Doctoral Dissertation.
Doctoral Program in Electrical, Electronics and Communications Engineering (36th cycle)

Title:

Molecular Sensors at the Nanoscale: Modeling and Technology

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Summary:

Molecular sensors or chemical sensors have recently achieved the ultimate sensitivity at the single-molecule scale. The electrical detection of single molecules of analyte enables the detection and quantification of rare events and real-time monitoring of (bio-)chemical processes, as well as the integration of sensors with front-end electronics. In this context, molecular electronics has been proven to be an effective means of performing electrical sensing at the single-molecule level, maintaining full compatibility with integrated circuit fabrication processes.

The thesis focuses on nanoscale chemosensors, enabling the electrical detection of analytes. The main topic is the investigation, with an engineering perspective, of single-molecule detection through molecular junctions (or molecular quantum dots). All simulations, modeling, and experiments collected in this work go in the direction of addressing prototypes rather than controlled laboratory proofs of concept.
Part of the work is dedicated to MOX nanowire sensors and the comparisons between molecular quantum dot sensors and MOX ones. The research develops both theoretical aspects of the mentioned sensors and preliminary fabrication attempts and characterizations.
The thesis is divided into three main parts and the conclusions:

I. Theoretical and Experimental Context (background)

The state-of-the-art in electrical single-molecule detection is summarized, along with the most common fabrication and characterization techniques and methods. The theoretical framework, simulation methods, and physical modeling approaches are addressed, as well as the used softwares and important physical quantities. A novel and simplified introduction to the NEGF (Non-Equilibrium Green's Function) theory is proposed, for readers who approach for the first time to the topic, exploiting analogies with linear system theory. The main literature lacks are identified and some of them are addressed in the following of the work.

II. Modeling (results)

The result part starts with the presentation of a holistic modeling approach proposed for MOX nanowire sensors for the detection of oxidizing gases like NO_2. The model links the macroscopic electrical response to the kinetics of the adsorption process. Then, C_{60}-based single-molecule junctions are considered for the sensing of NO, NO_2, and additional air pollutants. Novel sensing features are studied and clarified, and compared with MOX sensor features highlighting similarities and differences. An additional application is proposed for the sensing of AFB1 through a polypyrrole-based molecular channel. Some numerical experiments are finally performed to identify and clarify possible design guidelines for single-molecule chemosensors for the electrical detection of analytes.

The main outcomes of this part concern the clarification of the current modulation mechanisms, which are mainly of two types: (1) a target-induced orbital charge rearrangement, and (2) a target-induced conformational changes of the molecular detection element. The origin of the voltage-dependent response is also clarified according to the mechanism of electron transport through the junction. Analogies and differences between the Au-C_{60} dot and MOX sensors are highlighted, and they suggest further investigation in the direction of inheriting established modeling tools of MOX sensors for the emerging field of molecular junction sensors.

III. Experiments (results)

Preliminary experiments are based on an evaporated C_{60} layer on polycrystalline gold (chosen because most probable in an engineered production of real sensors). Experiments focus on the understanding of gold-C_{60} interaction to determine the regime of transport in real prototypes. The characterizations include: XPS, UPS, AFM, STM, current spectroscopy. The results are in good agreement with simulations, which are validated by experiments and provide a means of interpretation of them. The outcomes reveal information on the Au-C60 interaction, which primarily determines the regime of electrical transport in the Au-C60 junction. Also, they prove the possibility of performing electrical detection of CO through the Au-C60 interface and confirm both the current modulation mechanism and the success of statistical averaging to perform the detection.
Then, nanofabrication processes are used to fabricate gold nanocontacts (EBL + dry etching). The nanofabricated contacts are partially characterized through SEM, STM, AFM, XPS/UPS before and after C_{60} deposition, highlighting limits and fabrication challenges for small-scale production. In particular, good repeatability is found even if the resolution should be still improved.

Conclusions

Overall, molecular quantum dot sensors are promising candidates to perform the electrical detection of single molecules through integrated architectures, especially considering the recent rapid developments of AI-driven data processing, which can help in the quantification process. Such sensors are promising answers for future electronic noses relying on the electrical detection of low-quantity analytes. They present exclusive and interesting sensing properties, e.g., voltage-dependent response and calibration-free detection elements, also enabling new sensing paradigms.
Several are still the open questions, from technology, like the fabrication resolution, integrability, and practical measurement of the current vs. noise, to more theoretical ones, like clarifying the roles of some parameters on the sensing performance and the dynamics of the sensor response. Major challenges toward their engineering are still related to technological limitations in controlling all the parameters affecting the sensing performance with the desired (sub-nm) resolution.