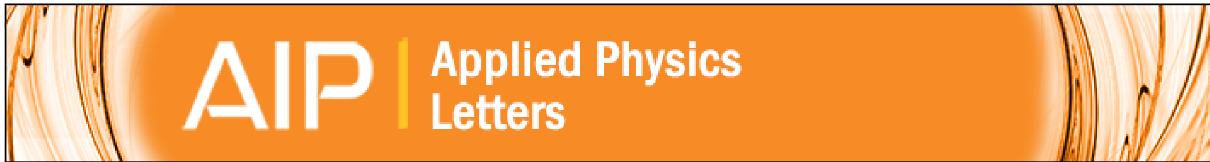

Voltage- and light-induced hysteresis effects at the high- k dielectric—poly(3-hexylthiophene) interface

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Voltage- and light-induced hysteresis effects at the high-*k* dielectric—poly(3-hexylthiophene) interface

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Capacitance-voltage (*C-V*) measurements have been undertaken on metal-insulator-semiconductor capacitors formed from atomic-layer-deposited films of aluminium titanium oxide as the insulator and poly(3-hexylthiophene) as the insulator. Upon cycling from −30 to +30 V in the dark, the *C-V* plots show large, temperature-dependent, reversible shifts in the flatband voltage to more negative voltages consistent with reversible, shallow hole trapping at or near the insulator-semiconductor interface. When illuminated with photons of energy exceeding the polymer band gap, even larger shifts to positive voltages are observed accompanied by inversion layer formation. This latter effect has potential applications in optical sensing. © *2007 American Institute of Physics*.
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The gate dielectric of organic metal-insulator-semiconductor field effect transistors (MISFETs) has received much attention recently. Evidence has been presented[1] that, insofar as amorphous semiconducting polymers are concerned, higher mobilities are obtained using low-*k* polymers (dielectric constant of ~2) as the dielectric. The situation is not so clear for inorganic insulators. In silicon technology high-*k* inorganic dielectrics are under intense investigation:[2] high dielectric constant leads to lower threshold voltages and reduced gate leakage for the same film thickness. These same attributes are also needed in organic electronics, and a number of reports on the use of such materials are reviewed by Veres *et al.*[1] Of interest here are the results presented by Swenson *et al.*[3] where the low mobility in their high-*k* devices arose from bulk traps in the active semiconducting polymer, F8T2, rather than from interaction with interface traps known to be present in Al_2O_3 and TiO_2 gate insulators. Bulk semiconductor traps can arise from several sources, e.g., polymer morphology in the neighborhood of the interface which may be influenced by the topography of the insulator surface. Atomic layer deposition (ALD) is known to produce high quality thin films, and careful control of deposition conditions allows mixed oxides to be deposited on various substrates. In the following we report *C-V* measurements on MIS capacitors formed from semiconducting poly(3-hexylthiophene) (P3HT) and transparent aluminium titanium oxide (ATO), a material being considered as the gate insulator for complementary metal-oxide semiconductor technology.[4] Measurements carried out both in the dark and under illumination with photons of energy greater than the semiconductor band gap confirm that shallow hole and electron traps exist at the ATO/P3HT interface (including states in the insulator close to the interface). In the dark, holes reversibly access these states under accumulation voltages causing a shift of the flatband voltage to large negative values. Under illumination, reversible electron trapping occurs but more importantly an inversion layer forms at the interface, similar to that observed when polysilsesquioxane was used as the gate insulator.[5–7] The concomitant change in device capacitance suggests that this effect could be harnessed in optical detection.

The substrates used in the present work (Planar Systems Inc, Finland) were composed of indium tin oxide (ITO)-coated glass (8 Ω/sq) onto which ~220 nm of ATO was deposited by ALD. These were cleaned by ultrasonication in a mild detergent solution, rinsed in ultrapure water and then ethanol, followed by drying using a hot-air blower. Subsequently, a P3HT film, ~100 nm thick, was spin coated onto the substrates from a chloroform solution (1 mg/ml). The capacitors were completed by evaporating a circular gold top contact, 1.1 mm in diameter, through a shadow mask onto the semiconductor. The samples were annealed at ~100 °C for 1 h under vacuum to remove any volatile impurities such as solvent residue and atmospheric moisture and oxygen. Capacitance measurements were made, without breaking the vacuum, using an HP4284A *LCR* meter with voltages applied to the ITO electrode. Devices were illuminated with monochromatic light through the ITO electrode, following our previously reported procedures.[7]

Figure 1 shows the *C-V* plots obtained at 130 Hz for a range of temperatures while cycling the gate voltage from −30 to +30 V and back to −30 V at a rate of 0.5 V/s. At the highest negative voltages the devices are in accumulation, yielding the insulator capacitance $C_I \sim 800$ pF (84.2 nF/cm^2) for the ATO, corresponding to a dielectric constant $\varepsilon \sim 21$ intermediate between those of Al_2O_3 ($\varepsilon = 8.4$) and TiO_2 ($\varepsilon = 41$). When measured using gold electrodes only, the dielectric constant of the ATO film was estimated to be ~16 and close to the value (~14) reported by Fortunato *et al.*[8] The higher value obtained from the MIS structure here is due to significant lateral conduction through the P3HT layer[9] at the low measurement frequency used here, which effectively increases the device area in the absence of a guard ring.

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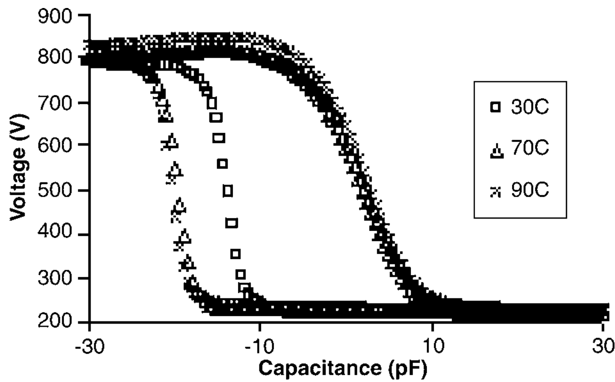

FIG. 1. *C-V* curves measured at 30, 70, and 90 °C during voltage sweeps starting at −30 V. The anticlockwise hysteresis here is caused by reversible hole trapping in interface states.

During the forward sweep toward positive voltages, the flatband voltage V_{FB} lies in the range from −15 to −20 V. From the relation $Q=C_I\Delta V_{FB}/A$, where ΔV_{FB} is the shift in the flatband voltage (V_{FB} is expected to be close to zero in an ideal device) and A the device area, the shift corresponds to $\sim 10^{13}$ cm^{-2} of holes trapped at the semiconductor-insulator interface. Increasing the device temperature (Fig. 1) and the hold time at ±30 V from 0 to 30 min (Fig. 2) cause further shifts to more negative voltages. This suggests that excitation of holes from the accumulation layer to interface (or insulator) states is a thermally activated process.

When the applied voltage is more positive than V_{FB} the device begins to deplete, the capacitance falling to a constant value. Over most of the depletion regime, the data followed the Mott-Schottky equation,[10] i.e.,

$$C/C_I=\left(1+\frac{2C_I^2}{A^2 q\varepsilon_S\varepsilon_0 N_A}(V-V_{FB})\right)^{-1/2}, \quad (1)$$

where q is the electronic charge, ε_S the dielectric constant of P3HT (∼3.5), ε_0 the permittivity of free space, and N_A the doping density. The results obtained for several devices under different sweep conditions and for temperatures in the range of 20–90 °C gave $3\times 10^{16} < N_A < 8\times 10^{16}$ cm^{-3}. Noting that the effective device area may be some 30% larger than assumed because of lateral conduction effects, so that the doping densities are overestimated by about 60%, then the values of N_A are similar to those in our previous reports.[5,6,11] From the minimum capacitance $C_{\min}=C_IC_D/(C_I+C_D)$ we estimate a depletion capacitance $C_D \sim 308$ pF in the P3HT corresponding to a depletion layer width of ∼95 nm, consistent with the film thickness of ∼100 nm estimated by atomic force microscopy. We conclude, therefore, that the minimum capacitance corresponds to complete depletion of the semiconductor, as observed in our earlier work.[5–7]

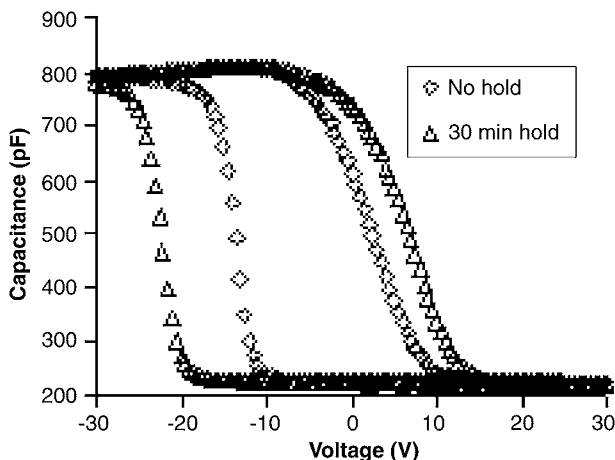

FIG. 2. Room-temperature *C-V* curves showing the effect of changing the hold time at ±30 V from 0 to 30 min.

On the reverse sweep from +30 to −30 V, a strong anticlockwise hysteresis is observed with the flatband voltage now seen at around −3 V. Furthermore, the slope of the *C-V* plot in the transition region is much lower but, interestingly, the return curve is almost independent of temperature and begins to rise at ∼10 V.

A similar hysteresis effect, confined mainly to negative voltages as seen here, was also reported recently by Yun *et al.*[12] for metal-insulator-semiconductor capacitors formed from a polyfluorene-based polymer spin coated onto Al_2O_3. As in their case, we observed a decrease of the "accumulation" capacitance with increasing signal frequency. Unlike Yun *et al.*, though, who suggested interface states as the origin, we[5–7] and others[13] attributed this to a Maxwell-Wagner-type dispersion arising from the inability of majority holes in the P3HT to follow the applied signal at the higher frequencies.

Citing earlier work,[14] it was assumed by Brown *et al.*[15] that the anticlockwise hysteresis in their P3HT-based MIS capacitors was caused by the slow migration of dopant ions. From Eq. (1) it is seen that any change in doping density will be reflected in the *C-V* plot. While dopant migration may occur, it cannot explain the present results. Firstly, the reduced slope on the reverse sweep would suggest a significant increase in doping density *throughout* the semiconductor. Secondly, the migration of dopant ions is expected to be a thermally activated process but, as seen in Fig. 1, temperature has little effect on the reverse sweep. Thirdly, introducing a hold time of 30 min at the extremes of the voltage sweep increases the width of the hysteresis loop but has little effect on the *shape* of the *C-V* plot obtained during the reverse sweep. We conclude, therefore, that since the lower part of the return curve is shifted to positive voltages, the reduced slope is likely to be caused by fast detrapping of electrons from interface states[15] during the return voltage sweep. Since V_{FB} is now close to zero, we further conclude that virtually all the holes trapped at the interface were either released or neutralized by electrons when depletion voltages were applied.

To confirm the presence of electron trapping states, the *C-V* plots were remeasured while illuminating the devices. When the photon energy exceeds the semiconductor band gap, bound electron-hole pairs (excitons) are formed, some of which will escape geminate recombination in the electric field of the depletion region.[6,7,16] Therefore, when illuminated with light of wavelength shorter than ∼650 nm, the optical absorption edge of P3HT, free electrons are expected to accumulate at the insulator/semiconductor interface. This same effect is utilized for imaging in charge-coupled devices. At sufficiently high free-electron concentrations, an inversion layer may form accompanied by a decrease in the depletion width and an increase in the depletion layer capacitance. If a fraction of the free electrons become trapped in interface states, a shift of V_{FB} to more positive voltages will also occur. Both effects are observed in Fig. 3. The minimum ca-

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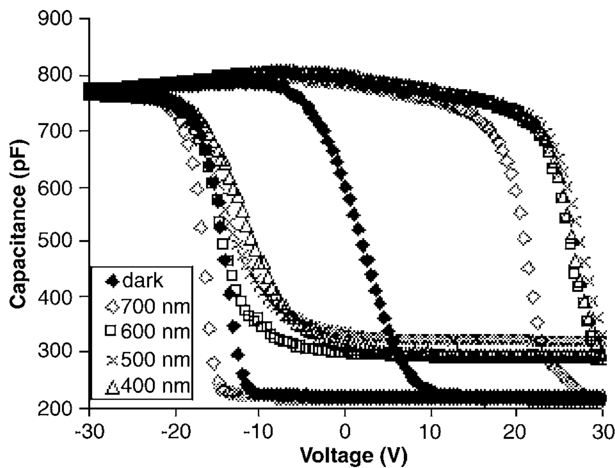

FIG. 3. Effect of photoirradiation on the room-temperature *C-V* curves. For wavelengths ≤600 nm the presence of both free and trapped electrons at the interface is evidenced by an increase in the minimum capacitance and a positive shift in flatband voltage, respectively.

pacitance increases from 217 to 290–330 pF, depending on wavelength, with the largest increase occurring at 500 nm and corresponds to a reduction, Δd=30–40 nm in the depletion width. The free-electron concentration at the interface, n_f, is exactly balanced by a reduction in space charge in the depletion region. Thus, $n_f = N_A \Delta d = (2-3)\times 10^{11}$ e/cm^2. From the flatband voltage shift $\Delta V_{FB} \sim 25$ V, we estimate that $n_T = (C_I/A)\Delta V_{FB} = 1.3\times 10^{13}$ e/cm^2 are trapped in interface (or bulk insulator) states.

Illumination with 700 nm photons, on the other hand, causes a shift in the flatband voltage, with no evidence for accumulation of free electrons. At this wavelength, absorption is weak and the exciton generation rate near the interface is too low to compensate for the loss of electrons to interface states or indeed to leakage through the insulator or along the semiconductor/insulator interface.

Figure 4 shows the temporal response of the MIS capacitor to illumination with 500 nm light. Within the time scale of the capacitance measurement, ~0.5 s, both the increase and decrease in capacitance are virtually instantaneous. However, for about 300 s after the initial sharp increase, the capacitance decreases slowly presumably caused by a loss of free electrons to trap states. The tail in the optical response when the light is switched off is then explained by the release of these trapped electrons. The rapid reversibility of the optical response here is in sharp contrast to the long-lived, photoinduced shift in threshold voltage in rubrene MISFETs (Ref. 16) and suggests that the ATO/P3HT interface is characterized by much shallower electron traps than the parylene/rubrene interface.

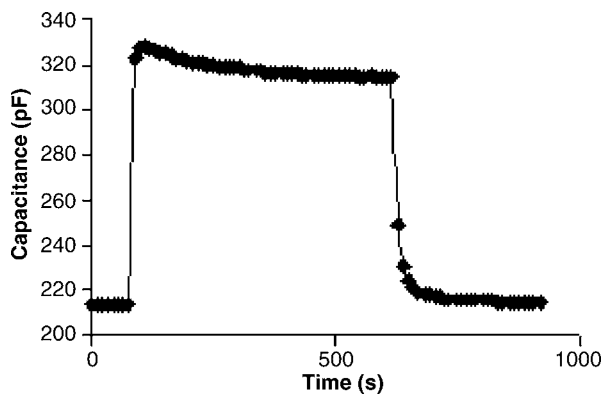

FIG. 4. Temporal response of the minimum capacitance when the device is exposed to 500 nm irradiation.

In conclusion, we have demonstrated that P3HT MIS capacitors formed on the high-*k* dielectric ATO are highly unstable in accumulation owing to a high concentration of hole traps at the insulator-semiconductor interface or in near-interface insulator bulk states. Unless a means is found to passivate these states, ATO is unlikely to be a good material for organic MISFETs. However, in depletion in the dark, the devices are stable and respond rapidly and reversibly to illumination by photons of energy greater than the semiconductor band gap, suggesting potential applications in optical sensors.

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