# PhD student position, LRN-Reims 2020

## Development of a near-field technique for local potential measurement by AFM/KPFM

The proposed subject concerns the instrumental development of an AFM / KPFM, adapted to the measurement of the surface potential of biased components, the improvement of its application potential, and its enhancement. This original technique has been developed by the team for several years and applied to the characterization of organic transistors, a project carried out in partnership with the Max Planck Institute in Stuttgart whose transistors present state-of-the-art performances. The proposed project aims to continue instrumental developments on new equipment with new features, to apply the technique to the characterization of new devices and to enhance the experience with equipment manufacturers.

The KPFM technique used in the laboratory is original, has been patented and uses a digital signal phase control to quantitatively measure the surface potential. This technique was developed on the basis of the experimental observation that commercial KPFM equipment does not, in most cases, allow quantitative measurement of the surface potential on biased components. The team therefore designed and developed an alternative technique which demonstrated its ability to quantitatively measure the surface potential profile of biased components. A PhD thesis is in progress, many results being acquired both on the characterization of the components and on the instrumental part. The ongoing collaboration has made possible to better assess the resolution limits linked to the approach used so far: around 30nm of lateral resolution.

New equipment has just been acquired by the NanoMat platform. It has the very interesting ability to precisely control the position of the AFM / KPFM probe (resolution in positioning on the order of a nanometer) using scripts. This possibility can be combined with the digital phase control technique to access new surface potential measurement techniques. We hope to improve the resolution of the current technique, but above all to access the location of the charges deep in the structure, which today is made difficult by the noise of the signals acquired in continuous scanning.

The technique developed in the laboratory has shown its interest in the study of the injection and transport of charges in organic devices. However, this single application seems too limited to motivate equipment manufacturers to develop the technique and market it, and the current resolution limit also seems to be a limitation factor. The second objective of the thesis will therefore be to broaden the field of application of the technique to the study of new objects, taking advantage of the collaborative projects underway in the team: on organic transistors of course, but also on component sensors volatile organics for application to the early diagnosis of lung cancer, and on the characterization of conductive films from agro-sourced materials. The thesis will therefore contribute to the study and development of these objects, and to the industrial development of the technique.

- 1. State of the art

We are interested here in local measurements of the surface potential of components or conductive materials, using an atomic force microscope (AFM) in KPFM (Kelvin Probe Force Microscopy) mode. These measurements allow access to the local potential of the surface, with a nanometric resolution depending on the measurement conditions (under vacuum or in an ambient atmosphere) and the technique used (contact, lift, type of modulation, etc.). They are mainly used on conductive or semiconductor materials, and find many applications, such as in the study of organic electronic components [1-4]. Burgi's work is a pioneer in this area.

Measurements under vacuum make it possible to reach the best resolutions but considerably complicate the implementation, in particular on biased components, which limits their practical application. We will limit ourselves here to measurements on biased components and in an ambient environment, because they correspond to the equipment available in the laboratory and to the objectives that it has set itself. Indeed we wanted to develop a technique as simple to implement as possible on various components, not requiring the mounting of the component to get out the electrical connections. We therefore opted for a technique using biased tips and in an ambient environment.

Numerous surface potential measurements have been made and published. The vast majority of them use a feedback loop to control the amplitude of the cantilever's oscillations, because it is the simplest method to implement (some AFM types does not provide any other method). It allows to obtain contrast images at the interfaces, which are often sufficient for some authors. However, it has been shown (see for example [5]) that this technique was not suitable for obtaining a quantitative measure of the surface potential, since it turns out to be far too sensitive to the interactions of the lever (of large surface) with the surrounding surface. The near field contribution of the tip is therefore polluted by the contribution of the lever, and the local measurement is no longer quantitative. Our own experiences have confirmed this fact.

Given the studies carried out by the team on the transport and injection of charges in organic devices, measurements of contact resistances or threshold voltages, there was a need for qualitative local potential measurements: a quantitative measure of the potential is essential for the exploitation of the measurements and for the modeling of the devices. To circumvent this problem it is preferable to detect the modulation of the frequency (or of the phase) of the oscillation of the lever in the presence of an electrostatic force [5]. This modulation is much more sensitive to the interaction of the apex of the AFM tip with the surface of the sample, than with the interaction of the lever body. Several techniques can be used for this purpose. In our method, the lever is set in oscillation by the application of an AC voltage on the piezoelectric element, as its excitation is in intermittent contact mode. The phase of the excitation signal is used as the reference and the phase of the signal from the photodetector is measured. A DC voltage is applied to the tip and controlled according to the phase measured to allow the measurement of the surface potential. The principle diagram of the system is given below, and its principle is described in detail in reference [6]. The key point of the method developed at LRN, which makes it original, even unique, lies in the fact that to work on biased electronic devices, using a source external to AFM, it is essential that the same equipment controls all the applied voltages to the device and to the tip, because it can come into contact with the sample and cause short circuits, or even damage the equipment. This strong constraint has conditioned the development of the laboratory method, in comparison to other FM modulation implementation modes.

We will return later to the phase control technique. The potential measurement is carried out in ‘lift’ mode during the second passage of the lever over the sample. The technique has demonstrated its robustness.

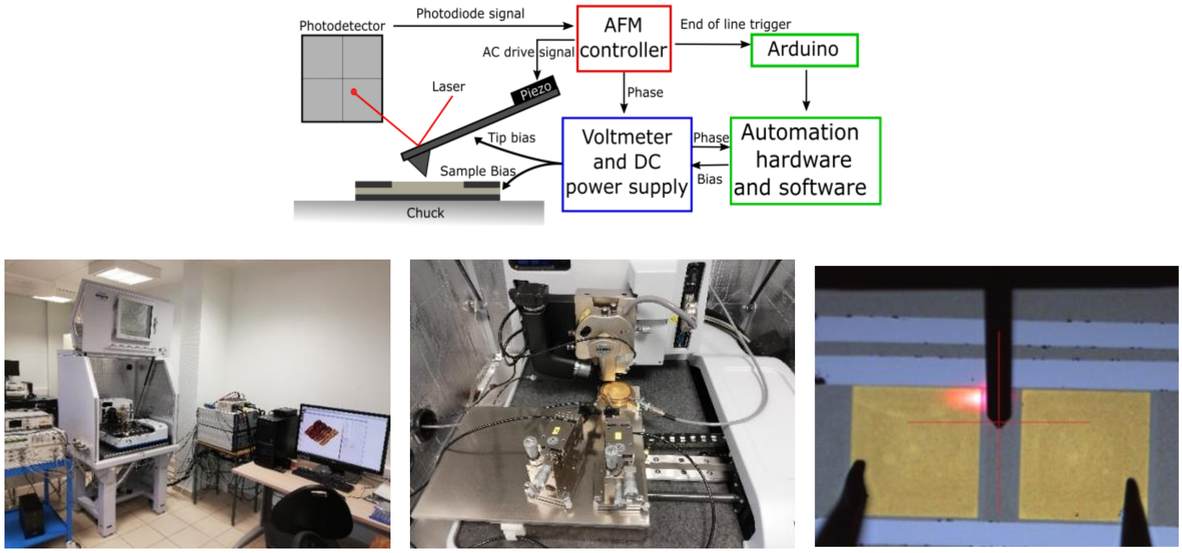



**Figure 1.** *Schematics of the working principle and photos of the existent KPFM setup*.

An example of potential profile measurement in the channel of an organic transistor is given in the following figure where the measurement is carried out on a component biased up to 35V (in ambient atmosphere). The electric field calculated from the derivative of the potential reaches 0.6MV.cm$^{-1}$. It is limited by the lateral resolution of the measurement and we will come back to this point also.

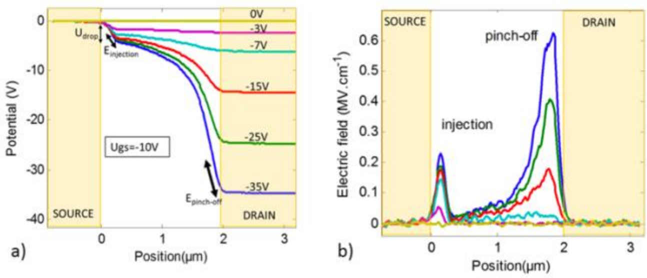



**Figure 2.** *(**a**) Surface potential measured by KPFM on an organic transistor based on PTAA and biased from UDS = 0 to UDS = -35V, and (**b**) calculated corresponding electric field.*

Working on components biased by an external source it is easy to demonstrate the fact that the developed technique allows a quantitative measurement of the surface potential, by showing that the voltages applied to the electrodes via the probers, are correctly measured the KPFM technique. The previous figure shows that the potentials measured on the transistor follow the applied voltages correctly.

The developed technique is currently used for the characterization of organic transistors in collaboration with the Hagen Klauk team at the Max Planck Institute in Stuttgart. The following figure shows the results obtained on components with linear or non-linear contact resistances, where the drop in potential at the source resulting from the reverse-biased source-channel rectifier contact is clearly observed. We can see that the contact resistance produces a voltage drop of more than half of the voltage applied between the drain and the source, which implies a significant degradation of the device performance.

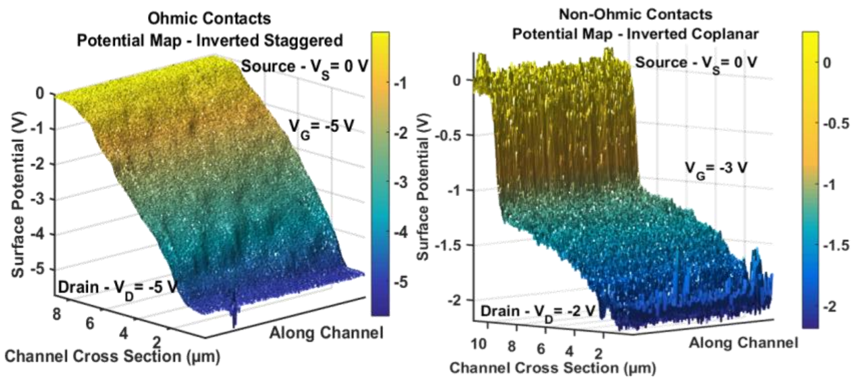



**Figure 3.** *Measured potential maps examples, measured on DNTT based transistors in planar or stacked configuration and showing ohmic (left) or Schottky (right) contacts.*

On the basis of these measurements, it is possible to extract vital information on the operation of the devices, such as the I(V) characteristics intrinsic to the contacts by circumventing of all the other effects which might hinder this measurement. An example is given in the following figure.

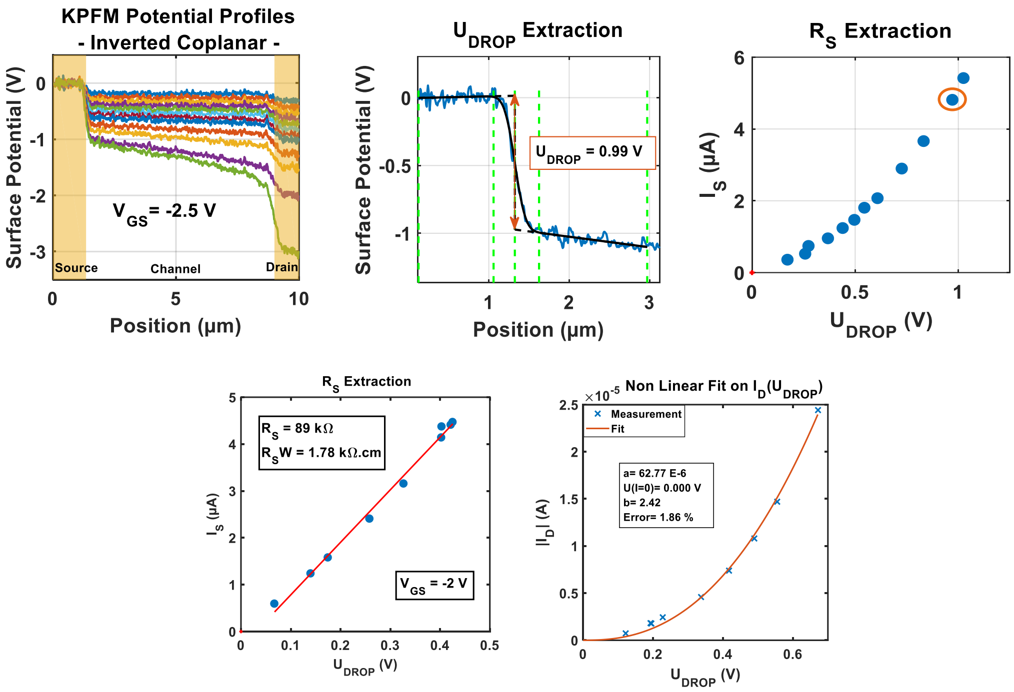



**Figure 4.** *Potential measurement along the channel of a DNTT transistor (top left), measurement of the potential drop at the source contact (top middle), and extraction of the intrinsic I(V) characteristic of the contact (top right). Application to linear or non-linear contacts (bottom left and right respectively) on DNTT transistors of different configurations.*

Therefore, it is of real interest to extend the use of the technique to other components as the slope changes observed on the potential profiles can be used to extract local mobility as well as the threshold voltages. An example of local conductivity measurement in the channel of an organic transistor based on PTAA is given in the following figure, in three different points of the channel, and as a function of the voltage applied to the gate. This transistor has inhomogeneities of local conductivity close to the source and drain electrodes, visible in the form of a change in slope of the potential profile. Mobility in these areas is three times less than mobility in the canal.

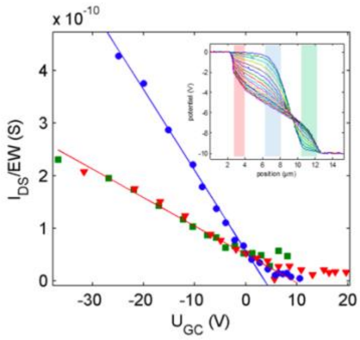



**Figure 5.** *Conductivity measurements in three regions of an organic transistor channel based on PTAA attributed to a disparity of the local mobility values.*

This type of behavior is also observed when grain boundaries modify the transport properties in materials. The slope changes observed in the potential profiles are correlated with the internal organization of the layer. The correlation between the local conductivity and the physical properties of the films is very important for the study and development of the materials and techniques for processing the films. We intend to take advantage of this point during the development of the active layer for the detection of volatile organic compounds or conductive films based on agro-sourced materials.

- Relevance, originality and objectives

The technique developed in the laboratory has no equivalent to our knowledge today. Other experiments of the same type have been demonstrated in various laboratories, in particular by the precursor Burgi [3-4], but do not seem to have been maintained. The technique used in the laboratory, digital phase control and double pass mode, has the advantage of its robustness. No prerequisite is required for the measurement: despite the intensity of the electrostatic forces, it is not necessary to know a priori the potential profile to perform the control. Furthermore, all the voltages are applied by the same equipment, up to several tens of volts, which ensures, via automatic and rapid compliance mechanisms, limiting the currents in the event of accidental contact between the tip and the sample, or dropout of the algorithm, guarantee of backup of equipment and components. Finally, the servo method is based on the measurement of the phase dish during scanning, as illustrated in the following figure (taken from [7]).

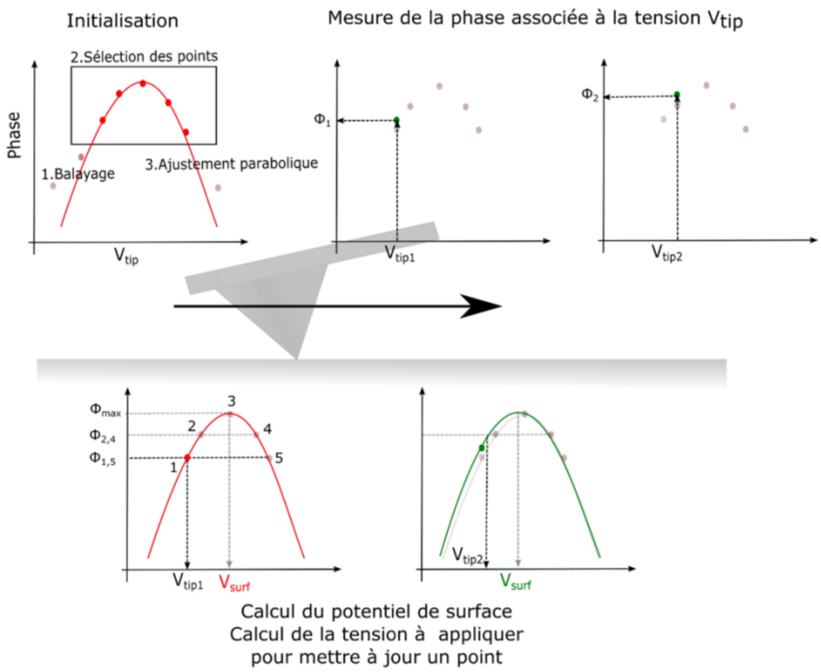



**Figure 6.** *Phase control method during scanning.*

From this measurement we obtain not only the surface potential, but also the second derivative of the phase (opening of the parabola). This data is rarely used, no doubt because the typical feedback loops do not allow it to be obtained. This constitutes another advantage and an originality of our technique. This second derivative is proportional to the second derivative of the force with the height and therefore strongly depends on the vertical distance between the tip apex and the electrical charges below the surface of the device. An illustration is given in the following figure, where a comparison of the measured potential and the second derivative of the parabola is provided with charges injected (or not) into the channel of the transistor.

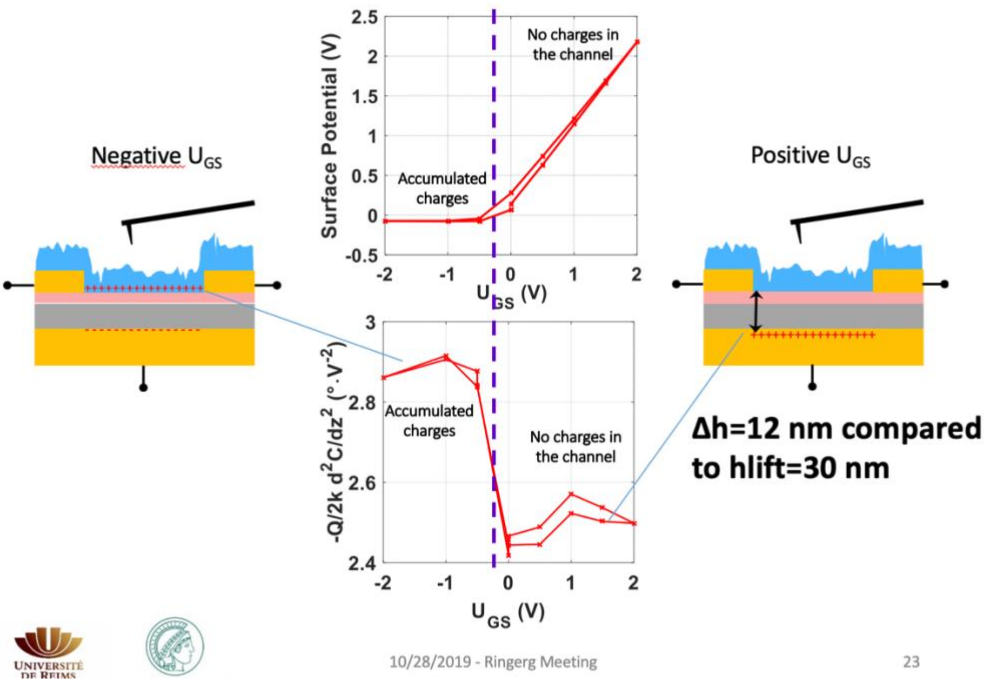



**Figure 7.** *Dependency of the second derivative on the tip to charge plane distance.*

The second derivative is very sensitive to the depth location of the charges. This can be used to better understand how the devices work. For example, in the following figure we show the mapping of the second derivative of the parabola in an operating transistor. We can see that the charges are not at the same depth in the channel: closer to the grid interface at the source, closer to the surface on the drain side. The second derivative of the phase therefore constitutes a complementary analysis tool to the surface potential for understanding the operation of the devices.

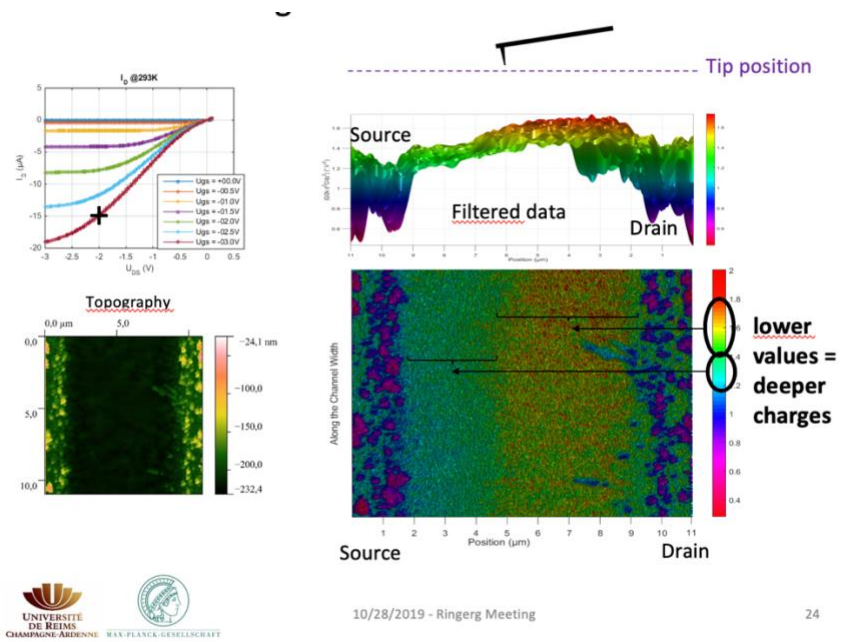



**Figure 8.** *Vertical position of the charges in an operating organic DNTT transistor channel obtained by measuring the second derivative of the phase parabola.*

Unfortunately in the feedback loop used today this second phase derivative signal is relatively noisy and can only be used after filtering, on a case-by-case basis. This is due to the trade-offs that must be made between the scanning speed (the tip is constantly moving in current experience), the integration times of the measuring instruments, the efficiency of the servo, the speed of variation of the potential, etc.

This is one of the main points that we wish to improve with the new equipment acquired this year, and which allows the creation of scripts in a fixed position, driving both the AFM and our equipment for applying voltage and measuring the phase.

The second point we wish to address is the lateral resolution. It is currently limited by the fact that we have chosen a double pass technique (lift mode). In this technique, the component is biased at 0V during the measurement of the topography, which avoids the electrostatic interactions at this time of the measurement, then during the transition to lift the component is again biased and the potential measurement is carried out. This method is robust and flexible to use in terms of polarizations applied to the component, but its disadvantage is that the potential measurement is carried out a few tens of nanometers above the surface, which obviously reduces the lateral resolution of the measurement. Typical values of lift height depend on the topography of the sample, and vary from 30 nm for favorable surfaces to 50-100nm for semiconductors such as DNTT. In the best conditions, we measured a resolution of 30nm for a PFQNE-Al tip (Bruker) at a lift height of 30nm, on a sample composed of electrodes spaced 12nm apart (made at MPI Stuttgart), (an example is given in the figure next for a SCMPIT Bruker tip).

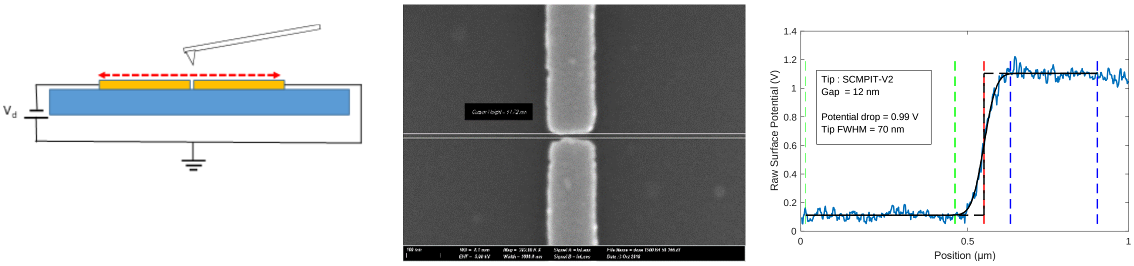



**Figure 9.** Structure of the sample used for the resolution measurements (left) and the SEM image of the device (center) whose measurements are presented (right) for a SCMPIT-V2 Bruker tip at 30nm lift height.

We believe that the resolution is decisive in extending the technique to other devices and to interest equipment manufacturers in industrial development. Also, the lateral resolution directly influences the maximum electric fields that the technique can measure. To give an order of magnitude, 1V of voltage drop over 10nm corresponds to 1MV.cm$^{-1}$. In the vicinity of a nonlinear contact, as illustrated in FIG. 2b), this field corresponds to the field of injection of the charges from the electrode to the semiconductor. The longitudinal electric field is a determining factor for the injection process, and its knowledge is essential for the modeling of this phenomenon, in particular in organic semiconductor components where it is still poorly understood. Improving one's knowledge would therefore constitute a significant advance.

We believe that the new laboratory equipment and its scripting possibilities will also make it possible to address the resolution by authorizing control and reduction of the tip-surface distance when measuring surface potential.

- Methodology and implemented techniques

We therefore plan to extend the possibilities of the current experiment by improving the measurement of the second derivative of the phase, and the resolution. These two improvements involve the implementation of AFM piloting scripts, allowing its control. Synchronization of scripts with our measurement equipment and the application of voltages is done via TTL signals which we use for synchronization of phase measurement. We don't see any difficulty on this side. The possible difficulties can come from the implementation of the scripts in the software of the AFM itself, which can always present ‘bugs’. Otherwise it will be necessary to find workarounds, which will be part of the software and instrumental development work.

The programming and validation of these scripts will take a few months. The validation will be done on organic transistors, because we have sufficiently stable and well known devices to validate the methods.

In addition, we explained how the KPFM technique made it possible to measure the surface potential, and how this measurement and its derivatives could be used to trace the local properties of the conductive materials analyzed, such as their local conductivity. We know that the local semiconductor or conductor properties depend on their morphology, notably crystalline or amorphous phases. Also, since these conductive materials must be used and therefore contacted, therefore forming components, it will also be interesting to characterize their contacts with the methods practiced in the laboratory.

Apart from the organic transistors, which constitute, as we will have understood, the insurance of an application component to the project, we wish to apply the technique to volatile organic compound (VOC) sensors that we will develop in partnership with IMT Lille Douai, as part of an Interreg 'Pathacov' project (2018-2022 [8]). Films must have low to very low conductivities to achieve the objectives in terms of sensitivity, which could pose problems of homogeneity. The synthesis of the sensor material will take place in Douai, and their implementation on transistor structures in Reims. A co-supervised thesis will start in early 2020 to support this project. Sensors will therefore be produced, and in addition to their conventional I(V) characterization we plan to use the KPFM to better analyze the conductivity, its uniformity, the accumulation of charges in the films, etc., and thus contribute to the development of the sensors.

The team also wishes to develop its skills in partnership with the FARE UMR of INRA (Reims) concerning plant fibers related subjects. In particular, lignocelluloses constitute one of the main sources of renewable carbon alternative to fossil carbon, but their transformation generates products whose applications and impact have to be studied. The study of the conductivity of lignin-based film and modified cellulose nanocrystals is part of the projects of the two teams [9-10]. Initial experiments were carried out between the two teams, showing films with conductive properties, but nevertheless weak and needing improvement. The influence of the composition and the structuring of the film, function of the deposition process, has not been evaluated yet and the KPFM must provide relevant information in the study of these compounds, in particular not the electrical morphology / property coupling that the technique naturally allows. This project is set to develop and will fall within the framework of the thesis. Currently, the means for its development are not available, but this subject constitutes one of the team's priorities in the long term.

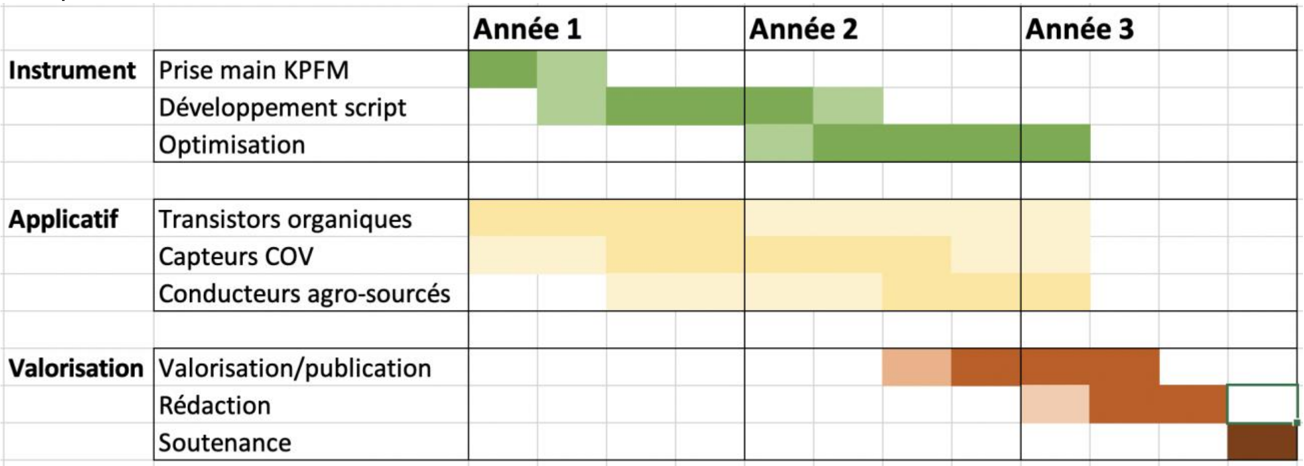
- Implementation plan (key steps and provisional calendar)

The first key step is the development of a script allowing the measurement of the phase parabola at fixed position and at different heights. This step is estimated to take approximately one year. Then it will be a question of exploiting the new possibilities on the available devices, and of optimizing the technique according to the needs of the different studies. This will constitute the second part of the thesis, more oriented towards applications.

From an application point of view, the KPFM measurement of organic transistors being already frequently used in the laboratory experimental work, they will constitute a first well-established element on which to base future experimental developments. They may be available to validate and enhance the technique throughout the thesis. Concerning VOC sensors, the Interreg project for 4 years, it will cover at least the first two years of the thesis. The study of agro-sourced conductive films will depend on the progress of developments and projects in partnership with the FARE laboratory at INRA.

Finally, writing will start at the start of the third year, along with writing articles. The writing will intensify in the 2nd and 3rd quarter to allow a defense at the end of the third year.

The provisional schedule is as follows




- PhD thesis management

The thesis will be directed by the team leader (70%), and co-supervised (30%) by the IR in charge of KPFM developments.

The equipment (AFM / KPFM) on which this thesis is based is integrated into the NanoMat platform, bi-site UTT / URCA, whose team is responsible for the Reims site, and which can count on the skills of 2 part-time engineers (IE and IR). The supervising team also relies on a part-time IE for technological achievements and maintenance of the clean room, and the co-supervising research engineer is in charge of maintaining and developing the (complex) management software digital phase control. These different people bring valuable skills, maintain theoretical and experimental know-how, and are able to provide daily support.

- Expected scientific results and impacts

The main expectations of this thesis are the development of an original and efficient operational experience, giving access to new characteristics of the components and functional materials studied, which can be put to the service of users of the NanoMat platform and beyond. Scientific publications constitute the first expected development: on the experiment itself, but also on the studied devices (organic transistors, VOC sensors, agro-sourced conductors). The potential for scientific development is therefore relatively open.

It is also expected that technical developments in experience may give rise to the filing of a patent in addition to the existing one. The same applies to the application domains for which the technique will be implemented, which can lead to new patents (especially on the VOC sensor aspects and agro-sourced conductive film).

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