

An inkjet-printed chemical fuse

M. F. Mabrook, C. Pearson, and M. C. Petty^{a)}

School of Engineering and Centre for Molecular and Nanoscale Electronics, University of Durham, South Road, Durham DH1 3LE, United Kingdom

(Received 27 September 2004; accepted 16 November 2004; published online 28 December 2004)

Inkjet printing of the conductive polymer poly(3,4-ethylene dioxythiophene) doped with polystyrene sulfonated acid has been used as the basis for a sensor for organic vapors. 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 vapors above a threshold level. © 2005 American Institute of Physics. [DOI: 10.1063/1.1846950]

Legislation concerning the permitted levels of chemicals in the atmosphere together with the public awareness of environmental and health issues have made the detection of pollutants a high research priority for scientists and engineers.^{1–4} There are many physical principles upon which sensing systems might be based; changes in electrical resistance (chemiresistors),^{5,6} refractive index (fibre optic sensors),⁷ and mass (quartz microbalance)⁸ have all been exploited. The main challenges in the development of sensors are in the production of cheap, reproducible, and reliable devices with adequate sensitivities and selectivities. Electroactive organic materials 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.^{9–13} 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 on large area and flexible substrates. Here, we describe a chemical sensing device—a “chemical fuse”—that can be fabricated by the inkjet printing of a conductive polymer on flexible substrate.

A commercial HP printer with a resolution of 600 × 600 dots/in. 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 × 4 mm sensing element onto polyester film (purchased from ISCA Papers). The PEDOT-PSS was dissolved in a mixture of organic solvents (mainly isopropanol) in the ratio 43% PEDOT:PSS to 57% solvent; the solution was purchased from Bayer AG. To the PEDOT-PSS solution further diluted with 50% water, 10% ethylene glycol and 1% dodecyl sulfate sodium salt were added to improve the viscosity and surface tension and prevent drying and clogging of the printer head. The measured values of these parameters for

the printing solution were: viscosity=3.2 cP and surface tension=41 mN m⁻¹. Multiple layers were made by repeated scanning over the same area of substrate. The inkjet printed films were dried under vacuum at room temperature for more than 12 h to remove any residual solvent.

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. The various vapor concentrations were produced using the permeation method.¹⁴ Here, the nitrogen was passed over a permeation vial containing a known quantity of the alcohol and held at a constant temperature of 25 °C. The direct current through the films was measured with a potential difference applied across the devices using a Keithley 2400 digital source meter. Atomic force microscopy (AFM) was undertaken using a Digital Instruments Nanoscope E contact mode instrument.

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, Fig. 1. The film morphology was also influenced by the nature of the flexible polyester substrate. Different roughness surfaces were provided by the manufacturer. 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. Figure 2 shows the dependence of the current versus voltage characteristics on the thickness of the PEDOT-PSS films, i.e., on the number of printed layers. The current through the organic film increases linearly with increasing voltage but in a nonlinear manner with the increase in the number of printed layers. These results are in good agreement with the observations from the optical micrographs in Fig. 1. Inkjet printing of one or two layers of PEDOT-PSS resulted in very thin films with a resistance of about

^{a)}Electronic mail: m.c.petty@durham.ac.uk

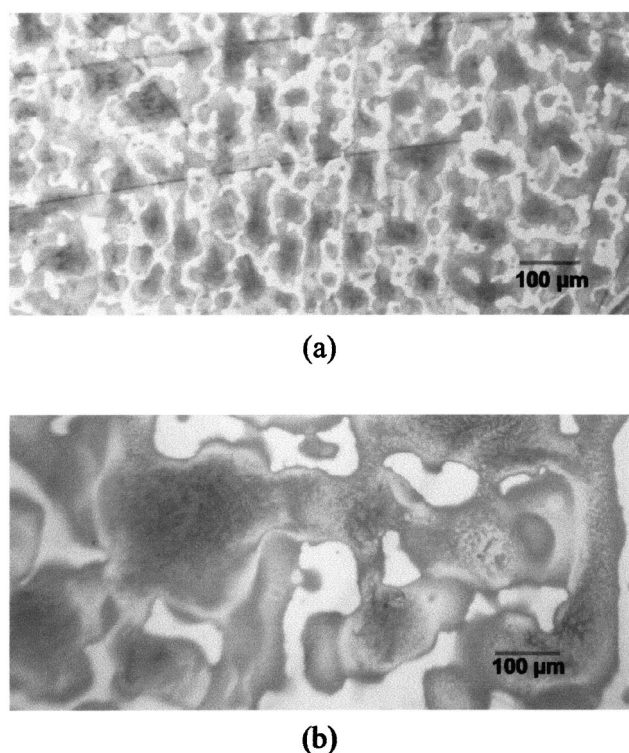


FIG. 1. (Color online) Optical micrographs of inkjet-printed PEDOT-PSS layers. (a) Three multiple layers and (b) five multiple layers. The dark areas represent the PEDOT-PSS material while the lighter background is the polyester substrate.

100 M Ω . Using substrates with rough surfaces made the charge transport in the thin films more difficult and the resistance of the films exceeded 1 G Ω .

Pulses of methanol or ethanol vapor were used to obtain information of the changes in conductivity of the PEDOT-PSS films in an alcohol ambient.¹⁵ To test the sensitivity and the response time of the sensors, the current through the film was measured as the concentration of the vapor in the nitrogen carrier gas was increased and decreased. After each in-

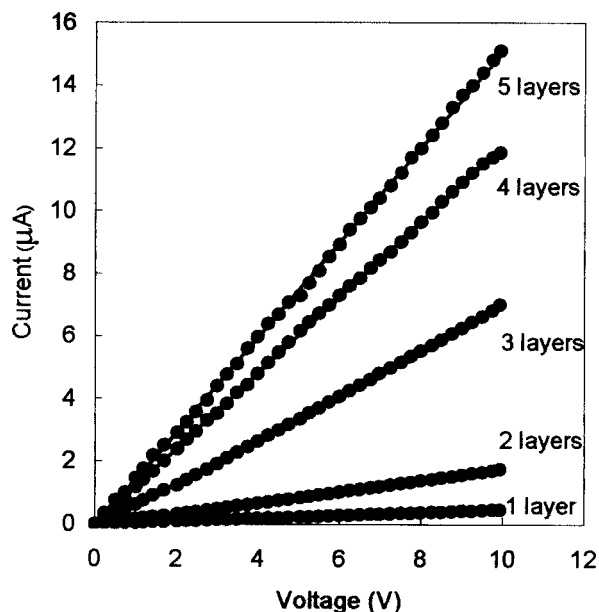


FIG. 2. Room temperature current vs voltage characteristics of inkjet-printed PEDOT-PSS layers.

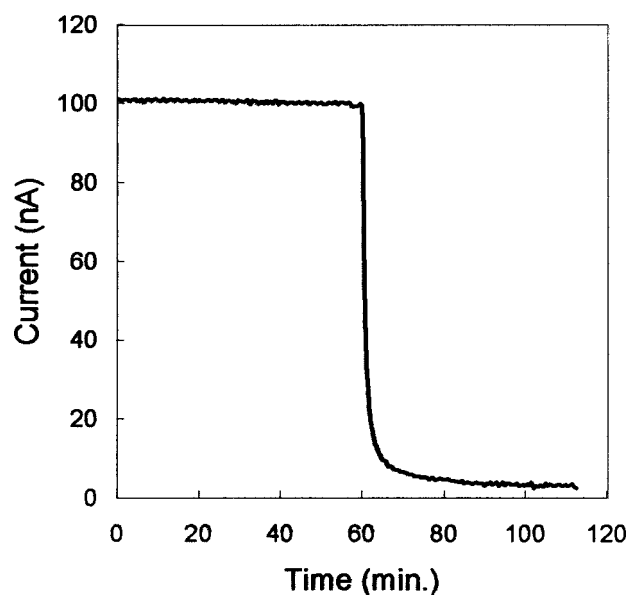


FIG. 3. The current response of thin PEDOT-PSS layer to the exposure of 5000 ppm methanol (chemical fuse).

crease in concentration of the vapor, the glass sample chamber was flushed with nitrogen. The measurements were performed on several thin films with thicknesses of one or two printed layers. The direct current through films was measured at an applied voltage of 10–100 V, depending on the film thickness and the type of substrate. Figure 3 shows the response of thin film (a single inkjet-printed layer) of PEDOT-PSS exposed to 5000 ppm of methanol. The initial exposure to the vapor resulted in a rapid and nonreversible decrease in the current. A similar effect was noted for films of two or three printed layers of PEDOT-PSS, but, generally, the thicker films exhibited longer response times (more than 2 h for a three-layer film). In our preliminary experiments, the inkjet-printed chemiresistors responded to both methanol and ethanol vapors. However, the devices were slightly more sensitive to methanol.

A completely different response was observed for thick films, greater than about five inkjet-printed layers. In these cases, *increases* in the conductivity were noted on exposure to alcohol vapor. These effects were reversible, apart from the initial exposure where a larger conductivity increase was observed, and are consistent with the suggestion that polar solvents with high dielectric constants can induce a screening effect between counter ions and charge carriers.¹⁶ This reduces the Coulomb interaction between positively charged PEDOT and negatively charged PSS dopant, thereby enhancing the hopping rate and dc conductivity.

The irreversible decrease in conductivity for the very thin inkjet printed sensor is almost certainly the result of a vapor-induced change in structure of the organic film. The morphology of the as-deposited inkjet-printed layer will depend on the contact angle between the PEDOT-PSS and the underlying substrate.¹⁷ This is influenced by the chemical (degree of polarity) and physical (degree of roughness) nature of the substrate. Figure 1 shows that first inkjet-printed PEDOT-PSS layer is in the form of a series of disconnected islands on the roughened polyester support. As further layers are printed, the individual droplets grow and coalesce until a continuous organic film is produced. If a one- or two-layer PEDOT-PSS film is exposed to the vapor of an alcohol, the

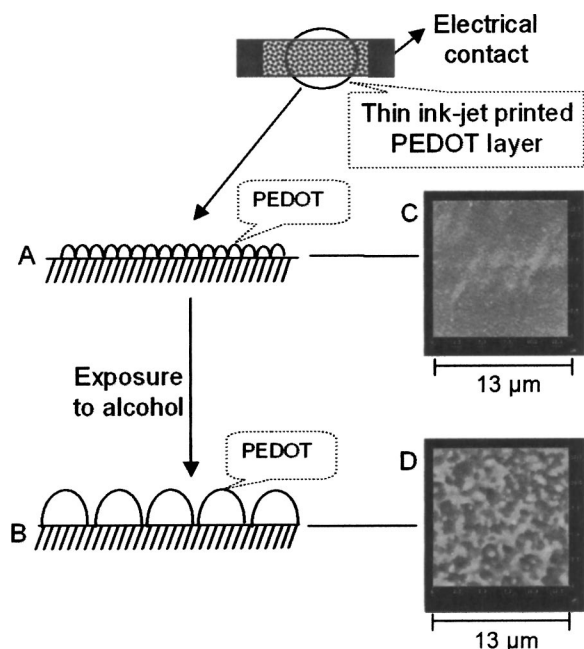


FIG. 4. (Color online) Schematic diagram of the proposed PEDOT-PSS chemical fuse. (a) Schematic diagram of an as-deposited PEDOT-PSS thin film. (b) Proposed reorganization of the PEDOT-PSS material where almost all the conductive paths in the film surface are broken due to the presence of alcohol. (c) Atomic force micrographs of one inkjet-printed PEDOT-PSS layer before exposure to methanol. (d) Film after exposure to 5000 ppm of methanol for 30 min. The lighter areas correspond to the presence of PEDOT-PSS.

vapor 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 vapor 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.

We propose that our inkjet-printed chemical sensor can be used as a type of “chemical fuse,” i.e., a single shot device to raise an alarm in the presence of organic vapors, especially alcohols, with concentrations above a particular threshold.¹⁸ The operating principle of the device, as described earlier, is illustrated shown in Fig. 4, which includes AFM images of a single inkjet-printed PEDOT-PSS layer before and after exposure to methanol (note the scale difference with Fig. 1). 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 morphology (a control experiment verified that there was no effect of the alcohol vapor on an uncoated substrate). As the response of the devices depends on the layer thickness, the sensitivity can be controlled by variation in the number of printed layers of the PEDOT-PSS. An analogy can be made with the choice of an appropriate thickness metal wire in a conventional electrical fuse. The nature of the substrate will also be important. For example, contact angles can be influenced by changing the roughness of a surface.¹⁷

In conclusion, we have demonstrated an inkjet-printed PEDOT-PSS chemical fuse to detect the presence of organic vapors with concentrations above a particular threshold. The sensor can be operated at room temperature and under normal laboratory environments. This particular device might find use as the sensing element in a disposable handheld breathalyzer or as a sensing element in an ALCOLOCK¹⁹ device. Other thin film deposition methods (e.g., thermal evaporation, Langmuir–Blodgett deposition, self-assembly) and/or different organic compounds might be used to provide a wide range of chemical fuse sensors.

This work was supported by Durham County Council under the Science and Technology for Business and Enterprise Programme SP/082. The authors would like to thank N. E. Widdowson for providing the software for the sensing equipment.

- ¹J. Janata, *Principles of Chemical Sensors* (Plenum, New York, 1989).
- ²S. Capone, M. Epifani, F. Quaranta, P. Siciliano, and L. Vasaneli, *Thin Solid Films* **391**, 314 (2001).
- ³M. Mabrook and P. Hawkins, *Sens. Actuators B* **75**, 197 (2001).
- ⁴M. C. Petty and R. Casalini, *Eng. Sci. Educ. J.* **10**, 99 (2001).
- ⁵M. C. Gallazzi, L. Tassoni, C. Bertarelli, G. Pioggia, F. De Francesco, and E. Montoneri, *Sens. Actuators B* **88**, 178 (2003).
- ⁶R. Rella, P. Siciliano, F. Quaranta, T. Primo, L. Valli, and L. Schenetti, *Colloids Surf., A* **198–200**, 829 (2002).
- ⁷B. Lee, *Opt. Fiber Technol.* **9**, 57 (2003).
- ⁸S. Maric, J. W. Lorgen, U. Herrmann, U. Schramm, and J. Bargon, *Sens. Actuators B* **101**, 265 (2004).
- ⁹H. Siringhaus and T. Shimoda, *MRS Bull.* **28**, 802 (2003).
- ¹⁰S. R. Forrest, *Nature (London)* **428**, 911 (2004).
- ¹¹Y. Yang, S. C. Chang, J. Bharathan, and J. Liu, *J. Mater. Sci.: Mater. Electron.* **11**, 89 (2000).
- ¹²D. Nilsson, T. Kugler, P.-O. Svensson, and M. Berggren, *Sens. Actuators B* **86**, 193 (2002).
- ¹³K. E. Paul, W. S. Wong, S. E. Ready, and R. A. Street, *Appl. Phys. Lett.* **83**, 2020 (2003).
- ¹⁴J. Namiesik, *J. Chromatogr.* **300**, 79 (1984).
- ¹⁵G. A. Sotzing, S. M. Briglin, R. H. Grubbs, and N. S. Lewis, *Anal. Chem.* **72**, 3181 (2000).
- ¹⁶J. Y. Kim, J. H. Jung, D. E. Lee, and J. Joo, *Synth. Met.* **126**, 311 (2002).
- ¹⁷A. W. Adamson, *Physical Chemistry of Surfaces* (Wiley, New York, 1990).
- ¹⁸M. F. Mabrook, C. Pearson, and M. C. Petty, *Chemical sensors*, UK patent application 0418945.2 (2004).
- ¹⁹S. Spagnoletti, *Alcolock car breathalyzer* (<http://transportation.engadget.com/entry/1127914145745557/>, 24 Aug. 2004).