Excimer-laser micropatterned photobleaching as a means of isolating polymer electronic devices

E. Itoh[1], I. Torres, C. Hayden, D.M. Taylor
School of Informatics, University of Wales, Dean Street, Bangor, Gwynedd LL57 1UT, UK
E-mail address: martin@informatics.bangor.ac.uk (D.M. Taylor).
1 Permanent address: Department of Electrical and Electronic Engineering, Shinshu University, 4-17-1, Wakasato, Nagano 380-8553, Japan.

Abstract

Results are reported of an investigation into the effects of UV irradiation on the electrical conductivity of poly(3-hexylthiophene) films and on the field-effect mobility in transistors formed from this semiconducting polymer. The UV source used was a pulsed excimer-laser (KrF, 248 nm) in a commercial, excimer-laser micromachining workstation. By limiting the fluence in the pulse to $\sim$50 mJ/cm^2 controlled reductions of up to 2 orders of magnitude in both the bulk conductivity and field-effect mobility were achieved before significant ablation took place. Changes in the UV–vis spectrum of the P3HT show that reduced electrical transport is accompanied by an increase in the optical bandgap which is attributed to a reduction in π-conjugation either by chain scission or photo-oxidation of the polymer. It is argued that photobleaching of selected regions of the semiconducting polymer film is a viable technique for isolating individual transistors in a polymer electronic circuit.

Keywords: Polymer field-effect-transistor; Poly(silsesquioxane); Poly(3-hexylthiophene); Photobleaching; Conductivity; Field-effect mobility; Excimer-laser micro- machining

1 Introduction

Thin-film, polymer field-effect transistors (pFET) are attractive devices for the production of low-cost circuits to be used in organic active matrix displays, RFID tags and electronic paper [1–5]. For such applications, solution-processable polymers are preferred, and one promising material that has undergone intensive study for pFET applications is regioregular poly(3- hexylthiophene) (P3HT) [5–8]. It is well-known, however, that leakage currents flowing through an unpatterned semiconductor layer can lead to significant increases in OFF-current in pFETs and hence a detrimental reduction in the device on–off ratio [9,10]. Furthermore, when whole circuits are based on unpatterned films, sufficient leakage current can flow between individual pixels in displays, for example, to cause a noticeable reduction in the contrast ratio of the display simply because pixels cannot be fully turned off. To optimize the performance of organic circuits, therefore, it is essential to devise an appropriate micropatterning approach that complements the solution-based fabrication technologies being developed in polymer electron- ics. Photolithography can provide the high-resolution needed, but it is a multi-step process requiring the application and removal of photoresist layers with the potential to impair the electrical properties of both the organic semiconductor and the gate insulator. Ideally, then, non-lithographic methods of pat- terning the organic semiconductor, as well as electrodes, are needed to avoid solubility problems, inter-diffusion of layers and possible chemical attack of previously deposited layers.

A number of novel approaches have been reported recently to replace traditional photolithography [11], for example, inkjet printing [12,13], direct writing of wax resists or selective dewetting [14], microcontact printing [15,16], screen printing [17] and micromoulding [18]. Although these techniques are all compatible with a low-cost production technology, difficult hurdles are yet to be overcome before high resolution patterns (<5 µm) can be obtained reliably on a commercial scale. For example, in inkjet printing there is a compatibility problem between materials in the print head and the solvents used to dissolve the polymer. Pre-patterning of surfaces is also necessary to confine the ink droplets either by physical barriers or by changes in surface energy [12]. Micro-contact printing can give errors in complex, large-area patterns due to deformation of the elastomeric stamp. While dry etching using laser ablation [19,20] can provide the necessary resolution and avoids the inadvertent doping of the semiconductor, there are problems to be overcome related to the debris produced during ablation [21]. Moreover, the high intensity of the laser radiation may cause serious damage to plastic substrates, an important consideration in a flexible electronics application.

On the other hand, Abdou et al. [22] showed that by limiting the fluence from a He–Cd laser (442 nm) to around 60 mJ/cm^2 it was possible to convert a spin-coated film of P3HT into a relatively insoluble gel while still maintaining a reasonable conductivity. Thus, after dissolving away the unexposed regions of film, and oxidizing the remainder, they were able to pro- duce conducting polymer tracks on silicon that were patterned to a resolution of 1 µm. A similar approach was taken more recently by Wong et al. for defining micron scale polymer lines [20]. Photobleaching of the irradiated polymer gives rise to a faint contrast in the P3HT film after exposure [22] and indeed UV-induced photobleaching of polymer or dye materials is a well-known technique for obtaining high resolution patterning and local refractive index changes in optical devices [23,24]. Of interest to the present work, though, is the observation by Abdou et al. [22] that increasing the radiation fluence above some threshold value resulted in a rapid decrease in the electrical conductivity of the P3HT owing to extensive disruption of the π-conjugated system. In the following, therefore, we report on an investigation to determine whether this is a feasible approach for isolating pFETs in polymer electronic circuits.

2 Experimental

The effect of irradiation on the electrical conductivity of P3HT films was monitored directly by spin-coating a 50 nm thick P3HT film over a pair of interdigitated gold electrodes patterned by photolithography on a glass microscope slide. The effective length of the electrodes was ∼20 cm with an inter-electrode gap of 60 µm.

Measurements were also undertaken on pFETs to investigate the effect of UV radiation on the field-effect mobility. For these latter measurements, pFETs were fabricated following the procedure outlined in Fig. 1. Initially, an indium tin oxide (ITO) coated glass slides (20 ▲ per square, Delta Tech. Ltd.), was patterned with hydrobromic acid to form a 1.6 mm wide gate electrode along the length of the slide. The gate insulator was then formed by spin-coating a solution of poly(silsesquioxane) (SST-3PM1, Gelest, Inc.) dissolved in ethyl-methyl ketone (5 wt%) onto the ITO and curing at 350 °C for 1 h in a conventional oven under a nitrogen atmosphere to yield an inert layer similar to silicon dioxide [25,26]. The thickness of the resulting layer was between 250 and 350 nm. A 0.5 wt% chloroform solution of regioregular P3HT (Aldrich) was then spun onto the insulator to yield a film that was ∼50 nm thick. After preparation, samples were placed on the *x–y–z* stage of an Exitech Series 8000 Microfabrication Workstation and exposed to between 1 and 64 pulses of radiation, ∼100 ns duration, from a Lambda Physik Compex 110 excimer-laser operating at 248 nm (KrF).
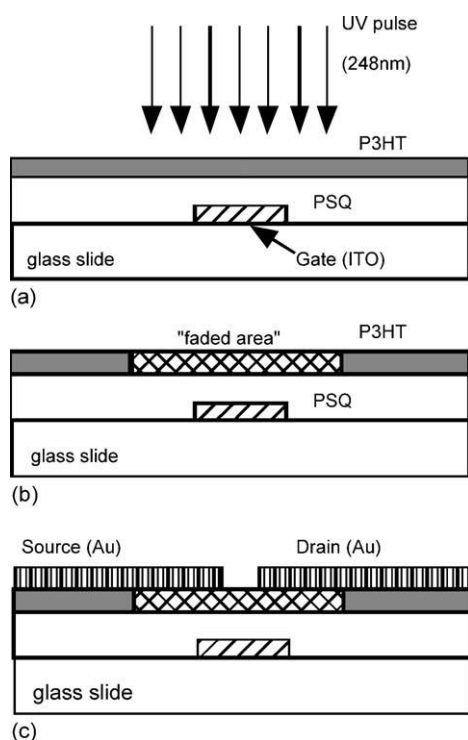

Fig. 1. Diagram showing the steps in the fabrication of the pFETs used in the present work. After forming the ITO gate electrode and PSQ gate insulator, a film of P3HT was spin-coated over the whole. To determine the effect of laser radiation on FET behaviour, the region above the gate was irradiated (a) prior to evaporation of source and drain electrodes (c).

Using the CNC capability of the system, the laser can be used to write any pre-programmed pattern in the sample. After pre- liminary testing using a test grid, the laser fluence was set to 50 mJ/cm^2 and square areas (1.2 cm × 1.2 cm) of the sample exposed. After irradiation, several pairs of 1.6-mm wide, co-linear gold stripes were then deposited by evaporation through a shadow mask onto the P3HT layer to form source and drain electrodes. These electrodes were aligned perpendicular to the common ITO gate electrode. The active channel thus formed was 100 μm long and 1.6 mm wide.

Prior to electrical measurements, all samples were heat- treated at 100 °C for 1 h under vacuum in order to remove residual solvent and/or adventitious dopants such as oxygen. Electrical measurements were then carried out under vacuum, in the dark, at 30 °C after heating at 100 °C step. The current–voltage (*I–V*)

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characteristics of the FET devices were measured using an electrometer (Keithley, Model 617) and a stabilized power supply.

3 Results and discussion

The problem caused by an unpatterned, semiconducting film is exemplified in Fig. 2 which shows the frequency-dependence of the capacitance, C, of two metal–insulator–semiconductor (MIS) capacitors formed by spin-coating P3HT onto a poly- imide gate insulator following the procedures described in our earlier publication [27]. Cross-sections (not to scale) of the two devices are shown inset in Fig. 2. The ohmic contact to the polymer in capacitor 1 is a circular gold electrode, 1.8 mm in diameter, vacuum evaporated through a shadow mask. In capacitor 2, the ohmic contact is surrounded by a concentric guard electrode spaced 150 μm away. In the unguarded capacitor at low frequency, the period of the applied voltage is sufficiently long for charge to flow out of the gold contact along the P3HT film, which behaves as a distributed transmission line effectively increasing the area of the capacitor. A related effect has been reported in silicon-based metal-oxide-semiconductor capacitors [28]. When such a device is inverted, the inversion region can extend beyond the gate area, particularly for p-type silicon in the presence of positive oxide charge. As a result, the response of the inversion layer to alternating voltages extends to much higher frequencies than expected since carriers can be drawn from the 'reservoir' of minority electrons present beyond the area defined by the gate electrode.
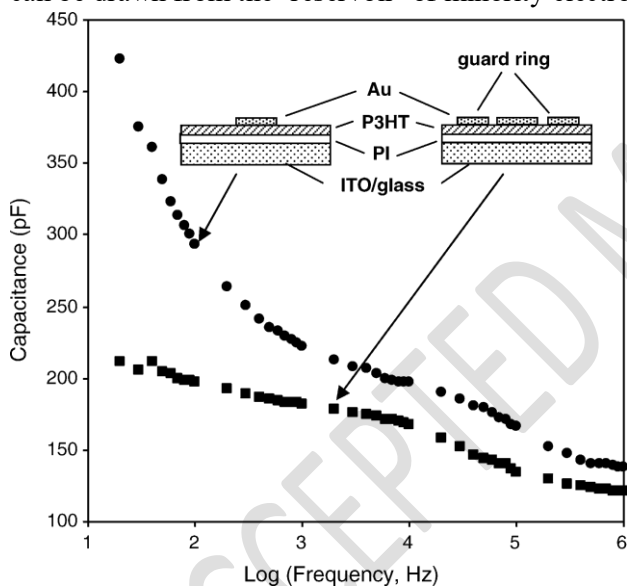

Fig. 2. Frequency-dependent capacitance of ITO/polyimide/P3HT/Au MIS capacitors showing that lateral conduction through the P3HT film increases the measured capacitance at low frequency when the ohmic contact to the P3HT is not guarded (●) and the reduction achieved when the electrode is surrounded by a guard ring (u). The inset shows cross-sections (not to scale) through the two devices.

In the present case, the presence of a grounded guard ring suppresses lateral charge flow through the P3HT so that the true capacitance and loss are measured at all frequencies. This has allowed the low frequency regime to be studied in some detail revealing the presence of interface state activity in addition to the Maxwell–Wagner-type relaxation at ~50 KHz [29]. Photolithographic removal of the semiconductor adjacent to the contact achieved the same result. Reducing the conductivity of the film adjacent to the electrode by photobleaching will also reduce significantly this source of leakage.

To test this hypothesis we began by determining the UV dose necessary to achieve the required reduction in conductivity with- out causing ablation. This was achieved by exposing the P3HT film in a programmed exposure in which the number of pulses and the fluence were increased in a regular manner over a test grid.
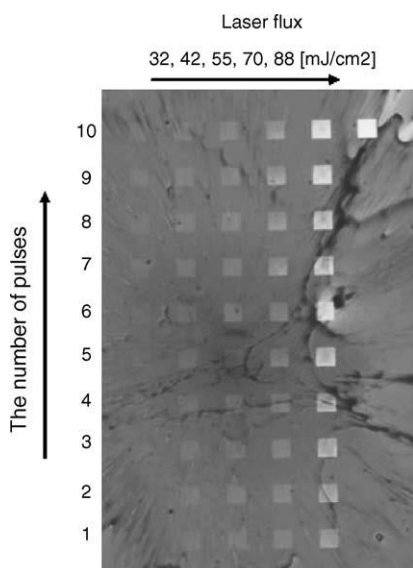
Fig. 3. Photograph of a P3HT film spin-coated onto a glass slide showing the result of running the test grid program. The columns represent fluences of (a) 32 mJ/cm^2, (b) 42 mJ/cm^2, (c) 55 mJ/cm^2 (d) 70 mJ/cm^2 and (e) 88 mJ/cm^2 while the rows represent the number of pulses used in the exposure. The single square at top right of the image is an alignment mark. The darker marks are processing residues present on the underside of the slide and are only visible when, as here, bottom illumination was used to enhance the contrast.

Fig. 3 is a photograph of a P3HT-coated glass slide after sequential exposure to a 2 mm × 2 mm square laser beam. Each column corresponds to a particular dose per pulse in the range 32–88 mJ/cm^2 and each row represents the number of pulses (1–10) used in the exposure. No visible changes occurred in the P3HT layer for doses less than 25 mJ/cm^2 per pulse. Photobleaching occurred between 25 and 65 mJ/cm^2 per pulse, the P3HT film fading gradually with either the incident dose or the number of pulses. Above 70 mJ/cm^2, ablation set in and a square cavity was micromachined into the polymer. It should be noted, however, that, up to ∼100 mJ/cm^2 per pulse no change was observed in the under- lying PSQ film. When irradiating P3HT films spin-coated onto a polyimide layer, though, severe damage to the polyimide film occurred even for a dose as low as 25 mJ/cm^2 per pulse.

The effect of increasing exposure on the UV–vis spectrum of the P3HT film was monitored with the laser set to 50 mJ/cm^2 per pulse, a value deemed to be sufficiently below the ablation threshold. In Fig. 4, are shown the spectra obtained from regions of the sample exposed to an increasing number of pulses. To eliminate effects arising from slight differences in sample thickness over the slide, the spectra have been normalised to the absorption observed at 200 nm. Prior to irradiation, the spectrum displays three main absorption bands at about 510, 550 and 610 nm similar to reports for high molecular weight fractions of regioregular poly(3-hexylthiophene) [30] and to poly(3-dodecylthiophene) [31]. Exposure, even to a single laser pulse, led to strong attenuation and elimination of the bands at 550 and 610 nm. The slow reduction observed in the 510 nm band which accelerated after 64 pulses probably arose from loss of material as a result of micromachining. After some 100 pulses the P3HT film showed visible laser damage.
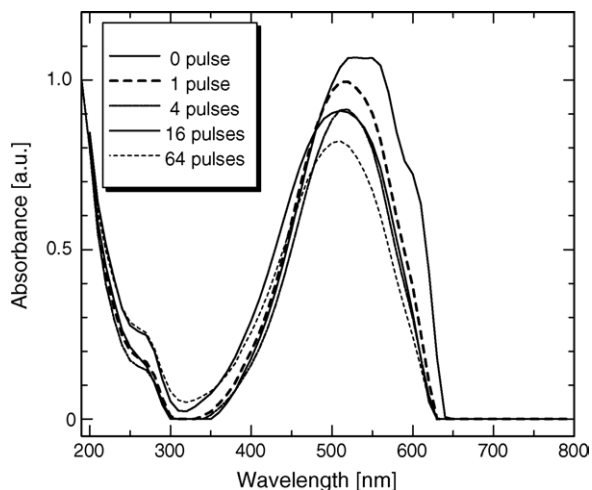
Fig. 4. UV–vis absorption spectra of P3HT, spin-coated onto a quartz slide, before and after exposure to the excimer-laser.

To understand the spectral changes we turn to the work of Trznadel et al. [30] who undertook a detailed characterisation of different molecular weight fractions of regioregular poly(3- hexylthiophene) that were extracted, using different solvents, from a batch of the polymer prepared by a Grignard-type poly-condensation. They showed that an increase in the mean molecular weight from ∼2000 to ∼20,000 produced a pronounced red-shift in the solution spectra indicative of a higher conjugation length. A much greater effect was seen in the solid state spectra. Of more interest to the present study, is that vibrational fine structure was only observed in the higher molecular weight fractions. For example, the absorption band corresponding to the energy of the 0–0 transition, i.e. the transition from the ground state to the relaxed excited state in the polymer, only just became discernible at 602 nm in the fraction of mean molecular weight ∼5000. In the higher molecular weight fractions, this band became much more distinct and displayed a bathochromic shift to 616 nm in the highest molecular weight fraction (M_W, ∼20,000) which again was attributed to an increase in the conjugation length.

Although in our study exposure to one pulse of the laser appears to totally quench this band, close inspection of the spectra reveals the remnants of the feature, albeit very weak, at ∼600 nm even after 16 and 64 pulses. We conclude, there- fore, that the laser radiation reduces the conjugation length in the polymer. This may occur through chain scission or through photo-oxidation of the polymer chain. This latter possibility would certainly be consistent with the photochemical reactions deduced from FTIR spectra of UV-irradiated P3HT [22] where one suggested mechanism involved the addition of photosensitized singlet oxygen to thienyl residues in the chain leading to the formation of C═O, C═C and C═S^+─O^- residues. A second mechanism involved the oxidative degradation and crosslinking of the alkyl side chains. The increase in optical bandgap produced by a single laser pulse is accompanied also by an increase from 4.85 to 5.0 eV in the ionization potential measured by photoelectron spectroscopy under ambient conditions using a Riken model AC-II instrument [32].

Based on the above findings, we proceeded to investigate the electrical effects of irradiation on both the conductivity of P3HT films and the field-effect mobility in P3HT pFETs again employing a laser fluence equivalent to 50 mJ/cm^2. This is well below the reported threshold for rapid loss of conductivity [22] and

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causes only limited ablation up to 64 pulses. However, it should be noted that Abdou et al. [22] employed a laser of longer wavelength (442 nm) than used in the present work (248 nm).

Fig. 5 shows the current–voltage characteristics of the P3HT film (a) before irradiation, (b) after 1 pulse and (c) after 64 pulses. As can be seen, the lateral current through the film decreases by more than an order of magnitude after just one pulse and is attenuated even further with additional exposure.
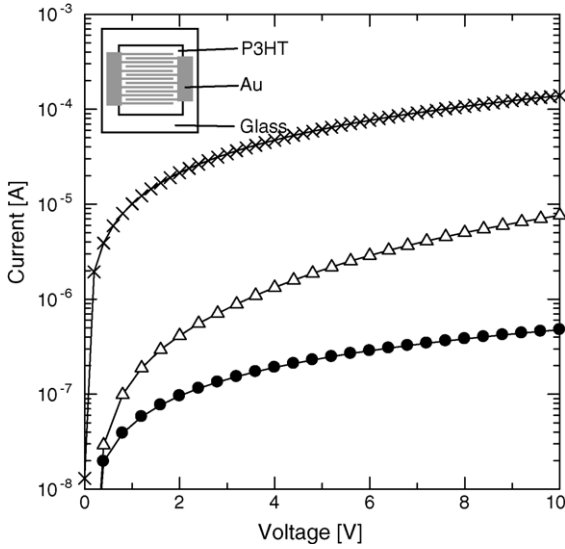

Fig. 5. Current–voltage characteristics of a P3HT film spin-coated over inter- digitated gold electrodes shown in the inset. The curves correspond to the unirradiated film (×), and the same film exposed to 1 (Δ) and 64 (●) pulses of UV.

Fig. 6 gives typical output characteristics, i.e. drain current I_D versus drain voltage V_D, obtained at various gate voltages, V_G, for a 100 µm channel pFET (a) before and (b) after 1 pulse of UV exposure. In both cases, reasonable transistor behaviour is observed despite the factor 6 reduction in drain current after irradiation. Prior to irradiation, a measurable gate leakage cur- rent flowed (non-zero I_D when $V_D = 0$ V). This is not surprising because the insulator area defined by the gate electrode and unpatterned P3HT film is much greater than the active channel area itself and is likely to have encompassed low resistance defects such as pinholes in the insulator. Thus, the measured gate leakage probably reflects the resistivity of the P3HT film rather than the intrinsic resistivity of the gate insulator. This is borne out by the fact that the reduction in leakage current in the irradiated device, from ∼0.06 to ∼0.01 µA (measured at $V_G = -50$ V), is in proportion to the reduction in lateral conduction induced by the radiation.

Although not shown here, the transfer characteristics displayed good quadratic behaviour at the higher drain voltages. From the capacitance per unit area, C_i, ∼7.2 nF/cm^2, of the PSQ layer and the device aspect ratio, $W/L = 16$, the field-effect mobility, μ, and threshold voltage, V_T, were estimated from the standard equation:

$$I_D = \frac{W}{L} \mu C_i \frac{(V_G - V_T)^2}{2}$$

describing the saturation current of a FET. For 10 nominally identical transistors, μ ranged from 1.8×10^{-3} to 4.4×10^{-3} cm^2/V s while the threshold voltage ranged from -1 to 3 V [26]. After exposure to one pulse of UV the mobility fell by an order of magnitude to ∼3.4×10^{-4} cm^2/V s and the threshold voltage shifted by as much as +20 V. After 16 pulses, μ decreased further to ∼7×10^{-5} cm^2/V s although after this degree of exposure it became difficult to measure device characteristics with any degree of accuracy.
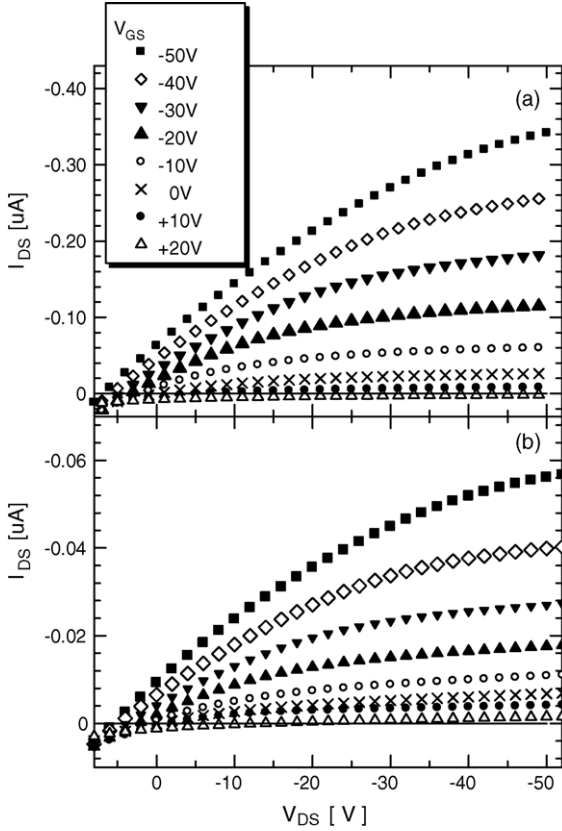
Fig. 6. Output characteristics, drain current I_D vs. drain voltage V_D, of a 100 µm channel FET obtained at different gate voltages, V_G (a) before and (b) after exposure to a single pulse of UV irradiation.

Since the reduction in field-effect mobility is of the same order of magnitude as the reduction in lateral conduction seen in Fig. 5, we assume that both effects are related and arise either from a reduction in conjugation length brought about by photochemical reactions of the type described above or from the photogeneration of trap sites in the bulk semiconductor and at the semiconductor interface. Although no specific studies were undertaken to determine the permanency of the changes we do not believe they are reversible. No changes were seen in irradiated samples after storage for several days.

Using either direct-write or projection mask approaches, the irradiation may be easily limited to those regions of the P3HT film outside the active channel. Thus, excimer-laser photobleaching can provide a rapid (1 cm^2 s^{-1}), high resolution (<1 µm), commercially viable patterning option for the isolation of FETs in polymer electronic circuits.

4 Conclusions

This study has explored the effect of UV photobleaching on the electrical properties of the semiconducting polymer P3HT. The results have demonstrated that by limiting the laser fluence to ∼50 mJ/cm2 per pulse and controlling the number of radiation pulses used in the exposure, it was possible to reduce the bulk conductivity of P3HT by up to 2 orders of magnitude before ablation became apparent. In pFETs exposed to similar radiation fluences, the field-effect mobility fell from (2–4)× 10−3 to (0.7–3) × 10−4 cm2/V s while the threshold voltage shifted to −20 V indicative of negative charge trapping at the interface. The study has confirmed that photobleaching of selected areas of a polymer circuit in an excimer-laser micromachining work- station is a viable means of isolating individual transistors in polymer circuits.

Acknowledgements

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