Doctoral School on Engineering Sciences
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Extended summary

Microwave Microscopy and Spectroscopy Techniques with Applications in Nanotechnology and Biology

Curriculum: Electromagnetics and Bioengineering

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Abstract. A Scanning Microwave Microscope was developed and applied within different contexts. It works through near-field microwave interaction between an emitting probe and a target sample. Its main application is the measurement, at extremely small scale, of electromagnetic features. Lumped and distributed circuit models allow getting quantitative data from measurements, although with limitations. Such models become even more complicated if considering different environments. This is fundamental for analysing biological samples (*in vitro* or *in vivo*). During this work, both applications to biological samples and "in-liquid" analysis were performed.

Another potentiality of the microscope is the microwave spectroscopy at atomic/molecular level. One of the topics of this research, performed at University of Maryland (USA), was the development of an instrument, working in cryogenic environment, for microwave spectroscopy of high-temperature superconductive materials. Atomic resolution would be useful in order to investigate non-linear phenomena at nanoscale.

Electron Spin Resonance detection through SMM was studied also in environmental conditions. The microscope was modified for jointly working with a magnetic head.

Furthermore, a more comprehensive description of the microscope resolution was investigated. Particular attention was given to the "in-depth" penetration of the evanescent field. This capability is extremely interesting in order to get a "short-range" tomography of complex samples (e.g., cells). A "time-domain" conversion of the frequency microwave data was applied.

Finally, the Scanning Microwave Microscope was employed in creating reproducible nanopatterns on graphene. This kind of patterning was observed experimentally, and then it was subject of theoretical and numerical investigation. This part of the research is supported by Oak Ridge National Laboratories (USA) within an active collaborative research.

Keywords. Carbon-Based Nanostructures, Microwave, Near-Field, Nanotechnology, Scanning Probe Microscopy.

1 Problem statement and objectives

Scanning Microwave Microscopy (SMM) is extremely attractive for nanotechnology applications: it could analyse complex structure behaviour at microwave frequencies through direct nanoscale measurements [1]. The electromagnetic interaction with samples occurs in the *reactive near-field* region, making its analytical description extremely difficult to solve, unless using tough approximations. Furthermore, both the sample features and the environment ones are determining for solving the electromagnetic problem [2]. During this research work, a SMM was designed and employed for nanoscale characterization of structured samples (*e.g.* Carbon-based nanostructures, cells). Analysis was performed in air and in liquid environment, taking into account the effect of fluid on measurements.
Once the field distribution is solved, the quantitative characterization of electromagnetic properties is possible. This is one of the most challenging issues related to the SMM; it has been studied from its discovery and it is still matter of research after 20 years.
Further topics stimulate research about SMM; for example, the concept of *resolution* of the microscope. In particular, the *in-depth* resolution of the microwave interaction, that could be extremely powerful in terms of "short-range" tomography [3]. Different approaches were proposed and analysed by Ancona microscopy group: one was based on time-domain conversion of frequency native data; the other was based on a revised holographic technique.
Additional interesting properties of materials arise at microwave frequencies, especially if considering interactions at molecular/atomic level (*e.g.* ferroelectricity, ferromagnetism, superconduction, etc.). The SMM is a suitable tool for this kind of applications [4]. Related experiments at cryogenic and standard conditions were performed during this research.
Finally, microwave disruptive interaction with matter is widely exploited for several applications [5][6]. Undesired effects have always been considered negligible during SMM scans because of the typical low intensities in use. In this work, the effects of the increasing power was numerically studied and exploited to create reproducible nanopatterns on graphene flakes.

2 Research planning and activities

The research activity has been structured on several sub-topics, introduced in the previous paragraph. During the first year of work, the candidate developed a technique for graphene flakes production from bulk graphite, by mechanical exfoliation. Then she analysed such samples through several Scanning Probe Techniques (mainly by SMM).
Briefly, the microwave microscope shares the emitting probe with a commercial Scanning Tunneling Microscope (STM) so it is able to record topographic data together with the microwave ones. The instrument performs raster scans of sample surfaces with sub-micrometric steps, up to several micrometres in size. In order to separate the tunnelling contribution from the microwave signals, the coaxial cables from PNA is capacitively coupled with the shared metallic tip. The microscope design is still improving, so part of this work has been dedicated to its tuning: "full-wave" numerical analysis, performed by electromagnetic simulators (*i.e.* HFSS, EM3DS), has been exploited in order to predict the spatial distribution of the field all over the system. Furthermore, it was possible to estimate the net power reaching the sample, and predict the focusing under the apex of the tip.

Due to the quasi-static nature of the localized field, the probe-sample interaction was modelled by a lumped element circuit. This approach was employed in order to get quantitative information about electromagnetic features from microwave recorded data (S11 complex parameter) in a more straightforward way with respect to numerical approach.
During the same year, the candidate gave support in testing a *complimentary* Scanning Microwave Microscope: in order to overcome limitations of the STM-based SMM, previously described, an AFM-based microscope was designed. The shared probe is replaced by a conductive AFM tip. The instrument was successfully applied to partially dielectric samples (structures of muscle cells grown over Carbon Nanotubes –CNTs).
Both these applications (graphene and CNTs+cells) showed a sort of "buried view" of non-topographic details. This fact witnesses that the microwave signal penetrates under the samples surface. Such SMM capability is intrinsically connected to the microwave-matter interaction, being the microwave radiation able to pass through almost all the materials.
During the following year, due to the capability of the Ancona microscope of working in liquid environment, an active collaboration with a research group in Oak Ridge National Laboratories (ORNL) – USA started. The aim of this cooperative research was the characterization of the microwave response of particular graphene samples, placed in different ionic concentrations. The samples consist in graphene islands grown by CVD on copper substrate.
The candidate developed a method for making STM/SMM tips suitable for liquid interactions, highly reproducible. Furthermore, she tested the system performances in performing large scans of graphene samples in fluid environment.
During the second half of the year, Monti was hosted by Prof. Takeuchi at University of Maryland - USA. There, she contributed to designing and testing a SMM working in cryogenic conditions. The main application of such instrument was the study of non-linear behaviour of superconductors at microwave frequencies. In order to perform such analysis, superconductive coils were inserted into the cryostat to apply an extremely high and localized magnetic field to samples. In such particular configuration, the extremely high resolution of the microscope would help in understanding phenomena at atomic/molecular level (*e.g.* Electron Spin Resonance – ESR).
Finally, the candidate explored the capability of the microwave microscope in destructively interacting with graphene islands on copper. Preliminary experimental analysis witnessed a destructive interaction with graphene flakes on highly corrugated substrate, so further studies were needed to clarify the contributions coming from tunnelling static potential and RF field. Once the microwave role has been found dominant over the tunnelling one, the microwave field were exploited to obtain reproducible patterns on the substrate.
The explanation of the chemical and physical phenomena involved in the etching process was deeply investigated. Significant support came from ORNL researchers. Analytical and numerical models were developed in order to predict the microwave density power distribution and to estimate the minimum level and exposure time to obtain the patterns.

3 Analysis and discussion of main results

For characterizing the microwave properties of graphene samples produced by mechanical exfoliation and deposited over a conductive substrate, the candidate solved a simplified lumped elements circuit with dominant conductive contributions. Without additional nano-calibration, through a *differential measurement* between known and unknown samples, it was possible to estimate the sheet resistance of graphene flakes. Furthermore, she proposed to use the microscope to generate micrometric maps of such electrical parameter (Fig.1). This data would be useful to test the spatial uniformity of current distribution (*e.g.* LED electrodes).

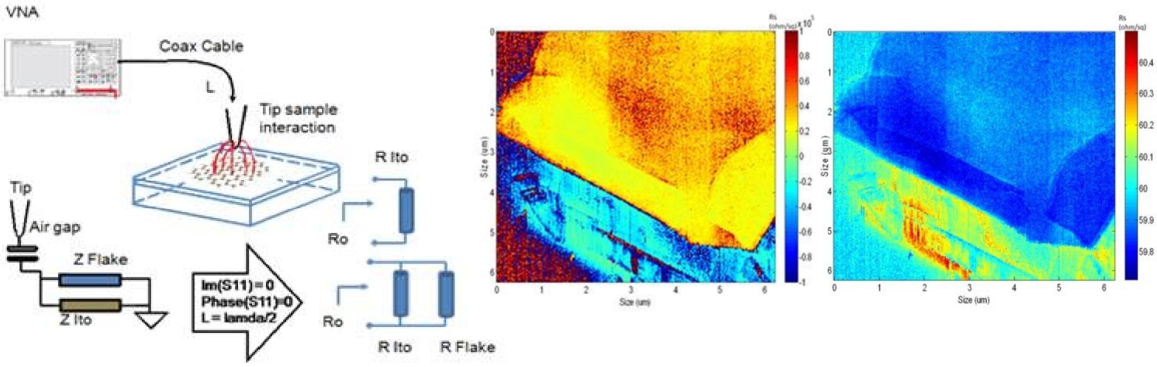

Fig.1 Schematic description of the lumped element circuit used to model the SMM interaction with graphene+ITO multi-layered sample. The approximation is valid only when the conditions in the arrow are satisfied (*left*). Maps of the spatial distribution of sheet resistance; graphene only (*centre*) and graphene+ITO case (*right*).

The application of AFM-based SMM allowed for imaging micrometric details of particular cells developed along Carbon Nanotubes structures. In particular, the SMM was able to clearly distinguish the dielectric contrast between elements at different depths, unrevealed by topography (Fig.2). In order to quantitatively evaluate the electromagnetic features of buried details, a "short-range" tomographic algorithm was needed: to this aim, the *in-depth* interaction of the near-field must be modelled. Although for metallic and magnetic samples, the traditional skin depth concept is still meaningful, different contributions become relevant in case of dielectric samples.
A *time-domain* approach was introduced and investigated to separate contributions coming from different z-planes of reflection; additionally, a holographic method for near-field microwave imaging and tomography was adapted to SMM imaging.

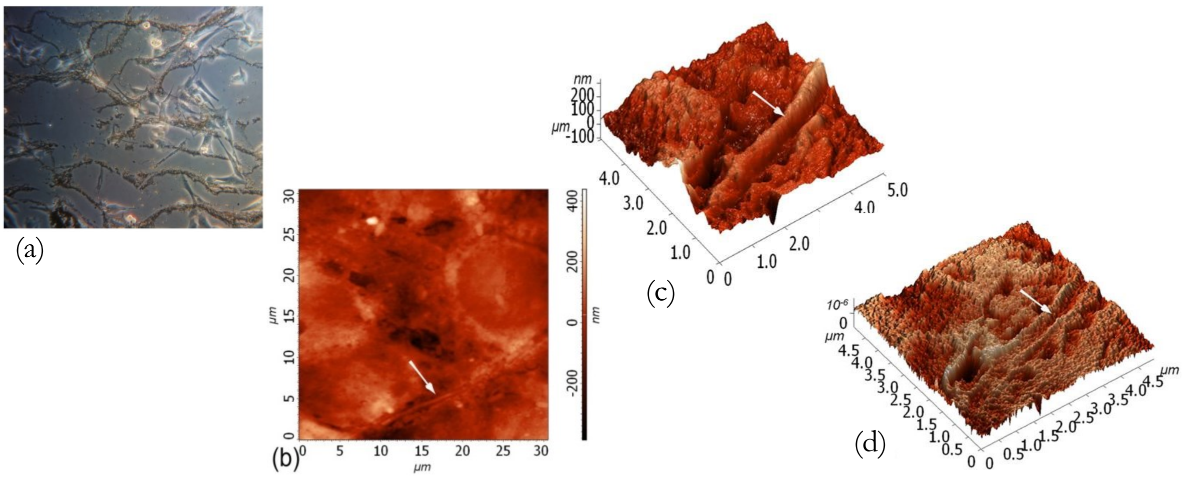

Fig.2 (a) Optical microscope image of complex structures made of cells and CNTs; (b) AFM image of such structures; (c) AFM detail of the previous image; (d) SMM image of the same detail. The latter image highlights features completely different from topography (c). These are ascribed to material dielectric contrast.

From SMM analysis in liquid environment of graphene islands grown on copper substrate, it was possible to clearly separate the fluid effects on microwave response, although further work is needed in order to quantify such contributions and make a general procedure to obtain quantitative results (Fig.3).

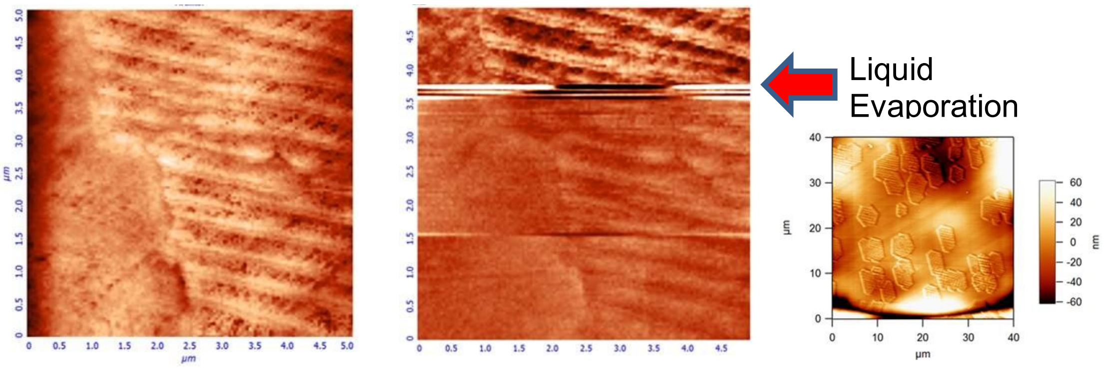

Fig.3 STM (*left*) and time-domain SMM (*centre*) images of a corrugated graphene island over copper substrate in liquid environment. The right image shows a wider topographic view of such sample. In SMM image different details are present in the upper and lower part, since the liquid evaporates during the scanning process. The STM remains unchanged. The presence of the fluid deeply alters the microwave response. Filtering operations in frequency-domain makes a clear separation between *air* and *liquid* details possible.

About the disruptive interactions between microwave field and graphene flakes, the candidate developed a reproducible method to obtain nanometric size "holes" on their surface. The cause of such holes was found in chemical reactions happening between graphene atoms and air molecules, since the tip worked without any contact with the sample.
A set of experiments were planned for optimizing the power and time of exposure. It was found that a minimum time is required for obtaining patterns with appreciable size; the long-term effect suggested again a combined thermal-chemical explanation rather than a mechanic one.
Furthermore, although the microwave density power was extremely focused under the tip, the graphene has a very high thermal conductivity, so the heating up effect should not occur. This was explained by the presence of an oxide layer naturally formed underneath graphene where the heating formed a *hot spot* and produced a very high thermal gradient (Fig.4).
The hypothesis was confirmed by a preliminary multi-physics simulation, but the accuracy of results must be improved.

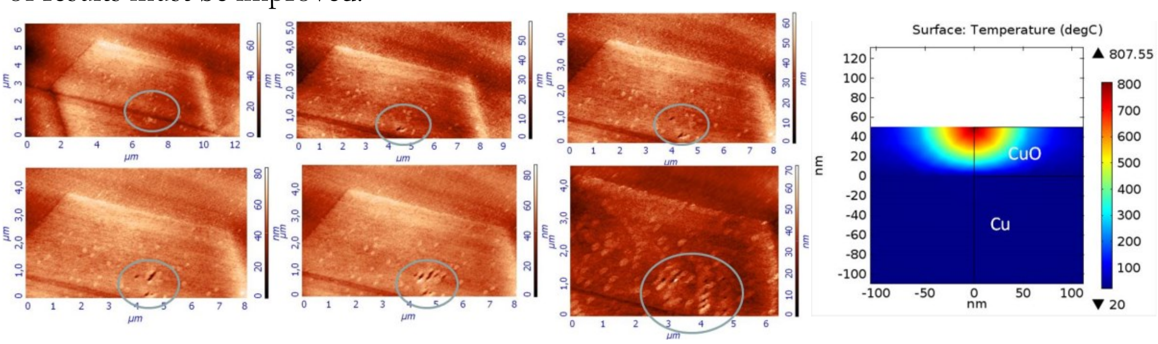

Fig.4 Consecutive scans of a graphene island on copper substrate, after localized microwave exposure through SMM tip (*left*). Each exposure generates a new hole on the surface. The process is highly controllable. COMSOL simulation: thermal gradient due to microwave localization (hot spot) (*right*).

4 Conclusions

The research issues related to the Scanning Microwave Microscopy development and applications hereby summarized are still under investigation; a more comprehensive "differential measurement method" is needed for applications to more complex conductive and dielectric structures (*e.g.* cells). As an example, a multi-steps procedure has been detailed in the referred thesis work.
Additional analysis is also needed in order to exploit the *time-domain* transformation of frequency native data for tomographic reconstruction. To this aim, the in-depth resolution of the microscope has to be defined in a more general way.
The Electronic Spin Resonance detection through SMM is still under investigation in Ancona microscopy laboratory: further research is ongoing in order to tune the magnetic head-SMM for applications at environmental temperature. Together with the cryogenic instrument at University of Maryland, comparative analysis in different environments will then be possible.
Finally, a set of experiments must be performed in order to understand the frequency dependence of the nanopatterning phenomenon through SMM. The candidate is still working on multi-physics numerical simulation of the complex system at nanoscale, in order to predict both thermal and electromagnetic mutual effects. The last aim of this study would be the employment of such technique for graphene and more general nanomaterials manufacturing.

References

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