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Electron trapping and inversion layer formation in photoexcited metal-insulator-poly(3-hexylthiophene) capacitors

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Photocapacitance measurements are reported on metal-insulator-semiconductor (MIS) capacitors employing polyimide (PI) or polysilsesquioxane (PSQ) as the gate insulator and poly(3-hexylthiophene) as the active semiconductor. By stressing devices into depletion while simultaneously irradiating with light of energy exceeding the semiconductor band gap, photogenerated electrons become trapped at the insulator/semiconductor interface or possibly in bulk insulator states. Additionally for the PSQ device, evidence is provided for the formation of a photogenerated inversion layer at the interface. The time dependence of electron detrapping in the PI case is similar to that observed for accumulation stress instability in organic MIS devices. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2382727]

Understanding and minimizing the effects of localized states at the insulator-semiconductor interface is crucial for the development of organic electronics. For example, the demonstration of *n*-channel behavior in *p*-type semiconducting polymer transistors[1] was possible only after careful preparation of the insulator surface to minimize the effects of minority carrier (electron) traps, e.g., –OH moieties at the insulator-semiconductor interface. Furthermore, there is evidence[2] that the threshold voltage instability reported by several authors[3–7] may be caused by water trapped at the interface. Although these findings were made using transistor structures, the silicon literature[8–11] suggests that more detailed information can be obtained from studies of metal-insulator-semiconductor (MIS) capacitors. Surprisingly, it is only recently[12,13] that such structures have been used to probe directly the presence of interface states using the complex admittance measurements advocated by Nicollian and Goetzberger (NG).[8]

However, the NG method probes only the interaction of *majority* carriers with interface states, since *minority* carriers make a negligible contribution to the overall response. This situation may be reversed by driving the device into depletion and irradiating with photons of energy greater than the semiconductor band gap.[9] In silicon, the combination of bias voltage and irradiation shifts the electron quasi-Fermi-level close to the conduction band edge while having little effect on the hole Fermi level. Although the localized nature of carrier transport in semiconducting polymers[14,15] may militate against the application of a strictly band energy approach, nevertheless the general principles will still be valid. Illuminating semiconducting polymers with light of energy greater than the optical band gap initially generates bound electron-hole pairs (excitons) some fraction of which escape geminate recombination in the presence of an electric field yielding free holes and electrons. The field-induced drift of such carriers leads to photocurrent and photovoltaic effects, for example, in the depletion region of polymer Schottky diodes.[16]

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Here we report on a photocapacitance study of polymer MIS capacitors in depletion. The results clearly demonstrate the presence of minority electron trapping states at the insulator-semiconductor interface (or in the bulk insulator). Such states have also been implicated in the photocurrent response of rubrene[17] MIS field effect transistors (MISFETs). Evidence is also presented for the formation of an optically induced inversion layer at the semiconductor-insulator interface analogous to charge-coupled device detectors where photoinduced electrons form the signal package.[18]

For the study we fabricated MIS capacitors on indium tin oxide (ITO) coated glass, incorporating a polyimide (PI) or polysilsesquioxane (PSQ) layer as the gate insulator and regioregular poly(3-hexylthiophene) (P3HT) as the active semiconductor layer following our previous methods.[12,13] The top electrode was an evaporated gold contact surrounded by a concentric guard ring to minimize lateral current effects. After preparation, the devices were heated under vacuum to 90 °C to remove adventitious dopants, e.g., atmospheric oxygen[19] from the P3HT and any residual moisture from the insulators. Device capacitance was measured, without breaking the vacuum, using an HP4284A LCR meter. Voltages were applied to the ITO electrode, with the detection circuitry connected to the circular gold electrode and the guard ring grounded. The signal frequency was kept to 1 kHz or less to avoid the dispersion due to limitations on majority carrier transport in the bulk semiconductor (Maxwell-Wagner effect).[12,13] The device was illuminated through the ITO electrode but confined to the region defined by the gold electrode. Monochromatic light was provided by a xenon discharge lamp and monochromator (Triax 320, J Y Horiba).

Capacitance-voltage (C-V) curves for the PI device, obtained at 1 kHz by sweeping the bias voltage from 0 to +40 V under illumination with light of different wavelengths, are given in Fig. 1. The curve corresponding to the longest wavelength, $\lambda = 800$ nm, was indistinguishable from that obtained in the dark and is similar to previously published results.[13] Below +10 V, the device is in accumulation and the measured capacitance is that of the PI insulator. Above ~10 V, the semiconductor starts to deplete. Between 14 and 24 V the Mott-Schottky plot, C^{-2} vs V, is

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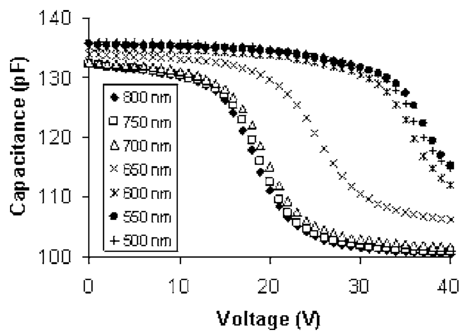

FIG. 1. Room-temperature *C-V* plots obtained for a PI device at 1 kHz while illuminating with light of constant intensity but different wavelengths.

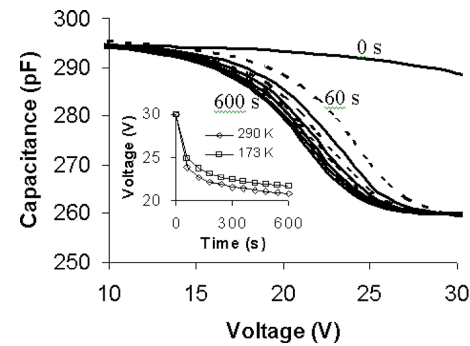

FIG. 2. Successive *C-V* plots obtained for a PI device every 60 s at 290 K after terminating the illumination. Each plot took 6 s to accumulate. The inset shows the time dependence of the voltage corresponding to $C=275$ pF at 290 and 173 K.

linear (not shown), yielding a doping density of $\sim 1.7\times 10^{16}$ cm^{-3} in the P3HT, consistent with previous reports.[12,13] Noting that the measured capacitance is the series sum of the insulator and depletion capacitances, we estimate a depletion capacitance of ~430 pF at 40 V, corresponding to a depletion width of ~170 nm and close to the thickness of the semiconductor layer. Thus for $V>40$ V, the semiconductor is fully depleted. Inversion may be ruled out since the capacitance asymptotes to the same bias-independent value measured at 1 MHz when majority carriers are unable to follow the signal frequency and the semiconductor behaves as an insulator. From the shift in the dark *C-V* plot, ~10 V, we infer that $\sim 3\times 10^{11}$ cm^{-2} electrons are trapped at the PI/P3HT interface.

Little change in the *C-V* curves was observed for wavelengths down to $\lambda=700$ nm, in contrast to shifts of ~10 V observed by Meijer *et al.*[20] in a P3HT MIS capacitor under a partial pressure of oxygen. This confirms the effectiveness of our procedures in removing adventitious oxygen dopant from our device.

A significant shift (~25 V) to more positive voltages is observed though when photon energies exceed the optical absorption edge of P3HT, i.e., for $\lambda<650$ nm, consistent with the trapping of $\sim 8\times 10^{11}$ cm^{-2} of additional minority electrons in the interface or bulk insulator states. Contrary to the results here, Meijer *et al.*[20] found that the shift in threshold voltage peaked in the range of 600–700 nm. However, their devices were illuminated through the bulk semiconductor which acted as an internal filter.[21]

Bias stress at elevated temperature can also lead to large threshold voltage shifts in the PI capacitors.[13] At room temperature, such shifts relaxed slowly over many hours. In contrast, on switching off the light, most of the optically induced shift observed here relaxed within a few minutes (Fig. 2), where successive *C-V* plots shift back smoothly with little change of shape. The time dependence of the relaxation was obtained by noting the voltage corresponding to 275 pF in each of the plots. This is given in the inset together with similar results obtained at 173 K. The relaxation appears to be composed of a fast and a slow component and occurs over several minutes similar to earlier measurements at 77 K.[22]

In such measurements, however, band bending in the semiconductor changes with time and certainly during the voltage scans, thereby affecting detrapping dynamics. In a second series of experiments, therefore, we maintained a constant depletion width and degree of band bending by utilizing a feedback arrangement to track the voltage necessary to maintain a constant, preset capacitance. The plot in Fig. 3 for the PI device was obtained by first optically charging interface states with a voltage of 40 V applied, then tracking a capacitance of 265 pF which is well into depletion. The relaxation of the threshold voltage, $V(t)$, as a result of electron detrapping is now seen to be part of a general logarithmic decay described by $V_T(t)=R\log(1+t/t_0)$ where R and t_0 are characteristic constants. A similar logarithmic dependence was observed in the accumulation-bias stress instability of V_T in sexithiophene thin film transistors[23] and in amorphous silicon transistors when charge trapping was dominant.[24] In the latter case, the logarithmic dependence was attributed to the increasing difficulty of electron tunneling into spatially deeper insulator states as traps close to the interface became occupied.

These same effects should manifest themselves in polymer transistors and indeed large photoinduced threshold voltage shifts have been observed in organic MISFETs.[17,25,26] Optically induced current transients following pulsed illumination of P3HT MISFETs show a similar decay to that seen in Fig. 2 (inset).[21] Significantly, the relaxation of gate-bias-induced stress in pentacene transistors[27] similarly shows a rapid decay for ~7 s followed by a much slower decay with a time constant between 120 and 150 s. Furthermore, the decrease in drain current as a result of accumulation-bias stress in polyfluorene MISFETs operating in the linear regime is characterized by a fast and a slow component.[28] Interestingly, at longer times (>100 s) the latter asymptotes to a logarithmic time dependence, suggesting a common origin with the behavior observed here.

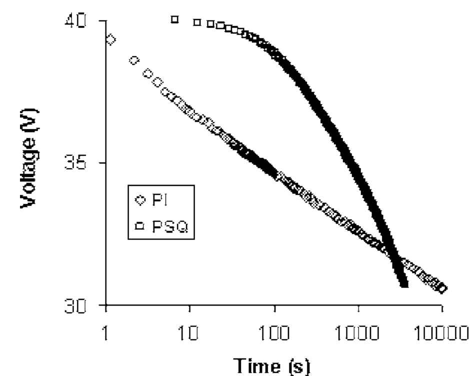

FIG. 3. Time dependence of the voltage required to maintain constant capacitances of 265 pF (PI) and 145 pF (PSQ) upon ceasing the photoexcitation.

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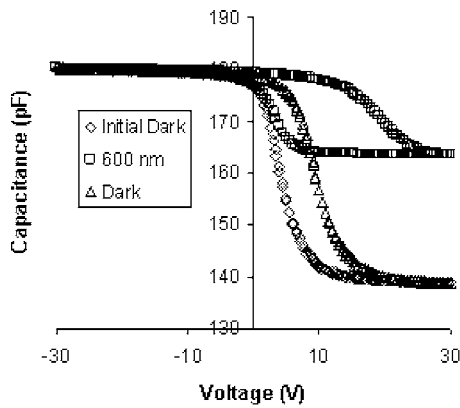

FIG. 4. Room-temperature *C-V* plots obtained for the PSQ device at 120 Hz (i) initially in the dark, (ii) under 600 nm illumination showing strong anticlockwise hysteresis, and (iii) subsequently in the dark showing a residual shift in threshold voltage. For the two dark plots the forward and reverse sweeps coincide.

The large voltage shift seen in our devices is likely to be related to the electronegative character of polyimide[29] which is expected to lead to strong electron trapping. The PSQ/P3HT interface, on the other hand, is more stable when subjected to depletion stress, suggesting a reduced tendency for electron trapping. The difference in behavior when irradiated (Fig. 4) is in marked contrast to that of PI. The initial dark *C-V* plot displays classical behavior, with full depletion of the bulk semiconductor setting in above 10 V. No hysteresis was observed on the reverse sweep. Upon illumination, the minimum capacitance on the forward sweep increased from ~140 to ~160 pF, consistent with the formation of an inversion layer. In subsidiary experiments, we have ruled out photoconduction in the insulator as the reason for the collapse of the depletion region.[30] On the reverse sweep, strong anticlockwise hysteresis occurred due to a fraction of the free electrons in the inversion layer becoming trapped either at the PSQ/P3HT interface or in the PSQ itself. Immediately upon terminating the illumination, the inversion layer is lost and a *C-V* plot obtained shortly thereafter is identical to that obtained preirradiation, albeit shifted by ~5 V to more positive voltages, consistent with $\sim 2 \times 10^{11}$ residual electrons per cm^2 trapped at the interface. Over the next 24 h further relaxation towards the initial dark curve was seen.

When irradiated for several minutes the threshold voltage shift for PSQ is comparable to that seen in PI. However, the resulting relaxation of the threshold voltage shift is initially much slower than observed for PI (Fig. 3) but becomes more rapid at longer times, indicative of different relaxation mechanisms in the two cases.

In conclusion, we have shown that photocapacitance measurements can be used for investigating the behavior of minority carriers at the semiconductor-insulator interface. The two insulator systems explored here show strong electron trapping (PI) and inversion layer formation (PSQ). The relaxation of the photoinduced threshold voltage shift in the PI devices and in work reported by others has a logarithmic dependence on time which is similar to that reported for accumulation-bias stress, suggesting a similar origin. The PSQ devices, on the other hand, show a very different time dependence, indicating different trapping dynamics. Understanding such effects is essential for the development of *n*-channel and ambipolar thin film transistors as well as organic phototransistors where the observed optical gain is obtained largely via the photoinduced shift in threshold voltage. We are now undertaking detailed experiments to identify the origin and nature of the electron traps.

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