A high spatial resolution measurement of trap states and charge motion in non-traditional semiconductors

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Introduction

Novel materials open up new functionality to nanoscale devices. Organic semiconductors offer the opportunity for lightweight and flexible devices, like the new Samsung Galaxy Fold, using Organic-LED technology. However, the efficiency of such materials remains limited by the formation of trap states, electronic states which are long-lived and localized, keeping the charges from contributing to the desired processes, and are particularly problematic for solar energy applications.

Most measurements used to investigate these states average over an entire device at steady state, unable to investigate the local, transient nature of the traps. We have developed a new measurement using scanning probe microscopy techniques to make high spatial resolution measurements of the effect of trap states on charges.

Scanning Probe Techniques

Scanning Probe techniques utilize a small probe brought near the surface to be studied. Light reflected off the tip onto a photodiode allows measurement of the tip deflection (Fig. 1), while the actuators which raster the tip over the surface and control the height of the tip record its x, y and z position. In order to measure a surface's height, we cause the tip to oscillate near its resonance frequency, and as we scan the surface, we raise and lower the tip to keep the oscillation at a constant amplitude (Fig. 2); an example height measurement is shown in Fig. 3(a).

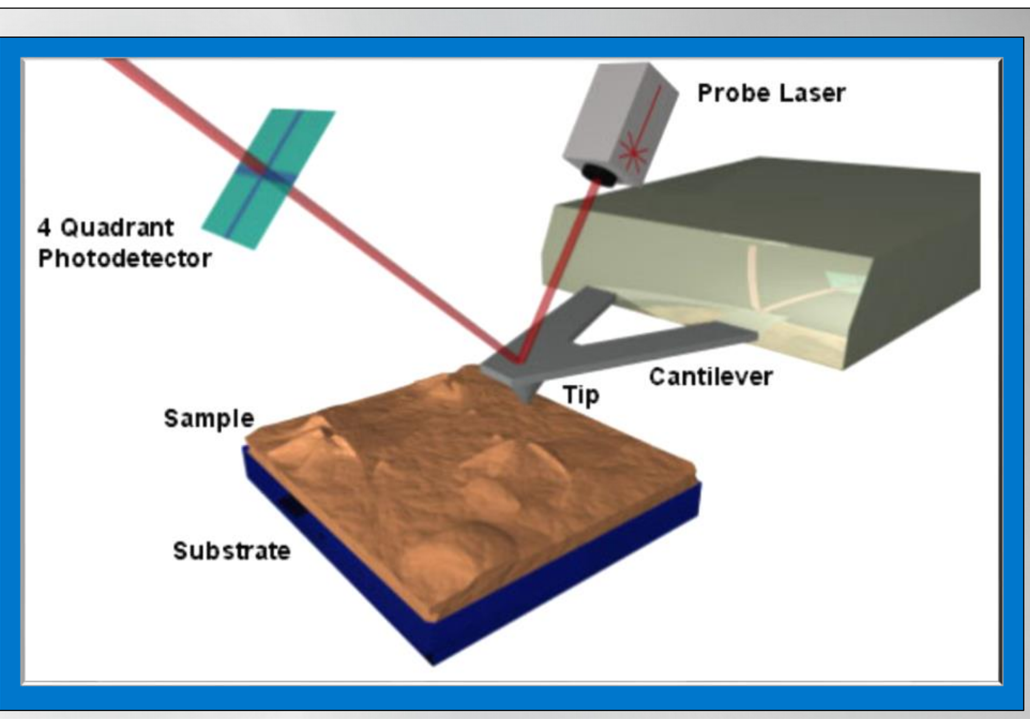

Figure 1. A schematic representation a scanning probe microscope. The tip is brought in near contact with the surface to be studied. The deflection of the tip is monitored by reflected laser light.

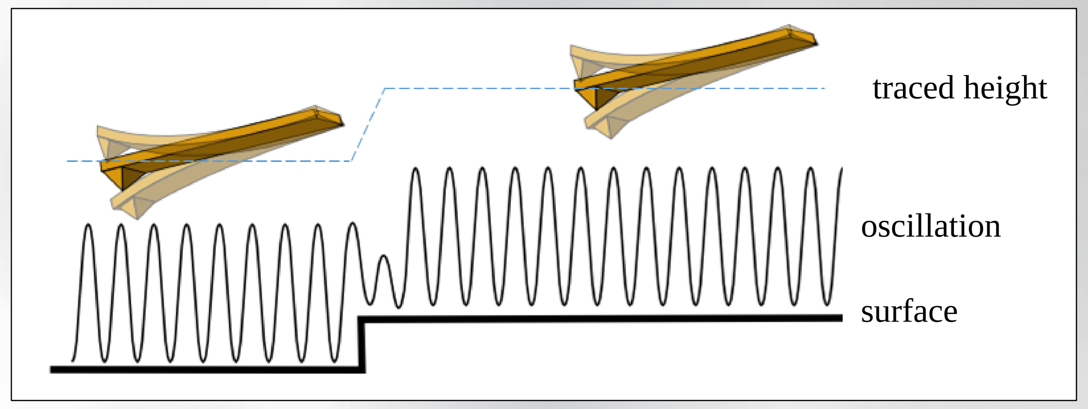

Figure 2. During a height measurement, a control loop raises or lowers the oscillating tip to keep the amplitude constant. Recording the height at each location creates a height map of the surface.

Kelvin Probe Force Microscopy

To detect charges, a technique must be sensitive to electrical potentials or fields -- Kelvin Probe Force Microscopy (KPFM) allows such a measurement. Applying an AC voltage to the tip causes it to oscillate if its potential differs from the surface.

$$F_{resonance} = -\frac{\partial C}{\partial z}\left[\left(V_{tip} + DC\right) - V_{sample}\right] * V_{resonance} * sin(\omega_{resonance} * t)$$

A control loop finds a DC offset to apply to the tip to minimize the oscillation, a condition which means the tip and sample are at the same potential. Recording that DC for all points in a scan builds the potential surface of the sample (Figure 3(b)).

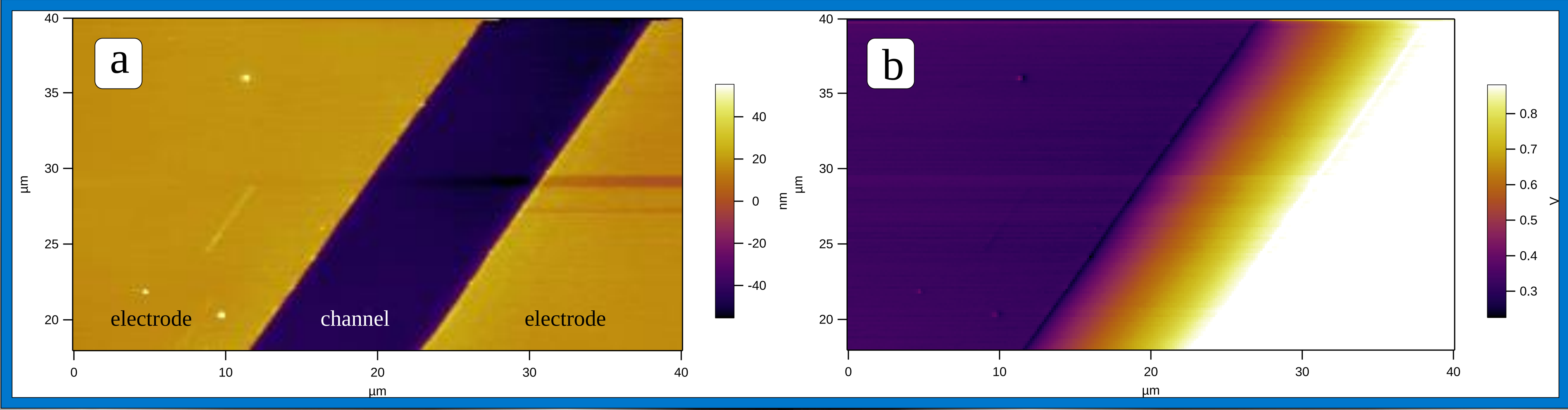

Figure 3. Example height (a) and potential (b) scans of a working field effect transistor device with a P3HT channel. The x and y scale are given on the outside of the scan, while quantitative height information given by the colour is described in the colour bar on the right of the scan. The gap between electrodes is 10 µm,(a) shows the electrode height is 50nm and (b) shows the device is functioning with a source-drain difference of 0.7V.

Time-resolved Kelvin Probe Force Microscopy

KPFM, while powerful, is too slow to catch trapping and de-trapping events, and measures steady-state conditions. We developed a time-resolved KPFM (tr-KPFM) technique, which focuses on how potential changes with time on the millisecond scale at user-chosen locations on the studied material.

We use a back-gated field effect transistor geometry to study the material. (Fig. 4(a)); these data show P3HT, an organic semiconductor and optoelectronic material commonly used in solar-cell research. We constructed a custom measurement cell to make the electrical connections for the measurement, and to protect the samples by maintaining a dry nitrogen environment; the bottom of this cell is show in Fig. 4(b). P3HT is a hole-carrier material, and the gate electrode can control the amount of current flowing through the active device (Fig. 4(c)). As the gate modulates the number of charge carriers in the P3HT, these charges can move in and out of trap states. We ground the electrodes during our tr-KPFM measurements, allowing us to measure charges being injected into or extracted from the film.

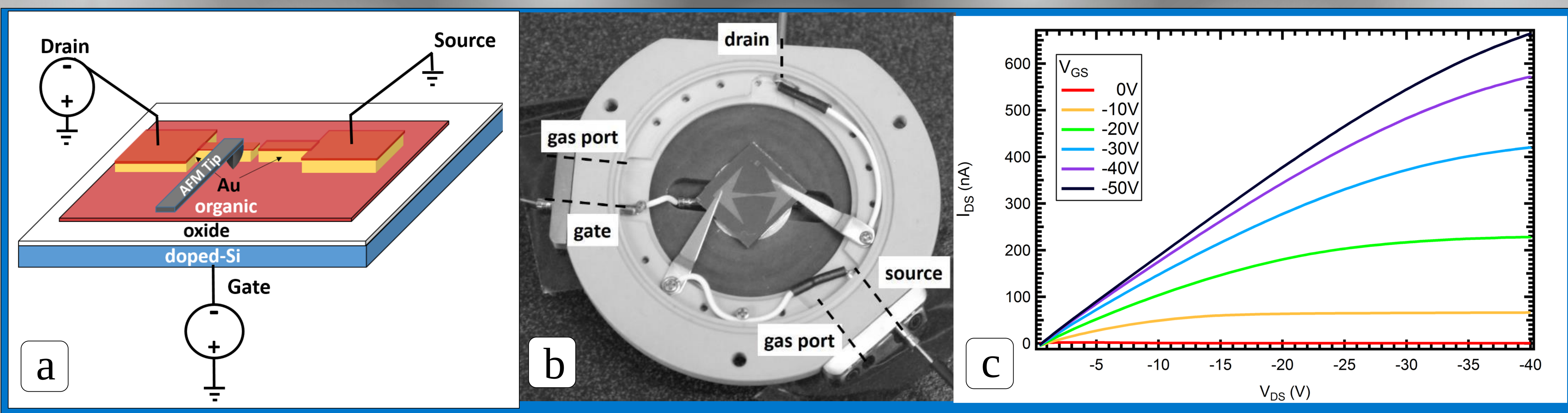

Figure 4. (a) Schematic of the FET setup. Current flows through the organic semiconductor (P3HT) between the source and drain. The gate is used to modulate the current, as shown in (c). The probe tip is shown where it will be used in the tr-KPFM measurements. (b) tr-KPFM requires updates to the microscope's hardware; shown here is the bottom of the custom measurement cell used to make the measurements. The chip is held in place via a magnetic chuck which also serves as the electrical contact between the gate and the electrical feedthrough leading out of the cell. Two clips contact the touchpads for the source and drain. Two other ports serve as the gas inlet and outlet, for continually purging the cell with N_2 to preserve the device. The scanning tip holder is mounted in a flexible membrane (not shown) to seal the cell. (c) The operation of the P3HT FET. The amount of charge carries present in the film, and therefore the amount of current flowing, is controlled by the gate voltage. Here the hole-carrier character of the P3HT is shown, as hole carriers are attracted by negative gates, increasing the current flow.

Measurement Results

Fig. 5 shows the result of the tr-KPFM measurement on a P3HT device. The dashed line (right axis) shows the applied gate voltage. The red curve (left axis) is the measured potential. $\bar{\tau}$ is a fit parameter representing the rate the charges move through the film, revealing that charges can easily move into available states in the film [(1) & (4)], but take longer to exit the film due to the trap states [(2) & (3)].

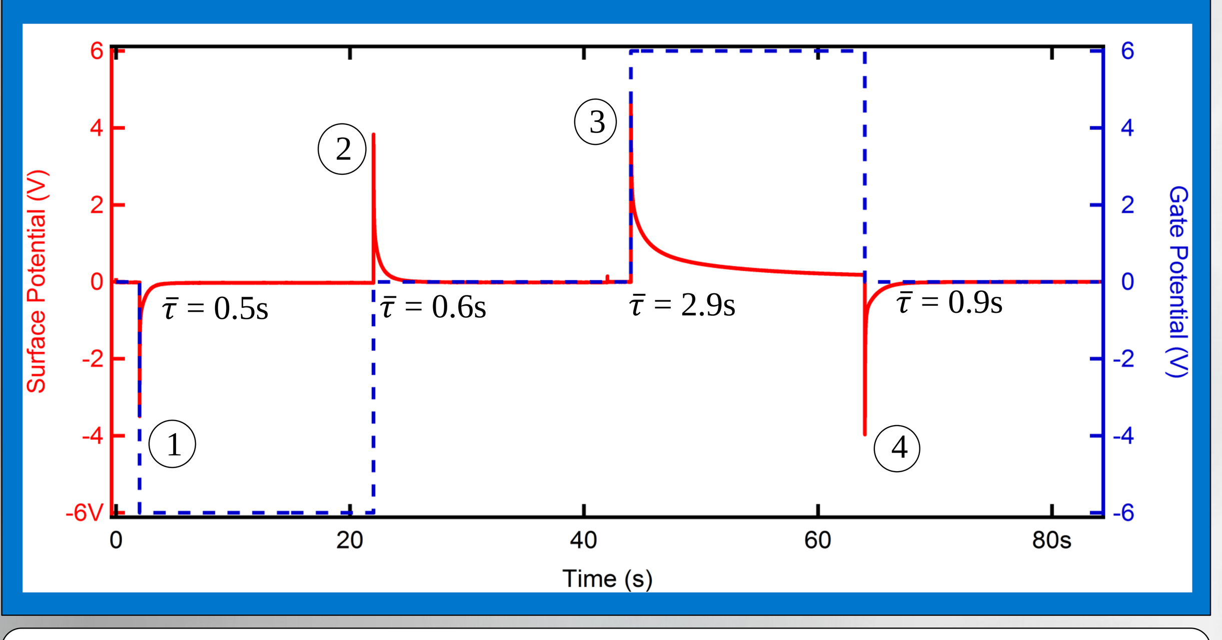

Figure 5. tr-KPFM of P3HT. (1) Under the influence of the negative gate, the tip measures a negative potential. That potential draws holes into the film, ultimately screening the tip. (2) The gate is switched off, now there is a net positive potential from the excess holes, which eventually go to ground. (3) The positive gate results in a positive peak which is screened as holes leave the film. (4) Finally, there is a negative peak as the gate is shut off because there are too few holes in the film, and the potential returns to neutral as holes enter the film.

Expanding Scope

Having shown the capability to perform position specific measurements sensitive to trap states, we are now working on not only refining the technique and applying it to new materials, but developing new metrics as well. Fig. 6 shows one such metric: position-dependent mobility measurements.

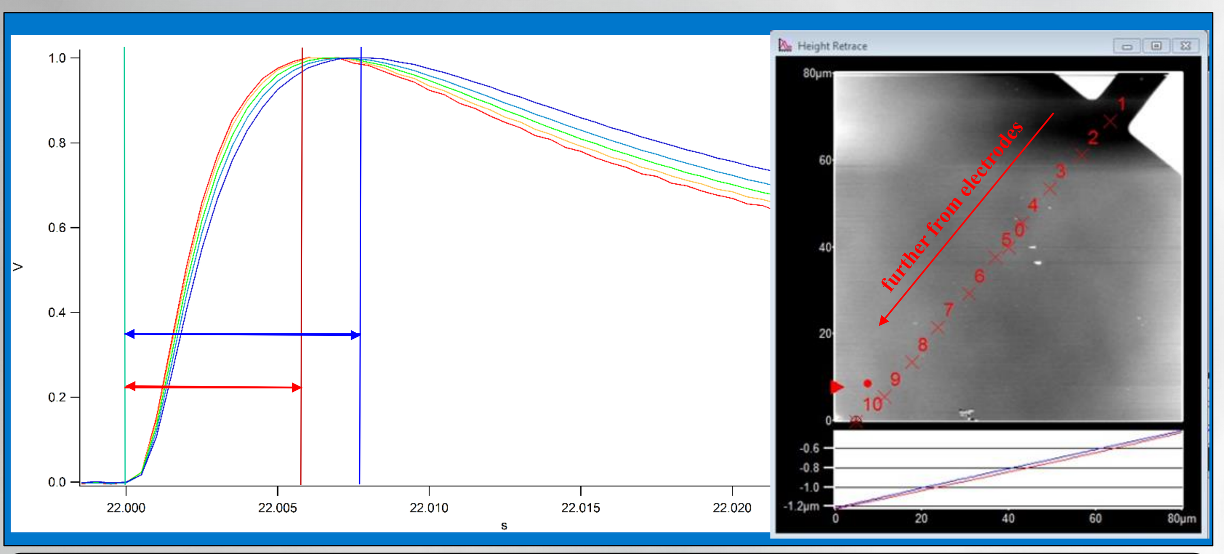

Figure 6. As we take tr-KPFM measurements further from the electrodes, it is clear the time for the potential to peak changes. The time-to-peak depends on the charge mobility, as it takes time for the charges to reach the tip and begin screening – this is a new way to measure mobility.

Acknowledgements

This work was supported by the National Science Foundation (CAREER Award DMR-0955348, and DMR-1708970), and all authors appreciate the support received via the NSF funded Center for Hierarchical Manufacturing (CMMI-1025020).