

CARBON NANOTUBES AS ELECTRODES FOR MOLECULAR ELECTRONICS: FROM SAMs TO SINGLE-MOLECULE CONNECTION

G. Robert¹, F. Moggia², N. Lidgi-Guigui¹, S. Streiff¹, V. Derycke¹, A. Filoramo¹, S. Campidelli¹, M.G. Goffman¹, B. Jousselme², S. Palacin², S. Lenfant³, D. Vuillaume³, and J-P. Bourgoin¹

¹Laboratoire d'Electronique Moléculaire, SPEC (CNRS URA 2464), CEA Saclay, 91191 Gif sur Yvette (France) - ²Laboratoire de Chimie des Surfaces et Interfaces, SPCSI, CEA Saclay, 91191 Gif sur Yvette (France) - ³Molecular Nanostructures and Devices Group, IEMN, CNRS, BP60069, Avenue Poincaré, 59652 Villeneuve d'Ascq (France)
gael.robert@cea.fr

While the use of molecules as building blocks for the development of new electronic devices has attracted a lot of attention for the past 25 years, one of the main challenges of the molecular electronics field remains the efficient connection of small assemblies of organized molecules and, ultimately, of individual molecules. For fundamental studies, several techniques to address either self-assembled monolayers (SAMs) on a nanometer-scale or single molecules have demonstrated their high potential, in particular those with adjusting electrode distances such as STM, Conducting-Probe AFM and mechanical break-junctions. From a device point of view vertical structures (such as nanopores) have been used but suffer from severe limitations related to the top contact formation - direct metal evaporation on top of SAMs usually resulting in the deterioration of the molecules. Even if a few methods were derived to limit this problem (indirect evaporation, conducting polymer inter-layer deposition...), the spatial resolution of the final device is limited by the patterning technique, which implies the connection of a very large number of molecules. Horizontal structures have also been developed, in particular micro-fabricated nanogaps, which have lead to fascinating results. In this geometry, the challenges concern both the control of the inter-electrodes distance and the reliable insertion of a known number of molecules, ideally a single one.

In this context, using carbon nanotubes (CNTs) as electrodes to connect molecules is very attractive with respect to their intrinsic nanoscale size, exceptional electronic properties and compatibility with most fabrication processes and substrate types (including flexible ones). Our work demonstrates the use of individual CNTs as electrodes in two configurations.

In the first one, an individual single wall CNT is used as top electrode in nanoscale metal-SAM-nanotube junctions (Fig 1.a). We first use a metallic CNT and compare the transport properties of a simple octadecanethiol (ODT) SAM with the more complex case of sigma-pi-sigma molecules with a terthiophene core (T3). The simple tunnelling regime of the first case corresponds to a barrier height of ~2.4 eV in strong contrast with the structured I-Vs of the second type of SAM, which includes hysteretic Negative Differential Resistance (NDR) behaviour (Fig 1.b,c).

Most interestingly, when a semiconducting CNT is used, the proposed device geometry combined with the insulating character of the ODT SAM enables the study of carbon nanotube field-effect transistors, in which the SAM serves as ultrathin and organic gate dielectric. These p-type transistors display excellent performances (very steep subthreshold slope, greatly reduced hysteresis and band-to-band tunneling) and allow the direct and quantitative determination of the efficiency of such molecular gate dielectric (Fig 1.d). Moreover, when converted into n-type transistors, these devices show an absence of gate modulation, which emphasizes the key role of the electrical dipole of the SAM in controlling the device switching behavior [1]. The tunability of this parameter associated with the high level of performances open new ways towards the realization of fully organic nano-scale transistors.

Very recently, nanotubes were also used by the Nuckolls group as electrodes for single molecule devices [2]. However the oxygen-plasma cutting technique results in the statistical fabrication of

different gap sizes, which are difficult to adjust to a specific class of molecules.

In a second step, we have thus studied and optimized a quantitative and selective chemistry route to covalently connect single molecules between CNTs, with preferential connection at the end of the CNTs [3] (Fig 2.a). We then show that the CNT-molecule-CNT junctions produced in solution can withstand the following process steps all the way to the device realization. We perform electrical measurements in the case of ethylenediamine (EDA) (Fig 2.c), which give conductance values in reasonable agreement with previous results from the STM-break junction technique [4]. The richness of the nanotube electronic properties together with the possible choice of the connected molecules offers a wide range of possibilities to study self-assembled single-molecule devices.

References :

- [1] G. Robert et al, *Self-assembled molecular monolayers as ultrathin gate dielectric in carbon nanotube transistors*, submitted.
 [2] X. Guo et al, *Science* **311**, (2006), 356.
 [3] J.-P. Bourgoin et al, *Electron Devices Meeting 2006, IEDM '06 Technical Digest* (2006), 435.
 [4] L. Venkataraman et al, *Nano Letters* **6**, (2006), 458.

Figures :

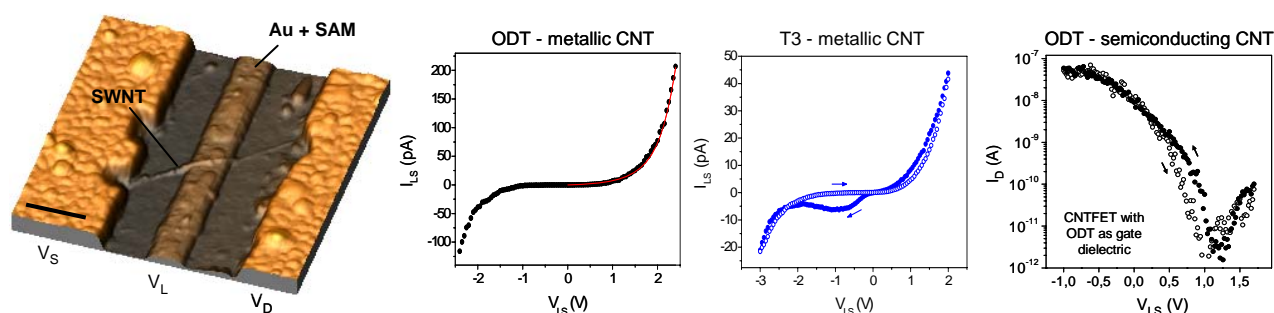


Figure 1 : **a)** AFM picture of a CNT-SAM device (scale bar 200 nm). **b)** $I(V)$ characteristic of a metallic nanotube-ODT SAM-gold junction and associated Simmons fit (red line). **c)** $I(V)$ characteristic of a metallic nanotube-T3 SAM-gold junction, forward and backward sweeps. **d)** ODT-SAM CNFET: $I_D(V_{LS})$ characteristic through the tube in both sweep directions showing the reduced hysteresis.

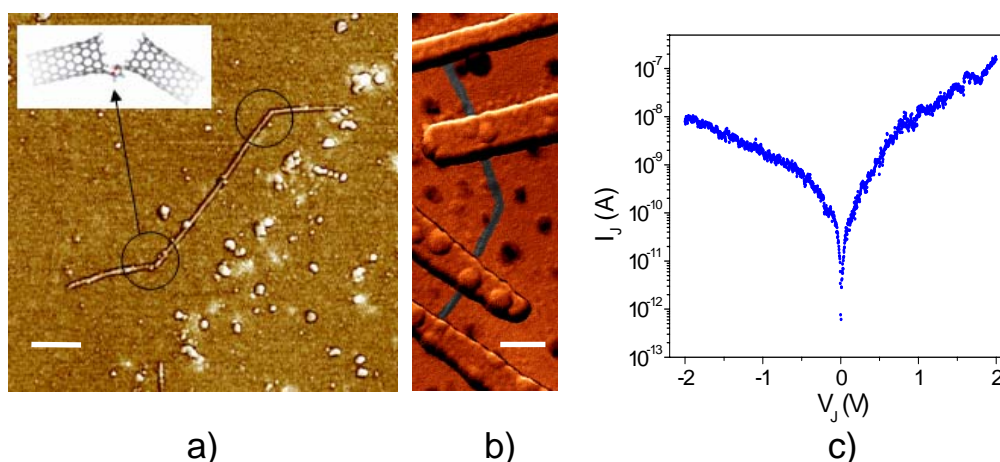


Figure 2 : **a)** AFM picture of multiple CNT-EDA-CNT junctions (scale bar is 200 nm). **b)** AFM picture of a connected CNT-EDA-CNT junction (the tubes have been colored for clarity – scale bar is 200 nm). **c)** $I_J(V_J)$ characteristic through the CNT-EDA-CNT junction