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Stable fully-printed polymer resistive read-only memory and its operation in mobile readout system

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ABSTRACT

The read-only memory (ROM) is a key component for a wide range of printed electronics applications. The resistive type ROM based on conductive polymer poly(3,4-ethylenedioxythiophene) doped with poly(styrene sulfonate) (PEDOT: PSS) would be a promising technology of choice, which can be "manufactured-on-demand" via digital printing for high throughput and material saving. However, the instability issues associated with the conventional PEDOT: PSS and its interface with contact electrodes would be a critical hurdle preventing the technology from practical applications. This work proves that, by removing the hydrophilic acidic groups in conventional PEDOT: PSS, these instability issues can be well addressed. The ROM tags fabricated based on the modified PEDOT: PSS of neutral pH and inkjet printed silver electrodes present extremely stable performance under both aging and electrical stress tests in air ambient. A self-designed memory readout circuit board, communicating with mobile phone through near field communication, is also implemented to demonstrate the feasibility of using the ROM tags in real mobile systems. It is shown that, without any encapsulation, the ROMs can have stable output under high humidity condition (>60% RH), after either being stored in the ambient condition for 30 days or being operated after 20000 reading cycles.

1. Introduction

The printed read-only memory (ROM) is a key component for many envisioned printed electronics applications such as item identification, anti-counterfeiting, brand protection and supply chain management [1–6]. Printed resistor structure would provide a facile and low cost approach to realize ROMs by interpreting the stored data based on the resistance value [7–9]. Conductive polymer poly(3,4-ethylenedioxythiophene) doped with poly(styrene sulfonate) (PEDOT: PSS) is one of the most commonly used materials for printed conductors in different applications for its low cost, tunable conductivity in a wide range, low temperature processes, and excellent transparency [10–13]. For resistive type ROM applications, the resistance values of printed PEDOT: PSS line structures could vary over orders of magnitude by using different ink formulations, post treatment and employing an over-printing technique [9,14–17]. Moreover, the ink formation of PEDOT:PSS can be modified to process the resistor structures with different coating and printing processes, including slot die coating, flexography, gravure, inkjet printing, and even screen printing by forming a high viscous paste [18–21].

For ROMs in practical use, especially those requiring large number of storage bits, the formed resistor structures need to have very stable electrical properties during the whole product life. Moreover, the ROMs need to endure enough times of data reading under electrical bias. However, the hygroscopic property of the conventional PEDOT: PSS could lead to poor stabilities of the printed resistors due to absorption of water from the ambient causing conductivity degradation of PEDOT:PSS [22]. Therefore, the instability issues would be a critical hurdle preventing PEDOT: PSS based resistive ROMs from practical applications.

In this work, resistive ROM tags were fabricated by dispensing PEDOT:PSS solution on plastic substrate to fabricate the resistor structures. For data readout, less resistive contact electrodes were formed by inkjet printing metal-organic precursor type ink to interface the dispensed PEDOT:PSS resistor structures representing different stored data. The combination of the two type "drop-on-demand" digital manufacturing approaches provides advantages of maskless patterning, great material saving for low

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cost and easy scalability towards mass production. It was found, with the conventional PEDOT: PSS, not only the resistance of the PEDOT: PSS resistor structures but also the contact resistance with the Ag electrodes could increase over time under storage or electrical bias in the air ambient, thus causing poor storage stability in the air ambient and also operational instability during the data reading procedure for the fabricated ROMs. The increase of the contact resistance is thought to be caused by acid corrosion of the Ag electrodes due to the acid property of conventional PEDOT: PSS [23]. To address these instability issues, a type neutral-pH PEDOT: PSS is introduced to fabricate the resistive ROMs, and can help to achieve stable intrinsic electrical property of the formed resistors and also stable interface with Ag contacts. As a result, excellent stabilities during operation and storage in air ambient are achieved. To demonstrate the functions of the printed ROMs in real system applications, a memory readout circuit board, communicating with a smart phone through near field coupling (NFC) communication, was designed. The operation of the neutral-pH PEDOT: PSS printed ROMs with the mobile readout system shows extremely stable properties during operation and storage. This work would open a route of developing low cost and reliable printed resistive ROMs in conductive polymer for practical system applications.

2. Experimental

2.1. Materials and processes

The PEDOT: PSS (Clevios PH1000) used in this experiment was provided by Heraeus Clevios GmbH with a pH value of 1.5–2.5. The neutral-pH PEDOT: PSS solution with a pH value of 7.0–7.5 from Shanghai OE Chemicals was obtained by adding guanidine aqueous solution into the acidic PEDOT: PSS. 5 wt% dimethyl sulfoxide (DMSO) solution was added to the neutral-pH PEDOT: PSS dispersion to increase the conductivity. 125 μm thick polyethylene terephthalate (PET) film was cleaned in acetone and isopropyl alcohol as the substrate. The contact pads were formed by printing a type metal-organic silver precursor ink (Jet-600C, Hisense Electronics, Kunshan, China) using a piezoelectric inkjet printer (Dimatix, DMP 2831) with a 10 pL cartridge, followed by a sintering process at 120 °C for 10 min in air ambient. For the inkjet printing process, a customized waveform was set with a drop velocity of approximately 5 ms, a jetting voltage of approximately 15 V, a cartridge print height of 0.8 mm and a jetting frequency of 5.0 kHz. After formation of the contact pads, either the PH1000 or the neutral-pH PEDOT: PSS dispersion was deposited between contact pads using a robot dispenser (Shanghai Pioneer Elec Tech Co. Ltd.), and then the samples were annealed on a hot plate at 120 °C for 15 min to form resistor structures.

2.2. Electrical characterization

The resistance measurements of the samples were carried out by a Keithley 2400 system. All measurements were performed at room temperature in air ambient.

2.3. Readout circuit board

The circuit board, as shown in Fig. 1(c) and (d), composes of a microcontroller chip, a NFC chip, a 13.56 MHz antenna and a 14-pin flexible flat cable (FFC) interface for reliable connection of the ROM tag. The MSP430F2618 16-bit microcontroller from Texas Instruments is chosen for its ultra-low power consumption and integrated functional modules including a 16-bit ADC and 48 I/O pins. The NFC controller chip was self-designed and taped out in Semiconductor Manufacturing International Corporation (SMIC), China. The data to be received and transmitted is stored in the data FIFO. The NFC chip communicates with the microcontroller through a serial peripheral interface (SPI) controller. A radio frequency (RF) interface in the NFC chip with the 13.56 MHz antenna is used to build wireless connections between the circuit board and the mobile phone.

3. Results and discussions

3.1. Device structure and the mobile readout system

The layout of the printed ROM is illustrated in Fig. 1 (a). 125 μm thick polyethylene terephthalate (PET) film is used as the substrate to fabricate the ROM tags. The resistor structures are defined by dispensing of PEDOT: PSS dispersion (PH1000 or the modified neutral-pH PEDOT: PSS). The chemical structures of the conventional PEDOT: PSS and the modified neutral-pH PEDOT: PSS used in this work are shown in Fig. 1 (b). The dispensed neutral-pH PEDOT: PSS line shows similar thickness, line width and surface morphology with that of PH1000, as compared in Fig. 2 (a) and (b), respectively. The contacts are formed by inkjet printing of Ag ink. The stored data is interpreted as a voltage divider of two resistor parts connected in series. The supply voltage (V_{CC}) is applied across the resistor pair with the output voltage (V_{OUT}) to be measured at the connection point between them. Different resistance values of the two resistor parts are defined by varying the number of printed PEDOT: PSS lines and the location of the Ag electrode for V_{OUT}.

To demonstrate the operation of the ROM tags in practical systems, both the fabricated PH1000 and neutral-pH PEDOT: PSS ROM tags are connected to a self-designed memory readout circuit board, which communicates with a smart phone through NFC as shown in Fig. 1 (c). Fig. 1 (d) gives the circuit schematic of the readout circuit board. When the phone touches the circuit board and sends a command for data acquisition, the data stored in the ROM tag is read out and transmitted to the mobile phone through NFC. A software developed in Android is run in the mobile phone to display the data on the screen.

3.2. Storage stability

For practical use, the stored data in the ROMs needs to be very stable during the whole product life under the ambient storage condition. In the fabricated ROM devices, the measured output data is determined by the PEDOT: PSS resistor parts and also their contacts with Ag electrodes, which could both vary over time in the air ambient. Fig. 3(a) compares the variation of the resistance for the printed resistors in PH1000 and neutral-pH PEDOT: PSS over time when being stored in air ambient at temperature of 25 °C and relative humidity (RH) of 60%. The initial resistance values of the PH1000 and neutral-PH PEDOT: PSS resistors with the same length of 0.5 cm are 6.8 kΩ and 5.4 kΩ, respectively. It can be seen that the resistance of the PH1000 resistor increases nearly 100% after 10 h due to absorption of water by the acidic PSS group in PH1000. After 10 h, the resistance of the PH1000 resistor tends to be stable because of water absorption approaching saturation. The PH1000 structures also present much larger dispersion of resistance values. The variation of resistance value over time and among different