

## Electrical bistability by self-assembled gold nanoparticles in organic diodes

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Electrical bistability is reported in metal-organic-metal diodes. The device consists of two Al electrodes separated by a layer of 2-amino-4,5-imidazoledicarbonitrile that contains embedded Au nanoparticles (NPs) supported by parylene nanopillars. Electrical characterization of the device shows two well-defined states with high (off) and low (on) impedances. The on/off ratio is about  $10^4$ . This conspicuous memory effect is rationalized in terms of charge storage mediated by the NP states. The fabrication method is general and provides a good control on both the size uniformity and the self-assembly of Au NPs embedded in the organic materials. © 2006 American Institute of Physics. [DOI: 10.1063/1.2372688]

Fabrication and characterization of memory devices using organic materials have attracted attention in the past few years. Different organic materials and device architectures have been explored for this purpose. For instance, organic bistable devices (OBD) made with a three-layer organic/metal/organic structures embedded between two electrodes was demonstrated by various groups.<sup>1-6</sup> The OBD switches between the off and the on conductive states when biased at a given threshold voltage and retains its programmed state even when the bias voltage is turned off. So far, the reported OBDs used small organic molecules such as 2-amino-4,5-imidazoledicarbonitrile (AIDCN),<sup>1-3</sup> aluminum tris(8-hydroxyquinoline),<sup>4,5</sup> and pentacene.<sup>6</sup> In all cases, the OBD intermediate metal layer is deposited on an organic layer by slow thermal evaporation. This method has the advantage of being simple and effective in preparing thin layers of metal nanoclusters. The size of the metal nanoclusters is controlled by the deposition rate and the final thickness of the films. However, it offers little flexibility in regard to the size distribution of the metal nanoparticles (NPs) and the control of the uniformity is poor. Hence, the performance of these OBDs varies from device to device. In this letter, we report on a method to achieve a control on the distribution, size, and position of Au NPs inside the organic matrix. We show that a simple self-assembly process allows the preparation of OBDs with reproducible and strong electrical bistability.

The device, which structure is shown in Fig. 1(a), was fabricated through the following steps: the Al bottom electrodes were first thermally evaporated on a glass substrate

through a shadow mask at a pressure of approximately  $10^{-6}$  Torr. Then, a parylene-C film (Cookson chemical vapor deposition system) was deposited on top of the electrodes by room temperature chemical vapor deposition. The thickness of this parylene layer was varied from 38 to 75 nm. The parylene surface was then modified with a 0.0002% solution of poly(vinylpyridine) (PVP) via adsorption for 1 h.<sup>7</sup> The samples were then thoroughly rinsed in alcohol in order to remove the weakly bounded polymer molecules leaving only a monolayer that serves as an adhesion promoter for the NPs to the parylene surface. To improve reproducibility, PVP modified samples were also annealed at 120 °C at ambient atmosphere for 2 h.<sup>7</sup> These freshly prepared surfaces were directly immersed in a solution of Au NPs for different times until the desired density was obtained. The Au NPs used in the present work were about 12–13 nm in size and they were prepared by the citrate route method.<sup>8</sup> The samples with self-assembled Au NPs were then rinsed with de-ionized water, dried in a nitrogen flow, and baked at 120 °C in an ambient atmosphere for 20 min.

A rf oxygen plasma etching was carried out on the Al/parylene/NP samples at 150 W average power and an O<sub>2</sub> pressure of 100 mTorr for 30 s at room temperature. The etching of the sample by the O<sub>2</sub> plasma needs special care in order to maintain conditions to avoid the oxidation of the Au NPs and to ensure that the parylene is etched down to the bottom electrodes. At this step, the samples were analyzed using x-ray photoelectron spectroscopy (XPS). XPS serves here as a useful tool to ensure that the Au NPs remain intact and to determine the best conditions for the plasma etching of the parylene layer.

The organic material used in our devices is AIDCN from Aldrich and was further purified using standard sublimation

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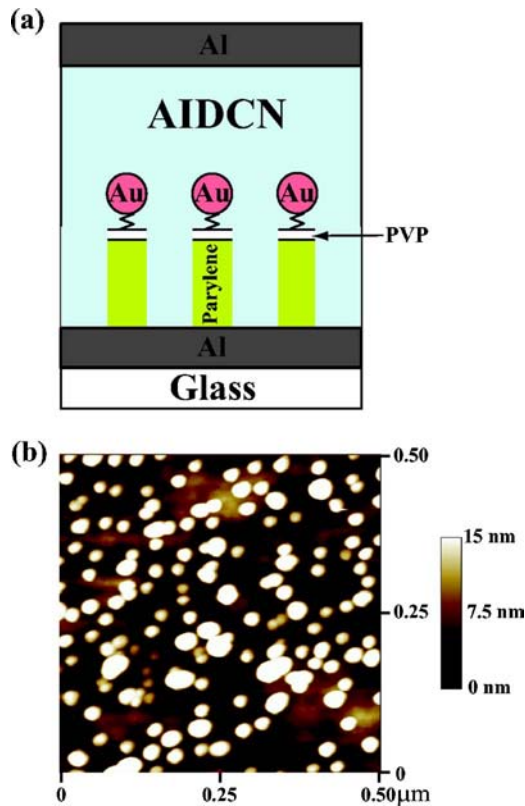


FIG. 1. (Color online) (a) Schematic diagram of the device structure. (b) Tapping-mode AFM image of the Au NPs self-assembled on a parylene surface obtained after 5 min dipping in a solution of Au NPs at a concentration of 17 nM.

techniques. The AIDCN was thermally evaporated at a rate of approximately  $0.4 \text{ \AA/s}$  on the samples and a pressure around  $10^{-6}$  Torr. The thickness of the AIDCN layer was varied from 80 to 150 nm. The thickness was chosen in order to ensure that the Au NPs were embedded at the center of the device structure. Finally, top Al electrodes were deposited through a shadow mask. These top and bottom Al electrodes were patterned as 1.5 mm wide lines and they were aligned perpendicularly to each other. This geometry produces a total active area of about  $2.25 \text{ mm}^2$ . The current-voltage ( $I$ - $V$ ) characteristics were measured using a Keithley 2400 sourcemeter in ambient atmosphere.

A typical result for the assembly of Au NPs on parylene/PVP surface is shown in Fig. 1(b). The atomic force microscopy (AFM) image of the surface was taken right after the deposition of Au NPs in a  $1.2 \times 10^{13}$  NP/ml (17 nM) solution for 5 min. The surface concentration of Au NPs achieved here is about  $5 \times 10^{10}$  particles/cm<sup>2</sup>, but this can be easily adjusted by controlling the deposition time in the solution. The measured size distribution on the surface is 11–22 nm due to some aggregation during the self-assembly process. As shown in the cross-sectional view of the sample taken by scanning electron microscopy (SEM) in Fig. 2, parylene pillars were created by this etching step with Au NPs on the top. The XPS results confirmed that the plasma process etched thoroughly the parylene down to the metal electrodes with the Au NPs remaining at the surface in their pristine metallic state. Therefore, the Au NP clearly acted as a hard mask for a selective etching of the parylene layer underneath.

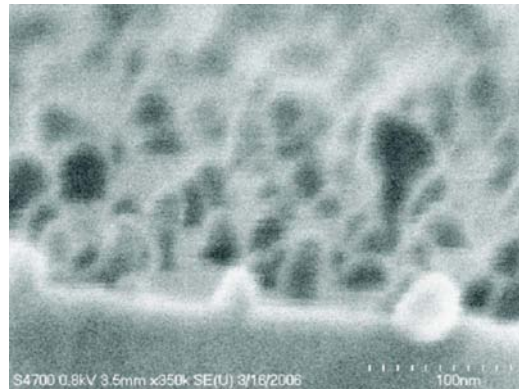


FIG. 2. Cross-sectional SEM image of a parylene/NP sample after etching for 30 s in an  $O_2$  plasma.

The typical  $I$ - $V$  characteristics of two electrical bistable devices A and B are shown in Fig. 3. They were fabricated with 75 and 38 nm thick of parylene, respectively. Continuous voltage scans for device A in Fig. 3(a) were carried out from 0 to 5 V, 5 to 0 V, 0 to  $-5$  V, and  $-5$  to 0 V, as indicated by the arrows and numbers. The current increases sharply by four orders of magnitude at a threshold voltage of about 3.5 V, which indicates a transition of the device from the off to the on state. The device stays in the on state even after the power is turned off. This reveals the nonvolatile nature of the memory effect. Decreasing the thickness of parylene results in devices with similar threshold voltages and higher off-state current, which negatively impacts the on/off ratio. For example, a comparison between devices A and B is shown in Fig. 3(b).

For most devices, the off state can only be recovered by an application of a reverse voltage at around  $-3.5$  V. This

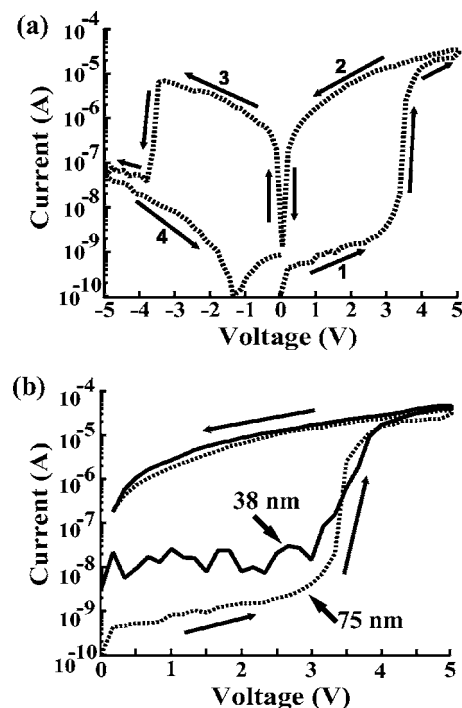


FIG. 3.  $I$ - $V$  characteristics of electrical bistable devices made of AIDCN containing self-assembled Au NPs. The arrows and numbers guide the directions of current variations with the applied voltage. (a) Device A with Au NPs supported by 75 nm parylene pillars. (b) Comparison of devices A and B with 75 and 38 nm parylene layers, respectively. Note that the drop in current at around  $-1.5$  V is caused by the range change of the instrument.

electrical bistable effect could last for a few days when the samples are stored without any further bias application. However, when continuous bias sweeping is applied to the samples in air for a few minutes, a slow increase of the threshold voltage was observed with a gradual decrease of the on current. This degradation problem is always present in our devices and seems to be related to the fabrication process of these devices in our laboratory. In fact, we have also observed similar degradation in other type of OBD devices made in our laboratory using the fabrication procedures described in Refs. 1–3, even though the devices were reported to be stable upon cycling. As this is not the case in any of our devices, we suspect that the degradation is caused by the breakage of vacuum during the fabrication process. We cannot avoid the air exposure with our current setup as the vacuum system has to be opened in order to change the shadow mask for making the top Al electrode deposition. Although this issue needs to be resolved, it does not impact the main conclusion of our study.

To further test the origin of the observed bistability, we prepared a set of control experiments using devices fabricated with only a single layer of AIDCN (no NPs) between two Al electrodes. Devices made with the purified AIDCN showed no memory effects, as expected. However, an electrical bistability was observed for devices prepared using the as-received AIDCN. The on/off ratio observed in this case was about  $10^2$ . It is clear from those experiments that the impurities in the AIDCN organic materials can produce the bistable memory effect. Because pure AIDCN-based devices produce no bistable states, we can therefore rule out charging effect coming from metal NPs diffusing from the top electrode. This was previously suggested to be the main origin of the observed bistability.<sup>6,9</sup> More details about these experiments will be published elsewhere.

The process responsible for the electrical bistable effect in our metal/organic-NP/metal layers is consistent with charge trapping mechanism in the Au NPs. The change of conductance can be rationalized by considering that the charge states of the NPs induce a space-charge field that inhibits or promotes carrier transport. In fact, the mechanism seems to be similar to those described in Refs. 4 and 10, although we did not observe the negative differential resistance in the  $I$ - $V$  characteristics. The process can be described as follows: the Au NPs act as floating gate capacitors that charge and discharge depending on the applied voltage between the Al electrodes. Their charge states modulate the field distribution in the AIDCN layer, which produces a dramatic change of the conductance of the layer. When the ap-

plied bias is removed, the electrons remain confined inside deep potential wells due to the large difference in energy between the lowest unoccupied molecular orbital level of AIDCN and the Fermi level of the Au NPs. This causes the nonvolatile memory effect.

In summary, we showed a device design for making organic electrical bistable devices. The approach is based on self-assembled Au NPs and provides a good control on the size and distribution of metal NPs inside the organic materials. It provides great advantages for charge storage, as compared to previous thermal evaporation methods. In principle, this allows for a better control on the capacitance coupling between the Au NPs and the Al electrodes, which appears to be central to the electron trapping effects required for making bistable devices.

*Note added in proof:* Further measurements done in vacuum on the device A that was kept for seven months in air show good bistability and no evidence of degradation. A negative differential resistance in the  $I$ - $V$  characteristics is clearly observed and the device switches off using a single bias voltage above 10 V.

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