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Research paper

Inkjet-printed resistive memory cells for transparent electronics

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ABSTRACT

This article describes completely inkjet-printed transparent memory cells consisting of a four layer structure of poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT:PSS)/Ag nanoparticles/spin-on-glass (SOG)/PEDOT:PSS. When targeting applications in transparent electronics, standard Electrochemical Metallization Memory (ECM) is constrained by its need for opaque metal electrodes. Therefore, we replace a bulk metal electrode by the conducting and transparent PEDOT:PSS covered with a submonolayer of Ag nanoparticles, which serves as active electrode for the filament growth while still preserving a high degree of transparency. Conductive atomic force microscopy (CAFM) measurements confirm that the Ag nanoparticles act as seeds for the filament formation. The cells show low switching voltages of approximately 1.2 V and a high OFF/ON resistance ratio of more than 100. The presented cell structure enables extremely cost-efficient memory for future applications in transparent electronics.

1. Introduction

The field of transparent electronics has gained a lot of interest due to its manifold applications such as transparent displays, intelligent windows and transparent solar cells [1]. Intense research has been conducted on transparent thin film transistors, which were first reported in 2003 [2]. In order to realize fully transparent circuits, every single circuitry element has to be transparent, including the memory unit. The resistively switching Electrochemical Metallization Memory (ECM) is non-volatile, shows low power consumption and has a simple three layer conductor-insulator-conductor structure [3]. Various oxides such as ZnO, SiO_2, and ZrO_2 have served as insulating layers [4–6] – all of them transparent, wide bandgap insulators. However, the ECM's switching principle is based on the formation and dissolution of a metallic filament through the insulating layer [7] and therefore ECM usually feature opaque metal electrodes. We replaced both metal electrodes with a layer of poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT:PSS), a highly transparent polymer. Since the memory cells require an electrochemically active metal as source for the metallic filament, the bottom electrode is covered with a sparse layer of silver nanoparticles to preserve a high degree of transparency, but also to provide material as a seed layer for the formation of a silver filament. The insulating SiO_x can show intrinsic switching through filamentary Si crystallization [8]. In our case, insulating spin-on-glass (SiO_x structure) only acts as matrix for the silver filament formation and requires the Ag nanoparticles for the switching. A schematic of the cell structure is depicted in Fig. 1.

Inkjet printing is an additive and extremely cost-effective deposition method and used for the fabrication of the whole device. Compared to standard photolithography, which requires four process steps under cleanroom condition, inkjet-printing only needs one additive process step at ambient conditions.

2. Experimental

In this study, we report on PEDOT:PSS/Ag nanoparticles/spin-on-glass (SOG)/PEDOT:PSS memory cells, which are printed on silicon wafers and glass substrates.

To exclude possible interference of sneak path issues in passive crossbar arrays during switching, the design consists of only one bottom electrode word line and several top electrode bit lines [9]. The intersection of bottom and top electrode, which makes up one cell, is shown in Fig. 2.

All four layers of the memory cells are printed with a FujiDimatix® DMP 2831 printer and a cartridge with a 10 pl drop volume.

The substrate is subjected to an oxygen plasma (100 W on a 4″ substrate holder) for 3 min to promote the ink wetting.

The first layer of the bottom electrode consists of PEDOT:PSS, a conducting organic polymer (Clevios™ P JET N V2) printed with two jets using a drop spacing of 10 µm. For optimized print quality, the substrate is heated to 60 °C during the printing process. A 30 min sintering step at 150 °C under ambient atmosphere results in a resistivity of

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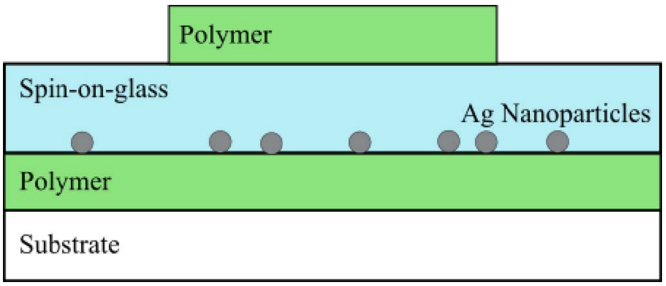

Fig. 1. Schematic of a cell cross section (not true to scale).

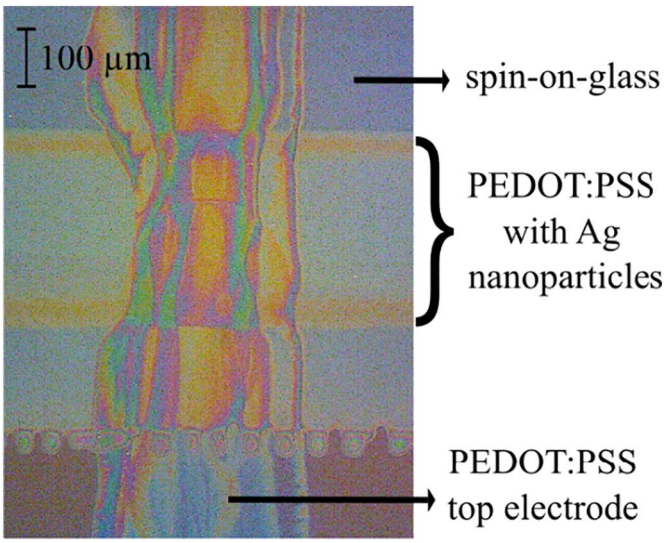

Fig. 2. Top-view photomicrograph of a cell on a Si wafer. The bottom electrode and the spin-on-glass layer are printed horizontally and the PEDOT:PSS top electrode is printed vertically. The intersection comprises one memory cell.

1.7×10^{-4} Ωm. A linewidth of 250 µm and a mean thickness of only 52 nm ensure a complete coverage of the SOG and prevent any short-circuit between top and bottom electrode.

In order to create an electrochemically active bottom electrode, Ag nanoparticles are printed on top of the electrochemically inert PEDOT:PSS.

Silver nanoparticles are fabricated in-house by microwave-assisted synthesis from silver acetate in ethylene glycol. A detailed description of the synthesis will be presented elsewhere. The silver ink is diluted to an Ag content of only 0.14 wt% which ensures a very low coverage of the bottom electrode with nanoparticles. The ink is printed on top of the bottom electrode with one jet and a drop spacing of 20 µm. The cartridge is heated to a temperature of 55 °C during printing to reduce the high viscosity of the ethylene glycol for optimal droplet formation [10].

Spin-on-glass, Honeywell Accuglass® P-5S is used as insulating layer. After a sintering step, this phosphosilicate polymer forms a SiO_x layer on the substrate. It is printed by one jet with a drop spacing of 5 µm on top of the bottom electrode. The manufacturer recommends a sintering temperature of 425 °C, which should result in a dense and chemically resistant SiO_x layer. However, the PEDOT:PSS bottom electrode excludes temperatures in excess of 200 °C as elevated temperatures tremendously decrease the polymer's conductance [11]. Thus, the SOG is sintered at 200 °C (3 h under ambient atmosphere).

Fig. 3 shows an atomic force microscopy (AFM) scan of the layer structure PEDOT:PSS/Ag nanoparticles/SOG on a silicon wafer. An AIST-NT SmartSPM system is used in tapping mode with Si tips of 8 nm tip radius. The nanoparticles are uniformly distributed on the bottom electrode and can be detected through the SOG layer. It is clearly visible that the low silver content of the ink results in a submonolayer of Ag nanoparticles on the surface.

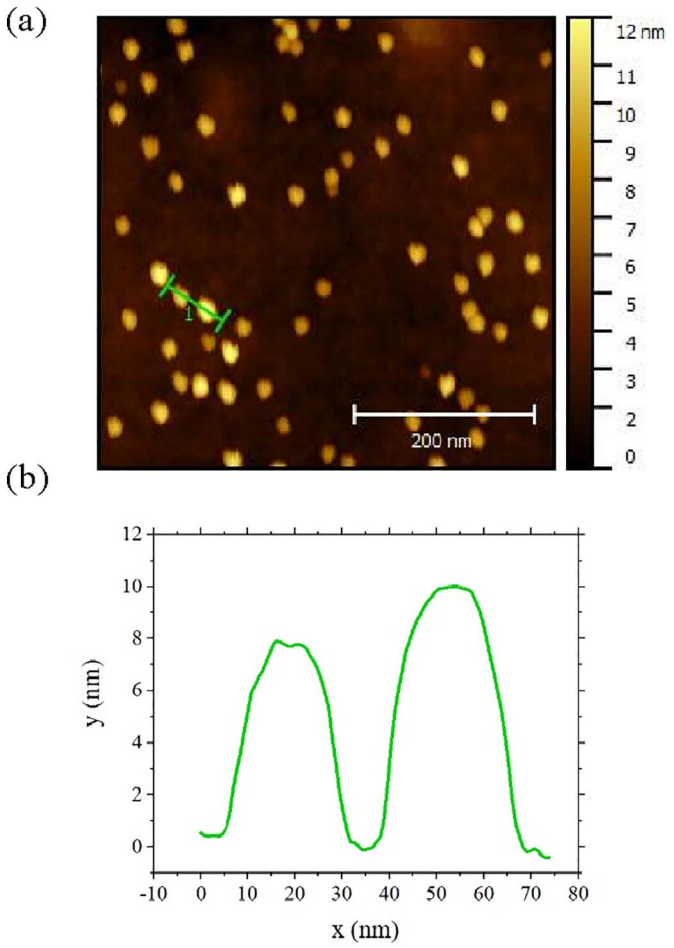

Fig. 3. (a) AFM topography image of printed silver nanoparticles on a PEDOT:PSS bottom electrode, covered with SOG, and (b) profile along the green line of the topography image. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

A second layer of PEDOT:PSS creates the electrochemically inert top electrode and is printed perpendicularly to the bottom electrode using the same parameters. However, four layers of the top electrode are printed to ensure good conductivity considering the roughness of the underlying layers.

3. Results and discussion

The cells are investigated by quasi-static electrical measurements using a Keithley 2400 sourcemeter with a voltage step size of 0.02 V and voltage sweeps between −0.5 and 3 V, starting from 0 V, and a current compliance of 10 µA. Typical switching characteristics are given in Fig. 4. The cell switches from the initial high resistance OFF state to the low resistance ON state at a voltage of 1.2 V and switches back to the OFF state at approximately −0.1 V. The resistance ratio of OFF to ON is larger than 100 (see Fig. 4(a)).

While the ON state clearly shows Ohmic conduction through the metallic filament, in the OFF state the current is directly proportional to $\exp(\sqrt{V})$ (see Fig. 4(c)). This indicates that the current flow for the OFF state is dominated by thermionic emission, where the electrons overcome the energy barrier at the conductor-insulator interface through thermal activation [12].

50% of the fabricated cells showed stable switching. The rest displayed short-circuits between the two electrodes due to insufficient coverage of the bottom electrode with SOG.