Extended Abstracts of the 2017 International Conference on Solid State Devices and Materials, Sendai, 2017, pp83-84

B-3-01 (Invited)

Fundamentals and Applications of Nano-molecular devices

Nicolas Clement[1]

[1] NTT Basic Research Labs, NTT Corporation
3-1, Morinosato Wakamiya, Atsugi-shi, Kanagawa, Japan
Phone: +81-46-240-2309 E-mail: nicolas.clement@lab.ntt.co.jp

Abstract

We used 10 nm-scale devices ―the typical length scale of a supramolecular organization phase― to investigate the charge transport properties of molecular devices. The high current densities through ferrocene-thiolated gold nanocrystals were suitable to demonstrate a molecular rectifier operating in the GHz regime. We also show that nanoscale transistors can be used to study and exploit molecular interactions in liquid for the development of versatile biosensor devices.

1. Introduction

Non-covalent molecular interactions play a key role in drug design, material science, protein folding, sensors, or organic electronics. The direct experimental measurement or the control of molecular interactions remains challenging, which potentially restricts the development of functional molecular devices. For example, the transfer integral *t* (or electronics coupling energy), a key parameter for charge transport through organic-based devices, is difficult to be assessed from electrical measurements due to molecular structural variability and the large number of parameters that affect the charge transport. Similarly, hydrophilic/hydrophobic molecular forces, that are expected to play a key role in the control of biomolecules structures and function, pose a major challenge for researcher. By using nanometer-scale devices and exploiting either a statistical degree of freedom or unique surface properties, we have performed complete studies starting from new insights into the above mentioned molecular interactions, to the demonstration of potential high-frequency organic electronics or biosensors applications.

2. Estimation of π-π electronics couplings from current measurements

Following the theoretical proposal described in [1], we have performed a statistical study to assess the π-π electronics couplings parameter *t* between neighboring π-conjugated molecules [2]. This was achieved by using a large array of Fc-thiolated gold nanocrystals, and sweeping a conducting atomic force microscope (CAFM) tip as a top electrode on the nanoarray (Fig.1). Nanoscale self-assembled monolayers are ideal for these experiments as they avoid the averaging over many molecular structures or defects, and the number of molecules ($\approx$150) is large enough for getting cooperative effects between molecules. The extracted value for $t \approx 35$ meV is in the expected range based on our density functional theory analysis. Further

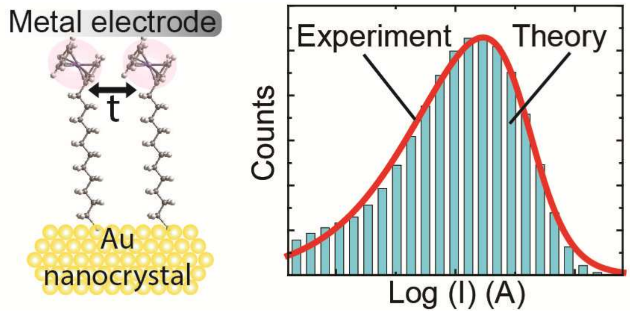

Fig. 1 Left: Schematic representation of a Fc-thiolated gold nanocrystal with electronics coupling between Fc molecule (parameter *t*). The metal electrode is a CAFM tip. Right: current histogram generated by sweeping the CAFM tip on the thiolated gold nanoarray. Histograms are fitted with a Landauer-type model that includes cooperative effects in a tight-binding model. Figure reproduced with permission from ref [2], Nanolett. (ACS)

-more, the *t* distribution is not necessarily Gaussian and could be used as an ultrasensitive technique to assess intermolecular distance fluctuation at the subangström level. This statistical analysis establishes a direct bridge between quantum chemistry, electrochemistry, organic electronics, and mesoscopic physics, all of which can be used to compare results in a quantitative manner [2].

3. A 17 GHz Molecular rectifier

Thanks to an asymmetrical molecular structure and difference in metal work functions, the device shown in Fig.1 behaves as a molecular diode [3,4]. The nanoscale molecular junction provides a gain of several orders of magnitude on the current density compared to micrometric molecular junctions [3,4], being as large as 0.36 mS at +1V. Such a large current density, combined with capacitances in the sub fF range, enable high-frequency operation. Direct current and radio frequency (RF) properties were simultaneously measured on a large array of molecular diodes measured using an interferometric scanning microwave microscope. The measured S_{11} parameters show a diode rectification ratio of 12 dB which is linked to the rectification behavior of the direct current conductance (Fig.2). From the RF measurements, we extrapolate a cut-off frequency of 520 GHz. A comparison with the silicon RF-Schottky diodes architecture suggests that the RF-molecular diodes are extremely attractive for scaling and high-frequency operation. There is a tradeoff to be considered in the design of molecules/electrodes electronics coupling strength to get simul

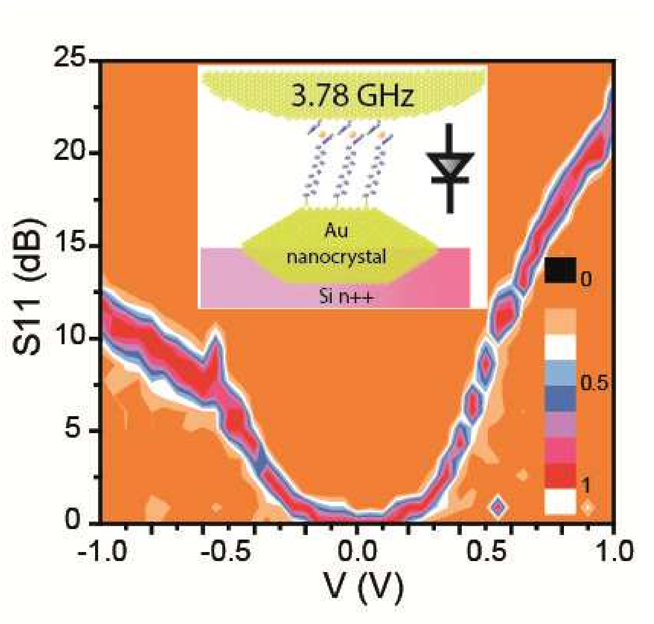

Fig. 2 2D $|S_{11}|$ 2D histogram (normalized to one) versus tip bias (V) generated from one hundred molecular rectifier junctions. The operation frequency was 3.78 GHz. Inset: schematic representation of the molecular rectifier composed of a Fc-thiolated gold nanocrystal and a scanning microwave microscope tip as a top electrode. Figure reproduced with permission from ref.[4], Springer-Nature.

taneously high-frequency operation and large rectification-ratio [5]. This can be potentially circumvented by using electrostatically reconfigurable molecule [6].

4. Biosensor based on specific molecular interactions

Nanoscale silicon transistors are sensitive to ions and show clear signatures of ion-specific effects in both measured signal and sensitivity. These effects, attributed to hydrophobic/hydrophilic molecular interactions, have been exploited to get insights in the nature of these molecular interactions, and to propose a selective-layer-free blood ionogram application [7].

5. Conclusions

The study of molecular interactions is a fascinating yet complex field of research. A better understanding and precise control/tuning of these forces will surely lead to a wide range of applications. We have shown that devices whose dimensions are in the 10 nm range are attractive for investigating and exploiting molecular interactions with potential applications in high-frequency devices or biosensors fields.

Acknowledgements

I would like express sincere thanks to Akira Fujiwara for continuous support and for all the other contributors of the papers related to this abstract, J. Trasobares, J. Rech, T. Jonckeere, T. Martin, O. Aleveque, E. Levillain, V. Diez-Cabanes, Y. Olivier, J. Cornil, J.P. Nys, R. Sivakumarasamy, K. Smaali, P. Leclere, D. Theron, D. Vuillaume, R. Hartkamp, B. Siboulet, J.-F. Dufreche. K. Nishiguchi, and also T. Hayashi, T. Yamaguchi and H. Tanaka for fruitful discussions. These works were partly supported by Marie Curie ITN grant and the EU-FP7 Nanomicrowave project, the iSwitch project, and Renatech.

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