Ionizing Radiation Detection Using Semiconducting Conjugated Polymers

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I. INTRODUCTION

There is currently an unprecedented expansion in the applications of polymer semiconductor technology: diodes (*incl* LEDs), transistors and even laser action have been demonstrated in this technology (see [1] and references therein) Liverpool Electrical Engineering & Electronics and Chemistry have been at the forefront of some of the most exciting developments [2,…,7]. The aim of this proposal was to develop substrate materials that would show sensitivity to ionizing radiation with a view to exploring the potential for finally developing cheap, large area arrays of sensors for use in particle physics and elsewhere. The first stage, to be addressed in this project was to attempt to build radiation detectors analogous to the silicon diode based detectors in common use in high energy physics. Whilst sensitivity to ionizing radiation in the form of X-rays using medical facilities with the University has been demonstrated, the technology will require further development to provide sensitivity to individual charged particles or short (ns - μs) bursts of light over the range of optical wavelengths.

II. DEVICE STRUCTURES STUDIED

Of the structures routinely produced for such measurements those with vertical Schottky contacts seemed to be more suitable for this application. In horizontal structures, due to larger distance between the contacts, higher voltage would be needed to maintain suitable electric field within the sample. In vertical structures, distances between contacts of up to a few microns can be readily achieved and high electric fields can be produced by applying a fairly low voltage across the sample. The Schottky barrier can even increase the field in the depletion layer when in reverse bias and the electric field can quickly and efficiently sweep any generated carriers towards the electrodes. Figure 1 shows the photograph of the test boxes designed and

produced in the Department of Physics for maintaining devices under an inert gas while testing with sources and light spots.

III. SUBSTRATE TECHNOLOGY

The key problem anticipated was in achieving a substrate material which demonstrated high bulk mobilities even after introducing the impurities which are needed to break the electron-hole bound excitons created by the passage of the ionizing radiation. Most of the research effort has been devoted to this issue resulting in several conference presentations [8,…,11].

The Schottky contacts are made of aluminium or titanium, and gold or indium-tin-oxide (ITO) is used to make the Ohmic contact electrode. The samples of fractionated sensing material was drop cast on metal coated glass substrates. Of the polyalkylthiophenes, P3OT was selected as offering high carrier mobility and good light sensitivity. After drying the polymer in the vacuum, the Ohmic electrode contacts were evaporated. Different materials were used to dope P3OT to enhance its carrier mobility and light sensitivity. The dopant materials studied were: 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ), bulkministerfluorine (C60), carbon single-walled nanotubes (SWNT), bormothiophene, and gold nanoparticles. These were mixed with different weight ratios with P3OT prior to casting to investigate the improvements due to the doping. Current versus voltage was measured in the forward and reverse direction using PC-controlled Kiethley electrometer and Kiethley programmable voltage source both with and without exposure to a calibrated light source. For X-ray measurements, the sample was reverse biased at 10 V through a load resistor of 10 MΩ and the current as a function of time was measured across the load resistor using a digital storage oscilloscope.

IV. RESULTS OF X-RAY AND LIGHT EXPOSURE

The *IV* characteristics of aluminium Schottky contact to P3HT is shown in Figure 2. There is an exponential rise at very low forward voltage. After that there is a drop in the rate of increase of the current with voltage probably due to an insulating interfacial layer on the aluminium surface. This so called ‘kink’ effect in the forward characteristics results in an increased turn-in voltage, which is one disadvantage of aluminium Schottky contacts. Titanium Schottky is preferred since it is less prone to oxidation and hence there is not a significant kink in the forward characteristics. Then the current follows the exponential trend again and becomes linear at higher voltages.

Polyalkylthiophenes are believed to become doped by oxygen when exposed to the air, deteriorating their performance. The *IV* characteristics of a P3HT/aluminium Schottky diode is shown in Figure 3, measured after fabrication and after one week exposure to air in a clean area. Both the forward and reverse currents are increased due to increase in doping concentration and consequently increase in conductivity. The sample then has been annealed at 150 °C in nitrogen atmosphere for 45 min. The kink effect has spread to higher voltages and the rectification has reduced as a result of increase in the thickness of insulating interfacial layer.

It has been shown that intentional doping of P3HT and other conjugated polymers could increase the carrier mobility as a result of increase in doping density. The *IV* characteristics of the samples with DDQ-doped P3HT as the semiconductor, with various ratios by weight are shown if Figure 4. By increasing the DDQ ratio, the kink effect spreads to higher voltages and some other kinks appear, the reverse current degrades with respect to the ideal, and rectification decreases significantly. It seems that DDQ has a strong influence on the interfacial layer. The forward characteristics are suggestive of a multi-trap space-charge limited current (SCLC).

The *IV* characteristics of DDQ-doped and undoped P3HT on aluminium and titanium back-planes show that the effect is specific to aluminium and no significant kink effect is observed in titanium samples.

Doping with DDQ increases the carrier mobility, however, it seems to have no effect on the sensitivity to light. The samples doped with C60 are more light sensitive due to photo-assisted splitting of excitons by C60. Single-walled nanotubes (SWNT) are supposed to have the same effect when mixed with polymer, with better carrier transport. However, the commercially available nanotubes we investigated were not pure enough to produce a good Schottky contact and need more purification prior to use in such devices.

The best samples were tested for X-ray detection. Undoped P3OT and P3OT doped with DDQ or C60 are nearly insensitive to X-ray exposure and no significant signal could be achieved for these samples. The other samples prepared by doping P3OT with bromothiophene and gold nanoparticles had measurable sensitivity to X-rays with the signal shown in Figure 5 resulting from an exposure using a 120kV 200mA 0.1s burst using a conventional medical tungsten target X-ray source. The signal shown is after background subtraction, measured with a LeCroy LC574AC Oscilloscope across a load resistor of 10 MΩ giving nearly 7nA. (10V bias was applied.) The corresponding signal without background subtraction seen with a commercial silicon photodiode of depletion depth ~20μm (OSD5.8-7Q) using 100 kΩ resistor is shown in Figure 6 and represents a current pulse of 160nA. Although sensitivity to ionizing radiation is demonstrated, the need for much thicker samples of the conjugated polymers is also suggested by these studies.

IV. SOURCE AND LIGHT-SPOT STUDIES

The set-up used to measure the signal induced by fast electrons from a ^{106}Ru β-source is shown in Figure 7. Figures 8 and 1 show the boxes for the silicon and polymer diodes, respectively. Here, 300μm thick fully depleted high resistivity silicon pad detectors were used for comparison. A wide bandwidth fast (0.1 ns rise and fall time) was used to amplify the diode output current to a level measurable with an oscilloscope. The noise level was <2 mV and the signal height about 5 mV. The measured signal is shown in Figure 9. The signal has been averaged over ~3000 sweeps with the Lecroy LC574AC oscilloscope. The averaging method proved necessary due to the small S/N ratio due to the high diode capacitance at the input of the amplifier. The ionisation charge induced by an electron crossing the detector is 23000 e^-. The same method was been applied to the study of the polymer detectors.

Due to the very thin active thickness (2 μm) the deposited charge is very small (the corresponding charge deposited in a 2μm thick silicon detectors would be ~150 e^- for a signal height of ~20μV). Moreover, the noise in the case of the polymer detectors is higher (~7mV) than for the silicon detectors, due to the higher capacitance (see Figure 10). Even by averaging the output of the polymer diodes over a large number of sweeps (10000) it is not possible to see any signal induced by the crossing β particles.

Different methods for depositing higher charge in the thin active volume of the polymer detectors have been tried. Alpha particles from a ^{241}Am source were used. The energy deposition of alpha particles in material has a sharp increase when the alpha particle energy has reduced to a few hundredth of keV (Bragg peak). The alpha particle range in air is about $0.56*E_a$ cm and $1.24*E_a$ - 2.62 cm (for energy (E_a) expressed in MeV ranging to 4 MeV or from $4<E_a<9$MeV respectively). The energy spectrum of alpha particles from ^{241}Am is centred to 5.48MeV giving a range in air of about 4.17 cm. Positioning the alpha source at 4.17 cm from the surface of the detector and scanning down to shorter distances, to allow for the higher energy loss in the thin window of the detector enclosure, should allow positioning of the Bragg peak within the sensitive volume. A strong enhancement of the deposited charge would than be expected (in the case of silicon a 50 times higher signal is measured with the alpha source positioned at about 1cm from the detector, as shown in Figure 11).

Varying the position in steps of 2 μm using a micrometer adjustment down to a distance from the polymer diode of a few mm has been tried, with no evidence of any signal coming from the diode. A different technique for inducing fast signals in the polymer diodes was also attempted. A higher generated charge is expected when the polymer diodes are illuminated by a source of yellow light. A pulsed yellow LED with a typical output of 3500 mcd, driven by a programmable pulse generator has been shone over the sensitive area of the polymer diodes. The trigger was given by the pulse generator driving the LED and the output was averaged using the oscilloscope. Different pulse rates and pulse duration have been used, ranging from 5kHz and 0.1μs to fractions of Hz (light switching for seconds duration did result in detectable changes in the diode current). A different set up with a charge sensitive preamplifier (Ortec 142) in place of the wide bandwidth preamplifier has also been tried. The slowest integration time (1μs) was used to try to detect intense light pulses from the yellow LED but no fast signals could be seen.

V. CONCLUSIONS

A large number of attempts have failed to demonstrate sensitivity of conjugated polymer diodes to single particle interactions, even using α-sources and carefully scanning the source - substrate distance. Other fast signals could not be seen either at the levels of sensitivity of standard equipment used for studying particle physics prototype detectors. The material used for the X-ray studies reported here was further found to show rapid degradation during X-ray exposure, with the sensitivity being lost for these intense bursts after about 10 exposures. Clearly, there is a lot of work to do to develop materials that could be of direct application to either large area X-ray or particle physics detector systems. Nevertheless, the anticipated low cost for large area applications, given the parallel developments for display screens using this

technology, make this an idea well worth taking further and there is enthusiasm within Liverpool to do so, particularly within the Electrical Engineering and Electronics Department where funds to do so are possibly available. The idea itself has led to the successful filing of patent 01934199.9-2213-GB0102457 on 04/06/01 with the European Patent Office. Furthermore, successful demonstration of the main objective, the detection of ionizing radiation with such materials has been achieved and it is now possible to build on this towards better detectors, with particular emphasis on solving one of our major problems, the development of much thicker substrates which will be vital for any applications to be of direct relevance to particle physics.

VI. REFERENCES

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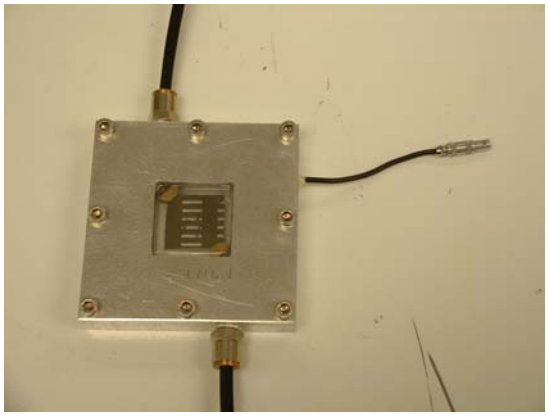

Figure 1 *Enclosure (with Nitrogen gas feed) of the polymer diodes. A thin plastic foil window allows the passage of light and electrons.*

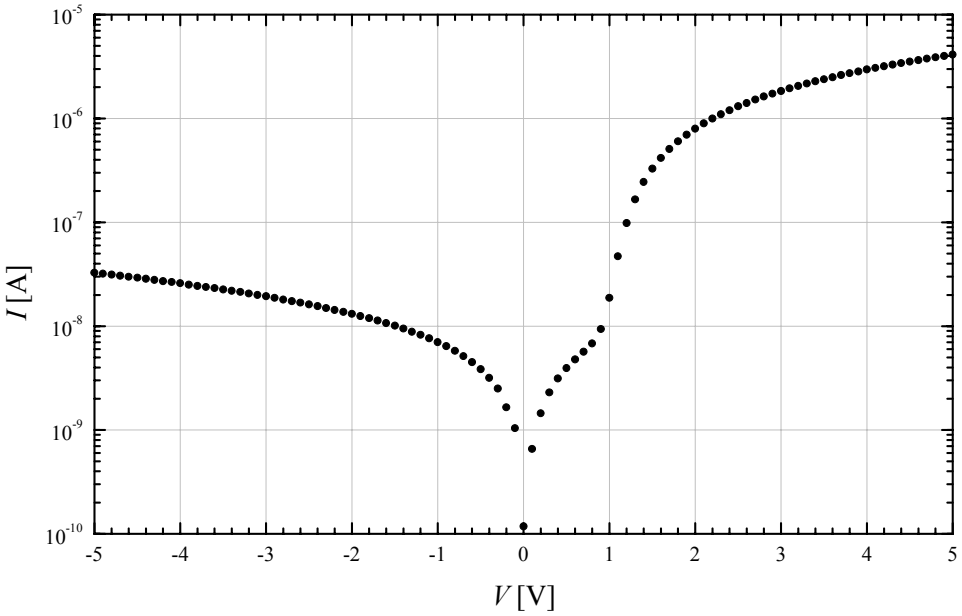

Figure 2 *IV characteristics of aluminium Schottky contact to P3HT*

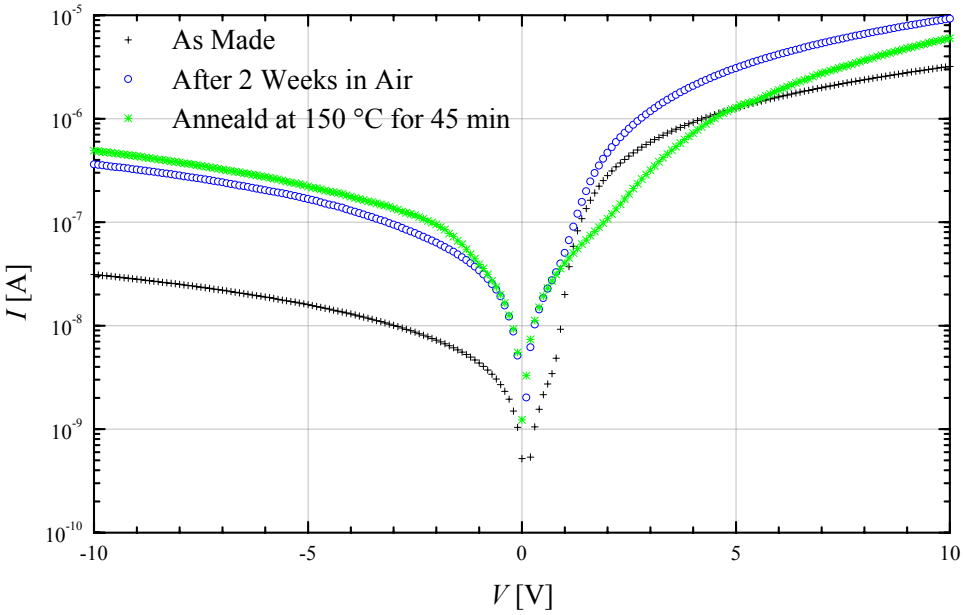

Figure 3 *Varying IV characteristics of the P3HT/aluminium Schottky diode*

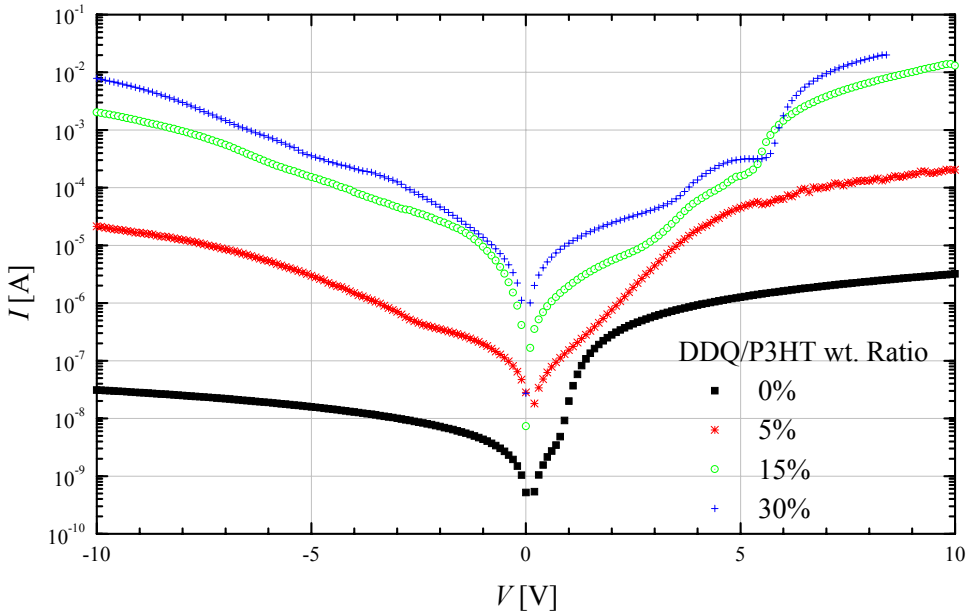

Figure 4 *IV characteristics of P3HT with varying DDQ doping*

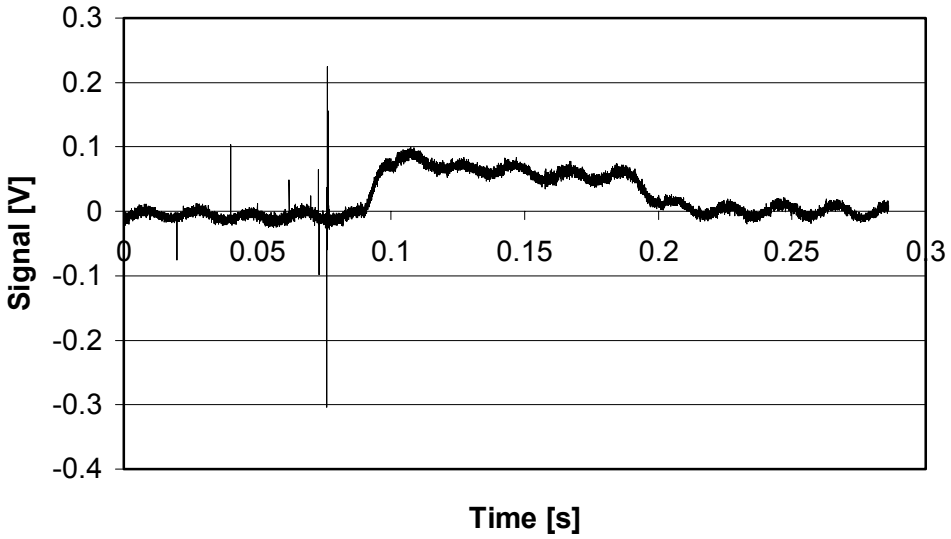

Figure 5 *Signal in bromothiophene-doped P3OT diode exposed to X-rays*

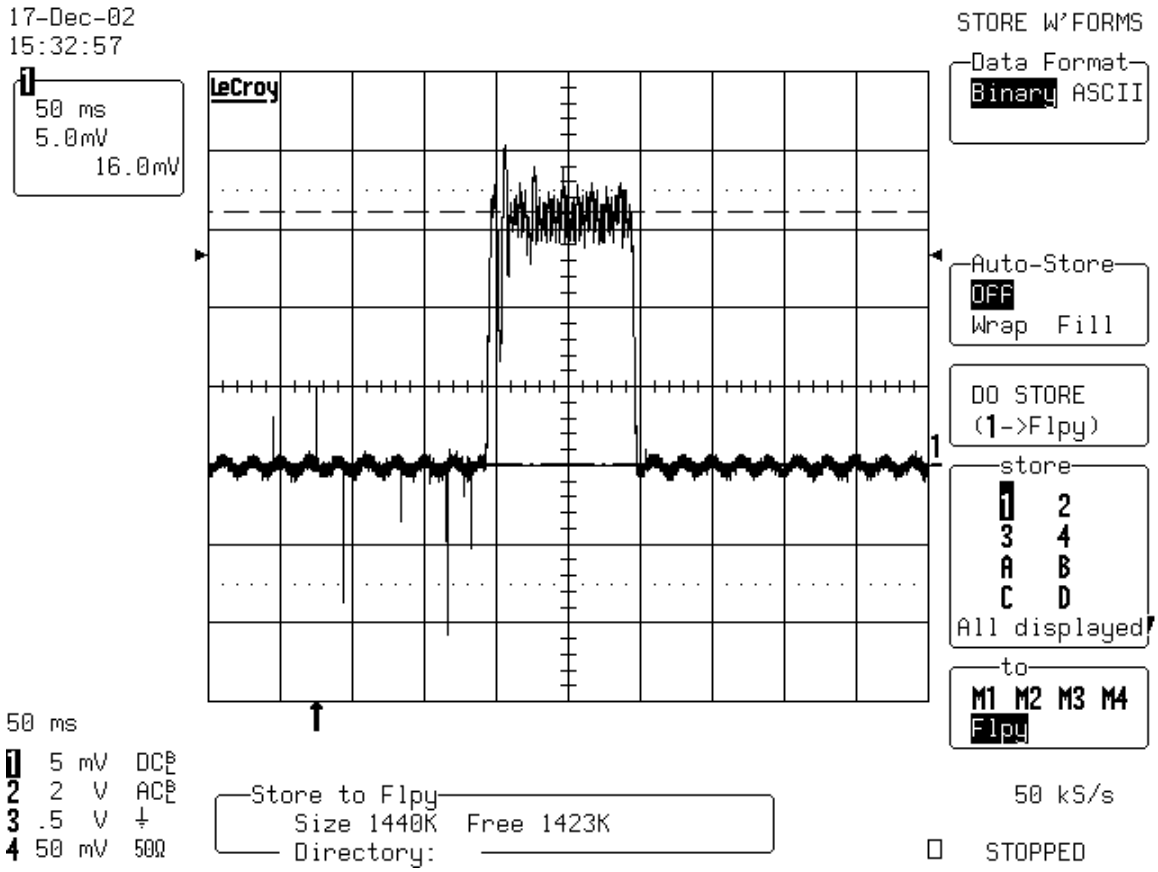

Figure 6 *OSD5.8-7Q silicon photodiode exposed to same X-ray burst as conjugated polymer diode*

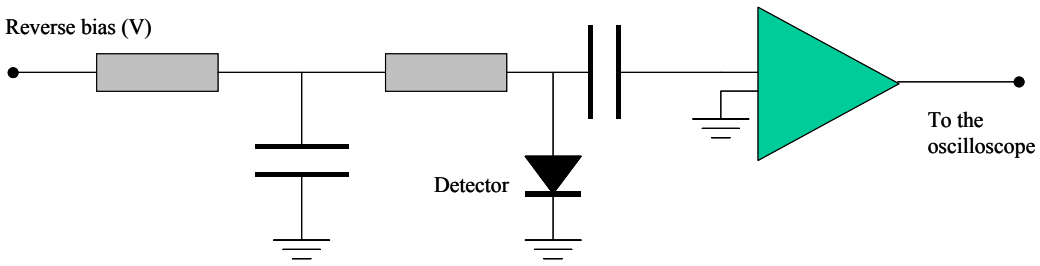

Figure 7 *Schematic of the circuit for measuring the signal induced by impinging radiation on a semiconductor detector*

Figure 8 *Box (acting as a Faraday cage when covered) for measuring ionising radiation with a silicon detector*

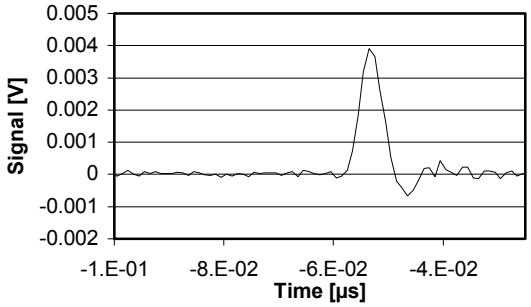

Figure 9. *Averaged (~3000 sweeps) signal induced by fast electrons from a ^{106}Ru –source in a 300µm thick silicon detectors*

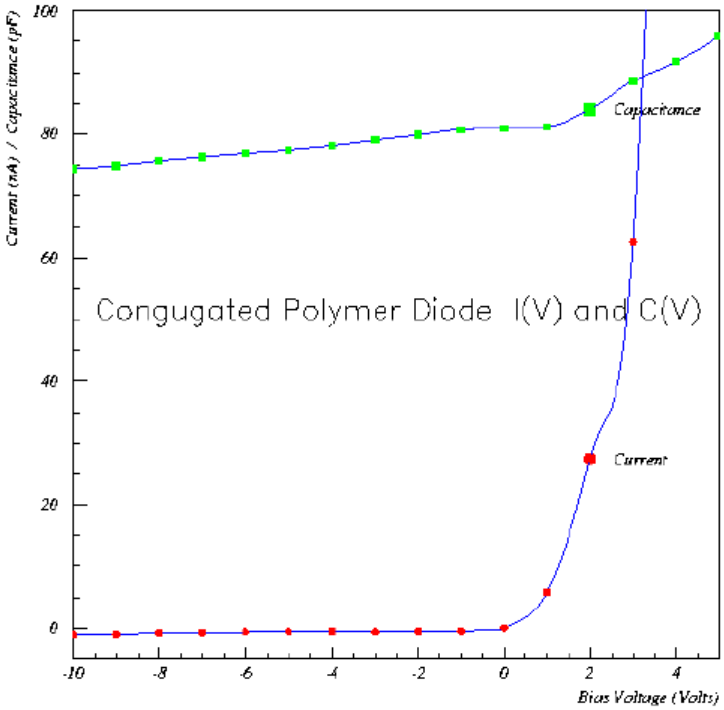

Figure 10. *Capacitance and current as a function of reverse bias for in bromothiophene-doped P3OT diode*

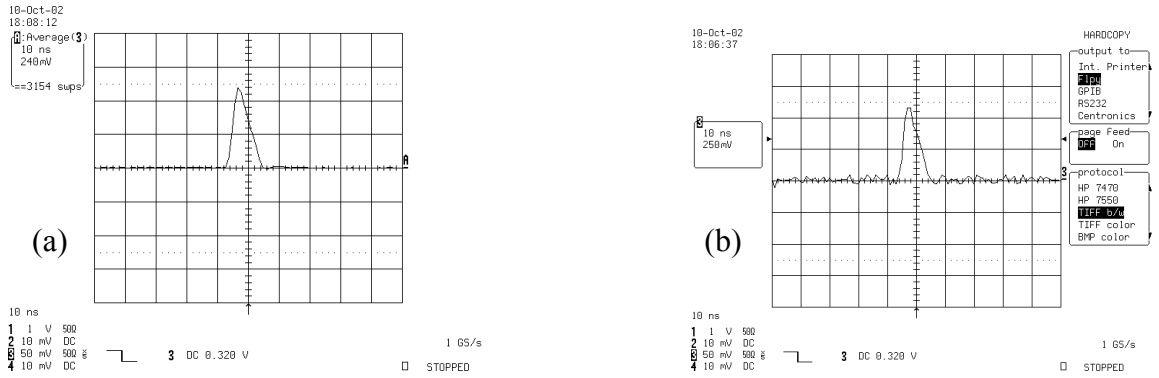

Figure 11 *Signal induced by alpha particles from a ^{241}Am source in a silicon detector: (a) signal averaged over ~3000 sweeps (b) single hit*