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Switchable Passive Wireless Vapour Sensors from Inkjet Printed Electronic Components on Poly(dimethylsiloxane)

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Abstract

A potential route to printed, inexpensive and disposable Radio Frequency Identification (RFID) sensor tags for chemical sensing such as the monitoring of food spoilage is described. The stimuli responsive material poly(dimethylsiloxane) (PDMS), is known to swell upon exposure to organic vapors. Colloidal silver ink solutions were printed and sintered onto surface modified PDMS to give conductive silver feed loops. These loops act as the active sensing component in antennae for passive (battery-free) (RFID) tags. When the tags were exposed to certain solvent vapors (e.g. ether, dichloromethane, acetaldehyde) the printed feed loop fractured. This was accompanied by a rapid increase in resistance and ultimately loss of conductivity. This led to a change in the transmitted power and read range of the wireless device. Remarkably upon removal from the vapor, the fractured feed loops reassemble and become conductive again, making them switchable and "multi-use". The selectivity for the response to the vapors could be directly correlated to a function of the Hansen solubility parameters and vapor pressures of the solvents giving rise to the vapours. Significant differences in the solubility parameters between PDMS and the organic volatile and/or low vapor pressures lead to no significant response (e.g. methanol, acetic acid, popan-1-ol). This work paves the way to a fully inkjet printed RFID substrate for vapor detection.

Introduction

The ability of poly(dimethylsiloxane) (PDMS) to absorb both volatile and non-volatile compounds[1] makes it an ideal candidate for a sensing component in RFID tag sensors. We have previously reported the use of PDMS as the active component in an RFID vapor sensor. In this previous work DMS swelled in organic solvent vapours and thereby acted as an actuator by displacing a feed loop that modified the antenna response. We showed that the degree of swelling, and hence RF response, was directly proportional to the Hansen solubility parameters and the vapor pressure of the organic vapor.[2] However, the displacement approach used in this previous work had limitations with respect to the manufacture of the sensor and its versatility in application. To construct cheap passive sensor tags a move towards an entirely additive manufacturing approach was required. In the following mansuscript we will outline the design of an RFID sensor based on the same principle (swelling of PDMS as a mechanical actuator) but constructed via ink-jet printing of the feed loop directly onto the PDMS substrate and briefly describe it's response as a wireless sensor.

RFID Sensor Design

The RFID sensor shown comprised four elements: (i) an antenna for RFID wireless communication, (ii) a sensing impedance transducer, (iii) a RFID integrated circuit (transponder chip), and (iv) a stimuli responsive polymer. The antenna is tuned to the UHF RFID band, the transponder chip modulates information in the reflected signal, and the feed loop connects the antenna to the chip. In this passive RFID system, the tag is energized entirely by power provided from an external reader which also receives the reflected tag signal. The feed loop transforms the impedance of the antenna in order to match that of the transponder chip and ensure maximum power transfer between the two.[3]

Maximum power transfer between the feed loop and the transponder chip is essential to obtain the minimum amount of reader power required to activate the tag. This is strongly affected by the loop conductivity and a change in the electrical properties of the feed loop will cause the tag activation power to vary and this can be detected by the external reader. The majority of the tag surface area is covered by the antenna which is an end loaded half wavelength dipole.

Printing of RFID Feed Loops

PDMS substrates were prepared by the reaction of silanol-terminated PDMS, tetraethoxysilane and the tin(II) 2-ethylhexanoate catalyst in PTFE molds (20 mm x 20 mm x 2mm) at room temperature for 2 hours and then overnight at 60 °C. To enable the printing of the silver ink on the hydrophobic the PDMS was rendered hydrophilic by UV-ozone treatment following techniques reported in the literature.[4]

Hydrophilicisation of the PDMS surface was confirmed by

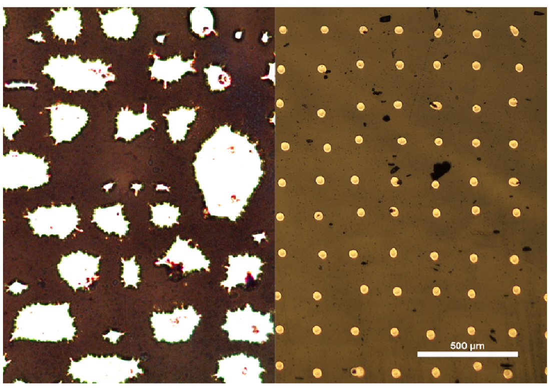

***Figure 1.** Droplets of silver on untreated (left) and UV-Ozone treated (right) PDMS substrates.*

(i) the appearance of peaks due to surface Si-OH groups in the ATR-FTIR spectra and (ii) a decrease in contact angles for water at the PDMS surface. The contact angle for the silver ink on the PDMS after UV-Ozone exposure was 34.0 ± 0.3° and a printed drop had a radius of approx. 50 µm and defined printed patterns were readily obtainable. An example of printed ink on PDMS before and after UV-ozone treatment of the surface is shown in Figure 1.

Further optimisation of the printing and sintering conditions was required to produce the low resistance needed for the RFID feed loops. The variables involved in the optimisation include the sintering temperature, the drop spacing and the number of layers of ink deposited. Sheet resistance of 20 Ω or less were needed for the efficient operation of the RFID tags and consequently the suitability of loops for application was assessed from four-point-probe sheet resistance measurements. Feed loops were ultimately created using a drop spacing of 35 µm with three printed layers and a sintering temperature of 150°C. Of a batch of 24 loops printed under these optimized conditions, 19 of them were seen to have resistances of less than 20 Ω and were considered suitable for incorporation into tags. A typical printed feed loop on a PDMS slab is shown in Figure 2a and the integrated PDMS feed-loop and antenna in the RFID tag is shown in Figure 2b.

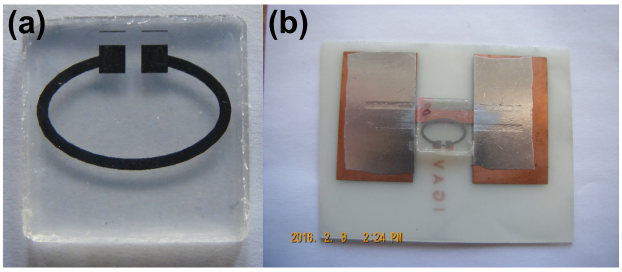

Figure 2. *Printed feed-loop on PDMS and complete RFID sensor tag.*

RFID tag sensing

PDMS swells in the presence of organic vapors and the expansion of the PDMS upon exposure to organic solvent vapours was observed to disrupt the conductivity of the printed conducting loop track. As a result the efficiency of the tag response was altered. This varying efficiency was detected by an external reader because the level of transmit power required to activate the sensing tag changed in proportion with the tag efficiency, which itself is a function of the exposure to the vapor stimulus. The tag efficiency is defined as the amount of power radiated by the tag antenna divided by the power flowing at its terminals connecting to the transponder chip.

Tags exposed to various vapors led to rapid increases in required transmitted power, typically reaching a maximum value in less than 10 minutes. Accompanying the increase in transmitted power was a corresponding reduction in read range recovery time after removal from solvent vapor, typically less than 10 minutes. Remarkably, repeated exposure to solvent vapor led to repeatable behaviour and a single tag could be exposed to vapor multiple times. An example of this recyclable response is shown for acetaldehyde in Figure 3. Optical microscopy and resistance measurements confirmed that the loss of conductivity caused by the fracturing of the feed-loop was the origin of the response (increase in power and

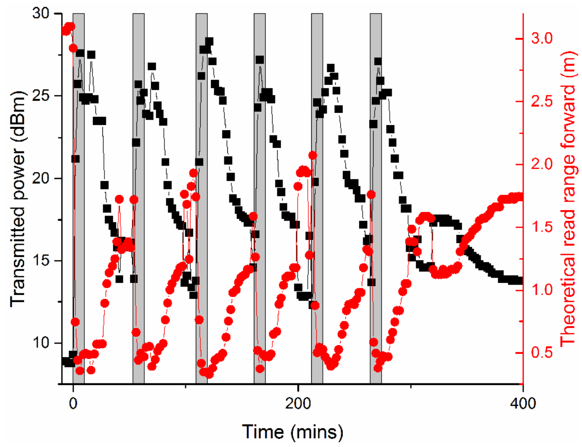

Figure 3. *Transmitted power and forward read range measurements for an RFID tag exposed to acetaldehyde.*

decrease in read range) and conversely the reassembly of the feed-loop upon removal from vapour led to the return of conductivity and decrease power and increase in read range.

Summary

We have demonstrated that we can print colloidal silver ink solutions using inkjet technology onto pre-molded PDMS substrates, and thermally sinter them to give conductive loops. With an end loaded dipole antenna, this produces a vapor sensitive RFID tag. These tags are shown to swell when placed in a solvent vapor atmosphere, which results in a dramatic increase in resistance across the printed loop. This corresponds to a significantly decreased (and ultimately, eradicated) read range, with a much higher transmitted power required to receive a response from the tag. Results from this study suggest that the large increase in resistance with swelling is a direct consequence of the fracturing/cracking of the printed silver loop that accompanies the swelling of the PDMS.

The reversibility of this vapour detection is demonstrated by the tag recovering from the loss of read range and increased transmitted power, returning to a working RFID tag after a period of time away from solvent vapor. This system could be used for numerous applications, such as the detection of food spoiling both on a small scale (in consumer's homes) and on a much larger scale (degradation of food during processing and transport). Further work is being carried out to enable this system to be made entirely by additive manufacturing.

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Author Biography

Simon Holder received his PhD in Chemistry from the University of Hull (1994) and since then he has worked in the Chemistry Department at Radboud University (Netherlands) and at the School of Physical Sciences at the University of Kent, Canterbury (UK). He is currently a Reader in Organic Chemistry at Kent.