An inkjet-printed chemical fuse

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Abstract. Inkjet printing of the conductive polymer poly(3,4-ethylene dioxythiophene) doped with polystyrene sulfonated acid (PEDOT-PSS) has been used as the basis for a sensor for organic vapours. The electrical resistance of the film was monitored as it was exposed to atmospheres containing alcohol. Ultrathin films exhibited a sharp and nonreversible increase in their resistance. This resulted from a change in the morphology of the organic layer, thereby disrupting the current flow through the polymer. An intended application for these inkjet-printed devices is in disposable handheld instruments to monitor the presence of organic vapours above a threshold level.

1. Introduction
Electroactive organic compounds such as phthalocyanine derivatives or conductive polymers are attractive materials for electronic applications as they can be dissolved in common solvents and processed in thin film form using methods such as spin-coating, thermal evaporation or inkjet printing. The latter technique is attracting considerable attention for ‘plastic’ electronics applications such as organic electroluminescent displays and field effect transistors.1 Inkjet printing is non-contact technology working on the principle of ejecting ink through nozzles of 10-200 µm diameter. The jetted stream is broken up into a series of droplets that can be deposited on flexible and non-flexible substrates. Inkjet printing offers particular advantages over other methods for forming thin films, namely: patterning capability; reduction in waste products; high speed and low cost fabrication; room temperature deposition; and printing onto large area and flexible substrates.

2. Experimental details
A commercial HP printer with a resolution of 600 x 600 dots per inch was used in this study. The only modification required was to replace the ink with the polymer solution. A water soluble conductive polymer poly(3,4-ethylene dioxythiophene) doped with polystyrene sulfonated acid (PEDOT-PSS) was used as the ink to print a 10 mm x 4 mm sensing element onto polyester film (purchased from ISCA Papers). The inkjet-printed films were dried under vacuum at room temperature for more than 12 hours to remove any residual solvent. Silver conductive paint was used to connect the sensor to the source meter.

The devices were mounted in a specially constructed glass chamber where nitrogen carrier gas containing known concentrations of methanol or ethanol was passed over the films. Here, the nitrogen was passed over a permeation vial containing a known quantity of the alcohol and held at a constant temperature of 25 ºC. The direct current through the films was measured with a potential difference applied across the devices using a Keithley 2400 digital source meter.

3. Results and discussion
The optical micrographs of the inkjet-printed PEDOT-PSS films revealed that thin films, one to three printed layers, of PEDOT-PSS were in the form of small poorly connected islands (average size of 75 µm) of the polymer, while films greater than five printed layers in thickness provided a significantly improved connectivity over the film surface.2 The film morphology was also influenced by the nature
of the flexible polyester substrate. Rougher surfaces invariably produced a more island-like surface morphology. The physical structure of the inkjet-printed PEDOT-PSS was reflected in measurements of the electrical resistance of the chemiresistor elements (in-plane measurements at room temperature). The highest electrically conductive films were produced when individual islands had coalesced to form a continuous film. To achieve this, all the inkjet-printed layers were printed in as short a time as possible, allowing the individual islands to merge before the evaporation of the solvents.

In order to test the repeatability of the fabrication of the sensors, the resistance of fresh ink-jet printed devices with different numbers of layers was measured. It was found that devices made from the same polymer solution had a variation in resistance of not more than ±10% depending on the number of layers; thin layers showed a larger resistance variation than thick layers in all our measurements. Devices made from different PEDOT-PSS polymer solutions (with slightly different surface tensions) resulted in greater resistance variations, as indicated table 1. To examine the stability of the sensors, some of the devices were stored for about three months in air and at room temperature. All the stored devices exhibited significantly higher resistances than the fresh devices and sensors consisting of one ink-jet printed layer showed very unstable resistances and could not be tested again, table 1. However, the response of the other devices to the presence of alcohol showed similar patterns to the fresh devices.

Table 1: The resistance of fresh and stored sensors as a function of number of ink-jet printed layers.

| No. Layers | Resistance of fresh sensors | Resistance of sensors after 3 months |
|------------|-----------------------------|-------------------------------------|
| 1          | 1-2.8 GΩ                    | Unstable                            |
| 2          | 30-40 MΩ                    | 350-400 MΩ                          |
| 3          | 3-5 MΩ                      | 40-50 MΩ                            |
| 5          | 1-3 MΩ                      | 20-30 MΩ                            |

To test the sensitivity and the response time of the sensors to the vapours, the current through the film was measured as the concentration of the vapour in the nitrogen carrier gas was increased and decreased. After each increase in vapour concentration, the glass sample chamber was flushed with nitrogen. The measurements were performed on several films with different thicknesses. In all cases, the initial exposure to alcohol resulted in a significant but non-reversible change in the current. These responses were dependent on the thickness of the PEDOT-PSS film and are described in the following sections. The direct current through films was measured at an applied voltage of 1-100 V, depending on the film thickness and the type of substrate. The current through films with a thickness corresponding to 4-5 multiple prints was measured at 1 V as the methanol vapour in the nitrogen carrier gas was introduced. The measured current increased significantly on the initial exposure to the vapour but did not recover to its original value, as shown in figure 1(a) for a five-layer film exposed to 5000 ppm of methanol. The variation of the sensor current (∆I) to the first exposure of 5000 ppm methanol was about 37%, with a response time (measured as the time taken for the response to change from 10% to 90%) of 8 minutes. Subsequent exposure of thick PEDOT-PSS films to alcohols resulted in a smaller but reversible response. The variations in the sensor current for the second and further exposures of a five-layer film to different concentrations of methanol are shown in figure 1(b).
The current through thin films of 1-2 prints was measured at higher applied voltages (>10 V) as the methanol vapour was introduced. Figure 2 shows the response of a single layer PEDOT-PSS film on exposure to 500 ppm of methanol. In contrast to the response seen for thick films, the current decreased significantly on the initial exposure to the alcohol vapour; the effect was irreversible. For the single inkjet-printed layer, the value of $\Delta I$ on exposure to 500-5000 ppm concentrations of methanol was about 95%, with a response time of 6 minutes. A similar behaviour was found for PEDOT:PSS films of two multiple prints. In this case, $\Delta I$ was about 75%, with a response time of 10 minutes.

**Figure 1.** (a) Current response for a five-layer PEDOT-PSS chemiresistor on exposure to 5000 ppm of methanol. (b) Current response of the sensor on exposure to step changes in the concentration of methanol.
Figure 2. The current response of a one-layer PEDOT-PSS chemiresistor on exposure to 500 ppm methanol (chemical fuse).

The irreversible change in conductivity of an as-deposited film on exposure to alcohol probably arises from a change in its surface morphology. It is well-known that PEDOT-PSS is soluble in water-miscible solvents, particularly high polar alcohols.\(^3\) Moreover, the relatively disordered and open structure of the inkjet-printed films is expected to give rise to rapid interactions between the organic layer and the vapour (one of the motivations for using inkjet-printed films for chemical sensing). Exposure to alcohols is likely to result in the penetration of the vapour into the organic film and in the re-dissolution of the film at high vapour concentrations.

In the case of thick films, the concentration of the PEDOT-PSS particles is very high as the small islands of each printed layer overlap with those of the underlying layers. In the presence of alcohol, some of the PEDOT-PSS will become more soluble and will diffuse to fill the existing voids in the film surface. This effect will improve the number of conduction paths in the film, resulting in an increase in the film conductivity. The reversible increase in current for subsequent exposures to alcohol vapours (figure 1b) can be attributed to the dielectric properties of the vapour molecules. Polar solvents with high dielectric constants can induce a screening effect between counter ions and charge carriers.\(^3\) This reduces the Coulomb interaction between the positively charged PEDOT and the negatively charged PSS dopant, thereby enhancing the hopping rate and dc conductivity. The higher sensitivity to methanol may be because of the small size of the methanol molecules, allowing them to interact and diffuse efficiently in the polymer layer. Furthermore, the high dielectric constant of methanol (~33) compared to ethanol (~23) probably results in better interaction between its molecules and the polymer film.\(^4\)

For inkjet-printed films of one or two layers, there are relatively few conductive paths through the film. Consequently, if such a chemiresistor is exposed to alcohol, the vapour can redissolve the organic film in the regions where it is very thin, i.e. between the islands of organic film. Therefore, the electrical connection between the PEDOT-PSS islands is lost and the current passing through the organic film falls effectively to zero (in the case of an insulating substrate). When the vapour is turned off, the polar PEDOT-PSS molecules are preferentially adsorbed onto the existing islands of the polymer rather than onto the substrate. The morphology of the inkjet-printed film has thereby been permanently altered.
From the above results, thin layers of inkjet-printed PEDOT-PSS can be used as a ‘chemical fuse’ (i.e. a single shot device to raise an alarm) to detect the presence of organic vapours, especially alcohols, with concentrations above a particular threshold. As the response of the devices depends on the layer thickness, the sensitivity can be controlled by varying the number of printed layers of PEDOT-PSS. The operating principle of the device, as described above, is illustrated shown in figure 3, which includes AFM images of a single inkjet-printed PEDOT-PSS layer before and after exposure to methanol. The AFM image of the as-deposited film shows little detail associated with the PEDOT-PSS and can be attributed to the underlying polyester substrate. However, following exposure to methanol, the AFM image reveals a distinct change in the thin film. Hence, the inkjet-printed thin films of PEDOT-PSS could be used as the sensing elements in a cheap, disposable handheld personal breathalyser to monitor the concentration of alcohol in the blood. These devices could also be used in ALCOLOCK devices, which can be connected to the steering wheel to prevent drink-drivers starting their cars.

Figure 3. Schematic diagram of the proposed PEDOT-PSS chemical fuse. A. Schematic diagram of an as-deposited PEDOT-PSS thin film. B. Proposed reorganisation of the PEDOT-PSS material. C. Atomic force micrographs of one inkjet-printed PEDOT-PSS layer before exposure to methanol. D. Film after exposure to 5000 parts per million of methanol for 30 minutes. The lighter areas correspond to the presence of PEDOT-PSS.

4. Summary
The work described in this paper demonstrates the possible use of inkjet-printed PEDOT-PSS chemiresistors to detect the presence of organic vapours. The resistance of thin films, one or two printed layers, increases sharply as the concentration of alcohol vapour in a carrier gas increases. In contrast, the resistance of thick films, four to five printed layers, shows a decrease in resistance with increasing vapour concentration. An intended application for this inkjet-printed device is a handheld instrument (either a single shot or multi-use device, depending on the film thickness) to monitor the
presence of organic vapours. For example, the PEDOT-PSS inkjet-printed chemiresistors could be used as the sensing elements in a cheap, disposable handheld personal breathalyser to monitor the concentration of alcohol in the blood or as the sensing elements in ALCOLOCK devices.

Acknowledgments
This work was supported by Durham County Council under the Science and Technology for Business and Enterprise Programme SP/082.

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