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Electrical bistability of polyfluorene devices

T. Ouisse [*], O. Stéphan

Laboratoire de Spectrométrie Physique, Université Joseph Fourier, Grenoble 1 and CNRS (UMR C5588), 140, rue de la physique, B.P. 87, 38042 Saint-Martin d'Hères Cedex, France

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Abstract

A specific layer transfer process is developed so as to obtain multi-layer devices based on spin-coated polymers. This process is put to good use for embedding fine evaporated Ag layers between polyfluorene (PF) films with cyano side groups. The resulting structures, which are a stack with sequence Ag/PF/Ag/PF/Ag, exhibit reproducible electrical bistability. The difference between the "off" and "on" currents may extend up to eight orders of magnitude. Hence this effect might be used for producing memory devices.

1. Introduction

Organic electronics has attracted much attention in the last decades. In particular, conjugated polymers offer specific advantages in terms of fabrication cost and technical performance [1]. Among them, the polyfluorene family is characterized by a good processability and resistance against oxidation [2,3]. Although the strongest activity is devoted to light-emitting applications (see e.g. [1–3]), a number of other domains are also emerging, such as, e.g., photo-voltaic devices [4] and transistors [5]. Besides, it has been known for a long time that some organic materials, when microscopically associated with a metal, may exhibit a negative resistance domain and/or electrical bistability, thus opening some interesting perspectives in the domain of electrical memories. Observation of this effect is most generally, but not always, correlated to the introduction of flat molecules with cyano molecular units, whose electron deficit makes them good electron acceptors. The most notorious example is probably the organic charge transfer complex which can be obtained from mixing a suitable metal with tetracyanoquinodimethane (TCNQ) [6–9]. Electrical switching in Cu-TCNQ thin films was reported as early as in 1979 [10], and is still being actively investigated [11]. More specifically, Gao et al. have first shown that introducing Ag nanoparticles into thin organic layers with cyano groups results in electrical bistability [12]. Recently, it has been convincingly advocated, through experiments conducted on small and flat molecule devices, that embedding a thin metal layer between two organic layers might be used for producing low cost plastic memories [13–15]. In this article we address two

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[*] Corresponding author. Tel.: +33-476-514771; fax: +33-476-635495.

E-mail address: ouisse@spectro.ujf-grenoble.fr (T. Ouisse).

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topics: the first one deals with stacking successive spin-coated polymer layers, even when they are soluble in the same solvents. The second one is the subsequent realisation of bistable polyfluorene devices, similar in principle to the ones proposed by Ma et al. in the case of small evaporated molecules [13–15]. Although spin-coating deposition is a main advantage of polymer device fabrication, it prohibits multi-layer deposition of polymers soluble in similar solvents. Reticulation or an adequate chemical modification of the first deposited layers may be an option, but it requires to change the nature of the polymer and may thus affect its physical properties. Hereafter we propose a simple layer transfer process, which relies upon the use of a sacrificial water-soluble polymer layer. This method keeps all the advantages of spin-coating deposition. Then we utilize this process for fabricating stacks of the type metal/polymer/metal/polymer/metal. We show that the resulting two-terminal devices exhibit reproducible bi-stability. Hence it represents a first step for the production of low cost, polymer-based memories. To summarize, the originality of our work is three-fold: (i) chemical synthesis of a new polyfluorene with cyano groups, (ii) development of a simple technical process, involving only spin-coating deposition, to make multi-layer polymer devices and (iii) fabrication of bistable devices from a polyfluorene derivative, instead of using small evaporated molecules.

2. Device fabrication

The generic process used to deposit successive polymer layers is described as follows: A first active polymer layer is spin-coated onto a first glass susbtrate (sample 1). Then, a layer of polystyrene-sulfonate (PSS), soluble in water, is deposited on a second glass substrate (sample 2); the rotation is typically 6000 rpm for 2 min, and the thickness is in the 100 nm range. After 1 h, 80 °C annealing of the PSS layer under vacuum, the next active polymer layer is spun onto the dried PSS layer. The polymer + PSS layer is annealed under vacuum at 80 °C during another hour. Then, the two samples are brought very close to one another, and progressively dipped into de-ionized water. As the water dissolves the underlying sacrificial PSS layer, the hydrophobic polymer layer on top of it gradually comes off and adheres onto the active polymer layer of sample 1, which stands in front of it. After the transfer is completed, sample 1, which supports the polymer layer stacking, is annealed under vacuum (for the polymer under study the temperature was 100 °C and the duration was 1 h). The process can be repeated as long as one wants to add new layers. We tested it successfully not only for producing polymer–metal layer stacks, as described below, but also for producing bi-layers with acceptor and donor layers, with the purpose of fabricating electroluminescent devices. The acceptable current drive capability that we obtained for this latter class of devices, as well as the data obtained with the polymer–metal stacks, which we detail below, demonstrate that the interface between the transferred layer and the underlying polymer layer exhibits satisfying electrical properties. It should nevertheless be noted that the water-related process may result in unwanted polymer or metal layer oxidation, and this can be avoided by the incorporation of small quantities of polymeric antioxidant. For organic LED's we typically incorporate commercial poly-TDP2000, purchased from Acros Organics, which is based on the use of thiol substituants. This product completely inhibits polymer oxidation during the water-related step taking place before carefully drying the samples. To check this, we transferred two photoluminescent alkyl-polyfluorene (alkyl-PF) layers onto two similar PF layers. In the first case no additive was present, whereas in the second case poly-TDP2000 was added in the solution to be spun. Fig. 1 shows the photoluminescence spectra of both samples. Only the sample without antioxidant exhibits the spectral shift characteristic of the creation of fluorenone segments [2,3]. In the case of cyano-polyfluorene, on which we focus in this article, we did not notice a substantial change in device behaviour when using poly-TDP2000 or not, so that we do not think that partial layer oxidation is as crucial as for LEDs, for which the slightest oxidation is highly detrimental to device performance.

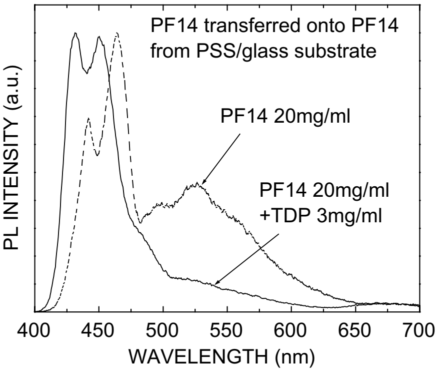

Fig. 1. Photoluminescence spectra of a spin-coated layer of polyfluorene with simple alkyl substituents transferred onto another PF layer (a side chain contains 14 carbon atoms). Full line: anti-oxidant poly-TDP2000 was added and dotted line: free from additive.

We note that in contrast with conventional wafer bonding techniques as applied to inorganic semiconducting materials [16], the process is not so strongly affected by the presence of microparticles, unless they lie precisely within the active area of a final device, since the soft polymer layer is conformally transferred onto the substrate. In principle, adequate modifications of this method would even allow one to deposit thin polymer layers on various non-flat substrates and objects, provided they are hydrophobic to some extent.

In this article we report more specifically on the fabrication of structures with a metal/polymer/metal/polymer/metal stacking sequence. First we synthesised a co-polymer of the polyfluorene family. One co-monomer consists in regular 9,9-dialkyl fluorene. It renders the co-polymer soluble in organic solvents. The second kind of repeat unit is obtained by converting fluorenone segments into cyano groups (Knoevenagel reaction) to obtain a molecular structure as schematised in Fig. 2. The synthesis of the initial fluorene–fluorenone co-polymer has been thoroughly described in [17]. It is worth noticing that the repeat unit is flat, thereby favouring π-stacking. The ratio of cyano-based units in the final random co-polymer, denoted cyano-PF, is estimated to lie in the 50% range. For fabricating the devices 1-mm-wide Ag stripes are initially evaporated under vacuum onto a glass substrate through a shadow mask; this substrate plays the role of sample 1 as described above. Then a chloroform solution containing typically 10 g/l of the co-polymer is spin-coated onto the substrate (the resulting layer thickness is close to 100 nm). A thin Ag layer (17.5 nm from quartz balance monitoring) is evaporated onto the co-polymer at a speed around 0.05 nm/s through a shadow mask with 1 mm^2 square holes, aligned with the first metal stripes, at a chamber pressure around 2×10^{-6} mbar. The low speed deposition is aimed at favouring metal penetration into the polymer layer [15]. The intermediate Ag layer is semi-transparent. The substrate is taken out of the deposition chamber and we transfer onto it a new co-polymer layer of the same thickness, following the method described in the previous paragraph. In our case, the use of Ag makes the possibility of metal oxidation in the low pressure chamber unlikely [18], but we cannot exclude a partial oxidation of the intermediate Ag layer during the water-related step. Eventually, we evaporate on top of the device a set of Ag stripes, perpendicular to the bottom ones and still aligned with the intermediate Ag squares. The electrical contacts are taken at the bottom and top Ag stripes, which define rows and columns. A schematics of the final devices is presented in Fig. 3. The tests are carried out with a Keithley 236 source-monitor unit, the devices being kept in a glove box under argon ambient, so as to partially avoid polyfluorene oxidation and a premature aging of the devices. We also produced the same stacking structures by using a homo-polymer containing only repeat units with alkyl side chains, as in Fig. 1.

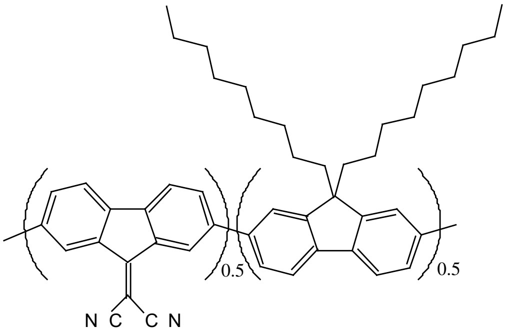

Fig. 2. Molecular structure of the fluorene units used to form the random co-polymer described in this study.

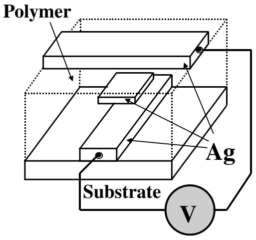

Fig. 3. Schematics of the polyfluorene bistable device.

3. Experiment

Typical *I–V* characteristics illustrating the hysteresis of the device are shown in Fig. 4. In such a plot the voltage is successively swept from zero to −4 V, from −4 to 4 V and from 4 V back to zero. As illustrated in Fig. 3, the device is initially in a low conductance state, and above a given voltage threshold it abruptly commutes to a much higher conductance state (close to −1.5 V here). The difference between the "off" and "on" states varies from one device to another, but the current jump usually covers several current decades, from 5 to 8. In the "on" state the current is ohmic. This high conductance state remains effective even when the device bias is swept back, thereby creating a hysteresis in the *I–V* curve. It is only when the voltage crosses zero or a voltage close to zero that the device is reset in the low conductance state. Then, in the positive bias range one observes a curve qualitatively similar to that of the negative bias, with a sudden current jump to a high conductance state, which remains effective until the device bias is swept back to zero. As can be seen in Fig. 4, the off current is in general noisy, but not always, and in many devices its average level was below the equipment noise limit, as illustrated in Fig. 5 with data measured from a better device. Although the current jump position as well as the "off" current value slightly vary when repeating the electrical test, the *I–V* curves are reasonably reproducible and can be repeated many times (at least a hundred) from a single device, thereby demonstrating that the jump is not due to an irreversible electrical breakdown of the layer. Due to the fabrication process the devices are not completely symmetrical, since the intermediate Ag layer is likely to penetrate into the bottom polymer layer, but not into the upper one, and the metal deposition on top of the device may also induce some metal penetration at the top Ag/polymer interface. This is probably reflected by the fact that the current jumps are not exactly symmetrical (see Fig. 4), and sometimes the difference may reach a few volts. Carrying the same electrical tests with a stack made from regular 9,9 dialkyl fluorene homopolymer does not lead to any hysteresis in the *I–V* characteristics (Fig. 5), and the overall current level remains much lower than in the on state of devices made from cyano-PF, whatever is the applied voltage. This is a strong indication that the role of electron acceptor usually played by cyano

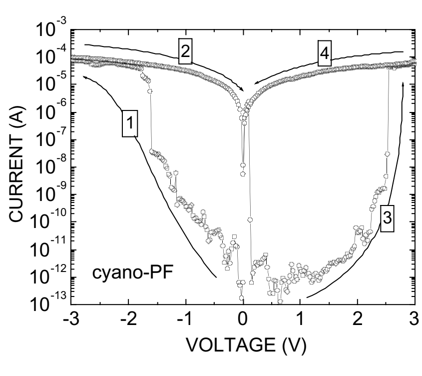

Fig. 4. Current–voltage hysteresis cycle of a device structure as in Fig. 3, made from cyano-polyfluorene and Ag metal layers. The numbers inside the figure indicate the chronological order in which are carried out the successive voltage sweeps.

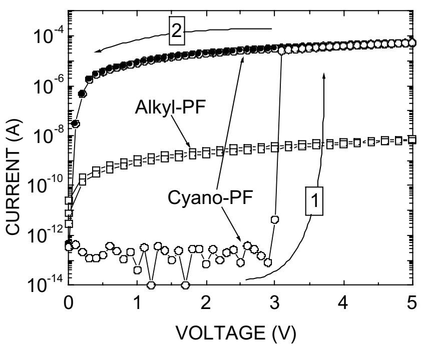

Fig. 5. Comparison between stacked devices as in Fig. 1, made from Ag and (a) Cyano-PF (circles) and (b) PF with simple alkyl side chains (squares).

groups is important for observing the electrical bistability phenomenon.

We did not obtain the same threshold value for all devices. We processed four different 2.5 cm × 2.5 cm square substrates containing each 25 devices. The threshold of different devices selected *from the same substrate* always remained in the same range. However, devices selected from different substrates did not necessarily exhibit similar thresholds, and there was indeed a marked difference between some substrates. Whereas for three substrates the jumps took place in the range of a few volts, considerably larger values were required for the fourth one, around 20–30 V (Fig. 6). In the bistable devices with higher threshold (Fig. 6) the current level was non-ohmic and smaller than in the other devices. We do not know whether this difference might be due to worse contacts, which would then support most of the voltage drop. Some of the devices from the wafer with higher threshold did not exhibit any current jump, always remaining in the "off" state. A possible explanation is a non-homogeneous bonding of the top polymer layer. In all substrates the off current level varied from one device to another, ranging from the sub-pA to the nA range at low voltage. Besides, and still for all substrates, we did not observe good retention properties when the device were turned on and then the bias was suppressed, as reported by Ma et al. in the case of similar structures based on small molecules [13]. In our case, the high conductance state is rarely maintained when the device is turned back to zero volts, although some retention is sometimes observed (see, e.g., the curve of Fig. 4 for which the switching back to the off state is obtained at a voltage slightly above zero when sweeping the bias towards the positive voltages). In general a device turned to the on state and then let unbiased was found in the low conductance state after biasing again at zero volts. Hence our devices cannot directly be used as a non-volatile memory in their present state.

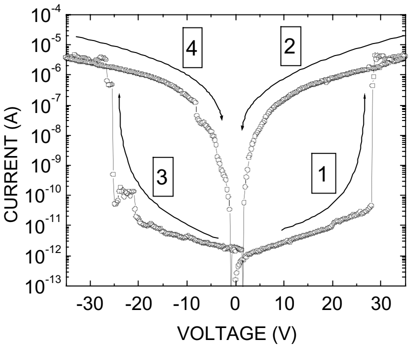

Fig. 6. Hysteresis cycle of devices exhibiting a higher threshold voltage (described in the text).

A detailed and *unambiguously proved* physical explanation of the bistable behaviour exhibited by organic materials with cyano groups is still lacking. Even in the case of charge transfer complexes involving TCNQ, most, not to say all of the proposed mechanisms remain highly speculative [7]. That some charge transfer occurs between the metal and the organic layer seems to be a necessary condition, since all the data that we are aware of involve organic materials containing electron acceptor groups. But the knowledge of the precise physical mechanism at the origin of the switching is still lacking, and unfortunately, our own data do not allow us to shed more light in this respect. However, in our case it is remarkable that we observe bistability with a spun on, almost amorphous polymer layer, even if our molecular structure obviously favours π-stacking. There is definitely no long range order, in contrast with devices built from small molecules. Hence this means that perfect crystalline order is not necessary to observe bistability. Our own experiment does not permit to draw firm conclusions with respect to the various hypothesis which have already flourished in the literature. In Cu-TCNQ and similar materials it has been argued that in the off state there is a complete charge transfer between copper and TCNQ, so that intersite coulomb repulsion between the electrons transferred to the organic material initially prohibits electrical transport. Above a given value the electric field would allow some neutral TCNQ sites to appear, thereby allowing the current to flow [10]. Some data support the hypothesis that in the on state the number of neutral TCNQ sites dramatically increases [19]. But the factors governing metastability are not known. In our case it is obvious that there cannot be a one-to-one correspondence between the Ag atoms and the fluorene units with the cyano groups, so that the same explanation cannot apply as is. Besides, in our somewhat amorphous materials a lattice stack dimerization resulting from Peierls instability cannot play any role, in contrast to the case of the various polycrystals built from TCNQ and metals or other organic materials. Nevertheless it is also tempting to ascribe the jump to the on state to a dramatic change in the charge transfer between the polymer and the intermediate metal layer. Ma et al. argue that the Al middle layer they use is oxidized and favours charge trapping into metal nanoparticles, which in turn dopes in some way the organic molecules [15]. The water-related step we use probably results as well in a partial oxidation of the intermediate Ag layer. But we note that in previous work they obtained the same behaviour with Au [13], for which the formation of an efficient insulating layer should not occur. Besides, they explain that charging of the metal nanoparticles through tunnelling must be easy to achieve. But then de-trapping should be as easy as trapping, and the retention properties they observe are difficult to explain. Clearly, additional experiments are required to thoroughly explain the behaviour of such devices.

4. Conclusion

We have proposed a simple method for transferring a spin-coated polymer layer onto another one. After having synthesised a fluorene co-polymer containing both alkyl side chains and cyano side groups, we used this method to fabricate devices which exhibit reproducible bistability. We have thus demonstrated that electrical bistability can be achieved with polyfluorene devices. In our case, the first points that we must investigate in further detail are whether it is possible to achieve good retention properties, and if the nature of the metal is important. Besides, it seems also necessary to investigate whether the current in the on state is filamentary or not, as well as its temperature behaviour. These points will be addressed in future work. It must also be noted that in order to develop reliable devices the jump voltage must be accurately controlled, and the current in the on state must not be too much reduced as the device area shrinks down to deep submicron dimensions.

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