Chair:
Prof. Paola Taroni

DOCTORAL PROGRAM IN PHYSICS

The Doctoral Program in Physics at Politecnico di Milano aims at attracting bright students with good scientific background and clear interest towards development and applications of new ideas and technologies. It offers a wide range of opportunities in the fields of advanced applied physics, such as photonics and optoelectronics (lasers, ultrafast optics), vacuum technologies (thin film depositions), material technologies (microelectronics and nanotechnologies, micromechanical processing), advanced instrumentation (electronic and atomic microscopy, nuclear magnetic resonance) and biomedical optics (optical tomography).

Scientific education and training to develop general research abilities in all areas of applied physics is increasingly needed by advanced technological companies. Through a general education in the basic areas of applied physics and a specific knowledge in condensed matter physics, as well as optics and lasers, the PhD Program aims at the development of an experimental approach to problem solving techniques and at the attainment of a high level of professional qualification.

The Doctoral Program has strongly experimental character. The contents are strictly related to the research activities carried out in the laboratories at the Department of Physics. They can be divided into two main areas:

a. Condensed Matter Physics, including photoemission; spin-resolved electronic spectroscopy; magneto-optics; X ray diffraction; magnetic nanostructures for spintronics; synchrotron radiation spectroscopy, positron spectroscopy, semiconductor nanostructures.
b. Optics and Quantum Electronics, including ultrashort light pulse generation and applications; UV and X optical harmonics generation; biomedical applications of lasers; diagnostics for works of art; laser applications in optical communications; time domain optical spectroscopy and diagnostic techniques.

All these research activities rely on advanced experimental laboratories located at Politecnico di Milano (Milano-Leonardo Campus and Como Campus) and are performed in collaboration with several international Institutions. Besides the experimental research, a consistent effort is devoted to the design and development of novel instrumentation.

The educational program can be divided into four parts: 1) Laboratory of Basic Physics, which allows the PhD students to join full time different experimental laboratories, guided by their supervisor and other colleagues at the Department of Physics; 2) Main courses specifically designed for the PhD program; 3) Activities pertaining more specific disciplines which will constitute the basis of the research work to be carried out during the Doctoral Thesis; 4) Doctoral Thesis. The thesis work is the major activity of the Program, it has a marked experimental character, and will be carried out in one or more laboratories at the Department of Physics.
The students are also encouraged to perform part of their thesis work in laboratories of other national or foreign Institutions. Collaborations that may involve the PhD students are presently active with several national and international research and academic Institutions, such as: ETH-Zürich, EPL-Lausanne, Lund Institute of Technology, University of Paris-sud, Ecole Polytechnique-Paris, University of Barcelona, University of Berkeley, University of Cambridge, Technical University of Wien, University of Bordeaux, Massachusetts Institute of Technology, Harvard University, INFM-CNR, IIT–Istituto Italiano di Tecnologia, European Space Agency, ENEA, Elettra–Ts, PSI-Villigen, Agenzia Spaziale Italiana, European Synchrotron Radiation Facility (ESRF-Grenoble).

The average number of fellowship/grants for students admitted to the PhD Program is around eight per year, while the average e number of available positions is more than double. At present, the overall number of students in the three-year course is fifty-seven.

Teaching and research activities of the Doctoral Program are controlled and organized by a number of Faculty members large enough to cover a wide spectrum of research fields. All members are highly qualified and active researchers. This ensures a continuous updating of the PhD program and guarantees that the students are involved in innovative work. A list of the Faculty members follows:

DOCTORAL PROGRAM BOARD		
Franco Ciccacci	Giacomo Ghiringhelli	Roberta Ramponi
Rinaldo Cubeddu	Guglielmo Lanzani	Paola Taroni
Sandro De Silvestri	Marco Marangoni	Alessandro Torricelli
Lamberto Duò	Mauro Nisoli	
Marco Finazzi	Ezio Puppin	

The Doctoral Program relies also on the advice of a Steering Committee, formed by distinguished experts (see table below) coming from R&D industries or research laboratories, taking care that the goals of the PhD program are in line with the needs of non academic world.

ADVISORY BOARD
Roberto Bez (NUMONYX, Scientific fellow - R&D)
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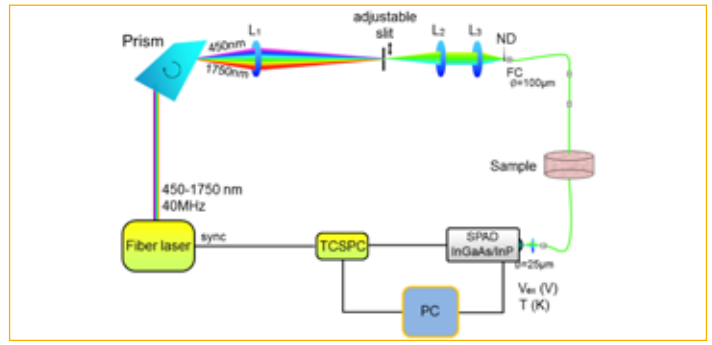
Emilio Parisini (CNST - Fondazione Istituto Italiano di Tecnologia (IIT), Team Leader (Biochemistry))
B Hans von Känel (ETH-Zürich, Professor)

ADVANCED TECHNIQUES FOR OPTICAL SPECTROSCOPY OF DIFFUSIVE MEDIA

Ilaria Bargigia - Supervisor: **Antonio Pifferi**

The research leading to this PhD dissertation has been accomplished in the Physics Department of Politecnico di Milano (Milano, Italy) and in the Division of Atomic Physics of Lund University (Lund, Sweden). The main framework of this work resides in the interaction of light with diffusive media (*e. g.* biological tissues, wood).
In recent years, there has been an increasing interest towards the non-destructive characterization of diffusive materials by means of optical methods and several advanced techniques have been developed based on Continuous Wave (CW), Frequency-Domain (FD) or Time-Resolved (TR) approaches. Although CW techniques are more common and can be found in different commercial systems, nowadays broadband time-resolved spectroscopic techniques are seen as valid alternatives for non-standard cutting-edge research and are applied and perfected in few centres of excellence around the world as in Lund University (group of Prof. S. Andersson-Engels) and in Politecnico di Milano by our group. Usually, broadband Time-Resolved Spectroscopy is performed in the wavelength range 600-1100 nm, the so-called therapeutic window, where the light is less attenuated by the main constituents of biological tissues.

Another advanced spectroscopic technique is the GASMAS - Gas in Scattering Media Absorption Spectroscopy, proposed by the group of Prof. S. Svanberg of Lund University. GASMAS, exploiting the scattering properties of turbid materials, is able to probe molecular gases trapped in pores of diffusive materials. Examples of application include the analysis of water vapour and oxygen in human sinuses, the investigation of gases in food packaging or the analysis of gases in nano-porous materials or pharmaceutical products.
During these three years, my work has been mainly dedicated to push the limits of Time-Resolved Diffuse Spectroscopy in terms of spectral range, portability of the instrument and of range of applicability (*e.g.* low scattering/high absorption samples). Moreover, I worked for applying this technique, together with GASMAS, in new innovative fields of investigation. In particular, this thesis consists of three main levels:
Exploration of applicability limits: critical situations for Time-Resolved measurements are taken into account, connected for example to high absorption and/or low scattering values of the sample. A study on the best operating conditions is presented, with the aim of finalizing the system for each particular application.
Instrument development: a portable time-resolved system and a laboratory workstation for time-resolved measurements in the extended spectral range 1100-1700 nm are developed. The first system meets the need for a portable as well as flexible solution for performing measurements in the field: it is a multi-purpose unit for time-resolved spectroscopy which can be easily and effortless modified to suit different applications, for example substituting the detector stage to investigate different wavelength range of interest. The second system works in the spectral region extending beyond 1100 nm, which up to now is largely unexplored by time-resolved diffuse techniques probably due to the uneasy combination of tunable laser sources and suitable detectors with sensitivity down to the single-photon level. A scheme of the set-up is reported in Figure 1.
Study of materials: results on the characterization of organic absorbers (as collagen and lipids) beyond 1100 nm and on the optical study of wood with combined measurements of time-resolved spectroscopy and GASMAS are presented. In particular, the first *in-vivo* measurements up to 1400 nm were performed on the breast and the arm of two healthy volunteers and we were able to attribute the main absorption features to the principal constituents of biological tissues as collagen, lipids and water. Other important results have been obtained from the optical analysis of wood. The measurements enabled us to monitor various properties of wood such as moisture content and oxygen diffusion. Moreover, valuable information could also be provided on wood internal structure, anisotropy, percentage of relative humidity, gas porosity and permeability. The optical analysis was also extended to archaeological wood. In particular, a first measurement on a sample from the shipwreck VASA proved the feasibility of time-resolved measurements in the range 1050-1450 nm to detect the presence of polyethylene glycol, a polymer used for conservation of wood.
As final application, a study on the feasibility of this technique for the *in-vivo* detection of carbon dioxide in tissues of rabbits is presented.
Future work will be done to increase the number of healthy subjects for the *in-vivo* investigation of tissues beyond 1100 nm and to determine the concentration of the main biological constituents. For what concerns the optical analysis of wood, the main future aim is to quantify its principal components, with a particular interest in the wood uptake of impregnants.



1. Figure of the experimental set-up for time-domain diffuse optical spectroscopy up to 1700 nm: the light source is a supercontinuum fibre laser, radiation is dispersed by means of a rotating prism and the diffused light is collected by a Single-Photon Avalanche Diode with active area in InGaAs/InP

DEVELOPMENT AND APPLICATION OF A RAMAN MAPPING INSTRUMENT FOR THE STUDY OF CULTURAL HERITAGE

Alex Brambilla - Supervisor: **Gianluca Valentini**

The thesis reports the project, the development and the application of a novel instrument for Raman spectroscopy. Based on a semiconductor laser and a pair of galvanometric mirrors, the proposed device is able to map an area of approximately 5 cm of a surface at a distance of 20 cm from the instrument: among the other features, the most striking characteristic of the instrument is its long depth-of-field, which makes it particularly suitable for the analysis of archaeological founds and of works of art.
In Cultural Heritage the necessity to monitor wide surfaces of heterogeneous artefacts is particularly urgent. The objects of interest, from paintings to frescoes, from mosaics to tapestries, can be characterised only by an extensive sampling over the surface, being a single-shot analysis not representative of the whole item. Moreover, only in rare cases an actual extraction of the specimen is allowed: an optical technique, such as Raman spectroscopy, is ideal for achieving chemical information without damaging or altering the analysed surface. The possibility to perform this measurements at a certain distance, without moving the sample, increases dramatically the number of possible applications; together with the already cited long depth-of field, this feature permits analysis of non-flat objects, such as bas-reliefs, stuccoes, sculptures and pieces of design objects. In addition the long working distance is necessary in order to allow the instrument to be employed on site, where physical and practical obstacles often prevent the adoption of a standard micro-Raman instrument.
The chance of performing remote measurements not only considerably widens the range of applications, but it also makes the device less affected by the vibrations which perturb contact analysis when performed out of the laboratory environment.
To permit the in situ application of the Raman device the project was specifically addressed towards a mobile layout, which consists of a probe head, mounted on a tripod, and remotely connected to the laser source and to the acquisition unit, both lodged on a mobile scaffold. The probe head contains the galvanometric mirrors which deflect the laser beam on the different points of the field of view and a custom optical system which is responsible of the focus and the collection of the backscattered light. The latter is the most crucial element of the whole set-up: it has been developed following an accurate study of the light path towards the sample and the reverse, for all the possible tilt angles provided by the mirrors. Simulations, run by the ray tracing software Zemax(R) permitted an optimization of the building parameters and an estimate of the collection efficiency. Light-weight materials, like carbon fibre reinforced plastic, and small-sized components have been chosen out of commercially available items; the selection followed the purpose of portability but the aim has been to maintain sufficiently good performances with respect to a similar desktop instrument. A custom-made software is adopted to manage the three computer-controlled devices (besides the galvanometric mirrors, the spectrograph and the CCD used to acquire and discriminate the Raman signal) with a unique virtual interface, specifically conceived for selective mapping measurements.
After an introductory chapter describing the classical and quantum theory of Raman scattering, with a particular glance on the information provided by the homonym spectroscopy method and on its critical points, the thesis focuses on the development of the instrument, previously synthesized. Then, a brief report of the tests for characterizing the effectiveness of the prototype instrument is given: spatial resolution, extent of the field of view and of the depth of field were assessed through dedicated tests. A measurement on a model painted panel determined the capability of the instrument to discriminate the spectral fingerprints of traditional pigments; this case study permitted, as well, to employ other non-destructive methods of analysis and compare the results with the spectral data obtained by the Raman spectrometer.
Spectra collected by different samples, extracted from real object of interests such as the Italian Auschwitz Memorial, or from white pigments of the last century, are reported and commented as examples of applications; in particular, the case study of the design telephone "Grillo" is presented to underline the effectiveness in the study of 3D objects.
The last chapter is dedicated to the application of another Raman portable instrument to amino acids, in the framework of a joint project with the Institute of Electronic Structure and Laser (IESL-FORTH) of Heraklion, Greece. The aim of the work is to help the detection of traces of organic materials in archaeological finds by exploiting the so-called Surface-Enhanced Raman Spectroscopy (SERS); this is an advanced method which employs a nano-structured metal as a substrate to boost the Raman signal of an analyte, adsorbed on its surface. The common background which links this research activity with the main object of the thesis is the search for new solutions in the application of Raman spectroscopy for *in situ* study of historical or artistic artefacts. The possibility to apply directly on the archaeological site a simple and reproducible technique for the detection of small organic molecules is here evaluated, starting with the analysis of amino acids in aqueous solutions. The goal is to achieve a significant detection limit for more complex substances, which will enable the researchers to identify traces of biological materials (e.g. wine, oil, honey) still present in some finds of ancient vessels or containers.
Globally, this thesis aims to show two novel applications of a consolidated technique, such as Raman spectroscopy, to the analysis of Cultural Heritage. The bulk of the work here reported is the project and construction of a new instrument, characterised by a different approach, not only from the commercially available devices, but also with respect to the spectrometers currently adopted for the diagnostic of precious artefacts. Thanks to peculiar features, such as the possibility to map a macroscopic surface without moving the sample and the stand-off character of the analyses, this instrument is an advantageous tool when analysing historical and artistic objects and it is particularly suitable for integration with other non-invasive techniques. Raman spectroscopy alone, indeed, is not usually enough for a safe identification; often, moreover, it can be hampered by competitive phenomena like fluorescence. An increasingly popular method such as SERS can be, in selected applications, a key to solve the intrinsic weakness incidental to Raman scattering: its employment with a portable Raman equipment has been, for the first time, successfully tested. Applications in the analysis of archaeological pottery are, therefore, foreseen .

DEPOSITION AND CHARACTERIZATION OF SILICON-GERMANIUM HETEROSTRUCTURES FOR THERMOELECTRIC DEVICES

Stefano Cecchi - Supervisor: **Giovanni Isella**

The increasing demand of energy, together with the environmental impact of fossil fuels in global climate change, have opened in the last decades a large discussion aimed to identify strategies to improve the sustainability of our energetic system. While fundamental research is focusing on new materials and new concepts development which could overcome nowadays electronics, a parallel approach consists in coupled systems capable of efficiency harvest wasted energy.

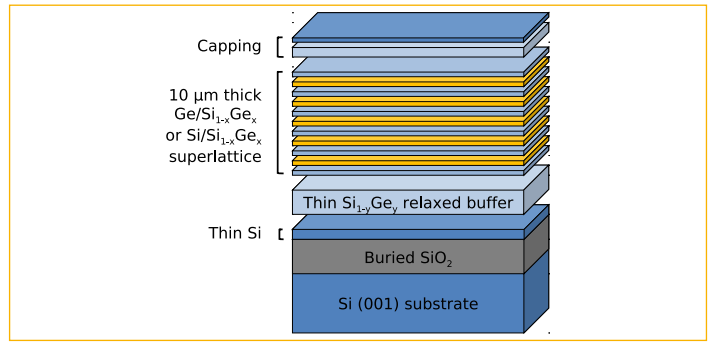
Germanium and silicon-germanium alloys have attracted in the last two decades the attention of the scientific community in many fields of technological research, such electronics, photonics, spintronics and more recently energy harvesting. The reason for such revamped interest is the improvements achieved in SiGe growth and fabrication technology, enabling the deposition of high quality epitaxial material and engineered low dimensional structures directly on Si. Indeed the strength of using the well-established and low-cost SiGe production techniques is the complete integrability with complementary metal-oxide semiconductor electronics based on Si.

In the field of thermoelectricity SiGe can play a primary role. Despite the significant scientific progresses reported in the recent years, one of the crucial issues to be overcome in thermoelectric devices is the relatively low efficiency which characterizes the actual technology. Indeed in bulk materials the thermoelectric efficiency, defined by the figure of merit *ZT*, is limited by conflicting parameters. Nevertheless, the use of low dimensional structures such as multilayers has demonstrated the possibility to overcome these constrains favoring the enhancement of *ZT*.

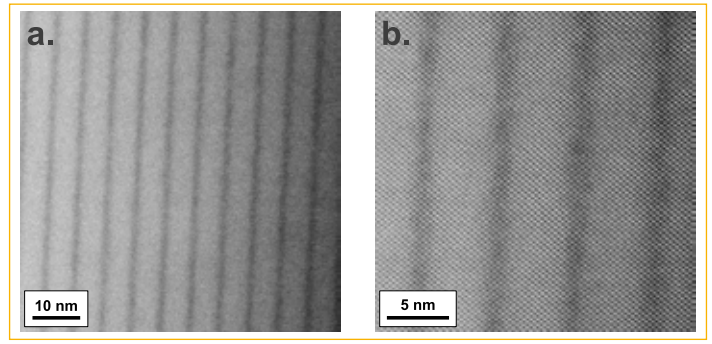
For high temperature applications (above 900 K) SiGe alloys have the best thermoelectric efficiency. Even though the efficiency at room temperature for the best SiGe alloy is substantially lower than that of other materials, the integration with Si-based devices together with the sustainability compared to the rare and often toxic materials used in state-of-the-art thermoelectric modules are key factors for the choice of SiGe. While nanostructured bulk materials seem to be promising for high-power high-temperature applications, thin film technologies constitute an interesting opportunity for the development of low-power thermoelectric generators. Integrated cooling and energy harvesting modules could be coupled to electronic devices, solar cells and autonomous systems such remote sensors.

We have deposited and characterized thick Ge-rich SiGe multilayer structures with the aim of demonstrating efficient, cheap and integrated thermoelectric energy generation. Two approaches have been followed in order to enhance the low efficiency characterizing SiGe alloys at room temperature.

Most of the experimental activity has been focused on lateral devices based on modulation-doped multiple quantum well (MQW) structures, where both electrical and thermal conduction occur in the in-plane direction (see Fig. 1). This solution is expected to improve *ZT* as well as the generated power. A great effort was made for the development of optimized procedures allowing the deposition of the required thick structures on silicon on insulator (SOI) wafers. Feedback from X-ray diffraction (XRD) and transmission electron microscopy (TEM) analysis was used in order to improve the structural quality and match the requirements for the different designs. The structural characterization of the optimized material confirmed



1. General schematic of the lateral structures. The 10 µm thick modulation-doped MQW stack is grown on top of a thin Si1–yGey relaxed buffer on SOI wafer



2. High-resolution TEM (a) and atomically-resolved scanning TEM (b) images of the thin layers characterizing the vertical structures, demonstrating a well defined Ge/SiGe structure.re, therefore, foreseen

the quality and the reliability of the structures deposited by low-energy plasma-enhanced chemical vapor deposition (LEPECVD).

The thermoelectric properties have been characterized using a micro-fabricated suspended device, allowing for the measurement of all the parameters entering the figure of merit *ZT* for the same piece of material. Although the measured *ZT* is far below the predicted value for equivalent MQW structures, the results demonstrate an enhancement compared to a reference SiGe alloy (also deposited by LEPECVD) and to literature data for p-Ge, encouraging further research.

The activity based on the second approach, consisting in the optimization of the thermal transport in vertical structures, where the heat and carrier transport occur in the cross-plane direction, has started only recently. This solution is promising for the development of higher *ZT* materials compared to the lateral one. A common feature for all the proposed structures is the need of a few nm thick layers. XRD and TEM data demonstrated not only the feasibility of growing such superlattice structures with LEPECVD, with a minimum layer thickness below 1 nm, but also the extremely high quality of the deposited structures (see Fig. 2). The characterization will be focused mainly on two aspects: the understanding of the mechanisms involved in phonon propagation in SiGe superlattices and the role of dopants in these vertical structures.

In conclusion, although many aspects still need to be clarified for a complete understanding of the involved thermoelectric phenomena and the optimization of the efficiency in these structures, the preliminary thermoelectric characterization of lateral multilayers demonstrates the viability of SiGe based devices as integrated thermoelectric generators.

SOLID/LIQUID ORGANIC DEVICES FOR ENERGY AND LIFE SCIENCE

Erica Lanzarini - Supervisor: **Guglielmo Lanzani**

In the thesis, the results obtained during my 3-years PhD activity in the two major research fields of renewable energy and organic bioelectronics are reported. In particular, two main topics are treated, such as 1. Organic semiconductor-based, photocatalytic water splitting and 2. Organic prosthetic devices for sight restoring. In the first part of the thesis, organic semiconductors are generally described from the point of view of their peculiar optical and electronic characteristics. Their capability of charge generation and transport upon illumination renders them particularly appealing for the development of any kind of application requiring a photovoltaic, low-voltage operating regime. For our projects, particular interest is elicited by polymers showing active functionality in the range of visible light. Besides photovoltaic cells applications they can, in fact, be originally employed in different fields currently mainly dominated by inorganic materials, such as water splitting and prosthetic devices realization. Biocompatibility and biostability properties of organic materials are moreover taken into account, providing an accurate view of the related current knowledge at the state of the art. Biocompatibility, in particular, is a peculiar characteristic of most organics; it descends from their carbon-based backbone rendering them similar to tissues´ structure and thus suitable for bio-mimetic applications and prosthetic purposes. After the introductory part, the first research topic treated, i.e. water splitting, is reviewed in detail. The water splitting phenomena is presented from both the theoretical and the devices` point of view. In reviewing the many different water splitting systems reported in literature at the best of our knowledge, most of which employing inorganic semiconductors such as titanium dioxide as active materials and operating upon external bias application, particular attention is devoted in the description of such systems which alternatively operate under photovoltaic conditions and/or employ organic materials as active layers. Consequently, the thin film, polymer-based, photocatalytic water splitting devices developed in our laboratories are presented. The description of such devices from both the realization and characterization point of view is organized as listed in the following: 1. Description of materials´ processing techniques for devices` realization, 2. Description of optical, electrical and electrochemical techniques and relative set up employed for devices` testing, 3. Presentation and interpretation of collected experimental data, with particular focus on the characterization of photogenerated chemical reactions taking place at the polymer/water interface. In particular, the innovative possibility to promote gaseous hydrogen from bulk water using a simple polymeric thin film as a photocatalyst under photovoltaic conditions (with no additional bias applied) upon visible light illumination is presented, 4. Characterization of the polymer/aqueous solution interface and development of a possible interpretation model, able to describe the charges exchange mechanisms at the polymer/water interface, not yet formalized in literature. Possible future developments of the devices` are moreover presented, with particular focus on the solar-to-hydrogen efficiency maximization. In the second part of the work, the field of organic bioelectronics is taken into account. A detailed review of literature regarding this field is provided, with particular attention to the areas of prosthetic devices and transistors for sensing. Our project´s aim concerns the realization of an all-organic, prosthetic device, totally operating under photovoltaic conditions, able to substitute a damaged human retina, subject of particular degenerative diseases which destroy the retinal photoreceptors, such as retinite pigmentosa. The organic artificial retina is conceived as a matrix of pixels, i.e. organic photodiodes, which act as photoreceptors and transduce optical signals into electrical ones. Two main results have been obtained until now within this project and are described in the thesis. The first one concerns the communication between a polymer-based organic device and rats´ hippocampal primary neurons. We in fact demonstrated for the first time how it is possible to obtain neurons´ stimulation using only visible light as an input and a simple polymeric thin film as a mediating platform. This result not only constitutes a fundamental and necessary step for the future realization of the prosthetic implant, but also establishes a new communication protocol between neuronal cells and prosthetic devices. The second fundamental result of our research concerns the stimulation of ganglion cells of blind rats´ explanted retinas. When retinal photoreceptors cells are damaged by certain diseases, blindness is caused in the patient. However, if all other retinal cellular layers are preserved, it is still possible to obtain photostimulated signals to be delivered to the optical nerve, able in principle to restore sight. A very simply structured, polymer-based, thin film device is thus demonstrated to be able to elicit stimulation of retinal ganglion cells (which are responsible for signals delivery to the optical nerve) in rats´ explanted blind retinas. Stimulation has been tested under visible light illumination for different light pulses even within the day-light limit. As a further development within the retina prosthesis project, results of our research for biomimetic and biocompatible materials to be used as scaffolds for polymeric thin film based devices in in-vivo implants are reported. As a conclusion, future perspectives for polymer-based retinal prosthesis are taken into consideration, focusing on the most relevant issues to be faced, such as biocompatibility and biostability over time. Necessary further improvements for the devices are also underlined, such as, for example, the necessity to realize a proper organic pixels matrix within the polymeric active device, in order to mimic the natural photoreceptor distribution in the retina.

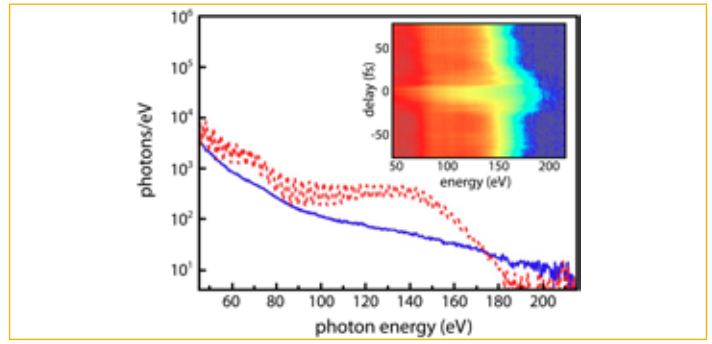
HIGH ORDER HARMONIC GENERATION DRIVEN BY A MID-INFRARED LASER SOURCE: A TOOL FOR ATTOSECOND SCIENCE AND MOLECULAR SPECTROSCOPY

Matteo Negro - Supervisor: **Salvatore Stagira**

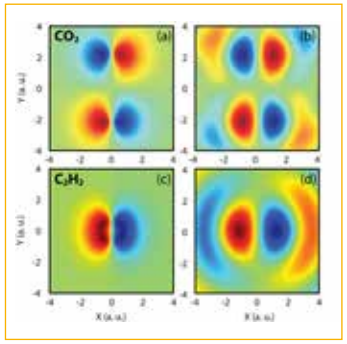
The development of ultrafast and intense laser sources has paved the way to the study of laser-matter interaction in the strong-field regime, where the amplitude of the laser field becomes comparable to the Coulomb field seen by the electrons in the proximity of their parent ion. The access to this regime triggered in the last decades the discovery of new nonlinear processes, like high order harmonic generation (HHG). This consists in the emission of bursts of extreme ultraviolet light (XUV) following the interaction of the electric field of an ultrashort laser pulse with a gas jet. The process can be understood in the framework of a semi-classical three-steps model: the outermost electron of the neutral species is ionized, accelerated and forced to recombine with the parent ion by the strong laser field. The recombination is followed by the emission of an XUV photon, whose energy depends on the kinetic energy acquired by the electron in the continuum. This picture of HHG is completed recalling that the laser pulse contains several optical cycles; thus the harmonic radiation appears as a sequence of XUV attosecond bursts, separated in time by half the optical cycle of the driving field. In the spectral domain, this to the emission of discrete odd harmonics of the fundamental frequency of the pulse. Up to few years ago, Ti:Sapphire lasers were the only candidates available for exploring the strong-field realm, and in particular the HHG process, due to their unsurpassed amplification bandwidth, that allowed to compress their intense pulses down to the single-cycle domain. In the last decade, techniques like polarization gating and spectral filtering of 800-nm few-cycle laser pulses successfully allowed the generation of 100 as pulses with photon energies below 100 eV and pulse energies of a few pJ. However, more recently, great effort has been spent in developing techniques for generating bright attosecond pulses with photon energies going beyond the 100 eV limit, and approaching the X-rays spectral range. This was made possible by the advent of high-energy mid-infrared (mid-IR) ultrafast optical parametric amplifiers (OPAs), operating in the spectral region between 1.5 and 3 mm, since the cutoff of the emitted XUV radiation scales as the square of the wavelength of the driving field. Part of my Ph.D. was devoted to the development of new approaches for the isolation of single attosecond pulses, by means of a high-energy mid-IR OPA. By combining different color pulses, it was possible to obtain the gating of the HHG emission over a single half-cycle, and generating continuous spectra, that are the signature of single attosecond pulse production, extending beyond 160 eV. Figure 1 shows the continuous spectrum (blue curve) generated in argon by mixing two mid-IR laser pulses with incommensurate wavelengths (1.35 mm, 35 fs and 1.75 mm, 32 fs), while the red line shows the discrete harmonic spectrum generated by the 1.35 mm pulse alone. The gating effect originates in this case from the shaping of the electron trajectories due to the two-color field.

HHG is intimately connected to the shape of the wavefunction of the bound state of the atom or molecule in which the process is triggered, through the recombination step. The emitted radiation contains a wealth of information about the structure of its generating medium. The first demonstration of the possibility of imaging molecular orbitals through HHG dates back to 2004.

In this study, a tomographic reconstruction of the Highest Occupied Molecular Orbital (HOMO) of nitrogen has been obtained by driving HHG into N_2 molecules, previously aligned by means of a first laser pulse. Indeed, if one assumes that the electron liberated by the laser field is not influenced by the Coulomb field of the ion during its motion in the continuum (i.e. it is a plane wave), the harmonic spectra can be expressed as a function of the spatial Fourier transform of the ground state of the molecule. By acquiring several spectra at different angles between the aligned molecules and the polarization of the driving pulse, and anti-transforming to the spatial domain, one is able to retrieve the HOMO. However, several issues have hindered so far the extension of this technique towards more complex molecules. First of all, in order to get a complete reconstruction, the information on the phase of the emitted harmonics needs to be present. This can be obtained by performing very sophisticated experiments. Moreover, despite providing an easy way towards the orbital tomographic reconstruction, the plane-wave approximation revealed inappropriate in molecular systems. Finally, in the last years, studies have demonstrated that high harmonic generation can involve more than one orbital, thus yielding information on the attosecond dynamics launched in molecules, following strong-field ionization. Although opening new and exciting perspectives in attosecond science, this findings have seriously called into question the original idea of HOMO tomography. During my Ph.D., we were able to introduce a breakthrough in the field of HHG molecular orbital tomography, which allowed to extend the concept to more complex molecules. The approach is based on the exploitation of a mid-IR laser source for driving HHG in aligned molecules, that prevented us from observing multi-orbital effects. We acquired a sequence of harmonic spectra as a function of the delay between the aligning and the driving pulse and from this all-optical measurement, by means of a mathematical algorithm, we retrieved the information on the phase of the emitted harmonic as a function of the frequency and of the angle. By introducing a correction that takes into account the molecular potential, we obtained a tomographic image of the HOMO of carbon dioxide and acetylene (shown in Figure 2), thus opening intriguing perspectives on coherent XUV imaging, eventually time-resolved, of complex species by high-order harmonic generation.



1. HHG spectra obtained in argon by 1.35 mm, 35 fs + 1.75 mm, 32 fs laser pulses (blue curve) and by the 1.35 mm pulse alone (red curve)



2. 2D projection of the (a) calculated by using a computational chemistry program and (b) retrieved HOMO of the carbon dioxide molecule. (b) and (c): same for acetylene

MAGNETIC, ORBITAL AND CHARGE FLUCTUATIONS IN LAYERED CUPRATES STUDIED BY RESONANT SOFT X-RAY SCATTERING

Matteo Minola - Supervisor: **Giacomo Ghiringhelli**

This thesis presents the results achieved on cuprates with resonant soft x-ray scattering (RXS) during my activity in the group of Prof. G. Ghiringhelli and Prof. L. Braicovich of the Physics Department of Politecnico di Milano (Italy). The group has a well-established experience in synchrotron-based spectroscopies for the study of magnetic and electronic properties of transition-elements and rare earth compounds. Recently they focused their activity especially on resonant inelastic x-ray scattering (RIXS), contributing to the development of the technique, both from the point of view of science and instrumentation. They designed and built two high resolution spectrometers dedicated to RIXS: AXES (Advanced X-ray Emission Spectrometer) and SAXES (Super-AXES). AXES is working since 1995 at the beamline ID08 of the European Synchrotron Radiation Facility in Grenoble, France. SAXES, which is the evolution of AXES, has been installed in 2006 at the ADRESS beamline at the Swiss Light Source in Villigen, Switzerland. It is working since July 2007 and by now it holds the world record of resolving power with a combined resolution of 130 meV at Cu L_3 edge (930 eV).
In this thesis I present some of the results obtained with these spectrometers on insulating and superconducting layered cuprates using Cu L_3 edge RIXS. This technique is shown to be the optimal probe to study magnetic, orbital and charge fluctuations in the CuO_2 planes of these compounds, allowing energy and momentum-resolved measurements and adding crucial pieces to the puzzle of high temperature superconductivity.
CuO_2 planes are the common feature of all layered cuprates where high-T_c superconductivity emerges: these planes consist of Cu^{2+} ions alternated to O^{2-} ions and they are separated each other by "blocking layers". Each CuO_2 plane is originally insulating, due to the large electron correlation typical of transition-element oxides. The Cu^{2+} ions ($3d^9$ configuration) have one unpaired spin-1/2 per site and they are coupled via superexchange interaction J, i.e. the exchange mediated by oxygen, so to produce a bidimensional antiferromagnetic (AF) lattice. The hybridization with the oxygen ions is so strong that the superexchange is exceptionally high in cuprates ($J > 100$ meV), allowing the study of the associated magnetic excitations without the need of a few meV resolution. When the insulating parent compounds are doped, the additional degrees of freedom from dopant charges further complicate the electronic situation. A critical doping is required to destroy the long range orders and superconductivity emerges when charges coming from the blocking layers dope the CuO_2 sheets in a number that alters the situation and triggers the transition.
Despite more than 25 years of studies, the origin of the superconducting state in cuprates is still unclear and remains the subject of intense scrutiny. One of the central unanswered questions concerns the nature of the spin fluctuations that may be responsible for the pairing. Because of technical limitations, the experimental investigation of doped cuprates has been until now restricted on low-energy excitations in a small range of momentum space.
In this thesis we used high resolution RIXS to show that a large family of high-Tc superconductors (HTS), i.e. $(Y,Nd)Ba_2Cu_3O_{6+x}$ (*R*BCO), exhibits high-energy damped spin excitations (paramagnons) over a wide range of doping, with dispersions and spectral weights closely similar to those of magnons in undoped cuprates.
The comprehensive description coming out from our experiments enables quantitative tests of magnetic Cooper pairing models and supports the paramagnons as strong candidates to cover the role of glue for the Cooper's pairs. Subsequently we have exploited the capability of RIXS to work very well on thin films, in order to study both insulating and superconducting cuprate-based heterostructures. Recently the technical progress in epitaxial growth has lead to the discovery of exceptional magnetic and transport properties in artificial heterostructures of 3*d* transition metal oxides in general. Electronic, lattice and orbital reconstruction occurring at the interfaces can in fact influence the charge transfer between the oxides, while the modified dimensionality can affect the magnetic properties of the oxides. Among these heterostructures cuprate-based superlattices (SLs) are particularly interesting since they can be considered as new, artificial HTS, offering the opportunity of freely choosing the two building blocks i.e., the superconducting CuO_2 planes and the charge reservoir blocking layers. We have carried out Cu L_3 RIXS measurements on both insulating and superconducting $(CaCuO_2)_m/(SrTiO_3)_n$ SLs and compared the results with those on a 14 nm thick $CaCuO_2$ film, in order to understand what happens to magnons when the CuO_2 planes are at the interfaces of a SL and if a (para)magnon-mediated superconductivity could still be possible. In all insulating samples spin excitations are in the form of dispersing magnons and in the SLs magnons have similar spectral intensity but reduced dynamics with respect to pure $CaCuO_2$. This is the demonstration that the AF order is preserved in the insulating SLs, down to very small cuprate layer thickness and despite the chemical and structural alterations at the interfaces. On the other hand the superconducting SLs exhibit dispersing paramagnons, similarly to the case of doped *R*BCO. Moreover the orbital excitations, visible in RIXS spectra together with magnons and due to the ligand field felt by Cu^{2+} ions, have revealed a pyramidal coordination of copper atoms at the $CaCuO_2/SrTiO_3$ interfaces. These findings open the way to the production of new, artificial HTS based on cuprate/noncuprate SLs where the charge reservoir layer is constituted by the interface itself.
Any successful theory for HTS should require a detailed understanding not only of the spin but also of the charge correlations in the normal state from which superconductivity emerges. Therefore we have studied charge fluctuations in the CuO_2 planes by means of RXS. Despite intense efforts, to the present date only two clear ordering phenomena have been reported for correlations in the copper oxide sheets of cuprates: the above cited uniform AF in undoped cuprates and a uniaxially modulated AF, combined with charge order, in the so-called "214" family [with chemical composition $La_{2-x-y}(Sr,Ba)_x(Nd,Eu)_yCuO_4$]. The latter is known as "stripe order", with a commensurate charge modulation with a period 4 lattice units, which greatly reduces the superconducting transition temperature of 214 materials at a doping level $p \approx 1/8$ per planar Cu atom. Incommensurate spin and charge fluctuations in 214 materials with $p \neq 1/8$ have been interpreted as evidence of fluctuating stripes. These findings have generated a long-standing debate around the questions of whether stripe order is a generic feature of the copper oxides and if stripe fluctuations are essential for superconductivity. We have used RXS to assess this issue and identify two-dimensional charge fluctuations with an incommensurate periodicity of 3.2 lattice units in the CuO_2 planes of the superconductors *R*BCO, with hole concentrations p of 0.09 to 0.13 per planar Cu ion. The intensity and correlation length of the signal increase strongly upon cooling towards T_c, while further cooling below T_c abruptly reverses the divergence of the charge correlations. In combination with earlier observations, these data indicate an incipient charge density wave (CDW) instability that competes with superconductivity and, for the first time, we have the evidence that the anomalously low T_c found in underdoped cuprates is due to CDW, and not other phenomena.

ULTRAFAST LASER-INDUCED DYNAMICS IN FERROMAGNETS: TOWARDS THE CONTROL OF THE SPIN ORDER FROM THE FEMTOSECOND TO THE SUB-NANOSECOND TIME SCALE

Christian Piovera - Supervisor: **Claudia Dallera, Ettore Carpene**

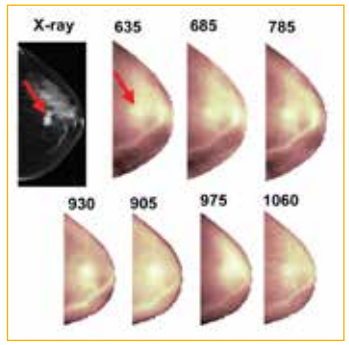
Time dependent mechanisms in magnetism cover a wide range of phenomena. The corresponding time scales embrace an extremely large window that can range from tens of years of logical bit lifetimes in data storage devices to the sub–picosecond rate of electronic interactions. From the technological point of view, the demand for increasing writing speed in memory devices boost the research towards the investigation of the fastest regime. However such a short timescale is connected to very fundamental processes at the microscopic and atomic level where our comprehension is still cloudy. The main limiting factor is the difficulty to experimentally access the correspondent temporal window. The study of the so–called ultrafast spin dynamics has been possible only recently, thanks to the development of femtosecond laser sources. The availability of ultrashort light pulses allows one to probe the evolution of the system properties via optical spectroscopies and with femtosecond resolution.
The first pioneering work was performed by Beaurapiere and coworkers in 1996. They shined a nickel sample with intense femtosecond pulses and observed a quenching of the spin order occurring in less than a picosecond after the optical excitation. This process has been called ultrafast demagnetization. Nowadays, it is a well–known laser induced effect in common 3d magnetic metals, however its comprehension is still under debate after more than 16 years. The work of Beaurapiere et al. raised interesting opportunities also for technological applications. Femtosecond laser pulses revealed to be capable of manipulating the spin order at rates several order of magnitude faster than modern magnetic computer components. One of the most intriguing possibility is to optically reverse the direction of the magnetization resembling the writing mechanism of memory devices. From the first experimental demonstrations of nanosecond laser–assisted magnetic inversion in 1997, up to now, picosecond switching has been achieved only in few cases, for instance, in specific ferrimagnetic samples or in low temperature ferromagnetic semiconductors.
In the present work we study laser induced spin dynamics in metallic ferromagnets.
We exploit the pump–probe technique to detect the transient modification of the magneto-optical Kerr effect (MOKE) within an extent time window from few femtoseconds to hundreds of picoseconds.
Three are the main purpose of the investigation: (i) disclosing the mechanisms underlying the ultrafast demagnetization process, (ii) developing a reliable experimental method to achieve the optical spin switching in the picosecond regime and (iii) studying optical contributions to transient MOKE signals.
First of all, focusing our attention on the femtosecond regime, we characterize the ultrafast dynamics of the magnetic order for different laser intensities and ambient temperatures in metallic systems. In particular the investigated samples are 8 nm thin iron films expitaxially grown on MgO in our laboratory. The observed temperature dependence of the ultrafast demagnetization and the slower remagnetization allows us to ascribe the former effect to the electron–magnon interaction while the latter to the Elliot–Yafet type electron-phonon scattering. On the other hand, ultrafast spin transport phenomena have been investigated during my six months visit at the Spectroscopy of Solids and Interfaces (SSI) group of Professor Dr. T. Rasing at the Radboud University in Nijmegen (Netherlands). According to recent theories the demagnetization may take place as a consequence of majority spin draining from the irradiated area. Therefore, we have studied the effect of laser excitation in tunneling magnetoresistance microstructures with the main scope of finding a correlation between spin currents and ultrafast dynamics. A non negligible possible outcome of such studies, combining ultrafast dynamics and electronic devices, could be the generation of electro-optical devices exploiting femtosecond laser induced spin motion.
However, our measurements are still in progress, thus only some preliminary results are shown and interpreted in the framework of the electronic superdiffusion theory.
Secondly, in the picosecond regime, we demonstrate the possibility to change the magnetization direction in thin iron layers using only ultrashort laser pulses. The sample heating due to photon absorption, results in coherent spin waves. With a proper orientation and intensity of the external field, we show that it is possible to control the magnetic precessional motion. In this way we can reproducibly and repeatedly commute the magnetic vector between preferential directions in less than 100 ps. This rate is more than ten times higher than the working speed of modern storage magnetic devices. In addition, ferromagnetic iron is characterized by an in–plane biaxial anisotropy, with the interesting technological follow-up of allowing one to record two bits of information on the same spot.
To conclude, we address the problem of optical artifacts in pump-probe magneto–optical experiments. The measured spin dynamics can contain a transient optical contribution not related to the true magnetic evolution that may lead to a wrong interpretation of the experimental data. This issue is of fundamental importance, since our knowledge about ultrafast phenomena is retrieved only via optical spectroscopies.
In particular concerning the TR-MOKE technique, many experimental works have already demonstrated that the measured magneto–optical Kerr effect may not follow the transient spin behavior in the first hundreds of femtoseconds. However in the picosecond time scale no experimental evidence of optical contribution has been observed up to now. We show that, under particular condition, the Kerr signal might considerably differ from the genuine magnetic dynamics also for a pump and probe delay longer than 50 ps. We have investigated this issue in two benchmark systems, Fe and CrO_2, that allowed us to to disentangle the magnetic information from purely optical one after a wide characterization of the TR-MOKE dynamics. This last work arises from a collaboration with the experimental groups of Prof. Dr. M. Münzenberg at the I. Physikalisches Institut of Georg–August–Universität Göttingen (Germany) and Prof Dr. A. Gupta from the department of chemistry of the University of Alabama (USA).

DIFFUSE OPTICAL IMAGING AND SPECTROSCOPY FOR BREAST CANCER DETECTION AND RISK ASSESSMENT

Giovanna Quarto - Supervisor: **Paola Taroni**

The PhD thesis is devoted to the development and application of diffusive optical spectroscopy and imaging devices for diagnostic purposes in the biomedical field, with particular emphasis to the investigation of the breast tissue.
Breast cancer is one of the most common tumors and one of the leading causes of death in women. Currently X-ray mammography is the gold standard for breast cancer screening and diagnosis, but it is less accurate in patients with dense glandular breasts so its effectiveness may depend on issues such as the age of the woman. Although it has high spatial resolution, a limit of X-ray mammography is due to the use of ionizing radiation, hence the inability to use it often.
Optical mammography is an interesting diagnostic tool which can provide information on breast tissue composition and related physiological parameters as well as tissue structure. A lot of interest in this diagnostic technique is at least in part due to its absolute non-invasiveness. The light is able to cross some centimeters of biological tissue offering a real opportunity to investigate the whole breast volume *in vivo*. Moreover optical mammography has the capability to investigate dense breast typical of young women and it has low instrumentation costs, covering X-ray mammography limits.
A seven-wavelength time-resolved optical mammograph operating between 635-1060 nm was developed at the Physics Department of Politecnico di Milano. Time resolved measurements allow us a quantitative estimate of the absorption and scattering properties. Moreover, multi-wavelengths measurements could provide the concentration of the five main breast tissue constituents (oxy- and deoxy-hemoglobin, water, lipid and collagen) and the values of the physical parameters *a* and *b*, which represent the amplitude and scatter power respectively.
Currently, the optical mammograph is involved in a clinical trial having two aims: the assessment of breast density and the lesion characterization.
Breast density is a recognized independent risk factor for developing breast cancer. It could be very important include the breast density as parameter into risk prediction models because this could be used to address high-risk women to screening programs and at the same time to personalized diagnostic path for the prevention of breast cancer. For the breast density assessment, results on 145 subjects on the direct correlation between mammographic density and tissue composition, in terms of all the main constituents (*i.e.,* water, lipid and collagen) and the optical parameter *b*, as estimated from optical data, combining them in an optical index, are shown.
Moreover we have shown that single point measurements proved by averaging data collected over small areas, which is essentially equivalent to perform a single measurement, can perform comparable results in the assessment of breast density. These results are very promising because, if no breast scanning is required, technical complexity, costs and measurement times could be significantly reduced.
The second aim of the clinical trial is important because the evaluation of lesion composition could lead to reduce the biopsy examination, which at present is the only one able to establish the histological nature of the lesions. The high examination costs and the invasive nature of biopsy, lead to develop other non-invasive techniques able to establish the composition of the tumor in order to discriminate between malignant and benign lesions. Optical mammography seems to be promising in the characterization of lesions in terms of constituents.
For this second goal, a new perturbation model based on the calculation of the internal pathlength spent by photons inside the lesion volume, was developed and tested on some malignant lesions. For the first time, in this work, we performed an analysis to get the constituent concentration of the lesion in terms of all the main components of the breast tissue: blood, lipids, water and collagen. Up to now, only blood parameters were estimated. Preliminary results of the absorption variation between lesion and healthy tissue, on 18 patients, are presented. Regarding the tumor composition, some common features are observed, in most of the cases: an increase in the oxy- and deoxy-hemoglobin and in the water and collagen content, which are the main constituents involved in the onset and progression of the breast cancer. This is reasonable since tumor is an area characterized by an increased vascularization and stromal tissue. An example of the absorption variation ($\Delta\mu_a$) maps between the lesion and healthy tissue of a patient with a malignant tumor in the left breast is reported in Fig. 1.

A clear white area in correspondence of the lesion, indicated by the red arrow, is evident showing a more fibrous tissue than the surrounding one. Moreover, since a lot of tissue spectroscopy devices are developing which require well-calibrated tissue phantoms for routine system comparison, evaluation and quality control; standardized phantoms to establish their accuracy and repeatability are needed. Organic phantoms, able to mimic biological tissue composition, are necessary to understand the capability of spectroscopy systems to estimate their composition. For this thesis work, new recipes based on the use of the main breast tissue constituents, water and lipids, to make phantoms mimicking the composition of the breast, are proposed and characterized in terms of optical properties for what concerns durability, homogeneity and repeatability. Moreover, it is also important in the optical field the development of devices able to work in a wide spectral range and at the same time having imaging capabilities in order to exploit their best advantage of being applied for different applications. Part of the thesis work was also devoted to the development of a new spectral imaging device to get spatial and spectral maps of the absorption and scattering spectra of different samples. The system was tested on home-made realistic tissue-simulating inhomogeneous organic phantoms mimicking the breast tissue with suspicious lesion.
The realization of organic phantoms and the development of a spectral imaging device to get spatial and spectral maps of biological samples pave the way to understand the capability of spectroscopy systems in the characterization of tissue in terms of composition.
Good and promising results were obtained for both the assessment of the breast density and lesion characterization, even if additional work is needed for the lesion discrimination.

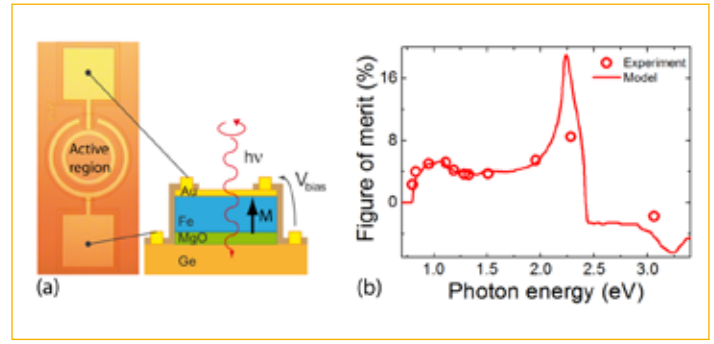


1. $\Delta\mu_a$ maps at the 7 wavelengths and X-ray image of the left cranio-caudal view of a patient with an invasive ductal carcinoma of 25 mm

GE-BASED PHOTODIODES FOR SPIN-OPTOELECTRONICS

Christian Rinaldi - Supervisor: **Riccardo Bertacco**

Spin injection and transport in semiconductors is under intense investigation by physicists around the world, motivated by the fascinating physics and the considerable potential for applications in novel devices.
In the past ten years, the focus has been on two technologically important materials: GaAs for the possibility to optically excite a spin polarized population (optical spin orientation), and more recently Si for its long spin lifetimes.
In this thesis we propose a new approach based on germanium. Ge is compatible with Si-based technology, it has higher room temperature hole mobility than GaAs or Si and a longer spin lifetime than GaAs. Noteworthy, the spin-orbit coupling enables a better control of the spin degree of freedom than in case of Si. Moreover, since optical spin orientation in Ge has been predicted to be as efficient as in GaAs, Ge is nowadays considered a promising material for optoelectronics applications. Exploiting SiGe heterostructure technology, sizable increases of the degree of spin polarization and spin diffusion lengths can be envisaged.
This thesis is in the context of spin-optoelectronics, a novel branch of spintronics aiming to exploit the coupling between photon and spin angular momentum in a new generation of magnetically controlled optoelectronic devices able to generate, manipulate and detect circularly polarized light. Spin-optoelectronics is based on the fact that the helicity of light can be maintained over macroscopic distances so that it can be used to transmit the spin information, overwhelming the electrical transport, which suffer from high spin relaxation rates and short spin diffusion lengths. Multiple-state logic and novel communication protocols can be implemented based on the capability of manipulating and detecting the different polarization states of light pulses (linear, circularly left and right) in integrated platforms without the use of external optical elements and with reconfigurable functionality depending on magnetization direction of the electrodes embedded in the emitters and detectors of the polarized light. Major future applications of such a novel approach comprise the areas of quantum computing and data-transmission cryptography based on the coherent interaction between qubits via photon-polarization effects.
In particular, we report on the growth, fabrication, characterization and modelling of spin-photodiodes (spin-PDs) based on fully epitaxial Fe/MgO/Ge(001) heterostructures. These devices convert the degree of circular polarization of light in a spin polarization (phenomenon called optical spin orientation) in the semiconductor, and thus in a modulation of the electrical current through the well-known Fe/MgO spin analyzer. Spin-PDs are thus detectors of the light helicity that can operate on a broad spectrum of wavelengths.
The growth of Fe/MgO/Ge(001) heterostructures has been performed by molecular beam epitaxy. Electron spectroscopies, diffraction and transmission electron microscopy allowed to verify the sharpness of interfaces, as well as to obtain the alignment of electronic bands.
The study of transport in the heterostructures has been carried out on tunnelling junctions fabricated by optical lithography. The measurement of current-voltage characteristic as a function of temperature allowed us to demonstrate that the tunnelling across the MgO barrier is the main transport mechanism.
Again by optical lithography, Fe/MgO/Ge photodiodes have been realized for spin orientation and spin detection measurements [Fig. 1(a)]. Spin-PDs are illuminated from the top with right and left circularly polarized laser light, while an external magnetic field keep the magnetization of the Fe film parallel or antiparallel to the wave vector of the incident light [Fig. 1(a)]. The voltage bias applied to the device permits to choose between the detection of holes or electrons. We studied the figure of merit of the device, defined as the percentage change of the photocurrent for complete reversal of the light helicity, depends on: (i) the Magnetic Circular Dichroism of Fe; (ii) the degree of spin polarization obtained by optical spin orientation; (iii) the spin diffusion length (i.e. the spin lifetime) of electrons and holes; (iv) the efficiency of the spin analyzer and (iv) the average resistance of the tunnelling barrier.
With Ge-based spin-PDs we provided the first demonstration of spin optical injection and detection in Ge at room temperature, both for electrons and holes. Noteworthy the figure of merit of our devices is significantly larger than that of previously investigated GaAs-based systems, and our spin-photodiodes can operate over a wide spectral range, from visible to infrared.
The analysis of the figure of merit as a function of the photon energy [Fig. 1(b)] and of the MgO thickness allowed us to gain a deeper insight into the physics of spin orientation and spin transport in Ge. To this scope we developed a diffusive model, adding the spin optical pumping term to the Fert-Jaffrès model for spin injection-detection at ferromagnet-semiconductor interfaces. By using this model to interpret our experimental data we were able to (i) confirm the predicted spectral dependence of the optical spin orientation in Ge; (ii) clarify the role of the MgO barrier resistivity on spin accumulation and filtering; (iii) determine the spin lifetime of both electrons and holes in Ge. Finally, from the *technological point of view*, the work presented in this thesis demonstrates that Ge-based spin-PDs can be used as integrated detectors of the photon helicity on a wide spectral range, spanning from the infrared (1550 nm) to the visible (530 nm). We obtained a device able to show up to ~10% of photocurrent variation upon complete reversal of light helicity at room temperature [Fig. 1(b)], without the need of external optical components. Spin-PDs are very reliable devices and able to detect optical powers down to 200 μW. The devices are scalable and can be fabricated in form of arrays. Ge-based spin-PDs pave the way to spin-optoelectronic applications.



1. (a) Sketch of a spin-photodiode. (b) Observed (dots) and model-fitted (solid line) figure of merit of spin-photodiodes for negative applied voltages

ON THE FABRICATION AND CHARACTERIZATION OF HIGH-PERFOMANCE GRAPHENE ELECTRONIC DEVICES

Laura Giorgia Rizzi - Supervisor: **Roman Sordan**

The activity here presented has been devoted to the fabrication and characterization of graphene-based electronic devices. Graphene is the name given to a single plane of carbon atoms arranged in an hexagonal lattice. Although graphene structure is theoretically known from more than 60 years, its experimental isolation has been reported only in 2004. Since its *discovery*, a variety of outstanding physical properties has been attributed to this crystal, stemming from its 2D character and the peculiar symmetry of its lattice. Graphene has a very high room temperature carriers mobility, which can range from 15,000 $cm^2/V{\cdot}s$ to 200,000 $cm^2/V{\cdot}s$ depending on the sample quality; moreover, a thermal conductivity up to 5000 $Wm^{-1}K^{-1}$, a breaking strength of 42 N/m with a Young Modulus of 1 TPa have been reported, conferring it the title of "wonder material". The thesis has been focused on four selected experimental projects (EPs) where important results have been achieved. The first EP was dedicated to the investigation of the mechanical properties of graphene membranes, which were suspended on a polymer substrate by e-beam lithography. Decoupling the crystal from the substrate allows to eliminate one of the major source of scattering for graphene carriers, thus giving access to its intrinsic properties. High carrier mobility together with lightness and stiffness make graphene an ideal building block of advanced nanoelectromechanical system (NEMs), whose archetype is a nanometric resonator which vibrates in response to an external force. Graphene could allow the fabrication of extremely thin NEMs, with large active area and high stiffness, which operate as gigahertz resonator exploitable as ultrasensitive sensors of mass, force and electrical charge. So far, most of the proposed suspended graphene devices were realized from mechanical exfoliated graphene flakes. Due to the low yield of this method, two were the main strategies towards the achievement of the suspended architecture: prepatterning the substrate with large matrix of holes before graphene deposition or introducing a wet etching step after graphene deposition. The first method does not provide a repeatable procedure to obtain suspended membranes. Moreover, since the substrate is covered by holes, the so-realized graphene device could not be integrate with other devices on the same substrate. The second method, relying on an isotropic etching, does not guarantee a proper control over the shape of the removed area, and it also requires a delicate critical-point-drying procedure to prevent graphene collapse, due to the development of strong surface tensions. The fabrication method here presented describes a simple procedure to fabricate multiple free-standing membranes from the same graphene flake. The method does not require critical-point-drying and provide full control over the shape and position of the suspended areas. The technique consists of suspending mono and bilayer graphene crystals deposited on a polymer substrate (polymethylmethacrylate, PMMA), whereas the suspended area are defined by e-beam lithography. The width of the suspended area ranges from 300 nm and 1.2 μm. Thirteen so-fabricated structures were tested with the nanoindentation technique through an AFM tip, resulting in a pre-tension value of T = 12 nN and an average Young modulus E = 0.43 TPa. This pre-tension is at least one order of magnitude smaller than values usually reported in literature for mechanically exfoliated graphene deposited onto SiO_2. The partial relaxation of the crystal has been attributed to the thermal treatment undergone by the second layer of PMMA together with the negative thermal expansion coefficient of grapheme. The low pre-tension allows to access the intrinsic properties of the crystal, because deposition-induced stress could alter graphene properties. The measured elastic modulus is in agreement with values previously reported in literature. In conclusion, the low pre-tension together with the high stiffness of these suspended graphene membranes support their use as ultrasensitive NEMs with repeatable performances. The second EP was devoted to the possibility of achieving voltage amplification through a graphene-based circuit, while operating at room temperature. Voltage amplification is an essential feature of every electronic devices, both analog and digital ones. From a circuital point of view, voltage amplification is represented by the voltage gain $A_V = dV_{OUT} / dV_{IN}$. In order to amplify signals, voltage gain must be above unity, i.e. $|A_V| > 1$ (0 dB). Due to the high mobility of charge carriers, graphene has been widely explored as conductive channel of field effects transistors (FETs) to realize several analog and digital electronic devices, behaving as a simple voltage-controlled resistor. However, voltage amplification at room temperature has been rarely reported. The main reason is imputable to the absence of an energetic band gap in graphene, which severely limits the extent of current modulation through gate voltage. In order to overcome this limit, two main strategies were implemented: the first one concerns the realization of the gate electrode, while the second one concerns the alignment of source/drain contacts with respect to the gate one. After graphene mechanical exfoliation and deposition onto standard SiO_2/Si substrate, top-gate electrodes are defined by e-beam lithography and realized by direct evaporation of aluminum; when the sample is exposed to air, a 4 nm layer of aluminum oxide will form on the whole surface of the Al electrode, thus realizing the gate oxide. In a second step, source and drain contacts (Ti/Au) are fabricated in the same way, but they are aligned in order to slightly overlap with the top-gate contact. In this way, complete channel coverage is realized, minimizing access resistances and maximizing the drain current modulation. The amplifier comprises two FETs integrated in a complementary configuration, such that $V_{OUT} = V_{DD}/(1+R_2/R_1)$, R_2 and R_1 being the variable graphene channel resistances. The best performance obtained was $|A_V| = 3.7$ (11.4 dB) for a supply voltage of 2.5 V. The gain is preserved in the whole audible range (< 20 kHz), which suggests the use of this kind of devices for high fidelity amplification of audio signals. Due to the success of this project, the following EP has been dedicated to the extension of the amplifier technology to a wafer scale, using CVD graphene instead of mechanically exfoliated one. Stemming from the high-quality of the graphene films used, it was possible to obtain even higher voltage gain ($|A_V| = 5$, supply $V_{DD} = 2.5$ V). This allowed to match input and output signals of a single amplifier stage, and also to cascade two different amplifiers fabricated on the same substrate, demonstrating that complex logic functions could be realized with a graphene-based circuit. The fourth EP was focused on the possibility to achieve a non-volatile memory effect through graphene, exploting the control of the transfer curve hysteresis with back-gate voltage. This mechanism is related to the presence of a thin SiN layer embedded in the substrate, which should act as a charge trap site. Mechanically exfoliated graphene has been patterned into *nanoribbons* (GNRs, width = 10-20 nm) to increase the transfer curve On/Off ratio, adopting a CdSe nanowire etching mask to protect graphene from reactive ion etching treatment. GNRs were exploited as conductive channels in a FET configuration. Although it was possible to detect a memory effect by triggering the FETs using a bipolar pulse-wave signal, this was volatile. For this reason, further investigations will be required to improve the efficiency of the mechanism for controlling the transfer curve hysteresis.

ULTRAFAST DYNAMICS IN MOLECULAR AGGREGATES AND INTERFACES

Ajay Ram Srimath Kandada - Supervisor: **Guglielmo Lanzani**

Light-matter interaction in carbon based molecular systems can be considered the primary reason for the birth and sustenance of life. It is also one of the driving forces of modern society through many ingenious applications. Yet, it remains one of the most intriguing and investigated subjects of material science, with the results having a deep impact on the development of cutting-edge electronic devices. Two inventions can be said to have fuelled the 'organic' revolution in opto-electronics: a) Discovery of electroluminescence in poly-p-phenylene vinylene (PPV) and its exploitation in the construction of Organic LED, b) Discovery of photovoltaic effect in organic bilayers and later the innovation of the famous bulk-heterojunction and dye sensitized solar cells. OLEDs have already moved from the laboratories to the markets mainly in the form of displays. Organic and hybrid photovoltaics are also advancing at a tremendous pace with the device efficiencies shooting above 10%. However, these technological advances and decades of extensive research in the field have not yielded a comprehensive picture of the photo-physical scenario.

The present thesis comprises of studies on the influence of the morphology, the intermolecular interactions and the composition on the branching ratio between neutral and charged photoexcitations in organic photo-voltaic systems. The experimental work combines the standard ultrafast spectroscopic techniques with novel tools developed for the specific purpose of elucidating the models of charge photo-generation.

This thesis can be divided into two parts:
i) Exciton dynamics in polycrystalline molecular films.
ii) Ultrafast dynamics at organic and hybrid photovoltaic interfaces.

The important results of the thesis are summarized below.

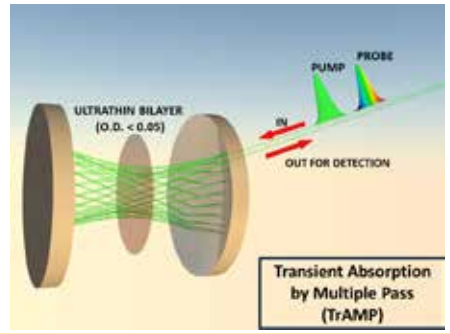
Exciton dissociation in Pentacene films:

Singlet fission is an interesting quantum mechanical phenomenon occurring in molecular crystals such as pentacene, wherein a single photo-excitation results in a pair of triplet states. By applying an external electric field, we are able to initiate and monitor the dissociation of the triplet states on ultrafast timescales. With singlet fission being viewed ~~upon~~ as a potential route to achieve internal quantum efficiencies above 100% in PV devices, our experiments provide new and crucial insights into the charge generation mechanism in such systems. In particular, our experiments show that the singlet fission process is in competition with the ultrafast generation of charges due to singlet exciton dissociation at the defects. The fraction of triplets that form by fission process can be further dissociated by an external electric field of 0.2MV/cm with an efficiency of about 10%.

Ultrafast dynamics at Organic Donor-Acceptor Interface

The quintessential component of an organic PV device is the interface between the donor and the acceptor molecular phases. The interface in a prototypical bulk heterojunction of P3HT (polymer, Poly 3-hexyl thiophene) and PCBM (fullerene derivative) is blurred due to molecular interdispersion of the PCBM molecules into the polymer phase. The photo-excitation dynamics at such an intermixed interface region are usually buried in huge bulk dynamics and hence not perceivable by any of the available techniques. Here, such interface dynamics are revealed by performing measurements on custom made ultrathin bilayers of P3HT and PCBM that can act as stand-alone interfaces. To perform the challenging transient absorption measurements on such samples which have extremely low optical density (in the order of 10^{-2}), we developed a new technique based on multiple pass (TrAMP), illustrated in Figure 1.

In this way, we discovered an efficient ultrafast energy transfer process from the polymer to the PCBM happening within 500 fs, followed by a much slower hole transfer back to the polymer leading to charge generation. This picture for the organic interface is quite different from the accepted view of ultra-fast electron transfer from the polymer to the PCBM and might provide a new direction for the development of efficient devices.



1. Illustration of the TrAMP system used to perform transient absorption measurements on ultrathin bilayers of organic donor/acceptor molecules to reveal the interface dynamics

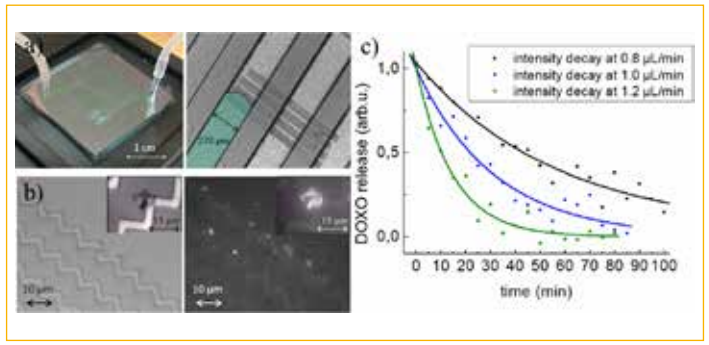
Ultrafast dynamics at Hybrid Photovoltaic Interfaces

Hybrid PV systems have been developed with the aim to combine the higher absorption cross-sections of organics with superior mobility of inorganics. We studied the ultrafast injection dynamics in two kinds of samples, with two different kinds of interactions between the organic and the inorganic parts.
a) *TiO_2 mesoporous films sensitized with black dye, a low band-gap Ru dye used in DSSCs.* In this case, the organic molecule is chemically attached to the oxide layer. By performing a pump dependence of the transient absorption, we identified ultrafast efficient injection from hot singlet excited states of the dye molecule to the acceptor states in the oxide. Usually, in this class of hybrid interfaces, charge injection is mediated from the triplet states and happens in hundreds of picoseconds. In our case however, due to the particular nature of the interaction between the black dye and the oxide, when pumped at higher energies, still within the visible region, we observe ultrafast charge injection without any triplet mediation.
b) *Interface between polymer(P3HT) and metal-oxides.* In this case, the interaction between the polymer and the oxide is physisorptive in nature with weak Van der Waal's coupling. By careful analysis of ultrathin bilayers of polymer and oxide, we found a strong correlation between the polymer morphology (P3HT) and the device performance. In addition, by extending the pump-probe technique in the UV spectral region we are able to monitor the electron injection into ZnO from the polymer, with the results showing an injection time of about 2 ps.

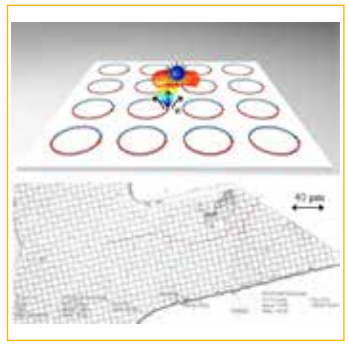
NOVEL FUNCTIONALITIES IN MAGNETIC DOMAIN WALL DEVICES ON-CHIP FOR BIOLOGY AND NANOMEDICINE

Andrea Torti - Supervisor: **Riccardo Bertacco**

My Ph.D. activity have dealt with the study, design and implementation of novel functionalities in domain wall (DW) based magnetic devices for application in the field of biology and nanomedicine. The devices allows for the manipulation of magnetic particles at the micro- and nano-scale through the coupling with externally controlled magnetic DWs.
This recent manipulation method has attracted a growing interest in biology and medicine, as functionalized magnetic particles are commonly used as molecular and cellular carriers or markers. However, until now, the features and the applications are still limited to linear transport of biomolecules or cells in non–microfluidic environments.
The aim of this research activity is twofold: on the one hand adding new features to DW magnetic micro- and nanostructures and, on the other their implementation in lab-on-a-chip systems to test medical nano-platforms for the controlled release of anti-tumor drugs.
Magnetic domain walls in confined magnetic structures form the fundamental core of the devices presented here. At the sub-micrometer scale the DW spin configuration starts to be dominated by the geometry rather than by the intrinsic properties of the material. In this framework the DWs behaves as quasi-particles, being sources of magnetic field that can be precisely manipulated by external magnetic fields. The design of the device is thus fundamental for the realization of additional features with respect to the traditional molecular or cellular conveyors. It has been recently demonstrated how micro- and nanofabricated, planar stripes made by Permalloy ($Ni_{80}Fe_{20}$) constitute excellent conduits where the DWs can be nucleated and moved between adjacent geometrical constriction, like corners or curves, under the action of external magnetic fields.
Methods for evaluating both computationally and experimentally the magnetic force on a superparamagnetic bead generated by DWs confined in Permalloy nano- and micro-corners are initially presented. Attractive forces in the tens of pN range are obtained for a 1 μm bead, with a spatial extension of few microns in the case of micro-corners which makes them suitable for displaying cells or trapping polymeric aggregates.
Using these structures microfluidic devices have been successfully implemented, mimicking the conditions of human capillaries, with switchable DWs based trapping sites, in order to study the controlled release of Doxorubicin (DOXO) from magnetic thermo-responsive nanocarriers. As a major result of this Ph.D. activity we studied the dynamics of the thermo-actuated release of Doxorubicin drug under different flow rate conditions and as a function of the thermo-responsive polymer shell of the nanocarrier. Fig. 1 shows the device with magnetic traps inside the microfluidic channel (panel a), nanocarriers-aggregates loaded with DOXO trapped at the corners imaged both in bright field and in fluorescence (panel b). The fluorescence decay due to the DOXO release for different flow rate is plotted in Fig. 1 (panel c).
In the second part of the experimental activity two novel functionalities in DW based nanostructures have been demonstrated. Bifurcated conduits, which combine zigzag shaped structures and curvilinear sections, have been designed and fabricated allowing for the creation of innovative single magnetic particles de-multiplexer. The single particle sorting of magnetic beads of different size (1 μm and 2.8 μm) on the same structure was obtained. Furthermore, by adding another DW injector pad to a zigzag shaped conveyor it was possible to trap couples of single particles and bring them in contact in a reproducible way.
A compatible microfluidic device allowing for the magnetically controlled meeting of two magnetic particles is currently under test.
All the above described magnetic conduits allow the motion only along a predefined path. Once the magnetic bead is trapped, it can be manipulated only along the direction imposed by the patterned structure.
A major achievement of this research is represented by the demonstration of a "free" 2-dimensional manipulation on-chip based on DWs.
Two-dimensional matrices of Permalloy rings allow the external user to trap and move magnetic particles without any predetermined paths, thanks to appropriate 3D magnetic fields sequences. Preliminary experiments have shown the successful handling of 1 μm magnetic beads along linear or pseudorandom paths.
Furthermore by transferring the magnetic rings pattern on the top of a PDMS microfluidic bifurcated channel, 1 μm magnetic beads have been trapped in the middle of the bifurcation and magnetically sorted to one of the two branches in static fluid condition (Fig. 2)
The coupling of a magnetic particle with a single domain wall in Permalloy micro- and nanostructures has proven to be a tunable and efficient way to study and manipulate biological entities at the nano-scale in microfluidic environments. This technological platform holds the potential for improving existing lab-on-a-chip applications and methodologies, paving the way to microfluidic tools for single molecule biophysics applications and drug delivery studies. Moreover the degree of complexity is much lower than other techniques for the single particle manipulation on-chip and they can be easily integrated in miniaturized systems.



1. a) Optical image of the microfluidic device. b) nanocarriers aggregates trapped by the magnetic array. The fluorescence is due to DOXO loaded within. c) Plot of the DOXO release as a function of time, monitored by the fluorescent signal decay



2. Top) sketch of the magnetic configuration of the ring array. DW generates an attractive potential well for the functionalized bead above. Bottom) Still picture of the bead motion on the ring array embedded in the PDMS bifurcated channel. The path is enlighted in red

DEVELOPMENT AND APPLICATIONS OF A MEDICAL DEVICE BASED ON TIME DOMAIN FUNCTIONAL NEAR INFRARED SPECTROSCOPY FOR BRAIN IMAGING

Lucia Maria Grazia Zucchelli - Supervisor: **Alessandro Torricelli**

Nowadays both research and diagnosis in the neuroscience field are performed with the aid of different technologies. First of all, Computed Tomography (CT) and Magnetic Resonance Imaging (MRI) significantly improve the *in vivo* anatomical imaging of the brain. Moreover, the increasing interest in the study of the brain activity has been reinforced by several functional methodologies arising in the last years. Besides invasive techniques such as Positron Emission Tomography (PET), it is possible to perform non-invasive measurements whether directly measuring the neuronal electrical activity by means of Electroencephalography (EEG) or Magnetoencephalography (MEG), or by localizing the hemodynamic response caused by a neuronal activation using the functional Magnetic Resonance Imaging (fMRI), becoming in the last years the golden standard for functional imaging studies.
Functional near Infrared Spectroscopy (fNIRS) is an emerging optical technique for the non-invasive assessment of the tissue oxygenation.
It is based on the fact that in the near-infrared spectral range the biological media are relatively transparent to the light, making feasible a non-invasive and *in vivo* investigation of relatively deep tissues (up to some centimeters). The absorption in this wavelength range mainly depends on the concentration of the two species of hemoglobin (oxygenated and deoxygenated). The bond between this blood component with the oxygen modifies the conformation of the molecule and consequently its absorption spectrum; hence an absorption measurement performed at two wavelengths allows to retrieve the information relative to the concentration of the two cromophores, to register their temporal evolution and thus to detect a localized hemodynamic response.
Because of the diffusive nature of the biological tissues, the photons travelling within highly diffusive media, such as biological tissues, experience many scattering events: the phenomenon, called Photon Migration, has to be conveniently modeled and handled in the spectroscopy measurements. The diffusion features allow working in reflectance geometry: light can be injected on the scalp, and photons, after having traveled for a while in the medium, can be detected some centimeters apart from the source point.
The fNIRS in Time Domain is based on the injection in the tissues of light pulses with a temporal width of some tens of picoseconds; with this approach it is possible to obtain a straightforward relationship between the photon detection time and its path within the medium, and thus to discriminate between absorption and scattering coefficient. It is possible to improve the depth sensitivity and distinguish the cerebral activity from superficial hemodynamic variations.

My PhD activity has been largely focused on the development an optimization of a multichannel medical device based on Time Resolved fNIRS. The system was further characterized by the well assessed MedhPhot protocol in order to evaluate its capability to measure the optical properties of calibrated homogeneous phantoms. Moreover two novel protocols have been developed: a first one for the assessment of basic performances of optical instrument (Basic Instrumental Performance protocol); a second one for the estimate of performances of optical brain imagers in the detection and quantification of absorption variations (nEUROPt protocol). Both protocols have been executed on our fNIRS device: These novel assays highlight the goodness of the presented work of instrument development and its comparability with other brain imagers based on optical spectroscopy. Work is now in progress to improve the instrumentation with the last generation of electronics and optics on the market, for the optimization of the performances in terms of signal quality, signal to noise ratio and stability.
Several *in vivo* measurements have been performed with the developed instrumentation, to validate its performances in a clinical environment. Different works have been accomplished, including neurofatigue experiments or cognitive experiments such as Go-noGo test, disgust perception and visual-spatial memory. The main campaigns I worked on have been focused to the assessment of the performances of our fNIRS device in a multimodality approach. The instrumentation was involved in two clinical campaigns: in the first one a control group of healthy volunteers and a group of patients with a motor disorder disease underwent to a motor task experiment; fNIRS data have been collected in coregistration with EEG, and all the subjects underwent an fMRI session and a TMS registration. The latter experiment involved a control group of healthy volunteers and a group of photosensitive subjects, undergone to three experiments of visual stimulation at different frequencies; fNIRS data have been collected in coregistration with EEG.
General linear model (GLM) was applied on fNIRS data at the single subject level and to the whole group, and statistical significance of the outcomes have been inferred and mapped over a three-dimensional reconstruction of the brain cortex.
The clinical employment of the medical instrument in the *in vivo* studies showed the good performances of the fNIRS technique, that can be easily applied and co-applied with other functional techniques. All topographic results (e.g. TMS center of gravity, maximum of fNIRS deflection and maximum of Event-Related Desynchronization in EEG) were related to and within the area of fMRI activation, assumed as gold standard, in agreement with literature. New clinical studies will be useful in order to increase the statistic significance of the collected data set.
Moreover work is in progress to develop and optimize data fusion strategies (e.g. fNIRS/fMRI GLM with EEG as regressors), and data comparison between the time courses of fMRI signals, time domain fNIRS and ERD-EEG.
Finally in my dissertation I present a different method for the assessment of the mean partial pathlength followed by photons in a multilayered medium. It takes into account the effect of system set-up (as described by the instrument response function) and the heterogeneous structure of the human head, for a more precise distinction between superficial and deeper contribution of absorption variations. The better accuracy in computing the optical pathlength would improve the NIRS data analysis, especially for the deeper layer. The model was validated with numerical simulations and then it was preliminary tested on *in vivo* fNIRS data, showing promising results.
In conclusion a medical device based on time resolved fNIRS was developed, characterized and successfully employed in several *in vivo* studies, demonstrating its potentialities and usefulness.