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Low-cost conductometric transducers for use in thin polymer film chemical sensors

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ABSTRACT

Low-cost conductometric transducers have been designed and characterised with a view to their potential use as chemiresistors in mobile sensor applications. Four different geometries of transducer have been evaluated by two different measurement techniques. Devices were fabricated by etching planar gold electrodes on low-cost glass-fibre substrates (FR-4) using a standard printed circuit board (PCB) photolithography, wet etching and electroless plating method. Thin films of the P-type semiconducting polymer poly(3,4-ethylenedioxythiophene)poly(styrenesulfonate), PEDOT-PSS, were cast onto the electrodes by spin-coating. The conducting polymer films were electrically characterised by measuring the film resistance from the underlying gold electrodes using a digital multimeter, and also by determination of the film's current–voltage transfer characteristic (*I–V* curve) measured with a precision laboratory 4-point probe instrument. This allowed the relative contribution of the contact resistance at the Au/PEDOT-PSS interface to be determined as a proportion of the overall measured resistance. Contact resistance is known to affect the analytical performance of chemiresistor type devices, so in this work the combined effects of electrode geometry, polymer film composition and ageing of the film on bulk film and contact resistances have been investigated. The applicability of the chemiresistor transducers for chemical sensing is demonstrated using a PEDOT-PSS thin film as an ethanol vapour sensitive coating in a simple vapour exposure test, where a reversible conductometric response was observed. Due to the simplicity, low-cost and ultra low-power requirements of these transducers, they may be particularly suited to battery powered mobile and wireless sensing applications, or to applications dependant upon energy harvesting.

1. Introduction

Conductometric (or resistive) and capacitive transducers based on conducting polymers (CPs) are among the most commonly utilised devices in switching and sensing applications, and are particularly attractive as chemical sensors, especially in electronic noses [1–4]. This is due to the relatively simple and inexpensive fabrication methods needed to produce them, such as ink-jet printing [5] and spin-coating, and the ease of interfacing them to processing electronics [6]. These features also make CP conductometric transducers interesting for deployment as low-cost disposable sensors, especially in mobile and/or wireless devices for the internet of things (IoT) [7], and as vanguard devices [8] in remote chemical analysis [9].

In its simplest form, a conductometric chemo-sensor consists of a chemically sensitive conducting or semiconducting material, layered between two electrodes. An excitation voltage or current is applied across the electrodes, and either the electrical conductance or resistance of the material, in the case of DC excitation, or the impedance or capacitance of the material, in the case of AC excitation, is determined. In the presence of a chemical analyte that modifies the conductance or dielectric properties of the film, an analytical signal component may be determined. Conductometric sensors can thus be arranged as simple variable resistors or capacitors in electrical circuits, in either single-ended or differential (Wheatstone bridge) type configurations. More intricate 3-terminal organic conductometric devices can also be fabricated that have greater sensitivity at the expense of increased device complexity, such as organic thin film transistors (OTFTs) and organic electrochemical transistors (OECTs) [10,11].

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A typical organic film chemiresistor consists of an interdigitated metal electrode array, usually microfabricated on an insulating substrate (quartz, glass, or alumina) onto which the organic chemically selective layer is deposited. Electrode features are usually in the 5–500 μm size range, and the thickness of the organic layer is typically in the range 0.01–1 μm. Total electrode areas are typically 0.1–1 cm^2 [12]. Electrodes are made by evapouration or sputter-coating of the electrode metal (Au, Ag, Pt, etc.) under high vacuum conditions onto the insultaing substrate. The final electrode shape is patterned in the metal layer using a lithographic process followed by wet chemical etch. The cost of fabricating chemiresistors in this manner can often be measured in thousands of dollars for prototype quantities due to the non-recurring lithography mask costs, and recurring thin-film deposition costs.

The overall resistance of a polymer based transducer is dependent upon several factors in addition to just the polymer bulk resistivity. These factors include temperature, the electrode material and geometry and the contact resistance. For example, it is known that the contact resistance between a metal electrode and the conducting polymer can become a significant proportion of the overall measured resistance when simple 2-point measurements are made on thin films [13]. The contribution of contact resistance can be removed by employing a 4-point measurement technique, where a stimulus current is passed between two drive electrodes, and the potential difference arising in the bulk material is determined between two sense electrodes. The 4-point technique is mainly used for characterisation of material properties, such as for example, measurement of sheet resistivity in "hard" semiconductors or semiconducting polymers like PEDOT-PSS [14,15], and is less commonly used for sensing. Nevertheless, the effects of contact resistance of polymer thin films on the response of conductometric chemical sensors are significant, and this complex issue has been studied in detail by Lange et al. [13]. In their work, they used microfabricated interdigitated planar electrodes to characterise bulk and contact resistances of thin polymer films of polyaniline [16], and polypyrrole [17] using both 2-point and 4-point methods. The effect of contact resistance in organic thin-film transistor (OTFT) sensors has also been investigated by Torsi et al. [18]. Material and geometry [19] of chemiresistor electrodes and the hydrophobicity/hydrophilicity of the substrate surface [20] have been identified as parameters which can considerably affect the sensor response. So, despite the intrinsic simplicity of these devices in terms of design and fabrication, the origin of the analytical signal in chemiresistors is rather complex and is affected by multiple factors including the conducting polymer film thickness and morphology or hydrophobicity of the insulating substrate. For these reasons, it is generally accepted that the functional relationship between the measured conductivity and the analyte concentration is always empirical, and that the rigorous interpretation of chemiresistor results is complex due to the combination of these different factors [3].

The aim of this work was to investigate the applicability of simple conductometric transducers specifically designed for use with low-cost mobile or wireless sensing systems. Transducers were fabricated on hydrophobic glass-fibre substrates (FR-4), each patterned with a unique electrode geometry onto which a semiconducting polymer film was deposited. The choice of materials and the design of electrodes allowed the electrical characterisation of the films to be performed using 2-point and 4-point techniques, so that both the bulk polymer and metal-polymer contact resistance could be determined. The transducer substrate material, FR-4, is the most commonly used printed circuit board (PCB) material from the electronics industry, and was selected because of its low-cost, ease of processing, and the future option of mounting electronic components directly on to the same substrate. These factors make the transducers ideal for emerging wireless sensing systems, and their intrinsic low-power consumption means these transducers could be powered in simple electrical circuits from energy harvesting devices (EHDs) [21]. PEDOT-PSS was specifically chosen as a model conducting polymer because of its suitable combination of properties, including chemical stability over a wide pH range, good film forming properties and processability, high electrical conductivity, and its general widespread use in plastic electronic devices and organic semiconductor sensors [22–26].

The results of the work presented here will contribute to optimising the electrode geometry, interface electronics and materials necessary for development of low-cost, conducting polymer chemical sensors suited to autonomous mobile and wireless sensing applications that are under development in our research group [27–29].

2. Materials and methods

2.1. Chemicals

Chemicals were used as received: PEDOT-PSS, poly(3,4-ethylenedioxythiophene) poly(styrenesulfonate) (1.3% in H_2O, dispersed in an aqueous solution, high-conductivity grade), ethylene glycol, mass fraction, $w \geq 99\%$, Triton® X-100 (4-(1,1,3,3-tetramethylbutyl)phenyl-polyethylene glycol), were from Sigma–Aldrich, ethanol ($w = 96\%$) from Gram-mol, Croatia, and DBSA, dodecylbenzenesulfonic acid (96% linear alkylbenzene sulfonic acid) from Alfa Aesar GmbH, Germany.

2.2. Electrode and substrate fabrication

Planar electrode structures were designed using commercial printed circuit layout software (EASY-PC Professional v11.0, Number One Systems Ltd., Gloucester, UK), and fabricated with a standard UV-lithography/wet chemical etch process followed by an electroless gold plating process on standard FR-4 glass-fibre printed circuit substrates (RAK Printed Circuits Ltd., Saffron Walden, UK). Substrates were coated with a hydrophobic solder resist to leave only the active gold electrode area exposed (Fig. 1).

2.3. PEDOT-PSS coating formulation

Chemical cocktails (coating formulations) containing different ratios of PEDOT-PSS, ethylene-glycol, ethanol, and either DBSA or Triton X-100 were prepared with the quantities shown (Table 1). Pristine PEDOT-PSS stock dispersion was stored at 4 °C, and therefore allowed to equilibrate at room temperature prior to use. Cocktails were mixed and homogenised for 10 min in an ultrasonic bath (Transsonic T 460/H, Elma Hans Schmidbauer GmbH & Co., KG, Singen, Germany).

2.4. Conductometric transducer fabrication

Electrode substrates were washed in ethanol and rinsed with distilled water, then oven dried at 100 °C for 10 min. Films were processed by dispensing either 100 μL of pristine PEDOT-PSS dispersion (M0) or one of the modified PEDOT-PSS cocktails (M1–M3) onto the substrate. Spin coating was performed with a laboratory spin coater (model KW-4A, Chemat Technology, Northridge CA, USA), with spin conditions as shown (Table 2). Film post-treatment consisted of an oven bake at 115 °C for 20 min. Processed substrates were stored in the laboratory at room temperature and pressure in non-hermetic glass containers, in ambient light conditions.