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Research paper

Spin-coated silver nanocomposite resistive switching devices

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ABSTRACT

A simple two-terminal resistive switching device is fabricated on the basis of a silver-based nanocomposite by means of direct processing through spin-coating technique. This work mainly focuses on the role of Ag in inducing a resistive switching in response to an applied electric field. Characterization results confirm the field-induced formation of a conductive filament along the silver clusters bridging two electrodes, which evidences the microscopic origin of bipolar resistive switching behaviour observed in our device. The morphological and electrical characterizations performed on the device support the hypothesis of field induced filament formation. The present study evidences a simple and low-cost material, easily processable to realize logic devices exhibiting a bipolar non-volatile switching behaviour that is controllable by means of the current compliance level.

1. Introduction

Memristor is supposed to be a fundamental part of future computing. During the year 1971, Leon Chua mathematically conceived the idea of a passive two-terminal electrical component featuring a linear relationship between flux (time integral of voltage) and charge (time integral of current) [1]. Until 2008 the term memristor was just used as a mathematical concept, until HP researchers came up with the development of the mysterious memristor [2]. From that time on, the field of resistive switching devices (RSDs) received unyielding attention. The exponential growth reported in Moore's law and more recently the saturation that was reached in the development of microchips in microelectronic industry, spurred further research in this topic. RSDs are considered to be a prospect replacement of standard memories in this regard, offering also a novel computational paradigm.

Resistive switching (RS) phenomena can be mainly categorized into two main types: filamentary type [3], and interfacial type [2]. The filamentary switching can be attributed to the formation of a local conductive filament. For interface switching, different mechanisms have been proposed such as migration of oxygen vacancies [4], charge trapping [5], drift of ions etc. [6]. So far there is no unified switching mechanism that has been proposed. Further research should be carried out in order to better understand RS behaviour. RSDs, with their simple two-terminal architecture, can be further divided in inorganic, organic and hybrid, depending on the type of active switching material present in between the electrodes. Inorganic RSDs are very well studied due to their well-controlled structure, ease of deposition in the form of thin films and, most of all, their compatibility toward CMOS processes [7]. On the other hand, a fundamental issue is connected to low power, low cost, and high integration density, necessary for the digital systems, especially portable ones. In this regard, organic RSDs, in which the active switching matrix is composed of a very thin film (100 nm or less) of polymeric material, are more advantageous [8]. At last, nanocomposite (NC) RSDs, otherwise known as hybrids, consist of a passive matrix containing active fillers dispersed as clusters or nanoparticles (NPs) [9]. Hybrid nanomaterials gained widespread interest due to their novel properties in various fields of science including optoelectronics, antibacterial, medicine, environment applications etc. [10–14]. Nanometer-sized materials feature quantum confinement of charge carriers and often result in amazing properties that could be exploited to realize electronic devices enhanced with innovative functionalities [15–17]. NCs can be easily prepared by blending polymers with inorganic NPs such as silver, gold etc. Such devices offer several potential advantages like reduced cost if compared to batch-processed inorganic materials, ease of additive manufacturing (i.e. printing) over large areas, high throughput processing, light-weight and flexible mechanical properties [18]. Nanomaterials used in this field include metallic NPs [19] as well as nanotubes, nanowires, nanorods etc. [20]. In the current scenario, the role of silver NPs in a polymer matrix to induce RS in a device is addressed. The incorporation of metallic NPs in an insulating matrix provides a conducting path between the electrodes when the concentration of particles is above the so-called percolation threshold [21]. We will see that by using a dissipative (hence not totally insulating) matrix enabling a certain current, it is possible to induce atoms/ions migrate and literally form aggregates of NPs, that create filaments

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bridging opposite electrodes. The metallic NPs can be added into the polymer matrix either directly (ex-situ method), where commercial NPs or NPs prepared separately are dispersed into the polymer matrix, or indirectly (in-situ method), where metallic particles are formed in the polymer matrix during their synthesis [22]. The preference of in-situ or ex-situ method depends on the particular application. The in-situ method allows to control the properties of the composite by controlling the reactions conditions and by choosing the appropriate route thus leading to a stable matrix [23], while ex-situ based composite preparation is less difficult when compared to in-situ. The geometrical structure of the device also plays a crucial role in the performance. Most of the recent work on RSDs was conducted on stacked structures, where the active switching matrix was sandwiched between two electrodes [20,24]. These devices have higher risks to undergo stresses during fabrication, and it is very difficult to probe the active matrix to identify any topological or morphological change occurring during switching. In the present study, the active switching NC is composed by ex-situ synthesized Ag NPs embedded in Polyvinylidene fluoride-hexafluoropropylene (PVDF-HFP). The NC was spin coated on the planar electrodes, optically lithographed on a silicon substrate, using inter-electrode distances in the order of 1 to 10 μm and thus at least two orders of magnitude bigger than usual sandwiched structures. Planar structures are said to have significantly lower intrinsic capacitance than sandwich-type structures, and thus said to have faster dynamic response [25]. In addition, such layouts have the active layer directly exposed and can be probed by a number of surface analytical techniques to identify and characterize topographical, morphological changes occurring upon RS. Very few studies have been reported so far in this regard [26–28]. Even though RS events are being studied in detail, no unique explanation has been provided for the bipolar resistive switching phenomena. Filamentary conduction model [27] which is very commonly used to explain switching is still not fully understood. Here we present a low-cost material suitable for the fabrication of RSD, which exhibits a bipolar non-volatile switching behaviour that is controllable by means of the current compliance level. The RS observed is explained by the field induced silver filament formation, which is substantiated by the electrical and morphological characterizations carried out.

2. Experimental details

2.1. Materials

Poly(vinylidene fluoride-hexafluoropropylene) (PVdF-HFP) Kynar-Superflex 2500 (pellets) with 20 wt% of hexafluoropropylene and a density 1.79 g cm^{-3} was purchased from Arkema. Polydispersed Ag NP suspension with an average diameter of 40 nm was bought from Politronica Inkjet Printing S.r.l.

2.2. Sample preparation

The RSD considered in this paper has a planar structure with identical gold electrodes The fabrication process started with the growth of a SiO_2 layer (200 nm thick) on both sides of a (100) oriented silicon wafer, by using a dry oxidation process in a quartz tube furnace. The gold electrodes were deposited using an electron beam evaporator (ULVAC EBX-14D). A Ti layer (10 nm thick) was used in order to promote the adhesion of the Au layer (100 nm thick) to the substrate. Both layers were grown using a deposition rate of 0.3 nm/s. Electrodes were patterned using AZ5214E photoresist (microchemicals) in a standard UV photolithographic process, with the aid of a Neutronix Quintel NXQ 4006 mask aligner. Then, Au layer was selectively etched using a solution made by Iodine (I_2) and Potassium Iodide (KI) in water, with an estimated etch rate of 0.2 nm/s. The underlying Ti layer was etched using a solution of Hydrofluoric Acid (HF) and Hydrogen Peroxide (H_2O_2) in water. Finally, the substrates were diced using a diamond dicing saw, in order to obtain samples with an area of 5 mm × 7 mm, each with three identical Ti/Au electrodes. The electrodes have a width of 300 μm, and they are separated by a 10 μm gap.

The active matrix used in the RSD was prepared as follows. PVDF-HFP/Ag NC was prepared by solution method. PVDF-HFP (10 wt%) was dissolved in DMF by vigorous stirring for 20 min at 30 °C. Finally, suspension of Ag NP was added to the polymer solution and sonicated for 20 min for improving dispersion. The exact composition of PVDF-HFP/Ag was 50/50. The Ag NC suspension was spin coated onto the devices at 3000 RPM for 20 s. A pictorial representation of the device with the spin-coated polymer NC is shown in Fig. 1.

2.3. Characterization methods

The electrical characterization was performed on the samples by means of a Keithley 4200-SCS semiconductor Characterization System, using standard 2-point setup and contacting the samples by tungsten microneedles placed directly on the Au electrodes. In the present set up, as the electrodes were symmetric, the application of positive and negative bias to a certain electrode was not significant. All the electrical characterizations were performed at room temperature.

Field Emission Scanning Electron Microscopy (FESEM, ZEISS Dual Beam Auriga) was used for morphological analysis of nanocomposite on the planar structure.

Optical microscopy image was taken on the sample before and after electrical characterization using Leica DFC295. Matlab environment was used in order to compute the algebraic difference between the characterized and not characterized sample.

Thermogravimetric analysis (TGA) was performed on the Ag NP suspension with TG-209 F1 Libra (Netzsch). The experiment was carried

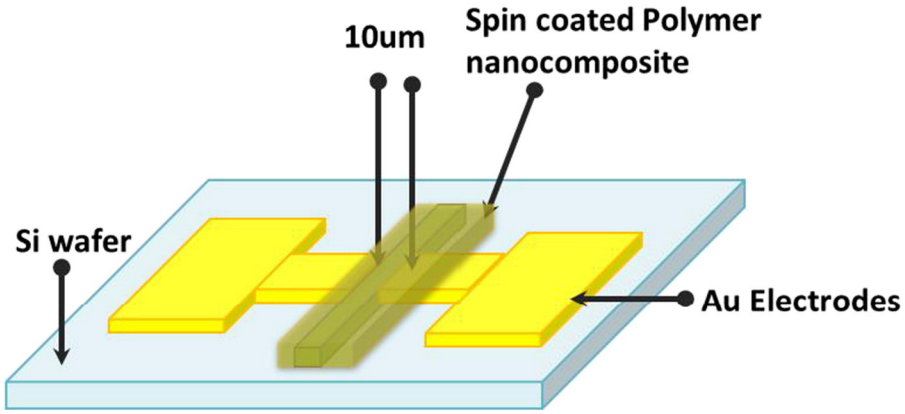

Fig. 1. Schematic representation of the RSD with Ag NC spin coated on the device.