Chair:
Prof. Franco Ciccacci

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, optical disks, optical communications), 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).

The PhD course is characterized by a strong experimental character. Its main purpose is the development of an experimental approach in problem solving techniques and the attainment of a high level of professional qualification. Scientific education and training to develop general research abilities in all areas of applied physics is increasingly needed by advanced technological industries. The PhD program aims at providing engineers and physicists, after a Bachelor of Science ("Laurea", 3 years) and a Master of Science ("Laurea Magistrale", 2 years), with a general education in the basic areas of applied physics and a specific knowledge in condensed matter physics, optics and lasers.

The contents of the doctoral program 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 biomedical applications of lasers, laser applications in optical communications; diagnostics for works of art; time-resolved optical spectroscopy; ultrashort light pulse generation and applications; UV and X optical harmonics generation.

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.

As for the educational program, it can be divided into four parts: 1) Laboratory of Basic Physics, implying that the students join full time different experimental laboratories, guided by their tutor as well as 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 (which constitutes the most relevant part of the program) has a marked experimental character and will be carried out in one or more laboratories at the Department of Physics. Based on the scientific collaborations of the Department, the students are encouraged to perform part of their thesis work also in laboratories of other national or foreign Institutions.
Numerous collaborations, which the PhD students may be involved in, are presently active with several national and international Institutions, such as: ETH-Zürich, EPL-Lausanne, Lund Institute of Technology, University of Paris-sud, Ecole Polytechnique-Paris, University of Barcelona, University of Berkeley, Technical University of Wien, University of Bordeaux, MIT-Cambridge, 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 mean number of fellowship-grants for students entering the PhD program is around eight per year, while the mean number of available positions is sixteen per year. At present the overall number of students in the three-year course is thirty.
The fellowship-grants presently active are funded by the following public and private Institutions:
Italian Ministry for University and Research (MIUR)
National Institute for the Physics of Matter - National Council for Research (INFM-CNR)
Istituto Italiano di Tecnologia IIT (IIT@polimi)
Scuola Interpolitecnica di Dottorato (SIP)

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		
Giulio Cerullo	Lamberto Duò	Roberta Ramponi
Franco Ciccacci	Giacomo Ghiringhelli	Paola Taroni
Rinaldo Cubeddu	Paolo Laporta	
Sandro De Silvestri	Ezio Puppin	

The Doctoral Program relies also upon a Steering Committee, formed by distinguished experts (see table below) coming from R&D industries or Research Labs, taking care that the goals of the PhD program conform with the needs of non academic world.

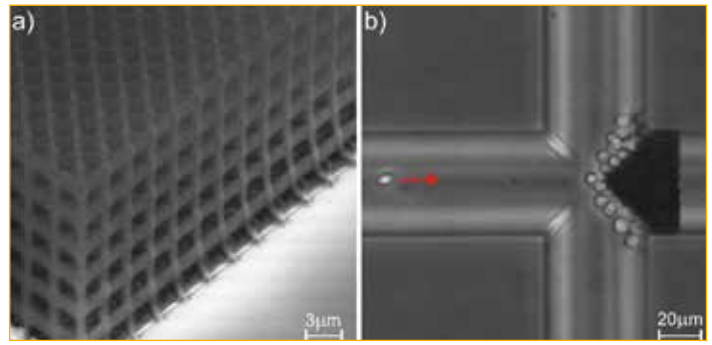
ADVISORY BOARD	
Roberto Bez (NUMONYX)	Hans von Känel (EpiSpeed AG (Zürich)
Gianfranco Canti (Dept. Pharmacology – Univ. Milano)	Marco Grioni (EPFL - Lausanne)
Bruno Ferrario (SAES Getters)	

INTEGRATED OPTOFLUIDIC DEVICES FOR BIOPHOTONIC APPLICATIONS FABRICATED BY FEMTOSECOND LASER PULSES

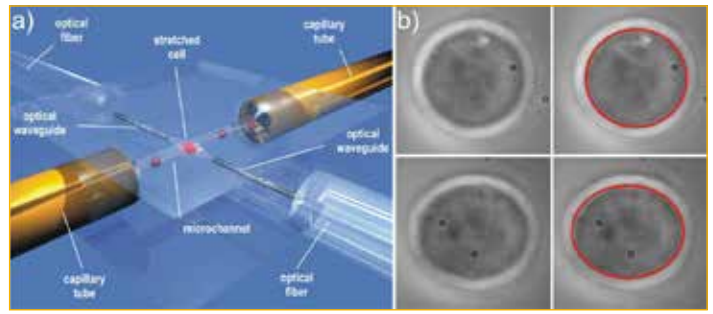
Nicola Bellini

Lab-on-a-chip (LOC) systems have been created to miniaturize several functions of a standard biochemical laboratory on a single small chip. These devices include complex structures to transport, mix, separate and make react biological samples. The sample analysis is typically accomplished through optical systems: measurements of absorption, scattering, fluorescence, elasticity, mobility and imaging provide a high amount of experimental data related to the sample features. If the integration of fluidic components in the micro-scale has already yielded good results in terms of compactness, optical detection systems are still composed of bulky external devices that strongly limits the great LOC integration potential.
Femtosecond laser micromachining is a powerful technique that allows the direct fabrication of optical devices, fluidic components and three-dimensional (3D) scaffolds.
Laser pulses, with a duration of the order of tens/hundreds of femtoseconds, are focused inside a transparent substrate and, through the activation of non-linear processes that occur only in the focal region, a permanent modification is induced in the volume. This technology permits to fabricate directly buried structures with any 3D shape, simply by controlling the translation of the substrate with respect to the beam focus. By tuning the irradiation conditions, different kinds of modification are possible: (i) optical waveguides are written by inducing a positive refractive index change; (ii) microfluidic channels are created in fused silica with the addition of a subsequent chemical etching step; (iii) two-photon polymerization can be activated in photosensitive resins by femtosecond laser pulses to produce 3D structures with resolution beyond the diffraction limit.
During my Ph.D. activity, I have exploited the potential of femtosecond laser micromachining to design, fabricate and validate integrated optofluidic devices for biophotonics.
We have proposed advancements in the fabrication processes to improve the flexibility of the technique. In particular, femtosecond laser writing was employed for the fabrication of advanced photonic devices in a single laser sweep by using a computer programmable spatial light modulator; we demonstrated the fabrication of directional couplers with variable coupling ratio.
Afterwards, we introduced an innovative method to control the shape of microchannels fabricated with femtosecond laser irradiation followed by chemical etching. By irradiating complex geometry paths it was possible to compensate for the intrinsic conical shape and to obtain uniform cylindrical channels. We fabricated also more complex structures, such as interconnecting channels, microchannel adapters and o-grooves for fiber-to-chip or capillary-to-chip fast connections.
Regarding two-photon polymerization, a 3D porous filter was fabricated inside an already sealed channel of a commercial LOC. The filter consisted in a 3D mash of intersecting lines in a cubic structure and the extreme spatial resolution of two-photon polymerization allowed a pore size of about 1 μm. The filter was tested with a suspension of 3-μm polystyrene spheres in a fluorescent solution: we showed separation of nanoscale (dye molecules) from microscale elements (polystyrene beads) and 100% of the beads were stopped by the filter. Preliminary validation of the filter for plasma extraction from whole blood was performed, demonstrating the filter effectiveness for softer particles such as red blood cells (Fig.1).

The potential of femtosecond laser microfabrication was exploited to achieve complete optofluidic systems for specific applications. Optical fluorescence sensing was integrated in a commercial chip for separation



1. a) SEM image of the 3D porous filter fabricated by two-photon polymerization in a commercial lab-on-a-chip; b) validation of the filter with whole blood sample.



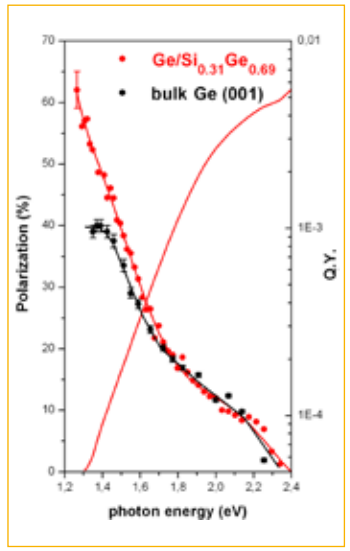
2. a) 3D rendering of the integrated optical stretcher for single cell analysis; b) stretching experiment on a leukemic cell (HL60) with automatic contour recover.

of DNA molecules through capillary electrophoresis.
Straightforward integration of optical waveguides enabled the detection of fluorescently labelled DNA samples containing different molecule sizes. Moreover, introducing a novel dual-point dual-wavelength setting, we demonstrated detection of single nucleotide insertion/deletion, as it is relevant for recognition of genetic anomalies.
We demonstrated a monolithic chip in glass for optical trapping and stretching of single cells for the analysis of the cytoskeleton viscoelastic properties: cell deformability is a reliable marker of the cell health status. We produced the integrated optical stretcher by first fabricating a square cross section channel chip and then by integrating optical waveguides in a commercial microfluidic chip. The optical stretcher was validated using red blood cells; then the chip was successfully tested on leukemic cells, confirming the potential to be applied for diagnosis in pre-clinical biological samples (Fig.2).
Femtosecond lasers were also exploited to fabricate adaptive optofluidic microlenses. Cylindrical microchannels, fabricated in fused silica, were filled with liquids at suitable refractive index forming focusing lenses for generation of planes of light. A monolithic illumination stage for selective fluorescence excitation was designed and realized, aiming to in-vivo 3D imaging of biological samples via optical sectioning.

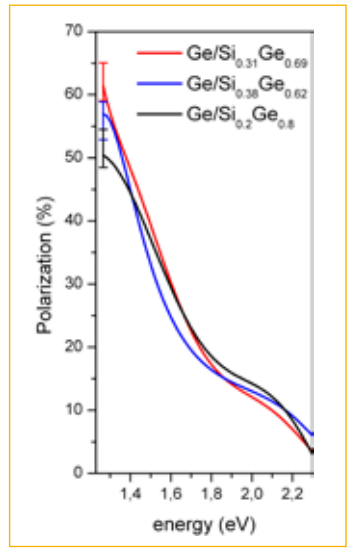
ELECTRON SPIN PROPERTIES IN GE-BASED HETEROSTRUCTURES

Federico Bottegoni

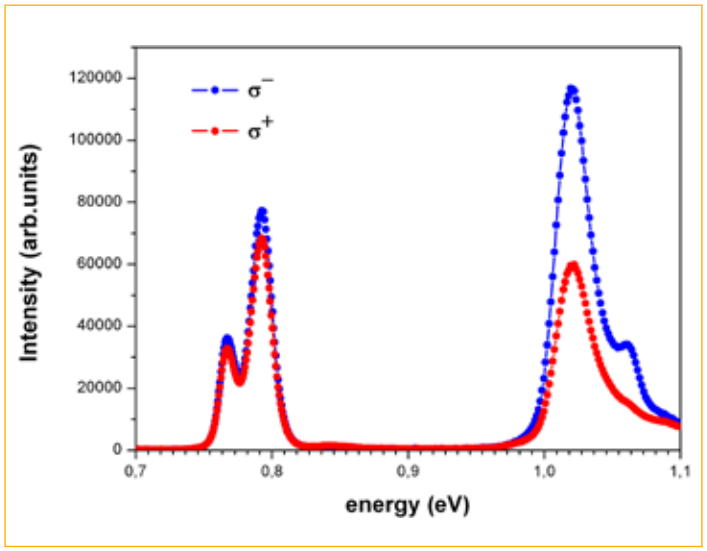
During my PhD activity, I have essentially built up and commissioned a compact experimental apparatus for the characterization of photocathode materials by means of quantum yield and electron spin polarization measurements, under the direct supervision of my PhD tutor Prof. Franco Ciccacci. The first step involved the planning of the experimental apparatus, included the mechanical design of vacuum components and measurement electronics suitable for my purpose. After all the elements of the measurement chain was separately checked up in order to ensure the attainment of their nominal work parameters. By the aforementioned experimental set-up, the electron spin properties of Ge-based semiconductor heterostructures have been studied. The in-plane compressive strain and confinement effects, which act on pure Ge grown on $Si_{1-x}Ge_x$ alloy, drastically modify the band structure so that a very high electron spin polarization can be found in the conduction band of Ge layer, when electrons are excited with circularly-polarized light. This allows the direct detection of optically spin-oriented electron population in the conduction band, which results higher than the bulk one, as shown in Fig.1, where the electron spin polarization spectra at low temperature (T = 120 K) of bulk p-doped Ge and pure Ge grown on $Si_{0.31}Ge_{0.69}$ alloy are compared. Furthermore it also possible to obtain an experimental determination of the orbital mixing between Light Hole (LH) and Split Off (SO) bands, away from the centre of the Brillouin zone, by symmetry analysis based on such spectra. By varying the stoichiometry of the $Si_{1-x}Ge_x$ alloy, the degree of compressive strain in the pure Ge layer can be modified so that it can be correlated to the maximum electron spin polarization in the conduction band of pure Ge thin film, as shown in Fig. 2: as result, it is reasonable to argue that the higher the compressive strain in the structure, the higher is the maximum electron spin polarization. Complementary information about Ge-based heterostructures can be obtained through Spin-Polarized Photo-Luminescence (SPPL). This technique detects the electron spin polarization, exploiting the recombination of the electrons with holes in the valence band, taking into account all the spin relaxation mechanisms, which involve polarized electrons and also polarized holes. Indeed the knowledge of these phenomena is essential in order to engine IV group-based spintronics devices. Spin Polarized Photo-Luminescence relies on the fact that the light, emitted during the recombination between excited electrons in conduction band and holes in the valence band, has a circular polarization degree, which is proportional to the spin polarization of the carriers inside the solid. This basically means that it is possible to deduce the spin-polarization of the carriers through the analysis of the circular polarization of the Luminescence light, emitted by the sample. Indeed Fig. 2 shows the Spin Polarized Photoluminescence spectra of ($Ge/Si_{0.15}Ge_{0.85}$) Multiple Quantum Wells.
Another aspect of my PhD research is related to theoretical studies on particle/spin transport and dynamics. I have developed all my theoretical work at Laboratoire des Solides Irradiés at Ecole Polytechnique, in the research group of Prof. Henri-Jean Drouhin. The common transport operator cannot be properly used, when dealing with Hamiltonian where Spin-Orbit Interaction terms are involved so that a novel definition of probability-current and spin-current operators is given, which satisfies the continuity equation for a general effective Hamiltonian up to the n^{th} order. A reformulation of the boundary conditions at the semiconductor heterostructure interfaces allows the correct determination of the envelope function for tunneling problems and these new findings are applied to the paradigmatic case of an interface, composed of a free-electron-like material and [110]-oriented GaAs barrier.



1. Polarization and Quantum Yield vs. exciting photon energy at T = 120 K for the $Ge/Si_{0.31}Ge_{0.69}$ sample (red dots and line), compared to the P of the thick Ge (001) sample (black dots). The compressive strain induces a net maximum P= 62% which is well above the one for the bulk structure. Dots represent the experimental points, the red line is obtained through polynomial fitting.



2. Electron spin polarization spectra of a collection of pure Ge epilayers grown on $Si_{1-x}Ge_x$ alloys with different stoichiometry. The maximum electron spin polarization can be correlated to the degree of compressive strain in the Ge layer.



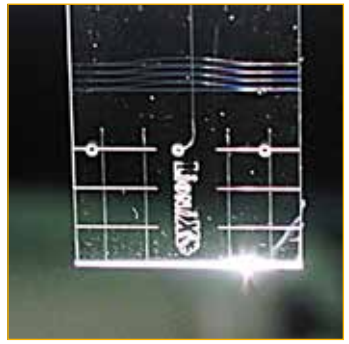
3. Spin Polarized Photo-Luminescence (SPPL) spectra of Ge/SiGe MQWs, measured at T = 15 K and under 1.165 eV excitation energy having a right-hand circular polarization (s^-). Direct and indirect gap features of the spectrum are resolved for left-hand, s^-(blue), and right-hand s^+ (red) circular polarization.

INTEGRATED OPTICAL CIRCUITS FOR BIOSENSING AND QUANTUM INFORMATION BY FEMTOSECOND LASER MICROFABRICATION

Andrea Crespi

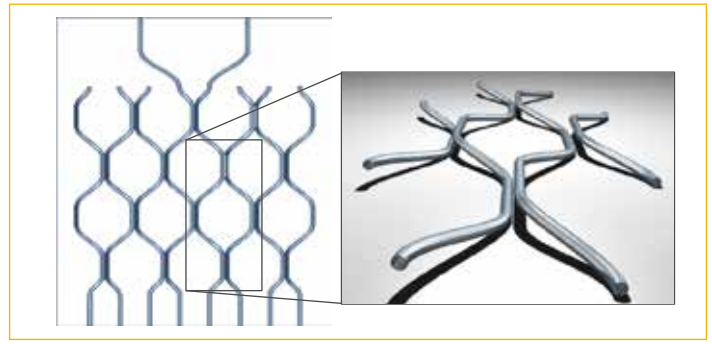
Femtosecond laser microfabrication has emerged in the last decade as a powerful technique for direct inscription of low loss optical waveguides in practically any transparent dielectric substrate, showing outstanding versatility. Prototyping of new devices is made rapid, cheap and easy: optical circuits are written in the substrate, in fully three-dimensional fashion, using the laser beam as an optical pen, without the need of the costly masks of conventional photolithography.
Many proof-of-principle demonstrations of the main integrated optics devices used in telecommunications have been successfully reported, including splitters, directional couplers, Mach-Zehnder interferometers and Bragg gratings. Furthermore, waveguides written in active materials have allowed to realize integrated amplifiers and laser sources. Anyway, the road towards applications has just been opened, and the unique capabilities of femtosecond laser micromachining will enable achievements inconceivable with other technologies.
In this thesis work, femtosecond laser writing is exploited to demonstrate complex photonic devices, which provide unprecedented functionalities in two applicative contexts: label-free sensing of biomolecules in microfluidic lab-on-chips, and integrated quantum computing and simulation.

For the label-free biosensing applications, integrated Mach-Zehnder interferometers has been demonstrated, interfaced with buried microchannels in order to measure the refractive index of the microchannel content by both classical and quantum interferometry.
In particular, a three-dimensional Mach-Zehnder interferometer has been directly inscribed in a commercial microfluidic chip for capillary electrophoresis (see Figure 1). The interferometer presents the sensing arm directly crossing a microchannel, while the reference arm passes above it. The sensitivity of the device has been benchmarked by measurements with glucose and peptide solutions, displaying a remarkable sensitivity down to 10^{-4} RIU. These results show not only the possibility of femtosecond laser writing to add new photonic capabilities to existing fluidic lab-on-chips, but also its ability to integrate specific sensing functions, hardly achievable with other technologies. In fact, the particular three-dimensional geometry of the device, impossible to realize by conventional lithographic techniques, conjugates the elevated refractive index sensitivity with high spatial resolution on the microchannel. Both characteristics are of crucial importance in applications such as detection in microchip capillary electrophoresis and multipoint real-time monitoring of chemical reactions inside a lab-on-chip.



1. Picture of the commercial microfluidic chip with four Mach-Zehnder interferometers inscribed by femtosecond laser micromachining.

A similar integrated structure has been also realized, combining a Mach-Zehnder interferometer with an etched microchannel, which has allowed to perform for the first time quantum interferometry measurements on biological samples. The refractive index of albumin solutions is retrieved using non-classical two-photon states of light, which give interference fringes with half the period of the classical ones. The main issues regarding this kind of measurements, which promise to beat classical sensitivity limits, has been investigated and a clear path towards real world applications of quantum interferometry has been indicated. In fact, optofluidics enables to combine the stability of integrated optical circuits with the superior capabilities of microfluidics in handling small volumes of analytes.
For the second kind of applications addressed in this thesis, namely quantum computing and simulation, devices with both polarization sensitive and insensitive behavior are required. In particular, a polarization insensitive directional coupler has been first realized, which enables integrated filtering of polarization entangled photon states. On the other hand, the development of polarization dependent directional couplers has allowed to realize a two-qubit integrated quantum logic gate, operating with qubits encoded in the photon polarization.
A network of directional couplers providing an enhanced polarization insensitivity, thanks to a peculiar three-dimensional geometry, has been also designed (Figure 2). This has enabled the simulation of the quantum walk on a line of two bosons or fermions, by injecting in the photonic structure entangled two-photon states with different symmetry.



2. Schematic of the network of directional couplers, employed to simulate the quantum walk of two correlated bosons or fermions. In the blow-up, detail of the three-dimensional design of the couplers.

The manipulation of entangled states is essential to implement many quantum information protocols for computation and communication. In addition, on-chip realization of the quantum walk model paves the way to the simulation of complexity physics and biophysics phenomena, such as Anderson localization and charge transport in light-harvesting complexes. The present results are significant from the point of view of the fabrication technique, since it is the first time that components such as partially polarizing directional couplers are realized by femtosecond pulses. More in general, this work proposes a quite innovative approach to polarization handling circuits, based on a kind of "universal" waveguide, with low and uniform birefringence. The polarization behavior of the devices is tailored, from a perfect polarization insensitivity to a fully polarization dependent operation, just by varying the device geometry, by exploiting the unique three-dimensional capabilities of the femtosecond laser writing technology.

Finally, the possibility of using femtosecond laser written waveguides to simulate quantum systems has been further explored, harnessing quantum-optical analogies. Here, the propagation of coherent laser light in properly designed photonic structures formally reproduces complex quantum dynamics. In particular, engineered arrays of waveguides has been realized, which allow to simulate the regime of "deep strong coupling" of the Jaynes-Cummings hamiltonian. This regime is extremely interesting due to the occurrence of highly non-classical and counterintuitive phenomena, and is still inaccessible in quantum cavity electrodynamics experiments.

ULTRAFAST DYNAMICS AT ORGANIC INTERFACES FOR PHOTOVOLTAICS

Giulia Grancini

The research work presented in this thesis is collocated in the current scientific effort of exploring the fundamental photophysical processes at the interface in organic-based systems for photovoltaics (PV), both in the context of bulk heterojunction and hybrid technologies. The tremendous advancement in the performance of polymer-based solar cells, now approaching a power conversion efficiency of 10% for both all organic and hybrid organic-inorganic systems, has motivated a deep research on elucidating the key feature governing the charge generation process, that directly influences the device efficiency.The peculiarity of polymer-based solar cells is that they mainly rely on self-organization of different active components, whose synergy delivers the final device functionalities. Therefore, the interfaces between the multi-components systems play the most relevant role, since they directly govern the functionality of the active film. For these reason, the main goal of this work is focused on understanding the ultrafast photophysical processes at the interface of different organic blends. To this regard, we have exploited the combination of ultrafast optical spectroscopy tools, that provides a wealth of information on the photophysics of excited state dynamics in molecules, with confocal microscopy, that allows for local imaging of the photophysical behaviour on a sub-micron scale. The derived information enable us to establish a link between the observed dynamical optical properties and the environment in which they occur, providing an important feedback to material scientists who strive to control the morphology and the supra-molecular organization of organic thin films in order to optimize the device performance. In this framework, we first highlighted peculiar inter-chain physics in a phase separated blend of Poly(9,9-dioctylfluorene)(PFO) with a polymethylmethacrylate (PMMA) inert matrix, used in photonic applications. We found that, depending on the chain conformation (i.e. isolated or aggregated polymer chains) the nature of the initial photo-excited states in PFO can be dramatically different. In particular, we highlighted an interface region at the border of phase-segregated islands, where the efficient mixing of the PFO with the PMMA results in the isolation of PFO chains. By imaging the interfacial local dynamics these isolated chains can support a stimulated emission band. This has important implications for photonics and optoelectronics, where conjugated polymer chain isolation and intimate polymer intermixing are crucial for gain properties in organic devices. We focus then on the interfacial processes in donor/acceptor systems for organic based PV. In these systems the "interface" photophysics governs the charge transfer mechanism: upon photoexcitation the exciton diffuse to reach the heterojunction where they can form an inter-molecular charge transfer states, precursor of free charge carriers. We investigated the role of the intermediate charge transfer state at D/A interface and its fate versus full ionization respect to geminate recombination, that ultimately dictates the device performances. In particular, we studied a light-absorbing electron-donor polymer (poly(3-hexylthiophene) (P3HT):[6,6]-phenyl-C61-butyric acid methyl ester (PCBM), acting as the electron acceptor, blend. We demonstrated that the local morphology directly influences the kinetics of charge separation and recombination. In particular, we highlighted peculiar interfacial dynamics at the border region between crystalline P3HT: PCBM microscopic phases, associated to the formation of a long lived intermediate charge transfer state, not affected by geminate recombination.On the other side, we have also investigated hybrid system based on inorganic nanoparticle blended with organic materials that represent interesting systems to create low-cost solar cells with performance and stability to enable wide-scale clean power generation. In this framework we have investigated the carrier dynamics in a new type of hyperbranched Cadmium Selenide (CdSe) crystal embedded in a regioregular poly(3-hexylthiophene) (P3HT) matrix. We demonstrate that efficient photo-induced charge transfer occurs at the hetero-interface, providing a clear picture on the charge generation mechanism. In both the study cases, thanks to the combination of ultrafast spectroscopy with fs time resolution and sub-micron spatial resolution, we shed light into the local photophysics of the interfacial charge separation process.The interface physics in organic blends is also monitored on an ultrafast time scale, aiming to understand the primary events upon excitation. We investigated the charge dissociation mechanism in an advanced copolymer for photovoltaics: the (poly[2,6-(4,4-bis-(2-ethylhexyl)-4Hcyclopenta[2,1-b;3,4-b']-dithiophene)-alt-4,7-(2,1,3-benzothiadiazole)] (PCPDTBT)), combined with PCBM. In particular, we monitored the charge generation process when an excess energy is released to the system upon impulsive photoexcitation to higher lying excited states. In this case, charge generation competes with energy dissipation through internal conversion to low-lying excited state. We demonstrated that in PCPDTBT:PCBM blend high energy excitation leads to enhanced charge dissociation via hot interfacial charge transfer state. The mechanism occurs in less than 30 fs, leading to weakly bound CT pairs that separate then on the hundred femtosecond timescale. In this blend, charge generation could thus benefit from dissociation of thermally excited charge transfer state, thus significantly enhancing the device efficiency. Finally, the work has been devoted to the direct realization and optimization of hybrid polymer/metal oxides devices. The hybrid solar cells are based on semiconducting polymers, acting as hole transporter and light antennas, infiltrated into mesostructured metal oxide electrodes (generally TiO_2). They offer great versatility in the task of interfacial engineering and device optimization, combining high electron mobility, low-cost and physical and chemical stability of the metal oxide nanoparticles, with the good light absorbing and hole transporting properties of semiconducting polymers. However, important issues related to inefficient electron transfer at the polymer/TiO_2 interface limits the power conversion efficiencies below 0.5%. With this knowledge, we implemented a new paradigm for a hybrid architecture by controlling the structure-function of the building blocks and by optimizing their chemical-physical interaction. We engineer the metal oxide surface with a self-assembled monolayer (SAM) of an organic electron acceptor, in order to activate the interfacial charge separation process. The proposed design takes advantage of the energy levels match between the electron acceptor SAM and the electron donor polymer (PCPDTBT, in our case), favouring efficient electron transfer. Indeed, we observed an enhancement of the device performances, which results in an increase of an order of magnitude in the photocurrent generation and power conversion efficiency. Moreover, aiming to extend the absorption spectral coverage, we upgraded the device architecture, exploiting a "co-functionalization" of the metal oxide interface with a mixed electron-acceptor and organic dye SAM layers. The new design leads to achieve "panchromatic" photo-response from the visible to the near IR region of the spectrum, thus further improving the device efficiency to more than 1.4%.

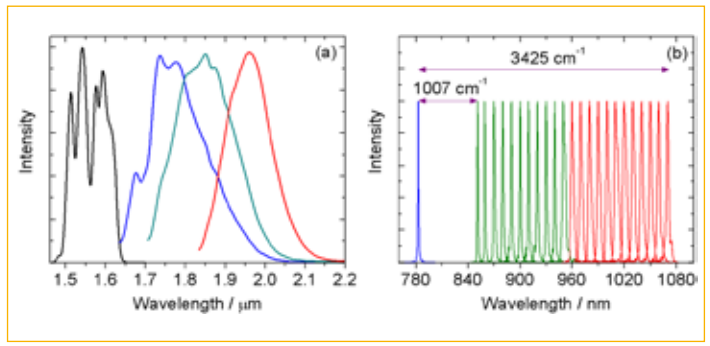
COHERENT RAMAN SPECTROSCOPY FROM A SINGLE FEMTOSECOND OSCILLATOR

Vikas Kumar

The thesis reports the development of three new approaches to Coherent Raman Spectroscopy (CRS), namely Coherent anti-Stokes Raman Scattering (CARS), Stimulated Raman Scattering (SRS) and Raman Induced Kerr-Effect (RIKE) spectroscopy, with overall much simplified laser excitation setups. CRS is a very powerful approach for label-free vibrational imaging of biological species and chemical compounds with high spatial resolution and acquisition speed.

Coherent Raman spectroscopy/microscopy in fact requires two synchronized trains of pulses with narrow bandwidth (a few cm^{-1}, corresponding to a few picoseconds pulse duration) and independent tunability over a wide spectral range (800-3300 cm^{-1}) in order to cover whole chemically important spectral region, which is typically achieved either by a pair of electronically locked picosecond Ti:sapphire oscillators or by an optical parametric oscillator pumped by a Nd:YVO_4 laser. Widespread application of such techniques is currently hampered by the use of such costly, complex and bulky laser excitation setups. This problem initiated a quest for simplified cost-effective solution.

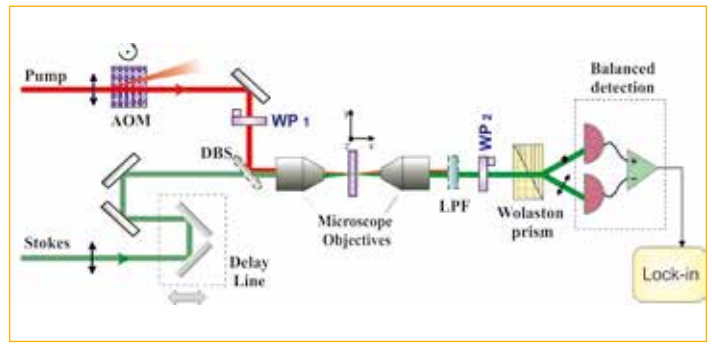
One solution makes part of the research activity reported in the thesis as the development of a versatile CRS setup based on spectral compression of femtosecond pulses emitted by an amplified "multiple"-branch Er-fiber oscillator to synthesize pump and Stokes pulses required for CRS[see Fig:1].



1. (a) Spectrum of the main laser output at 1560 nm (black line) and examples of spectra of the long-wavelength part of the supercontinuum(blue, cyan and red) generated in a highly-nonlinear fiber, tunable by acting on the input pulse chirp. (b) Spectra of the pump (green line) and of the tunable Stokes pulse (red lines), as obtained by spectral compression of the spectra reported in panel (a).

This new system can be easily reconfigured both for CARS (single-frequency or multiplex) and for SRS spectroscopy/microscopy with performances close to the current state of the art but with significant advantages in terms of compactness, higher power scalability and versatility. One of the most critical issue associated with CARS is the presence of a strong non-resonant background (NRB) generated from other simultaneously occurring nonlinear processes. Such background does not carry chemically specific information and, at low concentrations of the targeted molecules, can distort and even overwhelm the resonant signal. Many techniques for NRB suppression have been demonstrated so far: frequency-modulation CARS (FM-CARS) and interferometric CARS (I-CARS), time-resolved CARS (TR-CARS) etc. These NRB suppression techniques require the generation of a third (and phase-coherent in the case of I-CARS) colour pulses synchronized with pump and Stokes. One of the key features of the developed fiber-format CRS setup is the availability of the third branch phase-coherent with the pump-Stokes pair, which makes the setup suitable for straightforward implementation of NRB-suppression techniques for CARS. Experimental results of spectroscopy/microscopy on CARS, SRS and interferometric CARS performed on the setup are reported. The second approach that we pursued is still oriented to the solution of the most critical issue of CARS i.e. the presence of NRB. The approach is based on a time-resolved multiplex CARS spectroscopy setup where the required three synchronized pulses called pump, Stokes and the broadband probe, are all derived from a single femtosecond Yb:KYW laser. The 1-MHz repetition rate of the system allows very intense CARS spectra to be obtained in short acquisition times, while a delayed probe pulse ensures efficient NRB suppression.

The third part of the thesis gives theoretical explanation and experimental details of a novel CRS approach called balanced-detection Raman-induced Kerr effect (BD-RIKE) microscopy, as a new powerful coherent Raman imaging technique. It combines the advantage of CARS i.e. the absence of a linear background with the main advantages of SRS i.e. the linear dependence on the concentration of the targeted molecules and NRB-free response.



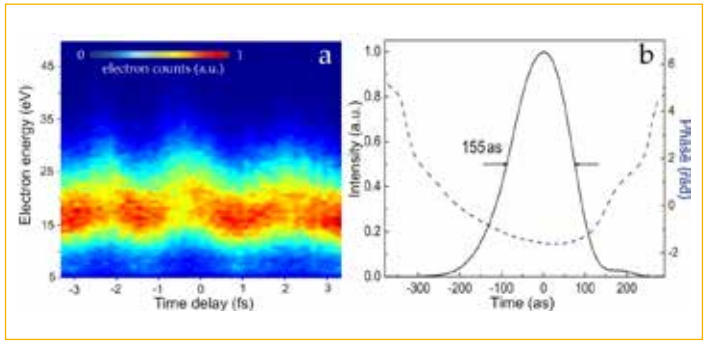
2. Schematic diagram for BD-RIKE. AOM: acousto-optic modulator; DBS: dichroic beam splitter; WP: waveplates; LPF: Long-pass filter rejecting pump photons.

Fig:2 demonstrates the schematic diagram of the setup for performing BD-RIKE microscopy. BD-RIKE microscopy allows mapping of different components of $\chi^{(3)}$ just utilizing four different combinations arise by using waveplate in excitation(WP1) as half-waveplate(linear RIKE) or quarter-waveplate(circular RIKE) and waveplate in detection(WP2) as half-waveplate/quarter waveplate followed by balanced detection of the two perpendicularly polarized outputs of a Wollaston prism.

MOLECULAR DYNAMICS IMAGING BY ATTOSECOND PULSES

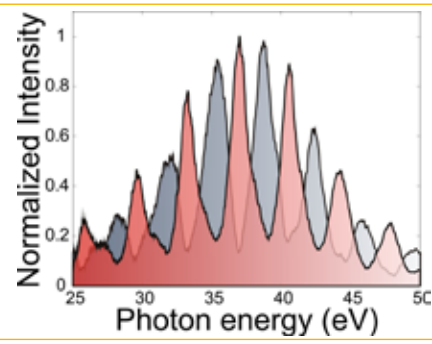
Matteo Lucchini

Between 1987 and 1988, two independent groups demonstrated the possibility to exploit the interaction between a strong infrared (IR) laser pulse and the atoms of a rare gas to obtain extreme ultraviolet (XUV) radiation characterized by a comb of odd harmonics. Only six years later the scientific community started to realize that the high-order harmonic generation (HHG) process could be suitable to obtain bursts of pulses with subfemtosecond time duration. Great effort was made to investigate more in detail the HHG process and the existing relation between the phases of each harmonic until the first experimental demonstration of attosecond (1 as = 10^{-18} s) pulses was performed in 2001. During the same year, for the first time a single attosecond pulse with a time duration of 650 as was successfully isolated from a train of attosecond pulses generated with the HHG process. These results paved the way for the birth of a new branch of ultrafast science: attosecond physics. Nowadays, the scientific community is well aware of the capability of attosecond pulses to probe ultra-fast dynamics. Due to the lack, at the current state of the art, of high-intensity attosecond light sources, attosecond pulses are typically combined with femtosecond IR pulses in order to have enough energy to perform pump-probe experiments but still preserving the attosecond resolution. Outstanding results have been obtained with the femtosecond-attosecond pump-probe experiments which allowed the investigation of ultrafast temporal dynamics like: the Auger decay times and the tunneling time in strong field ionization. Despite the positive results obtained, the attosecond science still has to demonstrate its full capabilities. In order to probe nonlinear effects in the XUV region or to perform attosecond-pump/attosecond-probe experiments, energies higher than few nanojoules (1 nJ = 10^{-9} J) are required. For these reasons a significant part of the research activity performed during my Ph.D. was devoted to the development of a new technique to generate high energy isolated attosecond pulses, based on a temporal gating scheme called ionization gating. Figure 1 displays the temporal characterization of the isolated attosecond pulses obtained with the new technique we proposed.



1. a) Portion of an experimental FROG-CRAB trace as a function of the temporal delay between the attosecond and the IR pulses. b) Reconstruction of the temporal intensity profile and phase of the attosecond pulses.

In order to measure the temporal characteristics of the attosecond pulses, the frequency resolved optical gating for complete reconstruction of attosecond bursts (FROG-CRAB) technique was used. The reconstructed temporal intensity profile of the XUV pulses, reported in Fig. 1b, confirmed the generation of an isolated attosecond pulse, with a duration of 155 as and a small residual chirp. In particular, for such a pulses, we measured an energy on target of 2.1 nJ per pulse, thus showing an increase of one to three orders of magnitude of the energy currently achievable with the other known techniques. Moreover, we demonstrated that the proposed technique can be exploited also to generate tunable XUV radiation. If the intensity of the driving field is slightly decreased, while keeping fixed the generating medium density, generation of high-order harmonics characterized by a complete tunability of their peak position occurs (see Fig. 2). The efficient generation of tunable XUV emission over a broad spectral range is of crucial importance in several applications ranging from femtosecond pump-probe experiment, to the seeding of free-electron lasers.



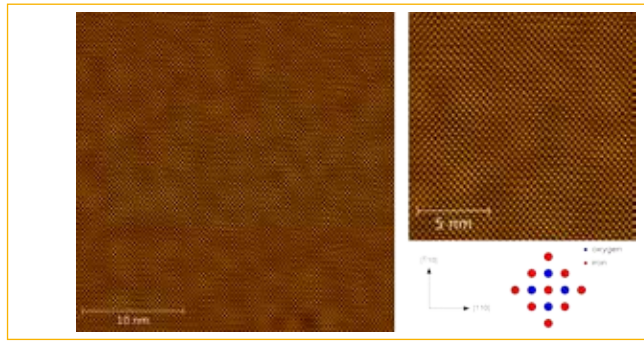
2. Experimental XUV spectra generated in a 2.5-mm-thick argon cell by 5-fs IR pulses with 3.3±0.3 × 10^{15} W/cm^2 peak intensity and two values of carrier-envelope phase separated by π/2.

In order to fully understand the role played by the electronic response in photochemical processes, both information about the time and space evolution of the electron wavepackets are required. This can be achieved by studying the peculiar features of the harmonic generated spectra, or by combining the attosecond radiation with a suitable position sensitive detector such as a reaction microscope or a velocity map imaging spectrometer (VMIs). Among all the available detectors the VMIs proved to be one of the most powerful in terms of versatility and accessible information. For this reason, during my Ph.D. experience I have worked at the FOM institute AMOLF in Amsterdam where we used the VMIs to study photoemission and ultrafast dynamics induced in small molecules (H_2, D_2, O_2, CO_2) by the harmonic radiation. Moreover, in the last part of my research activity I worked at the installation and optimization of the new VMIs in Milano. Such a spectrometer has been used to investigate the ultrafast relaxation dynamics in the nitrogen molecule. In this work we photo-ionized N_2 molecules with attosecond pulse tranis and we probed the ultrafast relaxation dynamics using strong IR pulses. In particular we demonstrated that autoionization in N_2 is energetically allowed even for short internuclear distances ~3.2 Å and that the time scale of the energy conversion of the manifold of high excited states of N_2^+ sharing the same symmetry is of the order of ~25 fs. Ultrafast dynamics in molecules initiated by sudden absorption of XUV or soft-X-rays photons, at the basis of a number of important phenomena in nature, can reveal a high degree of complexity. Generally many-body effects are triggered, where electron correlations play a crucial role. The imaging technique applied in this thesis to N_2 molecules, in combination with few-fs or sub-fs XUV pulses, can be extended to complex molecular systems. Particularly relevant is the time-resolved investigation of the relaxation dynamics of excited states in molecules with biological interest. Indeed, the understanding of the remarkable photostability of deoxyribonucleic acid (DNA) exposed to the ultraviolet photons from the Sun, is a very important research theme. Since high photostability is intimately related to ultrashort lifetimes of the excited states, the experimental technique and the theoretical analysis presented can have a useful application in the investigation of ultrafast relaxation dynamics in biological systems initiated by femtosecond or attosecond XUV pulses.

SCANNING TUNNELING MICROSCOPY AND SPECTROSCOPY STUDY OF THE OXYGEN-INDUCED EFFECTS ON THE FE(001) SURFACE AND 3D METALS/FE(001) INTERFACE

Andrea Picone

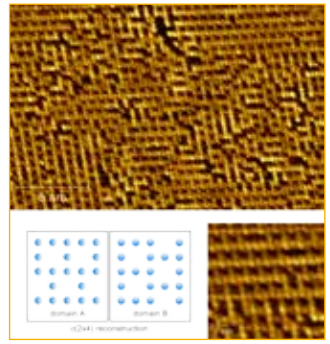
The experimental activity during the Ph.D. in physics, under the supervision of professor Lamberto Duò, has been mainly about the study of transition metal oxide ultrathin films grown on metal supports. In particular have been characterized nanostructured oxides like iron oxide, chromium oxide and cobalt oxide supported on Fe(001) surface, with a thickness ranging from the single atomic layer to few nanometers. Low-dimensional oxide nanostructures supported on well-defined metal surfaces have been the subject of intensive study because of their relevance both in fundamental physics and in technological applications.In technological applications they are employed as support surfaces in the field of heterogeneous catalysis, in the field of digital data storage and spintronics, as dielectrics in gas sensors, to name just a few. At a more fundamental level, there are a number of scientific challenges associated with oxide nanostructure. These include understanding the nature of oxide surface structures, surface electronic properties and the magnetic properties of oxide surfaces.The low co-ordination number, the reduced symmetry, the strain induced by mismatched substrates, the possibility to stabilize metastable states, and the presence of interface or surface states can profoundly alter the electronic and magnetic properties of thin films or surfaces with respect to the bulk, giving the possibility to create new classes of hybrid systems with tunable physical and chemical properties.The experimental techniques used are that typical of the ultra-high vacuum conditions. In particular the samples were characterized by a commercial available Omicron Scanning Tunneling Microscopy. In fig. 1 there is a an atomic resolved image of the oxidized Fe(001), the so called Fe(001)-p(1x1)O, where the surface is covered by a single layer of oxygen atoms.



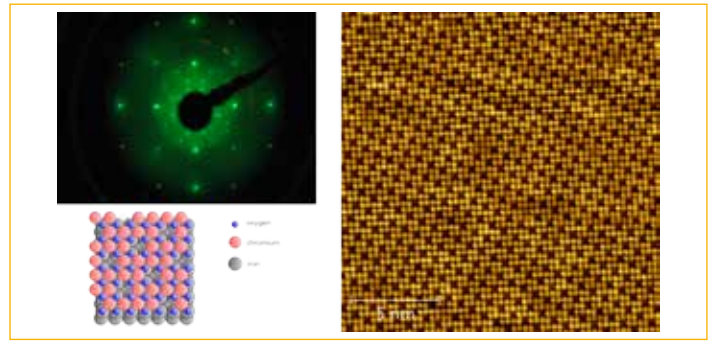
1. Atomic resolution of the Fe(001)-p(1x1)O. The oxygen atoms are located in the fourfold symmetrical hollow sites of the Fe(001) surface.

This surface has been used as a substrate to grow ultrathin chromium oxide films. After the Cr deposition we find that the surface is covered by bright spots embedded on the substrate, that are imaged as atomic corrugation (apparent height 50 pm). The bright spot number increases with the Cr deposition and is consistent with the nominal coverage. An interesting feature is that their disposition is somehow ordered.

In particular, when the nominal coverage is about 0.4 ML, there are clearly visible regions in which the bright spots form a c(4 x2) superstructure. When the Cr coverage is increased to 0.75 ML the c(4x2) structure covers the entire surface (see Fig. 2), as confirmed also by the LEED pattern (not shown) . After further deposition of Cr, a dramatic change takes place and the overlayer symmetry becomes p(5x5)R27°, characterized also by a very sharp LEED. What we observed is that the coverage at which the overlayer structure switches from c(4x2) to (5 x5)



2. The c(4 x2) phase obtained after the evaporation of 0.75 ML of Cr on Fe(001)-p(1x1)O.



3. The (5x5)R°27_ phase: (a) Leed pattern at 107 eV, (b) atomic resolution and (c) atomistic model.

R27 is about 1.2 ML, and that further increase of the Cr thickness does not change the overlayer structure, even tough the LEED pattern becomes weaker, due to the increased surface roughness and the spiral formation.The experimental data suggest the formation of an alloyed phase in the submonolayer range. The bright spots are related to the presence of the Cr atoms, even if we do not have the experimental evidence that what we image as protrusion are the Cr atoms. The XPS spectra taken before and after the Cr evaporation (not shown) are unchanged, thus we can state that we still have an oxygen monolayer present on the top of the surface.

Based on this experimental results, we suggest a model in which the Cr atoms replace 3/4 of the iron atoms present in the topmost layer, giving a formal stoichiometry Cr3FeO4. Notice that when we deposited Cr at 470 K on clean Fe(001) :(i) in the submonolayer range there is a strong Cr interdiffusion into the bulk of the iron and only one out of 4 deposited Cr atoms stays in the surface layer; (ii) the topmost layer is characterized by the formation of a disordered alloy. On the other hand, in the case of Cr deposition on the oxygen passivated surface, what we observed is that: (i) within the experimental error all the deposited atoms remain in the surface layer and (ii) the alloyed phase is well ordered, giving a c(4 x2) superstructure. The interpretation of the (5 x5) R°27 is quite different. In fact, the(5 x5)R°27 phase is present also on the oxygen covered Cr(001) surface, thus we can speculate that in this case the surface is composed only by Cr and oxygen atoms. A model of this surface is shown in Fig. 3. The dark spots are interpreted as Cr vacancies and the stoichiometry in this case is Cr4O5.In conclusion, during the first stage of growth at high temperature (470 K), there is an oxygen mediated Cr/Fe surface alloy, highly ordered and with a c(4 x2) symmetry. Increasing the Cr coverage gives the (5x5) R°27 overlayer. In this case the holes seen in the STM images are interpreted as chromium vacancies, and we can see the system as a Chromium oxide singlelayer accomodated on the top of the Fe(001) surface. During my last year I have spent 6 months in the group of professor Netzer at the Karl Franzens University of Graz. In this period we have studied cobalt oxide nanostructure grown on a vicinal surface of Pd(001), namely the Pd(1 1 19).

DEVELOPMENT AND APPLICATIONS OF A TIME DOMAIN NEAR INFRARED SPECTROSCOPY INSTRUMENT BASED ON WAVELENGTH SPACE MULTIPLEXING

Rebecca Re

Noninvasive monitoring of blood and tissue oxygenation is a research field where functional near-infrared spectroscopy (fNIRS) can be applied. This technique is employed both to experimentally and clinically investigate cerebral oxygenation and hemodynamic response to a wide range of stimuli in the human brain and to study muscle oxidative metabolism in healthy and pathological subjects. fNIRS is an optical technique that allows to non-invasively monitor the hemodynamic changes in human tissues exploiting the information (absorption and scattering) carried by light that has traveled through the tissue itself. The hemodynamic changes are well represented by the variations of blood volume and of the oxygen saturation that can be evaluated knowing the content of the oxy- and deoxy-hemoglobin. With the time-domain (TD-fNIRS) approach is possible to discriminate between absorption and scattering coefficient. The substantial advantage of the TD modality is the possibility to improve the depth sensitivity employing photons' temporal information encoded in the detected signal. Depth sensitivity improvement is a fundamental goal for near infrared spectroscopy because of the anatomical configuration of the tissue under examination, which is typically organized as a layered structure. Typically time-domain instruments use a Time Multiplexing (TM) approach to inject light of two different wavelengths into the tissue. Laser pulses are delayed and injected in the same optical fiber, and both the wavelengths are acquired in the same temporal window. With this modality problems of cross-talk between pulses might hamper the overall performances of the system. To avoid the cross-talk between the wavelengths and to increase the signal-to-noise ratio, we have introduced, for the first time, a new approach to inject and collect light into the tissue: the wavelength Space Multiplexing (SM). The two wavelengths are alternatively injected in the two optical fibers by means of an optical 2X2 switch. In this way, we acquire in each detection line and in each temporal window only one wavelength at a time, exploiting the full temporal and dynamic range of the Time Correlated Single Photon Counting (TCSPC) acquisition boards.The initial version of the instrument had two injection and two detection channels. It was characterized and tested during preliminary *in vivo* measurements. The final version of the instrument has 16X4 channels and is suitable for monitoring the hemodynamic changes in human tissues and to perform brain imaging as well.

In chapter 1 of my dissertation, an overview of the NIRS technique is presented. At first the optical properties of human tissues and how to extrapolate the hemodynamic parameters is shown. Then an explanation of the different NIRS approach, i.e. continuous wave, frequency and time domain is described. In the second part of the chapter, the radiative transport theory is introduced and the diffusion equation presented. Then the solutions of the diffusion equation for the continuous wave and time domain approach are extrapolated for a homogeneous medium. Finally we showed how the model has to be changed if we consider a heterogeneous medium and how we fit our time-domain data in order to obtain the optical parameters.
In chapter 2, the TD instrument based on wavelength SM, I developed during my PhD, is described.

In chapter 3, three different *in vivo* applications, performed with the instrument described in chapter 2 is presented. The applications are:

- TD-fNIRS vs. Laser Doppler Flowmetry (LDF): simultaneous acquisitions to provide an experimental evidence to the ``Time-Gated (TG) '' method we used to analyze data. TG method allows to separate from the whole signal the contribution coming from the deeper and the upper layers of a tissue, spreading the temporal information encoded in our signal. It was developed at our department and these measurements give an experimental evidence of it. From the TD-fNIRS signal is possible to extrapolate both the contributions, from the LDF the one coming from the upper layer, being the Doppler signal related to the surface flowmotion due to the peripheral autoregulation. During a Valsalva maneuver, i.e. a forced exhalation with a closed glottis, specific changes occur, which cause variations in the superficial perfusion. We took measurements on the prefrontal cortex of eight healthy volunteers and we found good correlations between the LDF signal and the TD-fNIRS signal coming from the upper layers, demonstrating the goodness of our semi-empirical method.
- TD-fNIRS vs. Electroencephalography (EEG): simultaneous acquisitions to test the feasibility of co-registration, on brain cortex, of these two techniques during a divided attention task. One of the goals of the modern diagnostics is to combine different techniques. This study aimed at the monitoring of both the hemodynamic and electrical activity on the prefrontal cortex, during a divided attention task. Divided attention is the skill to distribute the limited mental resources to different sources of information at the same time. Sixteen healthy volunteers were undergone to auditory and visual stimuli. Results suggest that there is a hemodynamic activation modulated by the task in the prefrontal cortex and that there is a temporal cascade among activations with different origin: electrical, systemic and hemodynamic.
- TD-fNIRS and Electrical muscle stimulation (EMS): hemodynamic response of muscle and brain during electrical stimulation at different current thresholds. During this study we monitored, on nine healthy volunteers, the muscle behavior during electrical stimulation, in order to understand muscle's hemodynamic changes when the stimulation current is varied through different thresholds. The electrical stimulation affects at first muscle but can also indirectly activate peripheral and association cortices. For this reason we monitored also the hemodynamics activations of the brain. Preliminary results are available on muscle but further investigations are still in progress.

In chapter 4, a report of my activity, during a six months period at the ``Abramson Center for Future of Health" (Houston, TX), is presented. Here I contributed to the development of a continuous wave (CW-NIRS) wireless prototype. With a single absorption CW measurement is not possible to determine simultaneously the absorption and the scattering coefficient's values. In order to obtain them is necessary to exploit the information coming from a third wavelength, for example the one around the water absorption's peak, to extrapolate a value for the scattering coefficient at that wavelength. Employing tabulated data is then possible to extract the entire scattering spectrum and compute the absorption coefficient's values at the oxy- and deoxy-hemoglobin wavelengths. Whit this method is however not possible to discriminate between superficial and depth signal. CW technique offers the possibility to have low cost, compact and wireless instruments but has still low depth sensitivity. To our knowledge, the instrument developed, is the first example of portable and wireless NIRS instrument for the real time monitoring of the hemodynamic parameters. In addition to the NIRS probe, we used a cardiovascular sensing system that includes an electrocardiogram (EKG) and a photoplethysmograph (PPG) sensor. At first, the instrument, in all its parts, is presented. After that, an in vivo application, during muscle incremental exercise, is presented. The final goal of the measurement campaign is to find new physiological indexes and correlations between them, to better identify and quantify the phenomenon of the muscular fatigue. These indexes can be applied in the cardiac rehabilitation, in the muscular training and in the evaluation of muscle performances during spaceflight.