device and the 6 V gate potential, approximately 10^{11} holes enter the film. As holes enter the film, some fall
175 into traps of varying depths. When holes need to exit from the film, some of these holes are trapped deeply enough to impact the amount of time that it takes to move in response to the change in the gate voltage. The effect is most prominent when applying the positive gate voltage, which pushes the largest number of holes from the films, presumably emptying them from deeper traps.

Figure 4: Time-resolved KPFM sequence for the P3HT device. The dotted black line displays the potential applied to the gate. An initial negative peak decays to a neutral potential as holes flow into the film from the electrodes. When the gate is turned off, there is initially an excess of holes (positive peak) that must leave the film. When applying a positive back-gate voltage, the second positive peak is more slowly screened as additional holes leave the film. When the positive gate voltage is removed, the initial negative potential due to too few holes is reduced as holes are quickly injected into the film. The weighted average time constant is indicated for each peak.

180 There is a slow migration out of the film, with a larger contribution from long-lived trap states. Given the minimal current measured for $V_G = 0$ V, there is not much mobile charge available to exit the film when a positive gate voltage is applied.

3.3. PDI-CN2 devices, electron majority carrier

185 To verify our description of the charge flow and the role of traps, we compare the p-type P3HT devices with n-type PDI-CN2 devices. We predict the same behavior for the electron majority carrier, but with longer time constants

Figure 5: Typical I_{DS} vs. V_{DS} curves for the PDI-CN2 FETs.

associated with applying the negative gate voltage rather than the positive - it will be faster to fill traps with the majority carrier than to empty them. The characteristic output curves of the PDI-CN2 devices are shown in Figure 5; electron mobilities were found to be $\approx 0.1 \text{ cm}^2/(\text{Vs})$, consistent with literature[26], with no evidence of hole transport; we do see evidence of a contact resistance in the IV curves. We were not able to perform KPFM scans across the channel to characterize the size or location of the resistance. Given the energy band alignments, it is more likely an electron injection barrier (workfunction of gold -5.1 eV and LUMO of PDI-CN2 of -4.33 eV) [27, 28], which would not lead to the observed KPFM signal.

Figure 6 shows the time-resolved KPFM of the PDI-CN2 device and the weighted average time constants. As expected, it is faster to draw the majority carrier electrons into the film during the positive gate (first peak, $\bar{\tau} = 0.024 \text{ s}$) than it is to remove them (second peak, $\bar{\tau} = 0.027 \text{ s}$). The same is true for

Figure 6: Time-resolved KFPM of PDI-CN2. The applied gate voltage (dotted black line) is screened by electrons injected and extracted from the film, resulting in temporary positive and negative measured surface potentials (red line) due to too many or too few electrons. Weighted time constants for each peak are indicated on the graph.

Figure 7: Time-resolved KFPM of PDI-CN2 with a larger applied gate voltage (dotted black line). (a) For $V_{GS} = +60$ V, the time constants are similar to $V_{GS} = +6$ V because there are many mobile electrons in the film. (b) When $V_{GS} = -60$ V, the screening of the gate voltage occurs over seconds as trapped electrons are forced to leave the film. The flat region is the maximum surface potential measurable by our KPFM feedback. As the negative voltage is removed, electrons are injected into the film much more quickly.

applying the negative gate voltage (third peak, $\bar{\tau} = 0.031$ s) and returning the negative gate voltage to zero (fourth peak, $\bar{\tau} = 0.030$ s), as predicted by our interpretation of the role of trap states.

205 However, there are differences when comparing PDI-CN2 to the P3HT case. The peaks are much smaller in voltage, the time constants are faster, and the time constants differ by a smaller amount. The PDI-CN2 FET has a mobility that is a factor of 50 higher than P3HT, and Figure 5 shows that an electron channel exists even with zero gate voltage, indicating mobile charges are present
210 until a negative gate is applied. These two factors would predict faster screening times, since more mobile charges are available and the mobility is higher. Since drift velocity is proportional to mobility ($v_d = \mu E$), in the absence of traps we would expect the time constant for screening with free carriers to be proportional to mobility, given the same electric field. The time constants of the screening
215 in the two materials differ by about a factor of 25 (24 ms and 30ms for PDI-CN2 and 0.5s and 0.9s for P3HT). Quoting a single mobility can be misleading, as these materials have field dependent mobilities, and traps play a role in the measured bulk mobility. We expect to see increases in time constants associated with screening when fewer mobile charges are available and trapped electrons
220 must exit the film.

To enhance the difference in time constants and the effect that the trap states play, we applied an order of magnitude larger gate voltage. Figure 7(a) shows the results with a +60V gate. There is little change in the time constants because the electrons are easily injected into the film, which already had mobile
225 charges at zero gate voltage and mostly filled trap states. Figure 7(b) shows a distinct contrast when applying a -60V gate. As the negative gate voltage is applied, the KPFM signal hits its maximum, preventing us from extracting a valid weighted time constant. However, the film takes about 7 s to fully screen the gate potential. Removing the negative gate voltage, causing electrons to rush
230 back into the film with zero gate voltage, reveals again a short time constant on a similar scale to the positive gate voltage peaks. By applying $V_{GS} = -60$ V, we deplete the film of mobile carriers, and electrons must escape longer lived traps

to exit the film and eventually screen the gate potential.

3.4. Bias Stress in P3HT

235 To further characterize and understand these time-resolved KPFM measurements, we studied P3HT films by stepping the gate voltage in 2.5 V increments down to -50 V and back up to zero. We repeated this measurement five times. (See Figure 8.) For each step, there is a temporary peak in the KPFM signal as holes enter or exit the film in order to return to a neutral voltage. When stepping
240 back up toward 0 V, more and more holes must exit the film. If the holes are free to move, we expect roughly the same time constants for the screening at each step. If a significant number of these holes are trapped at different depths, we expect that holes confined in the more quickly emptied shallow traps would first exit the film. As the gate voltage is stepped back to zero, more of the
245 deeply trapped holes must exit, leading to longer time constants as the gate voltage returns to zero.

Figure 8(a) shows the five sets of peaks that result when stepping from -50 V on the gate back to zero. The most striking feature is the increase in the screening time near $V_G = 0$ with repeated measurements. The red curve is the
250 first trial, and there is relatively little difference in time constant as the gate voltage steps from -50 V to 0V. The second (orange) through fifth (purple) measurements reveal increasingly longer time constants. Figure 8(b) extracts the weighted time constant for each trial, plotting only the first step from -50 V to -47.5 V (black dots) and then the four final steps to zero volts (from -10 V
255 to 0 V). For the first step back up from -50 V, all trials show approximately the same weighted tau. For the first trial from -50 V to 0 V, all the steps show approximately the same weighted tau. The large differences emerge for the fourth and fifth trials on the steps close to 0 V. Subsequent measurements reveal that holes take increasingly longer to exit the film near 0 V. We interpret
260 this result as a manifestation of bias stress. When the large negative gate voltage is applied for longer amounts of time, traps are created, or traps that are both statistically less likely to be filled and emptied are filled over time (e.g. traps

a short physical distance into the oxide layer)[29, 24]. Repeated measurements fill these traps, reducing the number of mobile and shallowly trapped carriers. The result is that when the last of the injected holes must exit the film as the gate voltage returns to zero, the amount of time required to screen the potential from the gate increases.

4. Conclusions

We characterize a time-resolved KPFM technique that records the motion of charge carriers in response to a changing gate voltage, measuring the potential at the surface of the film as the carriers screen the potential of the gate. For the tip and feedback parameters used, the mechanical bandwidth primarily determines the time resolution, which is approximately 3 ms. We demonstrate the ability to distinguish between populating and depopulating trap states, and the sensitivity of this technique to different ranges of gate voltage that push the device into different operating regimes. Repeated measurements reveal the effects of bias stress. As a scanning probe technique, KPFM offers the flexibility to determine contact resistance, and to examine location dependent variations in transport. The technique has the potential to differentiate among bulk contributions, interfaces at metal electrodes, and structures within the film such as grain boundaries. Further careful study examining a wider range of devices and the dependence on gate voltage and distance from the electrodes will more fully elucidate the contribution from the contacts, mobility, material non-uniformity, and traps.

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Figure 8: (a) Time-resolved KPFM of P3HT in response to stepping the gate voltage from -50 V to 0 V in twenty steps. The measurement is repeated five times. (b) Weighted time constants for selected peaks for each of the five measurements. "0" indicates the step from -2.5V to 0 V.

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