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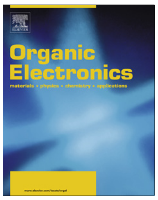

Air-stable, non-volatile resistive memory based on hybrid organic/inorganic nanocomposites

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ABSTRACT

A non-volatile memory element based on organic/inorganic nanocomposites is presented. The device can be operated in ambient conditions, showing high retention time and long-term life time. The formation/rupture of metallic filaments in the organic matrix is investigated by HR-XPS and ToF-SIMS analysis, and is demonstrated to be the driving mechanism for the resistive switching.

1. Introduction

Organic semiconductor devices have been widely studied for different applications, from sensing to optoelectronics [1–4]. Compared to the inorganic semiconductor technology, organic devices exhibit a variety of attractive advantages such as the possibility of low cost fabrication over large areas, of using flexible substrates, and of exploiting printing techniques [5–10].

In order to extend the application of organic semiconductors to more complex electronic systems, memory elements are essential. For these reasons, recently there has been a significant amount of research on memory devices based on organic materials [11–13]. Among them, organic Resistive Random Access Memories (RRAMs) [14] have emerged as promising candidates for future information storage media due to their attractive properties, including simple structure, good retention time, and high endurance. In addition, organic memories can show non-volatile characteristics or, in other words, can retain the stored information even when the electrical power supply has been turned off.

The key function of RRAM devices is the resistive switching: the resistance of the memory can be reversibly switched between two stable resistive states (low and high) by applying appropriate voltage pulses. So far, several materials have been studied for RRAM applications, and many groups have demonstrated the resistive switching in several types of organic and polymeric materials with different device structures [15–17]. Organic resistive

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memories were first introduced by Ma et al. [18] in 2002. They proposed a promising bi-stable device consisting of a three-layer-structure (organic/metal/organic) comprised between two metal electrodes. Initially, the idea was that the metal interlayer should be an ultra-thin continuous floating layer. However, detailed investigations revealed that this metal interlayer is electrically discontinuous, as it actually consists of small isolated metal clusters or nanoparticles (NPs) [19]. The Yang group extended this approach to different systems [20–23] and their research has stimulated strong interest in this field [24–26]. Recently, Liu and co-workers [27] proposed organic non-volatile memories based on Au/Alq_3/metal nanoparticles/Alq_3/Al. In particular, they concluded that the electrical characteristics of devices with gold NPs display much better performances with respect to those with aluminum NPs. These devices showed reproducible resistive switching, a high on/off current ratio of about 10^4, a retention time of 4 h and a reasonable stability under bias stress test.

Despite these promising performances, organic bi-stable memory devices are still in the exploratory stage of the research. Several important issues, such as the physical explanation of the resistive switching behavior, are still not clear. Although a remarkable amount of research has been made and many plausible mechanisms have been proposed by different groups, the understanding of the resistive switching phenomena is still controversial. Furthermore, their stability and reliability are still debatable. Indeed, organic memories should benchmark against inorganic FLASH memories in terms of data retention time, number of operation cycles, power consumption and stability in ambient conditions, in order to allow them to be employed in commercial products. However, one of the main issues concerning the real employment of such devices in operational environment deals with their long time stability. Indeed, many reported works show excellent behaviors but the devices have been only characterized and stored in inert atmosphere. Only few reports show a reproducible bi-stable behavior under ambient atmosphere. Among them, Jo et al. [28] developed a non-volatile memory element incorporating fullerene derivatives into the nanostructure of self-assembled poly(styrene-b-methyl methacrylate) (PS_{10}-b-$PMMA_{130}$) di-block copolymer. They demonstrated that such devices can be cycled more than 40 times and are characterized by a retention time of almost 1 h. Kim et al. [29] observed better results using a polyfluorene derivative film with silver nanoparticles, achieving retention time of 10^4 s with a reproducible behavior over more than 10^4 cycles. Very high retention times were also reported by Son et al. [30] using graphene sandwiched between two insulating poly(methyl methacrylate) (PMMA) layers. They demonstrated that these devices can be measured in ambient atmosphere with a number of ON/OFF switching cycles of around 1.5×10^5 and a (measured) retention time larger than 1×10^5 s. Hwang et al. [31] obtained highly environmental stable non-volatile memory elements with endurance cycle bigger than 10^2 and retention time in the order of 10^5 s, employing doped carbon nanotubes embedded into a polystyrene matrix. Summarizing, the demonstration of significant improvements in organic RRAMs in terms of retention time under ambient atmosphere should represent the main aim and motivation for further research in this area.

In this paper, a novel non-volatile memory device based on the combination of an air-stable organic semiconductor and inorganic nanoparticles is proposed. The device is particularly conceived for allowing long-term data storage in ambient conditions with high ON/OFF ratios. A complete electrical characterization of the memory element will be provided, together with an in-depth morphological investigation of the structure in order to precisely define its working principle.

2. Experimental section

2.1. Structure and materials

The memory devices fabricated in this study are two terminal elements, consisting of an hybrid layer between a cross-point array of top and bottom electrodes. The hybrid layer is a nanocomposite material obtained by sandwiching a metal nanoparticles interlayer between two organic semiconductor layers. The schematic view of the device structure is shown in Fig. 1. In particular, a commercially available perylene derivative, namely N1400 (Polyera), was used as semiconductor layer of the resistive memories. It is an n-type semiconductor, which can be deposited by thermal evaporation but also from liquid phase since it is soluble in chlorinated solvents. Moreover, it shows stable performances in ambient conditions. Indium Tin Oxide (ITO) and silver (Ag) were used as bottom and top electrodes, respectively. Two different types of metal nanoparticles, namely aluminum (AlNPs) and gold (AuNPs), were employed for the intermediate layer.

2.2. Chemicals

Gold nanoparticles were synthesized according to chemical reduction method previously described in [32]. Briefly, a mixture of sodium citrate tribasic dihydrate (0.9 g, 1 wt%, Sigma Aldrich $\geqslant$99.0%) and tannic acid (0.8 g, 1 wt%, Fluka) was added to the boiling aqueous chloroauric acid solution (98 g, 0.009 wt%, Sigma–Aldrich, $\geqslant$49%) under reflux. The color of the solution immediately changed from yellow to dark red, as a result of the gold NPs formation. Afterwards, the mixture was stirred for additional 15 min and then cooled down to room temperature. The NPs final concentration was 50 ppm with an average size of 9 ± 2 nm.

2.3. Device fabrication

ITO/N1400/NPs/N1400/Ag memories were fabricated on Indium Thin Oxide (ITO) coated glass (KINTEC) substrates ($2.5 \times 2.5\ cm^2$). The ITO bottom electrodes were patterned directly on the ITO coated glass substrates by means of photolithography. Chemical etching on ITO was performed using zinc powder and hydrochloridric acid. The first N1400 layer was thermally evaporated with a