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Photon-assisted capacitance–voltage study of organic metal–insulator–semiconductor capacitors

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ABSTRACT

The results are reported of a detailed investigation into the photoinduced changes that occur in the capacitance–voltage (C–V) response of an organic metal–insulator–semiconductor (MIS) capacitor based on the organic semiconductor poly(3-hexylthiophene), P3HT. During the forward voltage sweep, the device is driven into deep depletion but stabilizes at a voltage-independent minimum capacitance, C_{min}, whose value depends on photon energy, light intensity and voltage ramp rate. On reversing the voltage sweep, strong hysteresis is observed owing to a positive shift in the flatband voltage, V_{FB}, of the device. A theoretical quasi-static model is developed in which it is assumed that electrons photogenerated in the semiconductor depletion region escape geminate recombination following the Onsager model. These electrons then drift to the P3HT/insulator interface where they become deeply trapped thus effecting a positive shift in V_{FB}. By choosing appropriate values for the only disposable parameter in the model, an excellent fit is obtained to the experimental C_{min}, from which we extract values for the zero-field quantum yield of photoelectrons in P3HT that are of similar magnitude, 10^{-5} to 10^{-3}, to those previously deduced for π-conjugated polymers from photoconduction measurements. From the observed hysteresis we deduce that the interfacial electron trap density probably exceeds 10^{16} m^{-2}. Evidence is presented suggesting that the ratio of free to trapped electrons at the interface depends on the insulator used for fabricating the device.

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1. Introduction

The capacitance–voltage (C–V) measurement, the so-called Terman method [1], has proved particularly useful for characterising the silicon/silicon dioxide interface in metal–oxide–semiconductor (MOS) technology. However, it has been recognized for many years that when applied to wide bandgap semiconductor materials the method is severely limited by the very low rate at which minority carriers are generated thermally – it may take years to generate thermally an inversion layer at the semiconductor–insulator interface. Consequently, during a C–V measurement on metal–insulator–semiconductor (MIS) capacitors based on wide bandgap materials, the inversion plateau is not observed. Rather, the capacitance continues to decrease as the device is driven into deep depletion. However, it has been shown that this limitation may be overcome in materials such as gallium nitride [2–5] and silicon carbide [6] by increasing the rate of minority carrier generation through optical stimulation with photons of energy greater than the semiconductor bandgap. Even sub-bandgap light has been used, in which case band-to-band generation of electron–hole pairs in the semiconductor is precluded so that carrier generation presumably occurred from trap states [7].

Not surprisingly, since organic semiconductors tend to have relatively large bandgaps, 2–3 eV, a similar limitation is encountered in C–V measurements on organic MIS capacitors [8–10]. C–V plots measured in the dark do not display the inversion plateau but continue to decrease monotonically as the applied voltage drives the device into

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deep depletion. For sufficiently high voltages and a sufficiently thin semiconductor, a minimum capacitance plateau will be observed eventually when the depletion region extends throughout the semiconductor. Under illumination, though, a minimum capacitance plateau is observed well before full depletion is attained while strong hysteresis occurs on the return voltage sweep. Subsequent *C–V* plots obtained in the dark exhibit a long-lived shift in flatband voltage, V_{FB}, indicative of deep trapping at the insulator–semiconductor interface. Similar hysteresis and shifts in V_{FB} are observed also in the transfer characteristics of organic thin film transistors (OTFTs) [11–13].

These effects occur when devices based on *p*-type materials are illuminated while biased into depletion, so that optically-induced free electrons escaping recombination drift to and become trapped at the semiconductor/insulator interface or in insulator states. Such trapping has been implicated in threshold voltage instability in OTFTs [14–16]. On the other hand, long-lived charge trapping may be used to realise charge storage memory transistors [17]. It is important, therefore, to develop methods for investigating and understanding the mechanisms causing these effects. The photon-assisted *C–V* measurement on MIS capacitors is such a method since it avoids the added complexity arising from orthogonal current flow through the accumulation channel of an OTFT and also the parasitic source-drain photocurrent when illuminated.

In the following, we report the results of a detailed investigation into the photocapacitance effect in solution-processed organic MIS capacitors based on poly(3-hexylthiophene), P3HT, as the semiconductor and UV-cured photoresist as the insulator. We also develop a quasi-static model which, although not complete, explains the main features observed experimentally. Interestingly, the model shows that a minimum capacitance plateau in the photocapacitance–voltage plot can arise simply from deep trapping at the semiconductor–insulator interface. At a particular trapping rate, the concomitant shift of the flatband voltage tracks the applied voltage sweep thus maintaining a constant capacitance without the need to invoke the presence of an inversion layer.

2. Experimental

MIS capacitors were formed on precleaned and dried indium tin oxide (ITO) coated glass slides to act as a common gate electrode. The insulating layer was prepared from SU8 2000.5 photoresist (Microchem Ltd.) diluted in the ratio 50:50 (v/v) in cyclopentanone and filtered through 0.2 μm PTFE filters. Spin-coating in a nitrogen atmosphere at a final speed of 2000 rpm, pre-curing at 95 °C for 1 min, followed by UV curing (in air) and a post-cure bake at 95 °C for 1 min and 200 °C for 30 min under nitrogen, yielded a smooth, uniform 194 nm thick film. Regio-regular poly(3-hexylthiophene), P3HT, from Sigma Aldrich was prepared as a 1% solution in anhydrous chloroform, filtered and spin-cast again under nitrogen onto the SU8 layer at 3000 rpm for 1 min then dried in a vacuum oven at 90 °C for 1 h yielding films ~100 nm thick film. The devices were completed by thermally evaporating a 50 nm gold film through a shadow mask to form an array of 2 mm diameter circular contacts. Completed devices were placed in a bespoke sample holder and mounted in a cryostat (Oxford Instruments Optistat Model DN-V) located in a darkroom to eliminate the effects of stray light.

The optical experiments were undertaken over the range 400–700 nm using a xenon discharge lamp coupled to a monochromator (Jobin Yvon Triax 320). Monochromatic light was transmitted into the cryostat through a quartz window and illuminated the devices through the ITO contact (Fig. 1a). Since the main effects are expected to be associated with the insulator/semiconductor interface this arrangement minimized the 'internal filter' effect that would otherwise arise from absorption in the P3HT film [8] when illuminated through the upper electrode. The power of the light incident on the devices was measured using a sensor (Anritsu model MA9411A1) and power meter (Anritsu modelM-9001A) and could be set approximately by adjusting the exit slit of the monochromator.

C–V plots and admittance spectra (capacitance–frequency, *C–f* and conductance–frequency, *G–f*) were

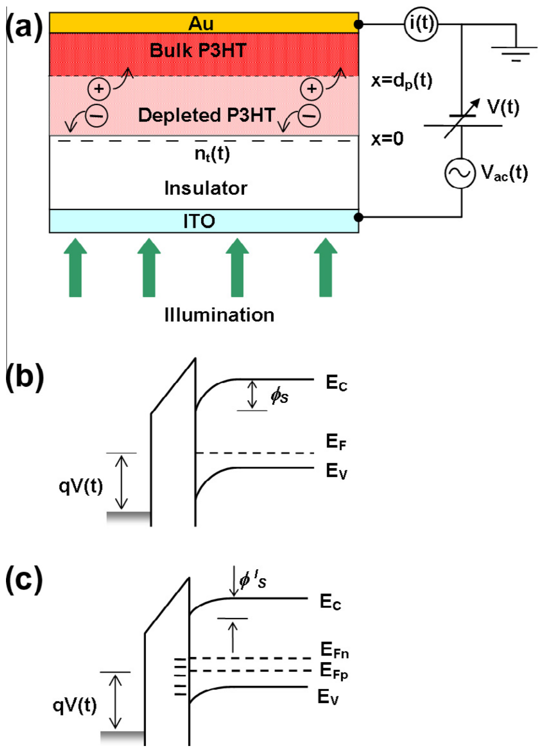

Fig. 1. (a) Diagram showing the measurement concept. Device capacitance is computed in the LCR meter from the ratio of the small signal current, $i(t)$ to the small signal voltage, $v_{ac}(t)$ while the applied bias, $V(t)$, sweeps the MIS capacitor from accumulation to depletion and back. Light enters the device through the ITO back contact and generates excitons in the P3HT depletion region which dissociate, releasing free electrons to become trapped at the interface. Also shown are classic band diagrams for a MIS capacitor based on a *p*-type semiconductor in quasi-steady state, (b) in the dark and (c) under illumination. In the latter case, illumination substantially increases the minority electron concentration thus splitting the hole and electron quasi Fermi levels, E_{Fp} and E_{Fn} respectively. Electrons occupy interface states up to E_{Fn}, their screening effect reducing the semiconductor surface potential from ϕ_S to ϕ^I_S.

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