PhD thesis proposal

Thesis title

Study of the mechanisms of injection at the electrode/channel contacts of organic transistors by techniques coupled in electrical and optical near-field

Keywords

"Organic electronics", "charge injection", "organic transistors", "organic semiconductors", "KPFM", "Raman/TERS spectroscopy"

Location

Université de Reims Champagne Ardenne

Laboratoire de Recherche en Nanosciences (LRN)

51100 Reims – France

Date

Planned start of the thesis: September 2023 – Duration: 3 years.

Supervisors / Contact

- Olivier Simonetti – olivier.simonetti@univ-reims.fr
- Nicolas Bercu – nicolas.bercu@univ-reims.fr

Profile and required skills:

Degree allowing enrolment for a PhD (such as Master 2 de Recherche or equivalent) in physics, materials science, Nanoscience or closely related science.

The candidate should be attracted by experiments.

During the thesis, the candidate will be involved in the fabrication of the polymer-based devices and the exploitation of the experimental setups to characterize the structural properties and the electrical properties of the polymer films.

English spoken and written is mandatory.

To apply

- A detailed Curriculum Vitae
- A copy of your official academic degrees (Master 1 and Master 2) and the corresponding transcripts
- One or two letters of recommendation
- A cover letter

Summary

This thesis falls within the field of organic electronics. It is oriented towards the study of mechanisms limiting the performance of organic transistors. The study focuses on the drifts under stress caused by the degradation of the contacts. It relies in particular on near-field techniques, an electrical KPFM technique and an optical TERS technique, which will make it possible to characterize these contacts at the nanometric scale. The organic transistor is an essential component for many applications. Its improvement is a major challenge to enable its commercial development.

This thesis is part of the research projects carried out by the 'Organic Electronics' team of the LRN. The team is particularly interested in the fabrication, characterization and modeling of organic transistors. A particular focus is now on the study of the limiting mechanisms of these components, in particular their drifts under electrical stress. We rely on KPFM (Kelvin Probe Force Microscopy) and TERS (Tip Enhanced Raman Spectrometry) techniques to perform local measurements under electrical stress. The project benefits from the favorable environment of the NanoMat platform, as well as collaborations with UTT and EUR NanoPhot for the TERS optical near field part. In particular, the LRN has developed proven know-how in the field of the electrical near-field characterization, correlated with a very good knowledge of the physics of organic transistors.

In addition, the LRN has established collaborations with renowned laboratories able to provide state-of-the-art components, in addition to the achievements of the constantly improving team.

The thesis project aims to support instrumental developments and their use for the characterization of the performance limiting factors of organic transistors. In particular, we wish to study, locally, the electrical and morphological properties of the interfaces of the contacts at the origin of the mechanisms of degradation of these components.

The student will be trained in I(V)-C(V), KPFM and TERS techniques for the first 6 months, as well as in the physics of organic transistors. The samples are transistors based on small molecules (typically sDNTT-10, pentacene and DNTT), made in the laboratory or from our partnerships. He/she will then focus his research on the methodological developments necessary for the study of the interfaces of the contacts of transistors under stress. The available instruments are already customized for the in-situ characterization of biased electronic devices, but further developments are envisaged (such as local electrical measurements using dedicated scripts for example or new electrodes design for specific TERS measurements). The following provisional schedule is proposed:

This PhD thesis topic addresses the problems of drifts and instabilities in organic transistors (OTFT) and has as its main objective the understanding of the degradation mechanisms that induce these problems. Several advanced physical characterization techniques will be involved including near-field techniques. Apart from the usual I-V and C-V electrical characterization techniques, the KPFM (Kelvin Probe Force Microscopy) technique and the NanoRaman/TERS (Tip Enhanced Raman Spectrometry) techniques will be used. The first, KPFM, is an electric mode of the atomic force microscopy (AFM) and allows the local measurement of the electric potential. This type of measurement provides valuable information on the charge injection, trapping and transport mechanisms. These measurements will be performed at the level of the transistor source and drain electrodes.

The second technique, nano-Raman/TERS, is an optical Raman spectroscopy using a conductive AFM probe that enhances the Raman spectral intensity. This technique provides information on the physicochemical structure of the sample (chemical structure, molecular disorder, dipoles orientation and opto-electronic properties). It will also be carried out at the electrodes. The originality of this study

is to use in-situ these techniques on operating OTFTs and therefore under electrical stress. This makes it possible to track the degradation mechanisms induced by the electric fields generated by the applied voltages. The PhD student will use these various techniques on OTFTs that will be produced in the laboratory or provided by our partners and collaborators.

In addition to the study described above, the doctoral student will also participate in the instrumental developments envisaged for this study. Specifically, he/she will participate to enable the transistor biasing during the TERS measurement. For the moment only the micro-Raman spectrometer is equipped to allow this kind of measurement.

This PhD thesis will allow a better understanding of the degradation mechanisms in OTFTs which are, at present, one of the technological issues that hinder the development of many applications targeted by organic electronics.

Detailed description of the subject

State of the art

Organic electronics uses organic materials with electrical and optical characteristics that have a broad field of applications: flexible screens, photovoltaics, sensors, biosensors, RFID tags [1] [2] [3] [4] [5]… These applications use OLEDs (commercial displays), solar cells (OPV) and organic transistors (OTFT), among others. The economic interest is obvious but many issues persist in the development of certain applications, in particular concerning the OTFTs that this project wants to study.

The factors limiting the performance of OTFTs are related to the low conductivities of organic semiconductors (SCO), the presence of contact resistance at the electrodes, and drift and stability problems. Even though the mobility of charges in these materials has not ceased to increase [2] and the contact resistances to decrease [7] (Figure 1), currently there is no commercial product using OTFTs. We attribute this fact to a lack of OTFTs robustness. In operating condition, OTFTs exhibit threshold voltage shifts, charge carrier mobility decreases, increases in sub-threshold slope, hysteresis and also changes in contact resistances. Reviews have discussed these issues [6] [8] [9]. We were able to test transistors from different laboratories, including those of H.Klauk's group at the Max Planck-Stuttgart Institute, undoubtedly among the most advanced devices available. All the measured devices showed changes in their IV characteristics and in their contact resistances when they are subjected to biasing cycles [10]. We think that these problems are accentuated by the strong electric fields present in the transistors with field effect, in particular in the vicinity of the contacts and in saturated regime. The project addresses the different aspects of this problem through a better understanding of the metal/OSC interface, obtained by different local electrical and optical measurement techniques, in particular KPFM and TERS. The TERS technique is still very little used in organic electronics and only a few works use it for the study of transistors [20] [11].

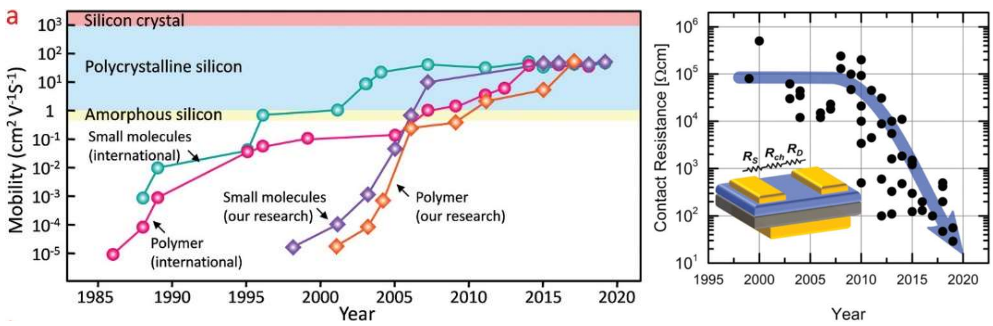

Figure 1: Increase in mobility [2] and decrease in contact resistances [7].

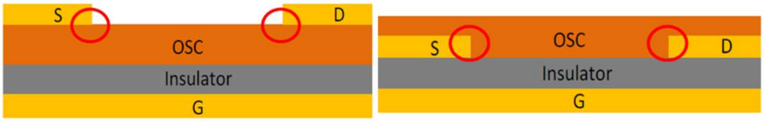

Figure 2: Architectures of organic transistors: a) Stacked structure (left) and planar structure (right). The red circles locate the contacts between the electrodes and the SCO channel of the transistor, where the electric field is likely to be very strong.

The characterization techniques implemented for the study of reliability are mainly I-V measurements. The proposed project wishes to take advantage of the laboratory's near-field tools, KPFM and Raman/TERS for a detailed analysis of the physicochemical phenomena at the origin of the measured drifts.

Relevance/originality/objectives

The laboratory is very well equipped for the electrical characterizations of OTFTs at room temperature and at low temperature (cryostat integrated probe station with a 77-450K temperature range), C-V (2Hz-2MHz frequency range), I-V (several Keysight E5270), AFM/KPFM (Bruker Icon customized and patented technique).

On the other hand, we are developing a µRaman experiment (LabRAM Horiba) on biased components (Fig.5), and have a nanoRaman/TERS (on the same equipment). The relevance and originality of the project lies in the joint implementation of these different techniques to obtain an enriched view of the operation of the interface, of the injection of charges from the contacts, of the drift observed in real time. In particular, we wish to correlate the evolution of the electrical characteristics of the metal contacts to the changes of the physicochemical nature of the interface. This point is the main objective of the thesis.

Methodology and techniques implemented

The studied devices will be either manufactured in the laboratory (Fig.3) or obtained within the framework of our collaboration with the H.Klauk group. These will be transistors based on small molecules evaporated under secondary vacuum such as DNTT or a derivative, or pentacene. Pentacene is more unstable in air but its technology is simple, inexpensive, and it makes it possible to develop the various experiments at lower costs. The (consistent) mobilities of the already available devices are 0.2-1 $cm^2/V/s$ (Fig 3) and 1-3 $cm^2/V/s$ for the H.Klauk group.

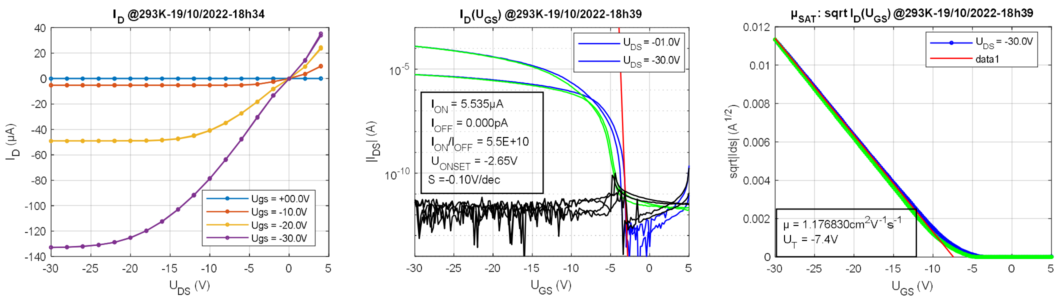

Figure 3: Example of electrical characteristics of an S-DNTT-10 transistor made in the laboratory (stacked structure). Mobility is close to 1 $cm^2/V/s$

The KPFM technique developed in the laboratory is based on a patented double-pass technique. It allows the measurement of the local surface electric potential on operating transistors, for bias

voltages greater than 30V (Fig.4) [12] [13] [15] [16] [17]. These measurements enable the extraction of many intrinsic parameters of the transistor: I-V and contact resistances, local mobility and threshold voltage and the estimation of the injection electric field at the interfaces [17].

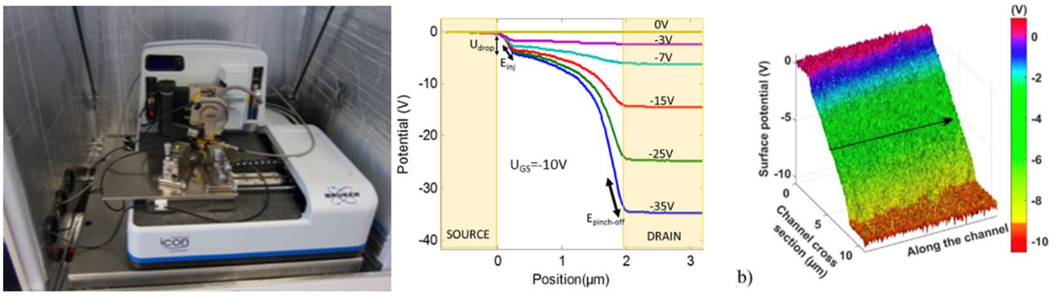

Figure 4: Photograph of the customized AFM/KPFM Bruker Icon, example of potential profiles and potential mapping measured with this technique on operating transistors.

The µRaman/nanoRaman spectrometer (TERS) was recently acquired by the NanoMat platform in Reims. This technique provides valuable information of the characterized sample (chemical structure, disorder, dipole orientation and opto-electronic properties [20]). A collaborative project with the Technological University of Troyes (UTT) is underway to apply this technique to the characterization of organic transistors (1 thesis and 1 post-doc in progress). The µRaman experiment has already been modified to allow biasing a transistor during µRaman analysis (Fig.5 (a)). This PhD thesis will continue these developments towards the implementation of a biasing system on the TERS technique in order to obtain a better lateral resolution of the Raman spectra.

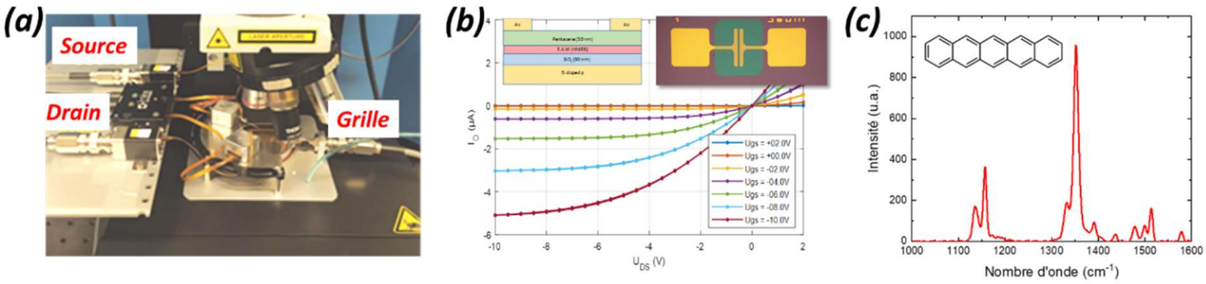

Figure 5: (a) Image of the µRaman system, (b) I(V) measurements and (c) Raman spectrum measured on a pentacene-based TFT.

The PhD student will implement these different techniques, supported by the permanent staff of the laboratory and the NanoMat platform (IE, IR and MCF). The objective of the work being to correlate the different measurement techniques for the analysis of the drifts of the components tested. He will have to divide his activity between methodological or instrumental developments, and the conduct of measurements and their interpretation.

Implementation plan (key stages and provisional timetable)

The student will be trained in IV-CV, KPFM and TERS techniques for the first 6 months, as well as in the physics of organic transistors. He will learn to make organic transistors, accompanied in this by the permanent staff. He will then focus his research on the methodological developments necessary for the study of the interfaces of the contacts of transistors under stress. He will contribute to the development of experiments, in particular TERS.

Human resources

The student will be supervised by Olivier Simonetti (MCF HDR), and co-supervised by Nicolas Bercu (IGR). He will be able to benefit from advice and will be trained in the production of components and their electrical characterization by members of the laboratory's organic electronics team (L. Giraudet, S. Potiron, F. Etienne). The strong LRN/L2n interactions of the UTT will also allow it to benefit from the proven skills of L2n, in particular on Raman spectroscopy.

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