MECHANICAL ENGINEERING / PHYSICS / PRESERVATION OF THE ARCHITECTURAL HERITAGE / STRUCTURAL, SEISMIC AND GEOTECHNICAL ENGINEERING / URBAN PLANNING, DESIGN AND POLICY / AEROSPACE ENGINEERING / ARCHITECTURE, BUILT ENVIRONMENT AND CONSTRUCTION ENGINEERING / ARCHITECTURAL, URBAN AND INTERIOR DESIGN / BIOENGINEERING /DATA ANALYTICS AND DECISION SCIENCES / DESIGN / ELECTRICAL ENGINEERING / ENERGY AND NUCLEAR SCIENCE AND TECHNOLOGY / ENVIRONMENTAL AND INFRASTRUCTURE ENGINEERING / INDUSTRIAL CHEMISTRY AND CHEMICAL ENGINEERING / INFORMATION TECHNOLOGY / MANAGEMENT ENGINEERING / MATERIALS ENGINEERING / MATHEMATICAL MODELS AND METHODS IN ENGINEERING

PhD Yearbook | 2020

Chair:
Prof. Marco Finazzi

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), biomedical optics (optical tomography), vacuum technologies (thin film depositions), material technologies (microelectronics and nanotechnologies, micromechanical processing), and advanced instrumentation (electronic and atomic microscopy, nuclear magnetic resonance).
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:
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.
Photonics 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 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. Consistent effort is devoted to experimental research, development of innovative approaches and techniques, and design of novel instrumentation.

The educational program can be divided into three parts: 1) Courses specifically designed for the PhD program as well transdisciplinary courses; 2) Activities pertaining to more specific disciplines which will lay the foundation for the research work to be carried out during the Doctoral Thesis; 3) 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 Berkeley, University of Cambridge, University College London, Massachusetts Institute of Technology, Harvard University, European Space Agency, ENEA, Elettra-Ts, PSI-Villigen, Agenzia Spaziale Italiana, European Synchrotron Radiation Facility (ESRF-Grenoble), IFN-CNR, IIT–Istituto Italiano di Tecnologia.

At present, the number of students in the three-year course is eighty-eight, and eighty-six of them have a fellowship.

The PhD Program Faculty, who takes care of organizing and supervising teaching and research activities, consists of members (listed here below), who are all highly qualified and active researchers covering a wide spectrum of research fields. This ensures a continuous updating of the PhD Program and guarantees that the students are involved in innovative research work.

FAMILY NAME	FIRST NAME	POSITION*
BERTACCO	RICCARDO	FP
BRAMBILLA	ALBERTO	AP
CERULLO	GIULIO	FP
CICCACCI	FRANCO	FP
CUBEDDU	RINALDO	FP
DALLERA	CLAUDIA	AP
D'ANDREA	COSIMO	AP
DELLA VALLE	GIUSEPPE	AP
DE SILVESTRI	SANDRO	FP
DUÒ	LAMBERTO	FP
FINAZZI	MARCO	FP
GHIRINGHELLI	GIACOMO	FP
ISELLA	GIOVANNI	AP
LANZANI	GUGLIELMO	FP
LAPORTA	PAOLO	FP
MARANGONI	MARCO	AP
NISOLI	MAURO	FP
RAMPONI	ROBERTA	FP
STAGIRA	SALVATORE	FP
TARONI	PAOLA	FP
TORRICELLI	ALESSANDRO	FP

***Position: FP = Full Professor; AP = Associate Professor.**

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, who take care that the goals of the PhD Program are in line with the needs of non-academic world.

FAMILY NAME	FIRST NAME	INSTITUTION
PIROVANO	AGOSTINO	Micron Semiconductor Italia s.r.l.
DONATI	FABIO	EPFL – Lausanne, CH
HECHT	BERT	Università di Würzburg, D
LURIDIANA	SEBASTIANO	Tecno Vacuum s.r.l.
BLANDINO	DAVIDE	Optec s.p.a.
MAJORANA	SALVATORE	IIT – Technology Transfer Office

INTEGRATED PHOTONIC DEVICES FOR QUANTUM INFORMATION PROCESSING

Simone Atzeni - Supervisor: Roberto Osellame

The second quantum revolution promises to change radically the paradigm of information science, exploiting quantum mechanical systems as information carriers and potentially leading to fundamental performance advantages in computation, communication and simulation. This prospective has triggered an enormous effort in the scientific community, from both the theoretical and the experimental point of view. Indeed, quantum technologies have experienced an exponential growth, achieving remarkable results in the creation, the manipulation and the detection of individual and complex quantum systems. Despite these results and the first proof of the so-called quantum supremacy achieved by Google, quantum technologies are still far from moving from the proof-of-principle level to real world applications and further developments are essential for the manufacture of devices with the proper number of components and functionalities.
A relatively new and compelling approach for facing this huge technological challenge is based on integrated quantum photonics, in which single photons are exploited as quantum information carriers. Quantum states of light are thus manipulated in small optical circuits, mainly composed of waveguides and interferometers. The intrinsic mechanical stability of this approach allows to control the phase of light in each spatial mode to an extent that is unreachable with the bulk optics approach. This enables the fabrication of complex interferometric structures, which represent the building blocks towards the realization of large-scale quantum optical processors.
In addition, propagation in highly confining waveguides provides an enhancement in light-matter interaction, leading to a remarkable increase in the efficiency of nonlinear processes. This kind of processes are at the basis of the realization of efficient integrated photon sources or frequency converters.
Lastly, leveraging the know-how, infrastructure and manufacturing system of classical optical telecommunications, the growth rate of integrated quantum photonics is expected to be significant.
In particular, femtosecond laser micromachining demonstrated in the recent years to be a very powerful technique for the design and the development of innovative optical circuits for quantum applications. This technique, in fact, presents several advantages over conventional lithographic processes, as the fast-prototyping capability, the low production cost and the unique possibilities to realize three-dimensional photonic structures. In addition, it relies on the non-linear multiphoton absorption of femtosecond laser pulses to induce permanent modifications in a transparent material, enabling the processing of a large number of different transparent substrates, from polymers and glasses to crystals, with the same setup. Furthermore, by properly choosing the material and the irradiation parameters, waveguides with low birefringence and high efficiency in the interfacing with standard optical fibers can be easily realized. However, the induced index contrast is typically rather low, which implies that the achievable density of components is quite limited.
In this thesis work, femtosecond laser micromachining is exploited for the realization of several integrated photonic devices with functionalities in the field of quantum information processing, with particular attention to the generation of quantum states of light and the manipulation of polarization entangled photon-pairs.
In addition, a higher-index-contrast platform, based on silicon oxynitride, was developed in the micro- and nano fabrication facility of Politecnico di Milano in order to potentially increase the complexity of photonic integrated circuits.
First, we proposed a novel Mach-Zehnder interferometer, based on the hybrid interfacing of photonic circuits realized in different materials, to enable the generation of wavelength-degenerate entangled photon pairs. Adopting this scheme, an integrated optical source encompassing three different components, as shown in the Figure 1, was realized by means of femtosecond laser micromachining. We show that the source, based on spontaneous parametric down-conversion, gives access to different classes of output states, allowing to switch from polarization-entangled to path-entangled states.
The realization of femtosecond-laser-written waveguides close to the surface may represent a challenging task, as the presence of defects can lead to distortion of the focused laser beam during fabrication and thus interruptions in the propagation path. However, they also represent a key component when reconfigurability is required. Exploiting bulk etching of the substrate, buried waveguides were brought close to the surface allowing the realization of an integrated reconfigurable circuit for mimicking and simulating the behaviour of quantum many body systems.
In order to further increase the reconfiguration capability of femtosecond laser written circuits, we developed a new design for integrated Mach-Zehnder interferometers, based on the combination of resistive microheaters and thermally-isolating 3D microstructuring. This allowed us to reduce more than an order of magnitude both the power dissipation and the thermal crosstalk between the active elements with respect to state-of-art devices for this technology. By operating these devices in vacuum, we also achieved record-low sub-milliwatt power dissipation.
Finally, we worked on the development of a platform based on silicon oxynitride. The process was optimized starting from the thin film deposition, going towards waveguide definition by lithography and etching and then proceeding with the capping exploiting a new class of materials, spin-on-glass. A preliminary set of measurements on the realized devices has shown promising values of propagation and coupling losses, even though further optimizations are necessary before the novel platform will meet the requirements of applications.

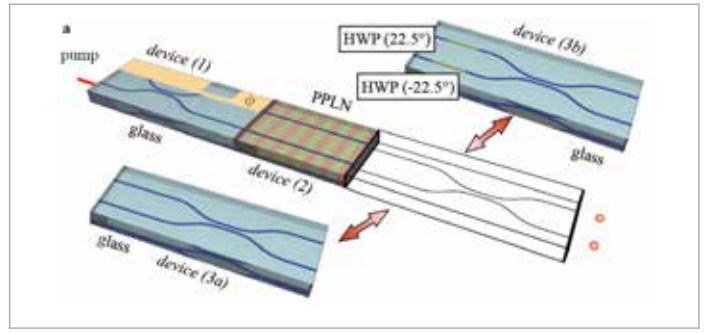

Fig. 1 - Schematic of the hybrid integrated source of entangled photon-pairs based on optical components realized through femtosecond laser micromachining.

DEVICES AND METHODOLOGIES IN DIFFUSE OPTICAL INSTRUMENTS

Anurag Behera – Supervisor: Alberto Dalla Mora

Light is a powerful non-invasive tool that can be utilized to probe biological tissue. Diffuse optics relies on injection of photons into the tissue and recollecting the back scattered photons. As these photons diffuse through the medium, they undergo many absorption and scattering events. By collecting statistically significant number of photons, it is possible to extract the background optical properties of the tissue. By monitoring the optical properties over time we can extract crucial hemodynamic changes in the tissue. Hence, diffuse optics can be exploited as a powerful clinical tool for neuromonitoring and neurocritical care.

Time domain approach in particular relies on the injection of a fast laser pulse into the probed tissue and recording of the photon arrival times of the backscattered photons over many cycles thus allowing for the reconstruction of the histogram of the distribution of time of flight (DTOF) of photons. The key components of this technique are pulsed laser source, time resolved single photon detector and time correlated single photon counting boards. The last decade has seen huge improvements not just in terms of performance but also in terms of cost and compactness of the sources as well as the detection chain.

The goal of my work revolved around exploiting the available technology to maximize system performance while maintaining low cost and compactness and to explore possible application of novel technologies which will act as a seed for next generation of time-domain instrumentation.

I began my work with a simulation study to evaluate the parameters that have the maximum impact on the overall performance of a time-domain diffuse optical system. All the associated parameters can be categorized into three namely: system parameters, geometrical and optical parameters and measurement strategies. All the parameters were evaluated on the basis of standardized figures of merit, contrast and contrast-to-noise ratio. Effect of critical parameters such as the instrument response function (which is the temporal response of the system to the injected laser pulse), the optical responsivity of the detection chain (which takes into account not just the photon detection efficiency but also the numerical aperture) and the noise present in the system (dark count rate and afterpulsing probability).

The effect of these parameters on contrast and CNR was studied under a wide range of background optical properties and inclusion size and depths.

The second phase of my work was to develop low cost and compact systems. These devices maintain the performance of traditional systems while drastically reducing the overall size, moving from a rack hosted system to a compact table top device. A huge step in this direction was the design and development of a Silicon photomultiplier (SiPM) based temperature controlled detection module. A SiPM can be considered as an array of Single photon avalanche diode (SPAD), with a global anode and cathode. SiPMs thus have a similar semiconductor based architecture while enabling the possibility of achieving active area close to photomultiplier tubes (PMT). The module is housed in a compact 91 mm x 50 mm x 40 mm aluminum case and is composed of 4 modular boards namely, the front-end electronics, an amplification board, a TEC controller unit to maintain the SiPM temperature with an accuracy of < 0.01°C and finally the power supply board that provides the biasing for all the components.

The improvement of an existing 8-channel SiPM based tomographic system was another thread in fabric of compact devices. The second generation of the 'Octopus' system uses dual wavelengths at 670 nm and 830 nm, 8 SiPM modules placed in contact to maximize the numerical aperture. The use of a fast optical switch allowed for short measurements times enabling monitoring of task induced hemodynamic changes in the motor cortex in healthy adults. The 8 detectors were spread over two probes each hosting four source points. 8 time-to-digital converters were used to collect the photon arrival times, which were then used for tomographic reconstruction.

The novelty of the system lies in its compactness and being cost effective while maintaining performance comparable to state-of-the-art systems. This work was carried out in collaboration with our colleagues at Commissariat à l'énergie atomique (CEA).

Finally, we developed a novel large area high throughput detection chain based on 3 x 3 mm^2 area SiPM. The goal of this activity was to explore the outer reaches of possibilities in terms of throughput. The large area SiPM, placed in contact, enabled a high optical responsivity while still maintaining a good timing response. This was coupled with a subnanosecond deadtime TCSPC unit which enabled achievement of unprecedented count-rates of up to 30 Mcps. This system showed substantial improvements over traditional fiber based systems. We observed an order of magnitude improvement in optical responsivity and an increase in contrast of 26% and in CNR of 250%. This work presented some unique challenges both technical and theoretical. However, it represents an important step in the move towards the use of high throughput systems which can open up new opportunities such as measurements in transmission geometry. To the best of our knowledge, this is the largest microelectronics based detector currently being in time-domain diffuse optical measurements.

In conclusion, this thesis starts with determining the parameters with maximum impact on system performance and then applied the results into the experimental work. First of which was the improvement of existing systems and technologies and second the exploration of novel technologies and techniques. It has presented some wonderful opportunities to collaborate with different scientific institutes and young scientists.

Silicon based detectors have come a long way in terms of performance compared to traditional PMT based systems. Adding to this their intrinsic advantages in terms of cost robustness and compactness makes ideal for future time-domain systems. The introduction of large area gated-SiPMs will represent a landmark in detector technologies for TD-DO.

This PhD work was performed in the framework of the European H2020 project BITMAP (Brain injury and Trauma monitoring using advanced photonics, grant N.675332).

STUDY OF PRIMARY MECHANISMS OF PHOTOSYNTHESIS IN GREEN ALGAE BY ULTRAFAST VIS-NIR SPECTROSCOPY

Gabriel José de la Cruz Valbuena - Supervisor: Cosimo D'Andrea

In recent years, the global energetic crisis has reintroduced the importance of looking for green and sustainable energy sources. Solar energy is the most abundant and renewable energy source and in fact, light conversion into chemical energy by photosynthesis constitutes the main solar energy conversion in our planet. Indeed, photosynthetic organisms such as plant or algae are able to produce between 30-80% of biofuel from biomass, which constitutes a promising way to possibly replace the use of fossil based fuels.

Among all the photosynthetic organisms, green microalgae stand as the most interesting candidates as they have a high photosynthetic efficiency and they can be cultivated in non-arable lands, not being in competition with food production. In addition, industrial gases and wastewater can be used to feed them and clean the environment. Nevertheless, in spite of its advantages, the use of algae for biofuel production is not industrially exploitable, mainly because their lower light use efficiency value observed compared to the theoretical one expected.

The principal reason for this difference lays on a photoprotective mechanism called Non-Photochemical Quenching (NPQ) which is activated under light stress conditions. NPQ consists in the release of excess energy as heat thanks to the action of a protein, LHCSR3, whose activation depends on the pH of the medium. LHCSR3 is a transmembrane protein who contains three helicoidal carbon chains with light-absorbing pigments, mainly chlorophylls and carotenoids, attached to them. The understanding of NPQ in LHCSR3 of green algae allows us to design mutants in which NPQ effect is not as strong, improving their light efficiency and the overall biomass production in the process

The principal objective of this work consists in the *in vitro* and *in vivo* study of NPQ in LHCSR3 of green algae *Chlamydomonas Reinhardtii* on its wild type and mutant strains from both biotechnological and physical points of view in collaboration with the group of professor Ballottari in Università di Verona. In particular, the main goal of this thesis is the understanding of the molecular pathways of NPQ in LHCSR3 using ultrafast spectroscopic techniques such as time-resolved photoluminescence (TRPL) and transient absorption (TA).

In TRPL, a light pulse interacts with the sample and promotes it to an excited state that eventually will be depopulated via spontaneous emission. Emitted light is then sent to a spectrograph and to a high-speed detection system to resolve it spectrally and temporally. On the other hand, in TA two pulses are needed: the first one is called pump and bring the molecule to an excited state whose decay pathways are tracked by the changes on the absorption of a second pulse, the probe.

First, we performed TRPL measurements on *in vitro* LHCSR3 samples at two different pH and protein aggregation conditions to simulate high/low stress conditions in the protein. We excited the sample at 400 nm and observed a quenching in the overall lifetime the closer we were to high stress conditions, or in other words, the lower the pH and the higher the protein aggregation were. In fact, the main reason for this quenching was the protein aggregation with pH playing a secondary role. However, these measurements do not explain the mechanisms that justify the observed quenching.

We thus performed TA measurements on the visible using a 630 nm pump to selectively excite the chlorophyll (Chl) and a broadband white visible light as a probe. We observed a ground state bleaching/stimulated emission (GSB/SE) at 680 nm and a wide photoinduced absorption (PA) from 470 to 600 nm associated with Chl a activity. Furthermore, we observed a carotenoid bleaching to the Car S_2 state around 500 nm which became stronger the lower the pH and the more aggregated the sample was.

In a longer timescale, we saw the formation of a Car triplet at 510 nm which was favored the less quenched the sample was. This triplet state was formed after a Chl intersystem crossing (ISC) and a Chl-Car triplet-triplet energy transfer following the scheme: ^{1}Chl → ^{3}Chl→ ^{3}Car. In addition, we could indirectly detect a weak energy transfer from the excited chlorophyll to the carotenoid first dark state S_1 as we saw a slight transition from the carotenoid S_1 state to a higher state, S_n. This transition was stronger at low pH conditions, pointing out a possible quenching mechanism.

We then extended our experiments to the NIR region, where carotenoid radical cations are formed, and we saw a bleaching at early times for all samples. Its time constant matches the one found for the carotenoid GSB in the visible, indicating that the main interaction between chlorophylls and carotenoids in LHCSR3 is the formation of a carotenoid radical cation. After careful inspection of the TA spectrum in the NIR we could conclude that the carotenoid involved in the radical cation formation was lutein. This data, however, does not fully explain all our signals, pointing out at a possible quenching mechanism related with protein aggregation as another energy dissipation pathway.

We then performed the same TRPL experiments with an *in vitro* LHCSR3 mutant, *bm6*, a LHCSR3 protein with less protonable sites. We observed that the mutant overall lifetime was longer than the wild type, regardless the pH conditions. In order to gain more insight in the quenching mechanisms we did the same kind of experiments we previously performed in the wild type, discovering that the same quenching channels both in the visible and in the NIR were also active in the mutant.

In this case, a more significant aggregation dependent mechanism was proposed to explain the experimental data: the lack of protonable sites favors protein aggregation and, subsequentially, the Chl-Chl interactions. This could explain why we observe a longer lifetime of the mutant respect to the wild type both in TRPL and TA when all the other quenching mechanisms remain the same.

In summary, we could disentangle the distinct molecular mechanisms responsible for NPQ in LHCSR3, revealing a lutein radical cation formation as the main quenching mechanism and a weak secondary ^{1}Chl-Car S_1 energy transfer.

DEVELOPMENT AND TEST OF NOVEL TECHNOLOGIES AND APPROACHES FOR TIME-DOMAIN MULTI-WAVELENGTH BREAST IMAGING BY DIFFUSE OPTICS

Edoardo Ferocino - Supervisor: Paola Taroni

Among women, breast cancer is the most common cancer and the leading cause of death: 1 woman out of 8 will develop breast cancer during her lifetime with a mortality rate around 13%. The primary method for assessing non-invasively the presence or status of a lesion is through breast imaging. The conventional techniques used are X-ray mammography, Magnetic Resonance Imaging (MRI), Ultrasounds (US) and Positron Emission Tomography (PET).
Though, X-rays are affected by low sensitivity on dense breasts, MRI has a high cost and long examination time, US has strong dependence on operator's experience for data analysis and PET requires the use of radioactive contrast agents.
Optical Mammography (OM) is a promising imaging technique that could potentially answer to most of the clinical needs: it is cost- and time-effective, health-safe, reliable even on dense breasts, and provides physiological information linked to breast tissue composition. OM is a specific application of Diffuse Optics (DO) which describes light propagation in diffusive media such as biological tissues: near infrared light (NIR, 600 nm – 1300 nm) is absorbed and scattered in the volume according to tissue composition (breast chromophores) and micro-sized optical heterogeneities, respectively. In the case of OM, the main chromophores in the NIR region are: Oxyhaemoglobin (HbO_2), Deoxyhaemoglobin (Hb), Lipid, Water and Collagen. The knowledge of tissue composition can be exploited for risk assessment (*e.g.* Collagen is an independent risk factor for developing breast cancer), lesion nature identification, therapy monitoring and prediction of therapy outcome. Thus, OM is a powerful tool for breast cancer management.
We focused the PhD activity on two instrumentations for time-domain (TD) multi-wavelength breast imaging by DO. The TD approach enables to decouple the absorption and scattering effects (contrary to CW approach). The use of properly chosen wavelengths highlights the above-mentioned components contribution to the absorption spectra. In the framework of OM, the two instrumentations are unique for the number and choice of wavelengths, giving access to the estimate of *all* the main breast chromophores at once, including Collagen, unlike most of similar instrumentations.
TD implementation requires pulsed laser as sources, single photon detectors for harvesting and proper timing electronics for diffused light pulse reconstruction. The first instrumentation is a 7-wavelength optical mammograph, developed in the years at Politecnico di Milano, that acquires projection images of the compressed breast: it is currently devoted to chemotherapy monitoring of patients diagnosed with breast cancer. The optical mammograph has undergone a substantial upgrade of the entire detection chain with the aim to improve the quality of the signal and overall robustness of the detection chain, features that are essential in a clinical environment. Silicon Photomultipliers (SiPMs) replaced the collecting fibre bundle and the two Photomultipliers Tubes (PMTs) as detectors, while a Time-to-Digital Converter (TDC) replaced the two Time-Correlated Single Photon Counting (TCSPC) boards for photon timing. These devices promote inexpensiveness, reliability and compactness. A big effort was made to acquire expertise and optimize these novel technologies.
The upgraded instrument was thoroughly characterized in each component following standardized performance assessment protocols. Results indicate that the instrument has good performances in terms of linearity (that indicates the ability to properly follow the changes in a specific parameter - absorption or scattering) and reproducibility of measurements on different days. Both features are essential for the clinical application of therapy monitoring. Also, the upgraded detection chain leads to a significant 2/3-fold increase of optical responsivity (which is a measurement of the overall photon detection efficiency of the detection chain) respect to the previous one.
Presently, the instrument has entered a clinical trial for neoadjuvant therapy monitoring and prediction of pathologic outcome.
The second instrument is being developed in the framework of the European project SOLUS and aims at combining Diffuse Optical Tomography (DOT) and US/Shear Wave Elastography (SWE) into a single hand-held probe to improve diagnosis capability and lesion identification: it acquires the light backscattered by the tissue performing a tomographic reconstruction of the optical properties of the volume beneath. Figure 1 shows a mock-up of the SOLUS probe: an US transducer is surrounded by 8 independent modules (optode) embedding the photonic devices for the DOT, namely 8 pulsed lasers, a gated SiPM detector and an integrated TDC for photon timing. Thus, each optode forms a standalone DO TD multi-wavelength device. The important technological novelties are the compactness of the building blocks for the TD approach and the combination of DOT, US and SWE into a single instrumentation.
Initial simulations were performed to validate the proof of concept and assess the estimated minimal measurement requirements and performances. Then, using optical bench instrumentation, we moved to validation on well characterized silicone phantoms and finally meat phantoms so to better mimic the heterogeneity of the human breast. The phantoms embedded an inclusion, mimicking a lesion with different optical properties respect to the background.

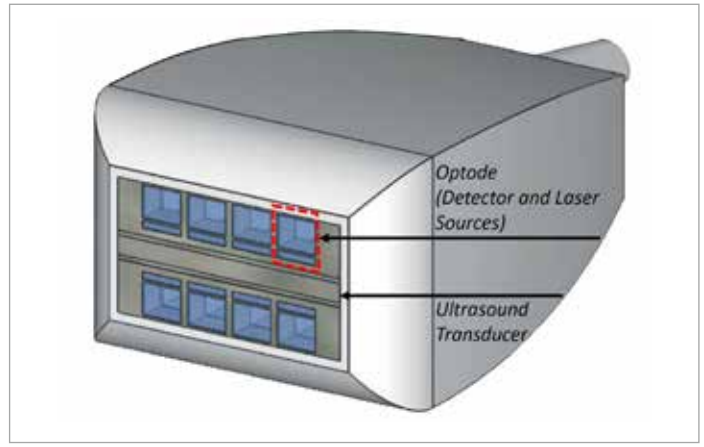

Fig. 1 - Mock up and schematic of the SOLUS probe

Results shows that using proper regularizations, the localization of an inclusion within the phantom is good with errors around 1 mm for each of the 3D dimensions up to 2 cm depth. For phantom measurements, surface artifacts are observed in the reconstruction, the inclusion is blurred and reconstructed at a shallower depth. However, using a morphological prior constraint (*i.e.* the exploitation of the a priori information on position and geometry of the inclusion) significantly improves reconstruction in terms of localization and quantification: the artifacts disappears, the inclusion is reconstructed without blurring in the correct position and quantification of the optical properties is improved. The morphological constraint was tested in view of information that in clinical settings could be obtained by US imaging. The obtained results are promising and indicate the proposed TD-DOT system suitable for breast imaging.

CUPRATE HIGH TC SUPERCONDUCTORS STUDIED BY POLARIZATION-RESOLVED RIXS

Roberto Fumagalli - Supervisor: Giacomo Ghiringhelli

More than 30 years after their discovery, Cu-based superconductors, commonly known as high T_c superconductors or simply *cuprates*, are still at the focus of intense research, both for their complex and fascinating physical properties and for the perspective of disruptive technological applications.
Cuprates have a two-dimensional (2D) layered crystal structure, with CuO_2 planes hosting antiferromagnetism and/or superconductivity. CuO_2 planes are usually separated by the so-called "charge reservoir" layers: the interaction between these intermediate layers and the CuO_2 planes plays a fundamental role in the physical properties of cuprates. In fact, superconductivity is usually achieved in doped samples, that are obtained by chemical substitution (or oxygen content tuning) in the spacing layers.
Despite the extensive scientific inquiry, both from the experimental and theoretical point of view, a consensus on the actual mechanisms of superconductivity in cuprates is lacking, making it one of the biggest challenges in contemporary solid state physics. The scenario is thus open to novel discoveries possibly coming from the development of new theoretical models and experimental methods.
Thanks to the recent improvements in the performance of the instrumentation in Resonant Inelastic X-ray Scattering (RIXS), especially in terms of energy resolution and efficiency, this technique has gained a lot of attention in the study of transition metal oxides, including cuprates. RIXS is a "*photon in-photon out*" synchrotron-based spectroscopy technique particularly suitable to investigate the elementary excitations in solids, which are related to the degree of freedom such as lattice, spin, charge and orbital. At the L_3 absorption edge, RIXS spectra are populated by peaks and features that can be assigned to phonons and magnons at the meV scale to orbital (or *dd*) excitations and charge transfer at few eV. To fully exploit the information contained in RIXS spectra one need to consider their energy, momentum and photon polarization dependence.
This thesis, besides presenting some important Cu L_3 RIXS results on cuprates obtained in the conventional way, *i.e.,* by summing over the polarizations of the scattered photons, presents a comprehensive review of polarization-resolved RIXS measurements. The experiments were carried out with the ERIXS spectrometer at the new ID32 beamline of the ESRF – The European Synchrotron, an instrument that, since 2015, has set new standards in high resolution soft x-ray RIXS: higher energy resolution, full control of the scattering geometry with diffraction quality standards, and linear polarization analysis of the scattered photon.
The thesis reports the first systematic high-resolution polarization resolved RIXS study of low energy (magnons and phonons) and orbital excitations in the high T_C superconductor $Nd_2BaCu_3O_{6-\delta}$ (Fig. 2), which serves also as a prove of the capability and reliability of polarimetric measurements. Here we used a pure ionic picture to study the experimental results calculating the theoretical RIXS cross sections for all the possible excitations. Furthermore, we are able to describe and interpret the different polarized resolved contributions in terms of Stokes' parameters. The thesis presents also other examples where the full polarization analysis has significantly contributed to the interpretation of the normal RIXS spectra. For example, polarization-resolved measurements confirmed the charge nature of the order parameter discovered in overdoped $(Bi,Pb)_2(Sr,La)_2CuO_{6+\delta}$, the assignment to spin excitations of the enhanced dynamic response at the charge order vector in $Nd_{2-x}Ce_xCuO_4$ and finally the confirmation of the charge nature of the fast-dispersing zone-center excitations in $La_{2-x}Ce_xCuO_4$. The polarization analysis has been applied also to systems other than cuprates, such as $CeRh_2Si_2$, where the use of the polarimeter allowed to assign the energy and symmetry of *ff* excitations. The thesis presents also the study of the momentum-dependence of orbital excitations in RIXS spectra of 1D and 2D cuprates. In correlated oxides electronic excitations tend to have localized a character and are usually described by orbital and spin quantum numbers in a symmetry adapted atomic picture: usually orbital excitations do not disperse, irrespective of their spin character. On the contrary, pure spin excitations have collective nature: spin-waves (or magnons) display large energy dispersion *vs* momentum. Theory predicts that at low dimensionality orbital excitations can split their orbital and spin components, giving rise to complex dispersion. So far orbital excitations with sizeable dispersion had been observed and theoretically analysed only in quasi-1D materials. We have investigated the Cu L_3-edge RIXS spectra of the quasi-1D AF Ca_2CuO_3 which display two dispersive orbital excitations (Fig. 3). Unexpectedly, also the data of the 2D infinite layer $CaCuO_2$ show a non-negligible dispersion of the *dd* excitations, a phenomenon that cannot be explained by the model used in the 1D case.

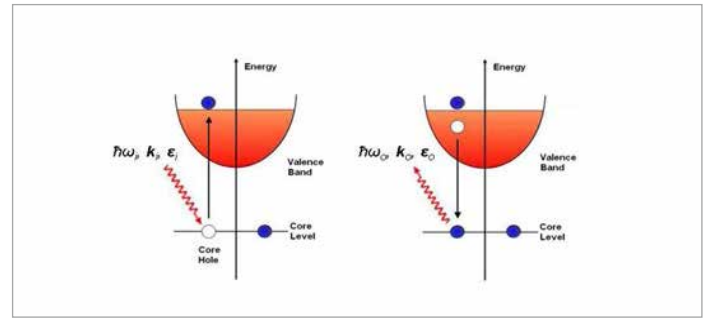

Fig. 1 - Scheme of the RIXS two-steps process

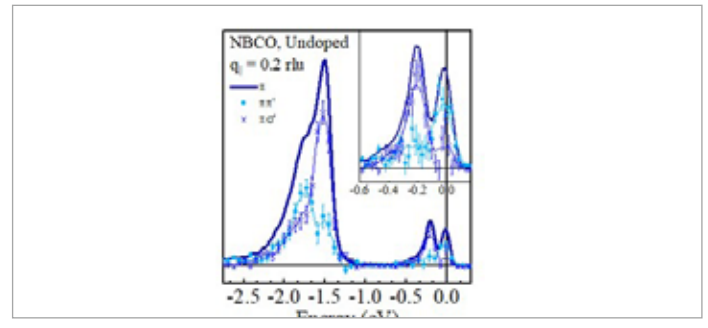

Fig. 2 - Example of polarization-resolved RIXS spectrum of $NdBa_2Cu_3O_6$

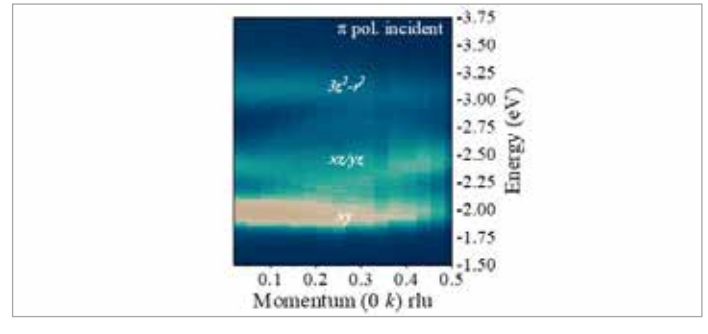

Fig. 3 - Close-up view of the orbital excitations in Ca_2CuO_3

ATTOSECOND TRANSIENT REFLECTIVITY SPECTROSCOPY FOR THE STUDY OF ELECTRON DYNAMICS IN SOLIDS

Giacinto Davide Lucarelli - Supervisor: Matteo Lucchini

The investigation of ultrafast electron dynamics in solids initiated by ultrafast laser pulses is fundamental for a deeper understanding of light-matter interaction processes and ultimately to advance toward the development of PHz electronics. So far, the most successful all-optical technique with sub-femtosecond temporal resolution is the Attosecond Transient Absorption Spectroscopy (ATAS). ATAS is a two-colour pump-probe technique; a pump pulse, usually in the Near Infrared (NIR) – visible (VIS) range with a time duration of few femtoseconds, induces a modification in the physical properties of the sample. These modifications are temporally resolved by detecting the variations in the transmittance of an attosecond probe pulse in the extreme ultraviolet region, as a function of the pump-probe delay. ATAS technique in solids is often used in combination with a so-called streaking measurement in noble gas in situ that allows one to measure precisely the NIR-VIS field acting on the sample during the experiment. The streaking technique consists in the measurement, by a Time Of Flight (TOF) electron spectrometer, of the kinetic energy of electrons coming from the photoionization of a target in the presence of an ultrashort CEP-stabilized intense infrared (IR) field, which gives a momentum shift to the photoemitted electron depending on the ionization time instant.

ATAS presents, however, a few drawbacks, mainly related to the fact that it can be employed only on very thin samples (typically from tens to few hundreds of nanometer thickness). First, heat dissipation in such thin samples is very inefficient, thus it is very difficult to avoid thermal effects on the sample during the experiment. Moreover, usually it is very difficult to grow monocrystalline samples of nanometric thickness, hence making impossible crystal-cut dependent studies. In order to avoid these drawbacks, it is possible to use reflection geometry. This approach allows one to perform experiments with sub-femtosecond time resolution on thick, monocrystalline solid samples. So far, no peer reviewed articles have been published, reporting applications of Attosecond Transient Reflectivity Spectroscopy (ATRS) technique. A possible limitation of this technique is that it is not possible to place a TOF spectrometer in front of the sample in order to acquire a photoelectron streaking trace at the same time of the ATRS trace. This restriction can be overcome by developing an attosecond beamline with two focal regions. The TOF can be placed in the first focal region, while the target is placed in the second one. This setup must be properly calibrated in order to take into account the phase accumulation due to the refocusing path. The first part of the PhD work was devoted to the development and characterization of a setup for ATRS experiments (Figure 1). A NIR pulse with stabilized CEP, compressed down to ~ 6 fs by using the hollow fiber compression technique, is split in two parts. One of them is focused onto a noble gas target to generate XUV Isolated Attosecond Pulses via a process called High-order Harmonic Generation (HHG). The other part goes through a delay stage and then recombines in a collinear geometry with the XUV pulse on a drilled mirror. The pulses are then focused on the first target, a noble gas jet, placed in correspondence of a TOF spectrometer, where a streaking trace is acquired. The beam is then refocused on the solid sample under study which is mounted on a roto-translation stage (in order to set the proper angle). The reflected XUV radiation is then recorded with an XUV spectrometer as a function of the pump-probe delay.

The second part of the PhD work was devoted to the realization of the very first experiment with the setup described above. The ultrafast electron dynamics around an excitonic feature in magnesium fluoride (MgF_2) has been investigated. Magnesium fluoride shows a double peak around 54.6 eV in his reflectance spectrum (Figure 2), corresponding to transitions from Mg 2p++ to two excitonic states below the solid conduction band. The system was perturbed by a NIR-VIS ~ 6-fs pump pulse, inducing multiphoton absorption and intraband motion within the conduction band and the excitonic states. The dynamics around the excitonic region are then probed by detecting the relative variation in reflectivity of a broadband attosecond XUV probe pulse (Figure 3). Experimental results show both a few femtosecond dynamics and faster oscillations at twice the pump frequency around the exciton and in the conduction band region. A collaboration with the research group of Prof. A. Rubio (Max Planck Institute for the Structure and Dynamics of Matter - Hamburg) has been established to develop a theoretical model that will be useful to extract information about the exciton dynamics and possibly the interaction between exciton and lattice from the measured trace. These results will offer unprecedented insights into core exciton dynamics in crystalline solids showing, at the same time, the potentials of Attosecond Transient Reflectivity Spectroscopy technique.

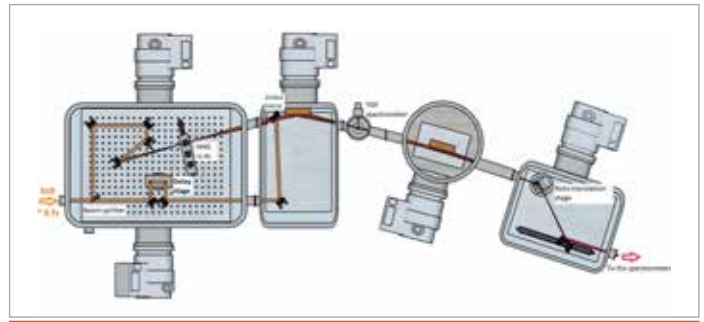

Fig. 1 - Two-foci setup for pump-probe Attosecond Transient Reflectivity Spectroscopy experiments.

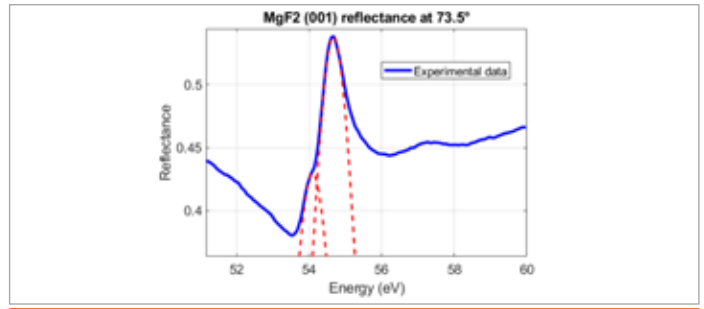

Fig. 2 - Blue solid line: measured reflectivity of the MgF_2 [001] sample at an angle of incidence of 73.5°. Red dashed lines: gaussian curves to guide the eye in the localization of the two excitonic peaks.

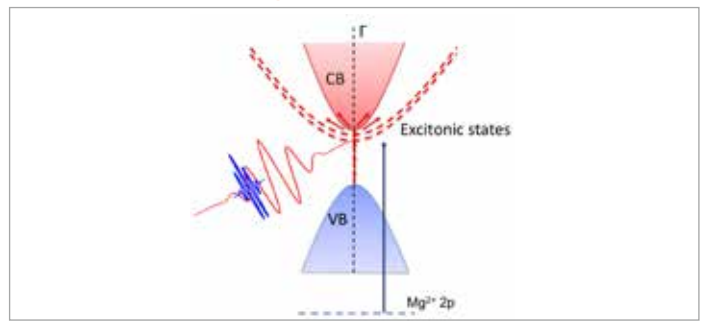

Fig. 3 -Symbolic representation of the pump-probe experiment on MgF_2. VB stands for Valence Band. CB stands for Conduction Band. Red arrows schematically represent the effects of NIR-VIS field on the sample (multiphoton absorption and intraband motion) around the Γ point. Blue arrow represents the XUV field probing around the exciton region.

PHOTONS QUANTUM INTERFERENCE INDUCED BY SPACE-TIME CURVATURE: A POSSIBLE VERIFICATION METHOD BASED ON A SPACE PLATFORM

Piergiovanni Magnani - Supervisor: Paolo Villoresi

Research Activity

The main subject of this PhD research has been to discuss the effects played by gravity on single photon interference in cases where photon propagation is over long distances (several thousands of kilometres) with large variation of General Relativistic (GR) fundamental tensor. In particular space-time metric theoretically affects phase coherence of photon wave packets propagating in quantum superposition along trajectories at different gravitational potential. Measurable interferometric effects are therefore expected with fringes and visibility characteristics depending on the specific experimental conditions. Gravitational 'red-blue shift', 'time dilation', 'photon trajectory bending' and 'classical observer-source relative motion (classical Doppler effect)' all contribute, to a different degree, to phase shift accumulation and 'which-way' information.

A reference experimental scheme to attain the large separation is shown in Figure 1 and involves the utilization of two segments: a ground segment (Ground Station - GS) and a space segment (Spacecraft – S/C) equipped with a duly designed optical payloads. In the shown configuration the photons are generated on ground and transmitted to the S/C where are processed. Interferometers, equipped with beam splitters, provide the necessary operations of states superposition and recombination.

Interferometric effects are strongly related to frequency variations induced by the experimental conditions. It is however noted that the frequency variations caused by classical 'observer-source relative motion' generates very large frequency Doppler effects and variations which mask and 'confuse' the relativistic ones. The classical Doppler effect has to be removed to a high degree of precision in order to discriminate the ones related to metric only.

It is evidenced that the first measurements related to gravity induced quantum interference has been performed by Colella-Overhauser-Werner (COW) in 1975 utilizing a Neutron Interferometer implementing quantum superposition along separate trajectories in a laboratory set-up; indeed it was a phase shift measurement on matter-waves. In this Research Thesis has been studied the detection of gravity induced quantum interference directly employing photons: this approach is sometimes named 'optical COW' and has already been suggested by the research community. Single photon conditions at the detecting interferometer are obtained, in the studied cases, by means of laser short pulses duly attenuated along the optical link.

Three experimental configuration variants have been evaluated: 'Oneway' (scheme given in Figure 1) utilizing two interferometers, one at the GS one on-board the S/C and two 'Twoways' utilizing one interferometer only (at S/C or at GS) exploiting a reflection (at GS or at S/C). The 'Oneway' configuration has been selected for detailed analysis.

The interferometric scheme for the selected configuration is shown in Figure 2 and consists of two Mach Zender Interferometers (MZI), one implemented at GS (photon emission) and one onboard the S/C (photon reception). The two interferometers are nominally 'equal' with a large arm unbalance (for example 400 m).

The approach specifically used in the analysis for the classical Doppler compensation is based on *ground intereferometer length control* driven by algorithms employing GS-S/C relative speed measurement. Other compensation techniques are possible.

Several factors affect the overall experiment performance and, to quantify the perturbations, an initial sensitivity analysis has been performed. Among the parameters considered are: interferometers length mismatch (calibration, stability related), errors in knowledge of Spacecraft position and speed, control errors in the implementation of the Doppler compensation scheme. The key technological aspects involved have then been analysed in more detail to allow a preliminary identification of specific development need.

A more complete analysis has then been carried out by considering photon counting at the two on-board detectors. This analysis accounted also for the characteristics of: laser pulses, attenuations and efficiencies, Single Photon Detectors. The (simulated) *photon counting*, allows to reconstruct the *probability curves* at the two detectors and then the *de-phasing curve* which can be compared against *the nominally expected curves*.

The simulations can be done for different GS-S/C orbital and experimental conditions. Indicatively assuming GS's placed around 40° N latitudes and S/C in elliptical trajectories (around 8000/22000 km, 28° inclination), maximum absolute de-phase determination error in the order of 0.03 (rad), plus a noise removable by filtering, are achievable. An example of performances is shown in Figure 3 comparing the reconstructed de-phasing with respect to the nominal de-phasing, for S/C elevation > 20° (above GS local horizon).

Whenever actual experimental data were available then the simulated performances could be compared to the actual measured performances for scientific analysis.

Should the experiment be of interest to the Agencies, and actually be pursued, then a detailed feasibility study, involving both Universities and Industries, is necessary. The objective would be to confirm the final configuration (including final choice of the Doppler compensation scheme), identify a detailed development plan and in general verify the experiment compatibility with medium size Spacecraft's and small launchers to limit the costs.

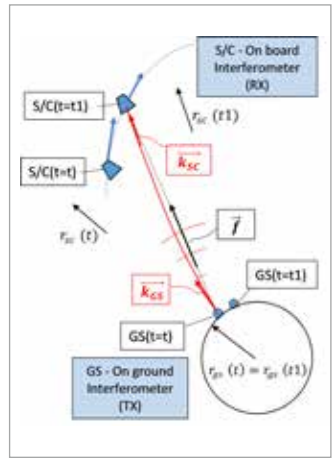

Fig. 1 - Schematics of main elements to attain large space-time separation

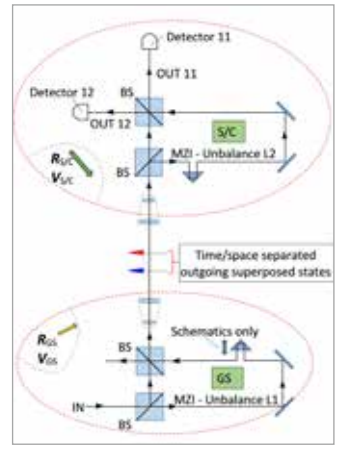

Fig. 2 - Interferometric scheme of the selected one-way experiment – Not to Scale

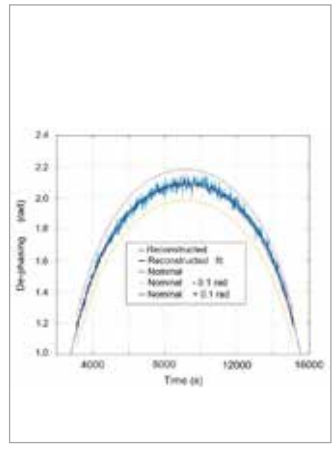

Fig. 3 - Example of performances (reconstructed de-phasing versus nominal)

ULTRAFAST RELAXATION DYNAMICS IN ETHYLENE AND CARBON DIOXIDE

Mario Murari - Supervisor: Matteo Lucchini

The understanding of ultrafast relaxation dynamics in highly excited states of molecules can shed light on many chemical reactions. The difficulties in performing these studies are connected to the need to create an electronic wavepacket on few selected excited states and to map its evolution on a femtosecond time scale. Using a pump-probe setup it is possible to study how does this system evolve. A first laser pulse known as “pump” will excite the electronic wavepacket and a second delayed laser pulse known as “probe” will trigger a second dynamics, made possible thanks to the previous interaction of the molecule with the pump. Since the excited states we want to study lie above the ionization energy of the molecules it is necessary that the pump pulse has a central energy in the extreme-ultraviolet (XUV) range. Exploiting high harmonic generation in noble gas, it is possible to obtain an attosecond pulse train composed by odd harmonics of the generating laser pulse (central energy = 1.55 eV) with corresponding photon energies in the XUV range. An attosecond pulse train will excite tens of electronic states making it impossible to identify the role played by each state. In order to have an higher energetic resolution without degrading the temporal characteristics of the laser pulse a time delay compensated monochromator (TDCM) able to select a single harmonic has been employed. The TDCM is composed by two stages divided by a slit. In the first stage the different harmonics are spatially separated using a grating. The slit performs the selection of the desired harmonic. Rotating the grating it is possible to change the harmonic centered onto the slit. The second stage is composed by the same elements of the first one but mirrored in order to compensate the temporal dispersion introduced by the first stage. The characterization of the XUV pulses have been performed by applying the FROG-CRAB technique, commonly used to characterize XUV attosecond pulses. We have employed extended ptychographic iterative engine to retrieve from a photoelectron spectrogram the temporal characteristics of the originating pulses. At the output of the TDCM the XUV pulses have a temporal duration of few femtoseconds, the shortest ever achieved with this kind of setup. This setup was developed thanks to a collaboration with the group of Dr. Poletto from CNR.

The first molecule we have studied is ethylene (C_2H_4). The exact relaxation mechanism of the first excited states of ethylene cation was not clear and different theoretical interpretations have been proposed. In order to understand this mechanism, we have performed a series of experiments with different harmonics, respectively with the 9th, 11th and 13th harmonics, to selectively populate the ground state and different excited states of the cation. A second IR pulse has been used as probe, to induce a change in the fragmentation yield of the molecule. Varying the relative delay between the XUV and IR pulses, it is possible to acquire a series of ion mass spectrograms and track the evolution of the excited wavepacket. The absorption of an IR photon by the cation in the ground state induces a bleaching in the generation of $C_2H_4^+$. Using as pump the 9th harmonic, the molecule is mainly excited to the ground state of the cation. This implies that the peak of the dynamic is centered at a relative delay of zero femtoseconds. Using as pump the 11th and 13th harmonics the molecule is ionized to the firsts excited states of the cation. This means that the molecule needs to relax to the ground state before to see the bleaching. We measured a delay in the bleaching of the $C_2H_4^+$ yield at about 20 femtoseconds delay, as visible in Fig.1. This corresponds to the relaxation time to the ground state. Other interesting information regarding the fragmentation process of the molecule are encoded in the dynamics observed for the different cations. We performed studies also on C2D4 in order to verify the effects of deuterium on the vibrational rearrangement of the molecule, discovering new interesting dynamics. We have also performed the first observation of ultrafast relaxation and vibrational dynamics of the superexcited states of carbon dioxide. Superexcited states are neutral electronic states with internal energy higher than the ionization energy of the molecule or atom under investigation. As one requires XUV pulses with time duration of few-femtoseconds, there are very few theoretical and experimental studies on the ultrafast relaxation dynamics of superexcited states.

In the case of carbon dioxide, the ionization energy is centered at 13.77 eV. Using the 11th harmonic that is centered at 17 eV it was possible to populate different series of Rydberg states and of electronic states lying just below the first excited state of the cation (HOMO-1 transition). With a synchronized IR pulse, it is then possible to ionize the molecule. In this case we have employed time-resolved photoelectrons spectroscopy to study the evolution of the excited electron wavepacket. as shown in Fig.2 in the acquired photoelectron spectrogram different oscillating signals are visible. Thanks to the collaboration with the group of Prof. Regina de Vivie-Riedle the oscillations have been explained as due to the symmetric stretching and to the bending mode of the molecule. Using a global fit analysis, it was possible to extract two decaying time, respectively 165 fs and 22 fs, due to the relaxation to lower energies states that can lead to the ionization or the dissociation of the molecule..

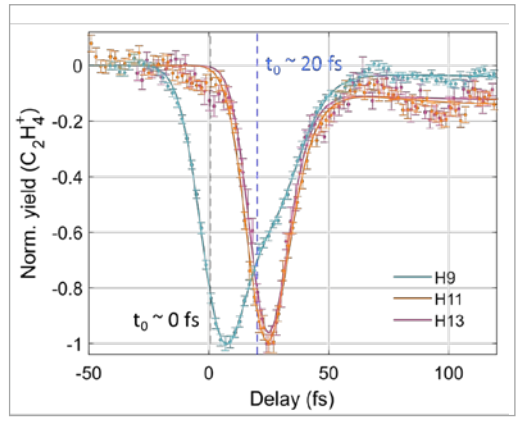

Fig. 1 - Delay in the bleaching of $C_2H_4^+$ yield

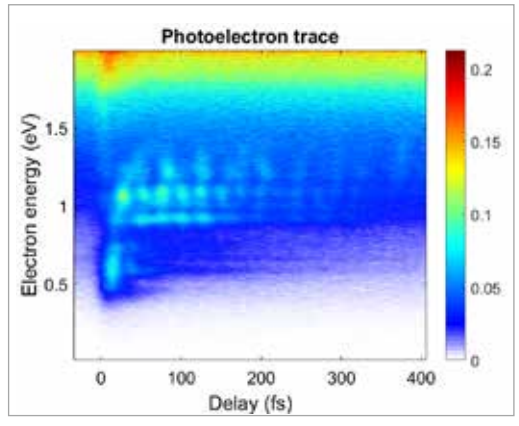

Fig. 2 - Photoelectron spectrogram of carbon dioxide

ULTRA-SCALED FIELD-EFFECT TRANSISTORS BASED ON 2D MATERIALS

Kishan Ashokbhai Patel - Supervisor: Roman Sordan

Silicon based electronic devices are rapidly approaching scaling limits. The main building blocks of Si electronics are transistors which are getting smaller every year. Continuous scaling of field-effect transistors (FETs) would there for require atomically thin semiconducting channels. However, making atomically thin channels from conventional semiconductors like Si, is unviable.

The atomic thickness of two-dimensional (2D) materials (such as graphene and MoS_2) make them ideal candidates for replacing Si in ultra-short (gate length ~10 nm) FETs. However, large scale fabrication of ultra-short FETs based on 2D materials is a challenging task. There have been several attempts to realize ultra-short FETs, but they either comprised several short-channel FETs connected in series or had very long access areas around the gate, making actual device dimensions much larger.

In this thesis, three different methods are demonstrated for the fabrication of ultra-short channel FETs without nanolithography. One such method is based on electromigration. In electromigration process strong electron wind creates nano scale break junctions in metal (e.g. Au) wires. These nano scale break junctions can be used to define the channel of ultra-short graphene field-effect transistors (GFETs). GFETs made by electromigration exhibited quasi-ballistic transport with very high transconductance, *g*m ~1200 S/m. However, such GFETs lacked drain current saturation due to their ballistic nature. This limits application of break-junction GFETs in electronics.

To make ultra-scaled FETs with MoS_2 a different technique was used, because electromigration did not provide satisfactory results. MoS_2 FETs with channel length as short as 10 nm were fabricated by shadow evaporation method. The ultra-scaled FETs were realized with exfoliated few-layer MoS_2 (thickness ~ 6 nm) and monolayer MoS_2 (thickness ~ 0.65 nm) grown by chemical vapor deposition, as the channel material. The 10 nm MoS_2 FETs exhibited drain current on/off ratio > 10^6 and maximum drain current I_D ~ 560 A/m, which is the highest reported drain currents for MoS_2 FETs measured in air ambient. The smallest subthreshold swing measured for such FETs was 120 mV/dec. Despite being very short, the 10 nm MoS_2 FETs exhibited a very good drain current saturation (output conductance ~2 S/m). Ultra-scaled MoS_2 FETs were also used to realize logic inverters in depletion load technology. The inverters exhibited a voltage gain as high as 50 at 1.5 V of the supply voltage, and in/out signal matching at a clock rate of up to 2 kHz. Finally, ultra-scaled FETs were also realized by using Van der Waals heterostructures, in which different 2D materials were assembled layer by layer. Superior electronic properties can be achieved by encapsulating 2D materials between two hexagonal boron nitride (hBN) layers. This is due to the atomically flat surface and absence of charge traps in hBN, which also screening the charge traps in the substrate. When graphene is encapsulated between two layers of hBN, it exhibits very high mobility at room temperature, typically > 12000 $cm^2V^{-1}s^{-1}$.

In this work, heterostructures were used to realize ultra-scaled GFETs. Two thin graphite (or even graphene) layers were encapsulated in hBN with a very thin separating hBN layer in between, and used as source and drain. CVD graphene transferred over the edge of the heterostructure and in ohmic contact with the thin graphite source and drain, was used as the transistor channel. The thickness of the separating hBN layer defined the channel length, typically between 5 and 10 nm.

The GFETs with the graphene channel placed over the edge of the heterostructure are perpendicular the substrate, making them first truly vertical transistors. By increasing the number of the thin graphite layers inside the heterostructures, multiple vertical GFETs can be realized. Such devices are stacked on top of each other and can therefore be used to realize high density chips for future nano-electronic devices.

Ultra-scaled FETs made of graphene and MoS_2 were realized using three-different methods. This work paves the way for the realization of future 2D nano-electronic devices and studies of fundamental concepts in physics and electronics due to the very small dimensions of the investigated devices.

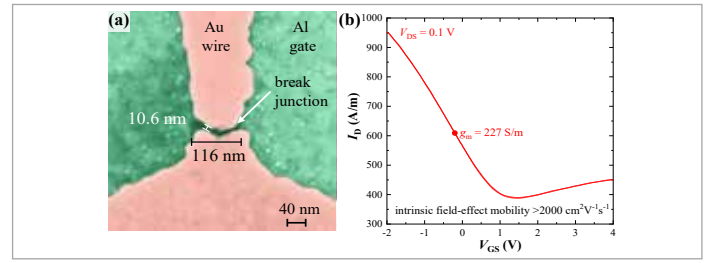

Fig. 1 - (a) False color SEM image of a break-junction GFET with a channel length of ~ 10 nm. (b) Transfer curve of the GFET, i.e., the drain current I_D as a function of the gate-source voltage V_{GS} at a drain-source voltage V_{DS} = 0.1 V.

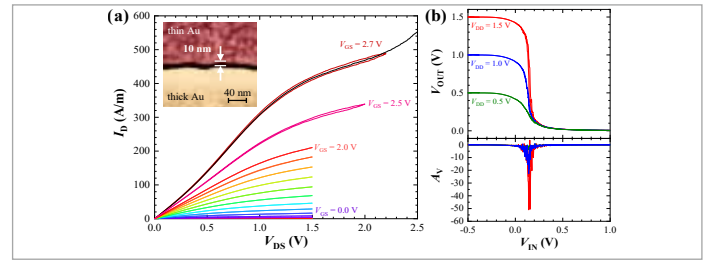

Fig. 2 - (a) Output curves of a 10-nm MoS_2 FET, i.e., the drain current I_D as a function of the drain-source voltage V_{DS} measured at different gate-source voltages V_{GS}. Inset image is false color SEM scan of the same device showing 10 nm channel length. (b) Inverter transfer curves (top graph; the output voltage V_{OUT} as a function of the input voltage V_{IN}) measured at different supply voltages V_{DD}, and calculated voltage gain A_v (bottom graph) of the same inverter exhibiting a maximum gain of $|A_v|$ ~ 50

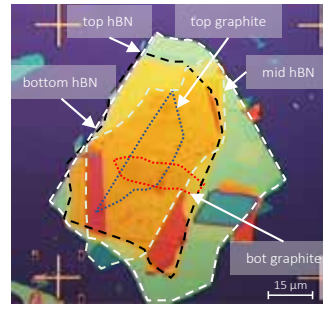

Fig. 3 - Optical image of a heterostructure made of thin graphite and hBN. Two thin graphite layers are encapsulated between hBN layers to make a vertical GFET.

HIGH-ENERGY ULTRAFAST TUNABLE MID-IR SOURCES FOR THE APPLICATION IN STRONG-FIELD PHYSICS AND SPECTROSCOPY

Prabhash Prasannan Geetha - Supervisor: Caterina Vozzi

Ultrafast spectroscopy in the mid-IR spectral range has several applications in the fundamental physics, chemistry and biological science. Vibrational and rovibrational resonances in several molecules appear in the mid-IR spectral region. Besides this, mid-IR pulses have several applications in strong-field physics. In particular they allow extension of the cut-off frequency of the high-order harmonics generation (HHG) process with respect to near-IR sources, thanks to the ponderomotive energy scaling, $U_p \propto \lambda^2$, of the ejected electrons during the tunnel ionization process. However up to now, ultrafast light sources in the mid-IR region have been inferior to those in the visible or near-IR spectral region in terms of peak power, bandwidth and pulse duration. These issues impose a limitation to the applications of mid-IR sources to ultrafast spectroscopy and strong-field physics.

The main goals of this research project were the development of a source of high-energy tuneable, ultrashort mid-IR pulses in the spectral range 2.8 to 4 µm and the exploitation of these pulses to strong-field experiments like HHG in molecules and bulk solid samples for spectroscopic applications.

The non-liner interaction between ultrashort pulses and gaseous matter leads to the emission of harmonics of the fundamental driving field. This harmonics generation process can be understood by a semi-classical three-step model. In the presence of high intense laser fields, the coulombic potential barrier gets modified and the electrons bound to atoms tunnel through the barrier. The freed electrons get accelerated and recombine with the parent ion. During this recombination, the excess kinetic energy gained during the propagation is emitted as an attosecond burst of high energy photons. The nature of the HHG process allow us to extract molecular structural information with high spatial and temporal resolutions. Analogous to this, HHG is in solids are also getting great interest in several aspects. For example, this technique may allow the all-optical band structure reconstruction of a solid sample, the observation of electron-hole re-collisions in real time, the enabling of quantum logic at optical-clock rate, the possibility of micrometre-scale extreme ultraviolet source development, and the possibility for developing table-top synchrotrons in the future. In solids, both inter and intra band phenomena contribute to HHG. Interband harmonics are generated due to the polarization build-up between the valence and conductions bands in the solids. Intraband harmonics arise from the motion of electrons/holes in the conduction/valence bands, which produces a non-linear current in the presence of the pulse electric field. Here, the harmonic cut-off is proportional to the driving field intensity. To study narrow band semiconductors, long wavelength drivers have been demonstrated as essential tools.

To generate laser pulses in the mid-IR spectral region, we exploit the optical parametric amplification (OPA) process in a second-order non-linear crystal. This is a non-linear optical process occurring in second order non-linear crystals involving the energy transfer between beams at different frequencies. We developed a two-stage OPA using Potassium Titanyl Arsenate (KTA) as amplification medium. The OPA was pumped with a portion of the laser beam from a Ti:Sa laser system which produces pulses with ~10 mJ energy at 1 kHz repetition rate. Figure 1 shows the characterization of the mid-IR OPA. The wavelength tunability of the OPA is from 2.8 to 4 µm. This source delivers pulses with a temporal duration of 52.5 fs (nearly 5 optical cycles at 3.4 µm) which is close to the transform limited pulse duration of 49.8 fs. The overall energy efficiency of the OPA compared to the total pump energy is about 5.9%, which is quite high compared to other OPA schemes pumped with Ti:Sa laser sources reported in the literature.

Using this mid-IR source, two main experiments were performed. In the first experiment, we combine this mid-IR pulses with 800 nm pulses and perform a two-colour experiment in different atoms and molecules in the gaseous phase. In the presence of mid-IR field, we observed a strong change in the HHG spectra, as shown in Figure 2. When the pulses are overlapped in time, the mid-IR component modulates the trajectories of the ionized electrons driven by the 800-nm field and due to the absorption of photons from the mid-IR pulse, non-integer harmonic orders of the 800-nm component were observed. Theoretical simulations using Lewenstein's quantum mechanical model for single atom response show good agreement with the experimental observations.

In the second experiment, we studied the crystal orientation dependence of high harmonics driven in ZnTe samples by mid-IR pulses. The output pulses from the mid-IR OPA are focused into a 500 µm thick ZnTe sample. The polarization of the mid-IR laser is rotated with respect to the axis of the crystal in order to study the angular dependence on the HHG from this bulk sample. The results are shown in Figure 3. Depending on the tilt of the crystal we observed a clear modulation in both even and odd harmonics present in the spectra. The efficiency and spectral shape of the harmonics depend on the crystal structure as well as on the electron trajectories that connect the neighbouring atomic sites in the crystal. Due to this, a possible application of HHG in solids is the retrieval of the interatomic potential and thus the access to the valence electron density and the electron wavefunction in the material.

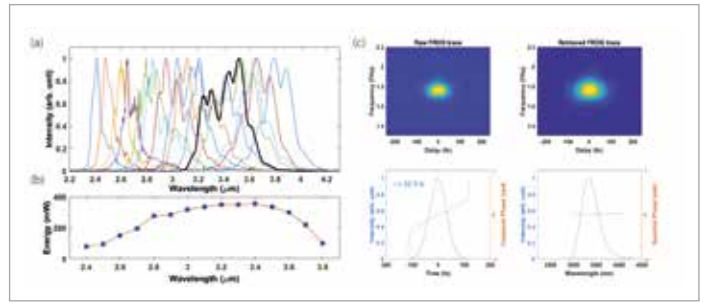

Fig. 1 - Characteristics of mid-IR OPA, (spectral tunability), (b) energy tunability, (c) temporal characterization using FROG.

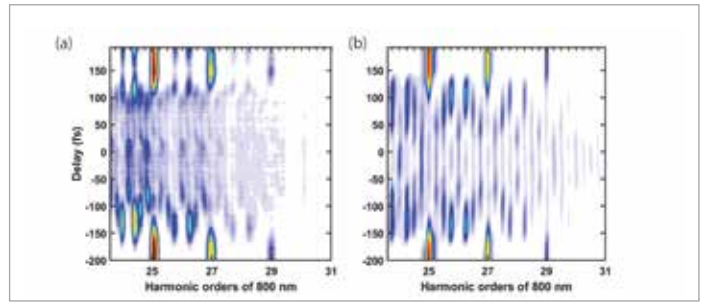

Fig. 2 - HHG spectra using two-colour field, (a) experimental and (b) simulation results

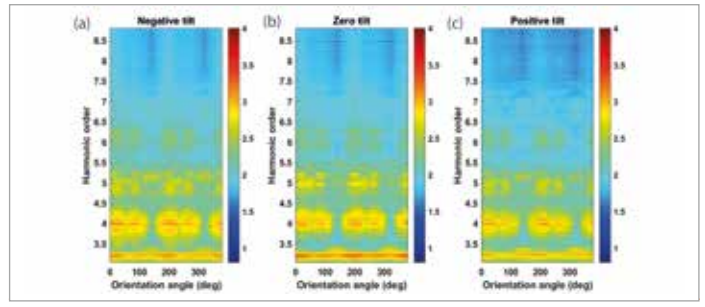

Fig. 3 - Orientation dependent HHG spectra of ZnTe <110> at different tilts of the crystal

VISIBLE AND NEAR-INFRARED FOURIER TRANSFORM SPECTROSCOPY WITH A COMMON-PATH INTERFEROMETER

Antonio Perri - Supervisor: Dario Polli

There are basically two way to measure the light spectrum of an emitting source. The first one is the dispersive technique where the light is divided into its spectral components by means of a grating or a prism and the intensity contribution of each component is measured by a multichannel detector array. The second one is based on the so-called time-domain approach and it employs and interferometer to create two replicas of the incoming light retarded by a variable delay. The interference signal between the two light replicas is measured by a single-pixel detector as a function of the variable delay and the spectrum is retrieved by performing a Fourier Transform (FT) of the measured signal. The dispersive technique is widely used not only in the academic field but also in the industrial one, especially in the visible spectral range, where multichannel detector arrays are not expensive, due to its compactness, and robustness. However, it has some limitations mainly caused by the entrance slit whose width is usually in the order of hundreds of microns. This small entrance affects significantly the light intensity at the detector, dramatically decreasing the sensitivity of the instrument. Moreover, the spectral resolution of the instrument is determined by the entrance slit size and this affect even further the performance of the instrument. This technique having no entrance slit, is not affected by the problems of the dispersive technique and has advantages in term of throughout and sensitivity. Moreover, the spectral resolution of this device does not affect the light throughput and the spectral accuracy is typically much higher. However, in a common double-beam interferometer the two replicas are created by means of a beam splitter and they travel along different paths. This causes problems because it is difficult to maintain interferometric stability between the two different arms of the interferometer, due to environmental vibrations and perturbations. Indeed, for this approach to work, the path length difference must not fluctuate more than λ/10, where λ is the radiation wavelength, and this is the main reason why this technique is de facto restricted to the infrared spectral region and can not be easily used outside laboratory environments. The interferometric stabilization of the interferometer is typically performed by complex and expensive feedback loop system, requiring a reference signal from an He-Ne laser, leading to costly and bulky instruments. The aim of my PhD studies has been to develop a device and several applications in which it was possible to combine the advantages of the two techniques, finally, bringing the advantage of FT-spectroscopy down to the visible and near-infrared spectral regions leading to the development of a compact, robust and cost-effective instrument. The drawbacks of the double-beam interferometers were circumvented by developing and using a Common-Path Interferometer (CPI). In this device the two replicas are not geometrically divided into two paths, but they travel along the same one. Therefore, the two replicas experience the same perturbations from the environment, keeping constant the relative delay between the two down to a sub-attosecond level. In this device, the replicas are divided in polarization rather than spatially and they are delayed by exploiting the birefringence of a uniaxial crystal. Being a CPI, this device does not require any active stabilization and He-Ne laser reference, leading to a compact instrument footprint. The device is unsensitive to environmental vibrations making it an industrial grade device.

During my PhD studies I have applied the device to several different applications showing the potential of this kind of interferometer as an enabling technology across several scientific fields. As a first application, the device was used to measure Excitation-Emission-Maps (EEM) of fluorescent samples as a substitute for the widely used wavelength-scanning systems. The CPI was also coupled to a confocal microscope in an international collaboration between Politecnico di Milano, University of Copenhagen and the Technical University of Munich. The device was tested down to the ultimate sensitivity limit leading to the measurement of the first ever measured EEM of a single molecule at room temperature. We studied several molecules with the same chemical structure being spreaded in different position of the microscope cover glass, noticing a great variability of their fluorescence behavior. This is because down to the nanoscopic environment each single molecule despite being chemically equivalent to the others feels a different nanoscopic environment. Therefore, this work paves the way toward the future use of single molecule as sensor for the nanoscopic environment.

The CPI being a high throughput device was applied as a replacement for monochromators in the collection path of a fluorescence spectroscopy setup to measure fluorescence Time-Resolved-Emission-Spectra (TRES). This was done by coupling the interferometer to a Single Photon Detector (SPD) and a Time Correlating Single Photon Counting (TCSPC) system. In this way, it was possible to combine in a compact and easy to use system, the spectral resolution given by the interferometer with the time resolution of the TCSPC system down to a nano-molar sample-concentration level.

Being a polarization sensitive device, the CPI was used to measure the chiro-optical activity of chiral samples, thus their ability to rotate and change the polarization state of the incoming light. Differently from commercial devices, the developed setup does not require the use of a photo-elastic modulator and a lock-in amplification system greatly reducing the cost and size of the instrument. Moreover, it was possible to measure simultaneously the circular dichroism and circular birefringence spectra. The CPI was used not only for single point spectral measurement but also to measure hyperspectral images, thus, developing a device capable of recording the light spectrum coming from each point of a scene of interest. As an example, this hyperspectral imager was applied in cultural heritage to assure authenticity of artworks and in remote sensing to detect the conservation level of buildings.

Finally, the interferometer was also used to measure the complex vibrational susceptibility using the Stimulated Raman Scattering effect and to measure Pump-Probe spectra.

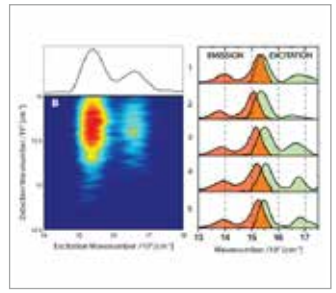

Fig. 1 - (LEFT) Excitation-Emission Map (EEM) of a single molecule of terrylene diimide molecules embedded in Polystyrene; (RIGHT) Emission and Excitation spectra as extracted from EEM's of several different single molecules with identical chemical structure, but in different nanoscopic environment.

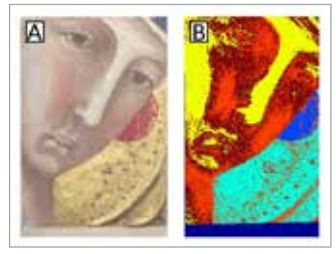

Fig. 2 - (LEFT) an RGB color image of a painting generated from its hyperspectral image; (RIGHT) segmented image in pseudo-colors of the same painting after automatic k-means cluster analysis; (RIGHT)

TIME DOMAIN NEAR INFRARED SPECTROSCOPY FOR MUSCLE AND CEREBRAL OXYGENATION MONITORING

Ileana Pirovano - Supervisor: Rebecca Re

Time domain (TD) functional near-infrared spectroscopy (fNIRS) is a non-invasive optical technique that allows to investigate the oxygenation status over time of different biological tissues, e.g. brain cortex and skeletal muscles. In human body, the oxygen is delivered to the tissues through the blood circulation, where the oxygen molecule is bound to the haemoglobin protein. Consequently, two different species can be identified: the oxygenated haemoglobin (O_2Hb) and the deoxygenated one (HHb). This two species show different absorption spectra in the spectral range 600 – 1100 nm (therapeutic window). Hence, injecting pulses of light at two wavelengths at least, usually around 690 nm and 830 nm, it is possible to exploit the diffusive properties of biological tissues and collect the re-emitted photons after they underwent different absorption and scattering events. At these wavelengths, the two haemoglobin species can be considered as the only chromophores contributing to the absorption of photons, while the scattering is mainly due to the structure of the tissue. O_2Hb and HHb concentrations can thus be non-invasively retrieved through the estimation of the optical properties, namely the absorption coefficient (μ_a) and the reduced scattering coefficient (μ'_s), exploiting the Lambert Beer's law.

The optical properties of the biological tissues can then be estimated fitting the obtained reflectance photons DTOFs with physical models derived from the Radiative Transfer Theory under the Diffusion approximation. A crucial step in the fitting procedure to perform quantitative measurements is taking into account the Instrument Response Function (IRF) through convolution/deconvolution strategies. In addition to the haemoglobin concentrations, derived haemodynamic parameters can be obtained, i.e. the total amount of haemoglobin (tHb), which is the sum of O_2Hb and HHb and represent the blood volume investigated, and the oxygen saturation (SO_2), defined as the ratio between O_2Hb and tHb.

In my thesis, I focused on the development of TD-fNIRS medical devices for studies on brain and skeletal muscles and their application directly in clinical measurements campaign on patients.

The first part of my thesis work refers to some improvements I did to an already existing in-house build TD- fNIRS device in order to employ it in a clinical environment. Particular attention was given to the implementation of custom-made 3D printed probes to hold the optical fibres used for inject and recollect light into and from the tissue, guaranteeing easy, fast and repeatable placement, no discomfort for the subject and avoiding movement artefacts. In Fig.1, an in house-built TD-fNIRS medical device and the probe suitable for muscle measurement is reported. Actually, the design was a non-trivial task. Geometrical constraints and the selection of the suitable 3D printing material for diffuse optics applications needed to be considered.

Moreover, an approach of IRF acquisition exploiting the same reflectance configuration of the optical fibres during tissue measurements was validate and implemented, leading to faster and more accurate acquisitions.

After these technical improvements, a series of pilot studies on healthy volunteers have been carried out in order to assess the best procedure to analyse the time-resolved fNIRS data, according to the different tissue investigated, i.e. brain or skeletal muscle. In fact, both brain and muscles can be reached by light only after it has travelled through an upper layer, the skull for the brain and the skin plus the subcutaneous fat for the muscle. Hence, these upper layers contribute to the signal acquired and have to be taken into account. On the contrary, brain and muscle differentiate for different aspects, such as the amplitude of the changes of the haemoglobin concentrations during tasks, which is lower for the brain, and for the structure, i.e. their optical properties and their relative variations are different. Skeletal muscles present a high oriented structure since are composed by fibres that can change orientation during exercise. I work in this thesis to establish the better method to correctly consider all these aspects in retrieving tissues optical properties.

Moreover, two clinical studies were conducted during my thesis. The first one was performed in collaboration with *ASST Sacco Hospital* and *Unit of Medical Statistics and Biometry, Fondazione IRCCS Istituto Nazionale dei Tumori* in Milan on 118 subjects, divided between healthy volunteers and patients affected by glaucoma. Glaucoma is a multifactorial optic neuropathy characterized by a progressive loss of retinal ganglion cells. In experimental MRI studies, also degenerative changes in the visual cortex have been found. Hence, in a panorama of gold standard clinical examinations for glaucoma diagnosis, we used the TD-fNIRS to investigate the effect of this pathology on the visual cortex during a visual stimulus (reversal checkerboard). From preliminary results of the variation of concentrations of O_2Hb and HHb during the task, control subjects show a higher cerebral activation (higher signals amplitude changes) with respect to glaucomatous patients.

A second clinical study has been performed in collaboration with the *ASST Gaetano Pini* in Milan and *CNR STIIMA* institute to monitor the effect of rehabilitation on 100 patients after femur fracture and surgery. The study is still ongoing and has the aim to quantify changes of *vastus lateralis* haemodynamic parameters measured at two different time points during the rehabilitation of each patient.

Finally, the last part of my thesis has been dedicated to development of a new TD-fNIRS medical device, which exploits high power laser sources. Light pulses at two different wavelengths are injected at the same time in the same location without the switching time limitation of a mechanical optical switch. Moreover, for the detection lines, cooled hybrid photomultipliers tubes have been chosen in order to guarantee a low dark count rate and a high SNR, even for fast acquisition. In fact, for particular applications (e.g. brain resting state oscillation monitoring or deep muscles/organs investigations), it would be necessary to increase the measurement sampling rate, usually set at 1 Hz for standard measurements, and the depth sensitivity still guaranteeing a high SNR. For this purpose, a technological improvement of the currently existing instrumentation is necessary.

The new high power device have been tested and validated according to standardized protocols to assess the performance of a TD device, while a sampling rate of 200 Hz has been reached in dedicated measurements. Thanks to the increased SNR, I also tested the possibility of performing measurements at 5 cm of interfiber distance, increasing also the penetration depth.

Fig. 1 - In-house built TD-fNIRS medical device and custom 3D printed probe for skeletal muscle measurements.characterization using FROG.

ELECTRONIC AND MAGNETIC PROPERTIES OF THIN AND ULTRA-THIN Co(Ni)-TPP MOLECULAR FILMS ON Fe(001)-*p*(1 × 1)O

Madan Sangarashettyhalli Jagadeesh - Supervisor: Alberto Calloni

In the last decade, organic semiconductors have been studied more extensively in order to optimize their performances in hybrid organic/inorganic devices. Organic molecules are thought to be the best candidates with respect to inorganic materials because of their flexibility and tailorability of physical, electronic and transport properties. Promising results in this research area of applied physics have been exploited in the development of high-performance devices for the advancement of commercial devices like sensors, solar cells, smartphone screens, etc.

Now a day's molecular magnetism has emerged to manipulate and control the spins of single atoms or molecules for the spintronic application, where the electron spin is used to carry information rather than the charge. One way to exploit these molecules is by growing them on a substrate, so that a fine control over the molecular growth, and their physical and chemical properties can be achieved. This depends on several factors, like their positioning on the substrate, as well as their electronic structure.

In organic based devices, the interaction between the molecular film and the substrate plays a significant role in charge injection. This may affect the device performance. However, the growth or adsorption of these molecules on a metal substrate can lead to chemical reactions, hybridization of the electronic states. From the magnetic point of view, this interaction between magnetic molecules and conducting substrate can result in a strong exchange interaction.

In recent times metal tetra phenyl porphyrins (M-TPP) molecules are getting much attention in the scientific community because of their physical and chemical properties, thermal stability and many advantages like its characteristics like planar ring like structure with a tetra pyrrole ring, called inner cavity, enclosed by four phenyl groups. The flexibility of choosing a different metal ion in the center allows to influence the properties of porphyrins, for instance by exploring different configurations of the molecular spin units. The functional groups and the type of metal ion can have a strong influence over the molecular reactivity. This possibility makes these molecules well suited for growing them on ferromagnetic substrate, which later can be exploited in order to build a next generation organic spintronic device.

The porphyrin planar structure and feasibility of tuning their peripheral groups allows them to assemble flat on the substrate. The growth of these molecules has been mainly focused on metal substrates but recently there has been an interest to reduce the interaction with the substrate and obtain a certain degree of decoupling, in order to preserve the molecular properties. This has been achieved by growing them on organic substrates or low interacting materials like Au. It is also shown that surface passivation is a one of the suitable strategy to obtain the molecular decoupling. This was attempted earlier by growing the organic molecules on passivated metal surfaces like graphene and ultra-thin metal oxides. This reduced interaction have the possibilities to grow magnetic molecules having a localized net magnetic moment on a passivated substrate so that a fine magnetic ordering can be obtained by choosing a ferromagnetic material. In this view, it is required to develop a strategy and a model to describe and characterize the organic/metal system. In particular, a specific focus should be given to their interface to determine the organic molecular properties. There are several adequate techniques used to investigate the interface of this system. In particular, area averaging surface sensitive spectroscopic techniques likes low energy electron diffraction (LEED) to investigate the structural arrangement, X-ray Photoemission (XPS) for elemental characterization, valence band photoemission (PES) and inverse photoemission (IPES) for occupied and unoccupied electronic states and also the magnetic properties by using SR-PES and SR-IPES techniques. The advantage of PES and IPES techniques is that they can also be made sensitive to the spin of the electron by proper modification of the experimental apparatus. For example, by exploiting the classical Mott scattering asymmetry it is possible to measure the spin polarization of the photoemitted electrons, and to obtain the magnetic properties of this hybrid organic-FM system.

We used Fe ferromagnetic substrate for the growth of Co(Ni)-TPP molecules, where the surface passivation was obtained by adopting a strategic method by passivating the Fe substrate with one atomic layer of oxygen called the Fe(001)-*p*(1 × 1)O, because it was proven that this passivation of Fe substrate produces a better morphology and enhanced magnetic moments. The LEED analysis of Co(Ni) TPP molecular film grown on ultra-thin Fe(001)-*p*(1 × 1)O shows a commensurate superstructure at the monolayer coverage. That is the molecules are arranged every 5Fe lattice steps thus forming a square superstructure. While, the core level characterization of this system shows that, when the molecules are deposited on Fe(001)-*p*(1 × 1)O shows reduced interaction with the substrate. Followed by this we also proved that this passivated Fe substrate tends to preserve the molecular electronic states by using PES and IPES techniques. This finding allowed us to characterize the magnetic properties of these molecular film.

The magnetic characterization by using SR-PES and SR-IPES measurement shows some polarization at their monolayer coverage but we found that our results were affected by the substrate contribution. We showed a strategy to characterize the molecular electronic states which are far away from the E_F so that the substrate contribution is negligible. This shows that Co-TPP molecules are magnetically ordered at their monolayer coverage, while Zn-TPP and Ni-TPP are not magnetically ordered. This is due to the fact that the Zn-TPP and Ni-TPP molecules have zero spin state, while Co-TPP has ½ spin state and the unpaired spin is localized to the central metal ion of the M-TPP molecule. This magnetically ordered surface can be used for future magnetic storage system where each molecule can be exploited as a magnetic bit.

ADVANCES IN BROADBAND TIME DOMAIN OPTICAL SPECTROSCOPY OF HETEROGENEOUS DIFFUSIVE MEDIA

Lanka Sri Rama Pranav Kumar - Supervisor: Antonio Pifferi

The study of photon propagation in highly scattering media (diffuse optics) is a very powerful tool capable of noninvasively investigating different kinds of diffusive media. It has a wide range of possible applications ranging from biomedical imaging and spectroscopy to pharmaceutical quality check, wood and art related testing and the food monitoring. Typically, the measurement scheme includes a light source and a detector placed at a known distance on the medium, and the acquired data is processed using diffusion models to extract the optical properties (absorption, scattering) of the medium under investigation. Based on the type of source used, instruments are classified into three modalities: Continuous Wave (CW), Time Domain (TD) and Frequency Domain (FD). Of these, Time Domain Diffuse Optical Spectroscopy (TD-DOS), which is also the technique used in this thesis, is known for its relatively better information content. Furthermore, measuring the optical properties of diffusive media over a wide spectral range allows for quantification of tissue constituents (chromophores) and gives crucial information on the microscopic structure of the medium.

While there is significant development in the field, it is still troubled by two critical issues; 1) the need for an accurate retrieval of optical properties when the medium is heterogeneous/layered and 2) a need for the standardization of performance assessment of instruments. This work mainly deals with exploiting TD-DOS to resolve these issues.
As a first step in this direction, we develop instrumentation to perform automized multi-distance broadband TD-DOS and used it for the broadband validation of an analysis model for layered/heterogenous media. The extra dimensionality provided by the 'multi' distance measurements aid in improving the accuracy of the retrieved optical properties. This instrument was then employed in some pre-clinical studies to monito non-invasively the human abdominal region or the human forehead which demonstrate a layered geometry.
In the case of the abdominal region the subcutaneous adipose/fat tissue, sandwiched between the superficial skin layer and the underlying muscle layer, was the tissue that we aimed to monitor non-invasively. This could be immensely valuable for the non-invasive detection of obesity and related pathologies. Similarly, in the case of the human forehead region, the aim was the decouple the influence of superficial layers of scalp and skull in the accurate retrieval of the optical properties of the underlying brain tissue, which are widely used to non-invasively monitor brain functionality and physiology. Also, simulations were performed to understand and correct for, the influence of the superficial scalp and skull layers and their geometries on the retrieval of optical properties and oxygenation of the brain tissue.

The diffuse optics group at Politecnico di Milano, is well known for its contribution in the development of performance assessment (PA) protocols for diffuse optical instrumentation. This is particularly necessary since these instruments are widely used in clinical scenarios and lack of PA could lead to wrongful results and diagnosis. In this spirit, a multi-laboratory exercise, involving 29 diffuse optical instruments from 11 institutions across 6 European countries, aimed at performance assessment of diffuse optics instruments was performed. As a first step performance assessment tests were performed on the instruments based on 3 well accepted protocols. The exercise was divided into 3 actions with the first action nearing completion. At this level, we have an inter laboratory comparison of the results obtained from the above-mentioned protocols. The results from one of the tests is presented in **Fig.1**. Here we compare the optical properties retrieved from the various instruments enrolled in the exercise, when used to measure an optical test sample also known as a phantom. Future actions aim at deploying these measurements onto an open data repository and investigate common analysis tools for the whole dataset.

Further, broadband TD-DOS was employed in a very interesting application aimed at monitoring Radio frequency (RF) based thermal treatment of tissue in real time. RF based thermotherapy is s a medical procedure in which dysfunctional tissues or tumors present in the body are ablated using the heat generated from a medium frequency alternating current. This technique has tremendous potential in the field of oncology. To avoid the risk of over or undertreating the target location, the electric or ultrasound characteristics of the tissue are generally monitored. These parameters however are not always reliable and there is a need for a more accurate monitoring of the procedure. Using the aforementioned instrument, we tried to monitor the broadband optical properties of ex-vivo bovine tissue when subject to thermal treatment and its usability as a complimentary alternative to monitor the treatment. **Fig. 2** shows the results for ex-vivo bovine liver when it is thermally treated at 105°C. In total, the absorption spectrum experienced five key variations with treatment time while the reduced scattering spectrum sustained two key variations. In the absorption spectrum, a red shift of the hemoglobin peak (@760nm) and a blue shift of the water peak (@970nm) was observed with significant change in the peak widths. A new peak around 840nm and a valley around 910nm were observed that intensified with treatment. A fifth changein the absorption spectrum was an increase in the absolute value of the property below 910nm (water peak region). The reduced scattering mainly experienced a drastic increase in the intital part of the treatment followed by a gradual decrease. These changes could be arising due to the multiple physical and chemical changes occurring in the tissue with thermal treatment like, denaturation of protein, carbonization or charring, evaporation and change in the chemical nature of primary tissue constituents like a conversion of hemoglobin to methemoglobin. While further research is necessary to understand the origin of every observed trend, these results demonstrate that time domain DOS could give multiple reliable biomarkers to monitor and therefore guide RF based thermal treatment in real time.

All these studies show the width and the depth of advancements and range of applications of TD-DOS. Future directions should be aimed mainly at exploiting the technological advancements to develop compact, standardized multimodal, application specific TD-DOS devices.

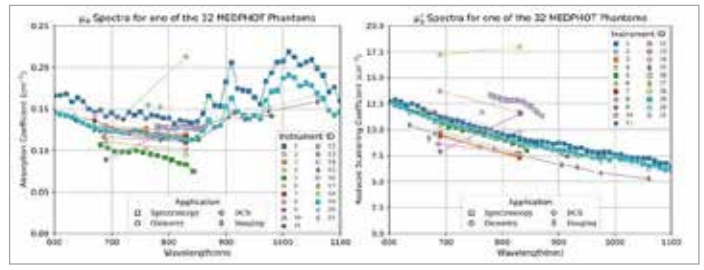

Fig. 1 - The absorption and reduced scattering coefficient spectra obtained by the different instruments on one of the 32 phantoms as a part of the first protocol: MEDPHOT. The legend corresponds to a unique identifier and the application of each instrument enrolled. The results of this test are shown here for only 21 out of the 29 instruments.

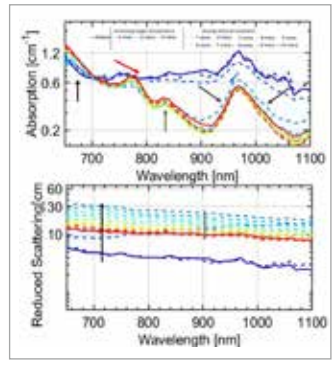

Fig. 2 - Broadband absorption (top) and reduced scattering coefficient (bottom) spectra of bovine heart tissue during the RF based thermal treatment at the two temperatures. The colored arrows indicate key spectral changes observed.

LOW VOLTAGE PRINTED ORGANIC ELECTRONICS

Elena Stucchi - Supervisor: Mario Caironi

Two of the most significant advances that characterized the twentieth century are the development and diffusion of synthetic polymers and the evolution of electronics. The first started with the discovery of polyethylene in 1939, followed by the discovery of isotactic polypropylene by Natta in 1954, and has seen a steady increase during the last decades, covering needs in a wide variety of fields such as packaging, automotive, and many others. The electronic age, on the other hand, started with silicon, from the invention of the transistor in 1947, to the development of integrated circuits and the tools for microfabrication, which have led to the widespread use of this material for a variety of applications.
Most of the known plastic materials act as dielectrics. In 1954, organic conducting materials have been synthesized for the first time, and the possibility to have conducting and semiconducting polymeric materials lead to the realization of organic electronic devices, with the first organic field effect transistor in 1987. The main advantages of carbon-based devices compared to standard silicon ones are related to their mechanical properties, being flexible and ductile, and in some cases even stretchable and conformable, as opposite to the brittle crystalline silicon, their lightness, biocompatibility and optical transparency. Additional advantages are related to the fabrication techniques, which are solution-based methods that allow for an efficient use of raw materials, limit the required thermal budget and are easily customized thanks to their digital nature, leading to low-cost, large-area compatible and highly efficient production, with improved environmental friendliness compared to silicon devices.
Plastic electronic devices can be used for a wide variety of applications such as flexible and rollable displays, RFIDs (radio-frequency identification tags), wearable systems, intelligent packaging and textiles, interactive surfaces, disposable diagnostic devices and sensors, to be employed in the fields of security, diagnostics, automation, health-care and many other. In this thesis, focus will be on Organic Field Effect Transistors (OFETs), which form the building block for the development of the next generation of thin film electronics.

One of the main limits hindering the success of organic electronic circuitry is related to the operating voltage. These devices need to be portable, to allow for an easy integration into consumer products, and as such should be powered by energy harvesting devices, such as plastic solar cells and/or thin film batteries. The maximum operating voltage and power consumption allowed are low, limited to few volts. Most of the devices presented in literature, on the other hand, have operating voltages of tens of volts, which strongly limit their portability and diffusion on the market. A reduction of this parameter is thus a key enabler toward the diffusion of organic electronic devices in the consumer market. During the first part of this work, this issue has been tackled, with the implementation of a high-capacity dielectric bilayer, composed of PMMA and parylene, and its integration in flexible OFETs and complementary integrated circuits. The yield of fabrication, the uniformity and the mechanical stability of the printed complementary OFETs have been tested, and the first demonstration of printed, transparent, flexible and all-polymeric ring oscillators and D-Flip-Flops operating at voltages as low as 2V has been presented.

Flexible electronic devices play a crucial role in the transition from rigid silicon-based electronics to applications with more appealing mechanical features. In recent years, the field expanded even further with the realization of devices with ever increasing mechanical characteristics, such as ultra-flexibility and conformability, and the creation of the so-called epidermal or imperceptible electronics. Devices have a thickness lower than 10µm and improved lightness and form factor, and are thus capable of adhering to irregular surfaces. The realization of ultra-flexible and biocompatible electronics is of great interest for the healthcare industry, with the possibility of developing conformable devices for a wide variety of applications. In this work, a strategy for the realization of ultra-flexible electronic circuitry is presented, employing ultra-thin parylene films, with a thickness of 2µm, both as substrate and as encapsulation layer. In this way, the first demonstration of printed, all-organic, transparent and ultra-flexible complementary OFETs and inverter has been realized. The mechanical performances of these devices have been analyzed with two main tests, rolling and crumpling, and no significant loss in performances has been recorded.

Now that organic electronics is approaching its commercial phase, problems and challenges not yet considered need to be addressed, and one of them deals with the disposal of broken and old devices. In order to tackle this issue, biodegradable electronics has been proposed, with the employment of biodegradable materials for the realization of environmentally friendly and disposable electronic devices. In this way, not only the amount of e-waste and plastic waste generated is reduced, but there is also the possibility to widen even further the field of organic electronics, with the realization of medical applications, environmental sensors, food packaging, use-and-throw-away devices and security applications. In the last part of this work, this new field has been explored, with a review of the materials for organic electronics and the strategies to be used in the transition from recyclable to biodegradable devices. In the first step toward the realization degradable and compostable electronic devices, the realization of printed OFETs on a Mater-Bi substrate is presented, with the integration of organic transistors onto a commercial degradable film.

The results presented in this thesis, together with all the achievements reported in literature in the last decades, show the feasibility of organic electronics as a main player for the realization of flexible and low-cost electronic devices. Some issues are still to be discussed, and obstacles need to be overcome before plastic electronic devices could be integrated into consumer products, but the path is clear and the widespread integration of organic electronic devices into consumer products will soon become reality.

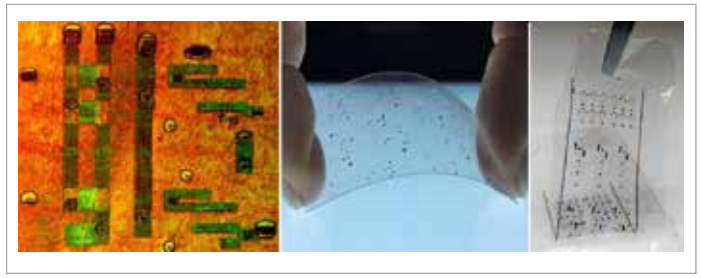

Fig.1 - (left) Optical microscope image of a printed all-organic D-Flip-Flop on plastic substrate, (center) printed organic devices onto a flexible plastic film, (right) ultra-flexible printed OFETs and circuits.

INVESTIGATION OF CHARGE TRANSPORT PHENOMENA IN POLYMER MONOLAYERS

Anupa Anna Thomas - Supervisor: Mario Caironi

Over the past few decades, developments in high mobility donor–acceptor semiconducting polymer-based field effect transistors (OFET) have favoured the enhancement of performances in printed and flexible polymer electronics. These discoveries have led to the realization of such devices entering the market of flexible and wearable electronics which are employed in everyday life as well as integration into complex biological systems. The possibility to fabricate solution processable devices in general opens an arena of applications with an additional range of curiosities associated with the device physics which drives the research in this field to grow forth. A wide range of investigations have been carried out in the last 35 years on semiconducting polymers for their application in roll to roll, flexible and conformable devices. In order to improve the numbers for various figures of merit like mobility for instance, various steps are followed like controlling the deposition techniques, doping, substrate treatments, so on and so forth. However, structure-transport property relationship is still intensively investigated, with the aim of providing a rationale for further development of the field.

One of the most extensively studied copolymers is Poly{[N,N′-bis(2-octyldodecyl)-naphthalene-1,4,5,8-bis(dicarboximide)-2,6-diyl]-alt-5,5′-(2,2′-bithiophene)} (P(NDI2OD-T2)), an n-type conjugated copolymer system that stands out yielding mobility values (> 1cm^2/Vs, while displaying a considerable amount of disorder. So far, the studies have suggested how intra-, inter- and supra-molecular features, like chain elongation, alignment or entanglement can have drastic effects on charge transport. In order to elucidate how such different aspects determine the formation of efficient carrier percolation pathways, in this work we have exploited the pre-aggregation properties of P(NDI2OD-T2) for controlling the formation of sub-monolayer sparse networks of polymer fibrils with a different degree of substrate coverage, up to a uniform thin film.

We have demonstrated a new and simple outlook on the understanding of polymer aggregation behavior and fibril growth for the investigation of transport properties without the use of complex methodologies or processing techniques. The results we have accumulated helps to extend the rich database we already have on P(NDI2OD-T2). Even though it is an extensively studied material, our results play an important role in defining the importance of certain parameters like orientation order of aggregated phases when it comes to a different regime of transport like the monolayer and sub-monolayer regime of charge carrier percolation.

In our experimental work, we first tune the fibril networks to make them reproducible and reliable for investigation with several trials of substrate surface treatments and solvents .We then move on to incorporating them into the active layer of an OFET. We demonstrate a non-ideal OFET with sparse networks of polymer to an ideal OFET with fully covered network and estimate the percolation threshold of coverage for the charges to start their transport in such systems. We explore the different regimes of transport where we see a linear increase in current to a regime where the currents not scaling much with coverage hinting how the charges are relying on more underlying parameters than just the coverage/material at stake.

From our GIWAXS results, we demonstrate how a face on orientation for the fully covered film transits to an onset of edge on orientation probably a bimodal distribution of orientations at 83% coverage where there are areas of both a monolayer and bilayer. However, we see a strong crystallinity until 40% coverage which is a pure monolayer that is edge on which is lost at 27% of coverage of polymer. This point is also where the orientation order (OP) drops drastically. At this point, we wrap up our investigation by demonstrating how the order-disorder in these networks change with coverage which is responsible for the variation in currents extracted from various networks.

This motivates the investigation to explore more variables that can affect the transport of charges like the orientation of fibers based on morphology and stacking or crystallinity available in the networks. We mainly discuss the importance of how the orientation order for coverage/material is higher for the networks that showed higher currents/conductance, implying that it has a strong role in pushing charges through even when they differ from each other by double the coverage of polymer. The two films which shows similar currents differ in coverages yet show an order of current which is comparable. We demonstrate how an orientation order parameter (OP) of higher than 0.8 ensures a better conductivity which means that the charges are path selective based on the degree of orientation available to them.

The next crucial evidence we bring into light is the spectroscopic traces of charge carriers in the film which was extracted from the UV-Vis spectra which directly hints the amount of aggregates in the film and a general idea on how much order -disorder can be seen. Charge modulation spectroscopy was the next step we undertook which is essentially resolving the spectra to derive more information on the mobile charges that take part in the real charge transport in the OFET. From the main bleaching peaks of CMS, we see evidences of how the CT states lose their intensities and how the inter-intra molecular transport changes with changing the available coverages. Through this analysis, we acquire more hints on how there could be a different stacking in lower coverages compared to a fully covered film and essentially enter a region of lower crystallinity or more disordered regimes as we reduce the amount of coverage/material of P(NDI2OD-T2). The progresses reported in this work provides a fresh perspective on charge transport in polymer networks and the various factors involved in selection of pathways for percolation by the charges. This knowledge can come in handy to the further advancement in improving the current performances of organic electronic devices.

We further employ the acquired knowledge on how to form fibrils which is a monolayer thick and the result of doping them and how essentially it can lead to forming a depletion-mode operating organic field effect transistor. We also demonstrate how it is useful to have a thin layer of organic material rather than a thick one when it comes to controlling the device characteristics like threshold voltage V_{th}. By changing the amount of dopant concentration in the polymer material from 1% to 5% by weight, we show how it is possible to shift the threshold voltage in a controlled manner to negative voltages and thus realizing a depletion mode OFET. By doing so, we also open an opportunity for P(NDI2OD-T2) monolayers to be employed in one of the basic building blocks of logic circuits which is an inverter. We also demonstrate the use of these devices in a Zero-V_{GS} depletion load inverter. Here, we employ the doped monolayer transistor and the 'load' and the undoped (pristine) transistor as the 'driver' unit. We also show a working device measured at different V_D to demonstrate it is operation as an inverter. Additionally, we carry out Charge Modulation Spectroscopy (CMS) in the doped monolayers to investigate if there is a difference in transport when a pristine layer is doped with nDMBI. We confirm that the charges see the same states for intra and inter-molecular transitions as in a pristine monolayer. Thus, it does not produce any kind of hindrance or traps when it comes to charge transport. This work opens the door for having a single semiconductor for the whole logic circuitry where parts of the logic can be doped and the others pristine for inverters instead of going for the usual CMOS inverters with the need for p and n type semiconductors.

ULTRAFAST SPECTROSCOPY OF 2D MATERIALS AND RELATED HETEROSTRUCTURES

Chiara Trovatello - Supervisor: Giulio Cerullo

The discovery of graphene (GR), a two-dimensional (2D) hexagonal sheet of carbon atoms exfoliated from graphite for the first time in 2004, has triggered a revolution into the research of low-dimensional materials. GR possesses astonishing properties, like remarkably high electrical mobility $\mu > 15000$ $cm^2V^{-1}s^{-1}$ (10 x GaAs), high thermal conductivity (10 x Ag) and high mechanical strength (higher than steel!). Moreover, GR is a gapless semimetal with an ultrabroadband, almost featureless and constant absorbance of ~ 2.3% per atomic layer, and it is also very light and flexible, opening up the possibility to be integrated not only in novel photonic and optoelectronic components, but also in wearable and flexible devices.

Along with GR, transition metal dichalcogenides (TMDs) constitute a class of crystalline 2D materials which can be reduced to the form of monolayers. TMDs are MX_2 compounds, where each metal atom M (Mo, W, etc.) is sandwiched between two chalcogens X (S, Se, etc.). Therefore, each single layer (1L) of TMD consists of three atomic layers, resulting in a thickness ~ 6.5 Å. Since in bulk TMDs the constituting single layers are kept together by weak van der Waals (vdW) forces, 1L-TMDs can be exfoliated from their bulk counterpart. Indeed, the most interesting properties arise when the system undergoes a transition from bulk to 1L configuration. The breaking of inversion symmetry induces an indirect to direct bandgap transition, making 1L-TMDs truly 2D direct bandgap semiconductors, with near infrared-visible gaps.
Excitons, bound electron-hole pairs, are the main photoexcited species in 1L-TMDs, being stable even at room temperature. Different from standard 3D semiconductors, like Si or GaAs, whose exciton binding energy (E_b) is ~ few meV, in TMDs the extreme quantum confinement gives rise to an abrupt reduction of the Coulomb screening, increasing the electronic bandgap as well as the E_b, which can be as high as 0.5-1eV. Excitonic transitions, namely A, B and C, strongly renormalize the optical absorption spectra of 1L-TMDs and they largely determine the optical/electronic properties of such low-dimensional materials. For this reason, due to their peculiar band structure 1L-TMDs constitute a unique platform for studying exciton physics in semiconducting systems at room temperature.
Thanks to the weak interlayer vdW forces, 2D materials can be stacked together forming the so called vdW heterostructures (HSs) (Fig.1a), bypassing any lattice mismatch limitation. vdW heterostructures can be formed by exfoliation and stacking process, or by growth of the different constituting 2D layers, directly one on top of the other. The possibility to create an innumerable quantity of new tunable quantum materials which are nanometer thick is opening new fascinating opportunities in the field of photonics and optoelectronics (photodetectors, LEDs, plasmonic devices, sensors, tunneling devices, etc.), and also integrated linear and nonlinear optics.
Understanding the physical mechanisms at the heart of the non-equilibrium optical response of 2D materials is of paramount importance, not only for fundamental knowledge, but also for integrating these new materials into next-generation technology. Many of the processes occurring at the nanoscale after the photoexcitation of the system, like bandgap renormalization, bright/dark exciton formation, hot carrier thermalization, charge transfer, intra-inter valley scattering, are driven by electron-electron and electron-phonon interactions, whose characteristic timescale ranges from tens of femtoseconds (fs) to hundreds of picoseconds (ps). In order to reveal and study such processes, both in frequency and time domain, in this PhD activity I have exploited ultrafast broadband transient absorption and reflection spectroscopy with extremely high temporal resolution, i.e., sub-20fs.

In the last years, the transient optical response of TMDs has been extensively studied, but the typical temporal resolution of the experiments (i.e. ~ 100 fs) has not allowed to clearly resolve those physical processes, like exciton formation dynamics, which are supposed to occur on a much faster timescale. In the first project we overcome this limitation by pushing the temporal resolution below 20 fs. From the rise time of the transient dynamics of A (1.88eV) and B (2.03eV) excitons, we reveal that the timescale for the exciton formation process ranges from ~15 fs, when carriers are excited close to the excitonic transitions (2.35eV), to ~35fs, when we inject carriers at higher energies (2.75eV). Our experimental observation is consistent with a scenario where initially excited free carriers relax towards lower energy states and finally form the exciton via Coulomb interactions (Fig.1b).

The second project focuses on the investigation of coherent optical phonons in 1L-MoS_2, which has two Raman active optical phonon modes: A'_1 (out-of-plane) at 406cm^{-1} and E' (in-plane) at 387cm^{-1}. Upon exciting 1L-MoS_2 with a sub-20-fs pulse, we detect strong coherent optical phonons modulating the electronic relaxation across the whole absorption spectrum of 1L-MoS_2 (1.8-3.1eV), but predominantly around the C exciton. This coupling is further increased when the pump photon energy is also tuned around the C exciton. The oscillation period of 82fs matches the period of the A'_1 mode, while no signature of the E' mode is detected, revealing that the generation mechanism of coherent phonons in 1L-TMDs is not impulsive stimulated Raman scattering (which activates all the optically active modes), but is instead displacive excitation, which indeed forbids the excitation of E modes for symmetry reasons.

The third project investigates the ultrafast charge transfer dynamics in GR/1L-WS_2 HSs. By selectively exciting GR with infrared light, with energy below the WS_2 bandgap, we observe an ultrafast signal, appearing within 20 fs across WS_2 resonances. From the strongly nonlinear intensity dependence of the signal we reveal its origin as due to hot electron/hole transfer.

In the fourth project, which I have been working on from March to September 2019 during my stay as a visiting PhD at Columbia University, we demonstrate single-pass optical parametric amplification in 1L-TMDs, also providing the absolute efficiency and the polarization of such second order nonlinear process.

All the described experimental findings are fully supported by ab initio calculations and numerical simulations.

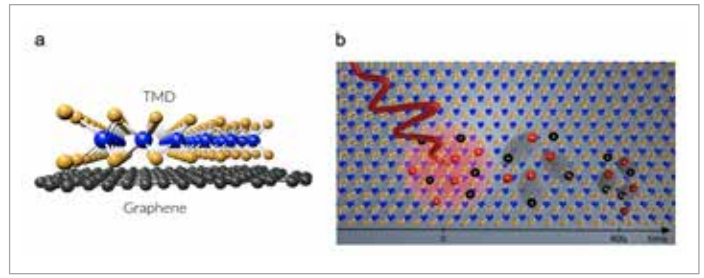

Fig.1 - (a) graphic representation of a van der Waals heterostructure formed by a 1L-TMD and a graphene sheet; (b) sketch of the exciton-formation experiment: an ultrashort pulse (sub-20fs) excites free electron hole pairs, which collapse into tightly bound excitonic states in few tens of fs.

NONVOLATILE CONTROL OF SPIN AND CHARGE TRANSPORT IN FERROELECTRIC RASHBA SEMICONDUCTORS

Sara Varotto - Supervisor: Christian Rinaldi

Artificial intelligence is nowadays growing more and more in importance and its unprecedented potential is involving every aspect of our society, including health. Just few months ago, researches from CEA in Grenoble (France) created a whole-body exoskeleton that allowed a tetraplegic patient to move and walk again using his mind, which was connected to a neural network with learning capabilities. This is just an example of the emerging success of neural networks, which although is now encountering a serious issue. For instance, circuits with about 104 processors and hundreds of kW are required even for simple operations (e.g. recognize a cat from one image). As X. Xu, "CMOS scaling does not offer much help in meeting the increasingly demanding requirements for computation density and energy efficiency, so innovations in architecture, circuit and device are required instead." Indeed, the scaling of Complementary Metal–Oxide–Semiconductor (CMOS) transistors based on Moore's law is slowing down as the size is reaching its physical limit of about 10 nm. The technological need for high computing capability and density scalability served as the springboard for the discoveries of multifunctional materials and nanodevices implementing innovative physical concepts. Among the most significant, resistive-switching memory (RRAM) devices and spin-orbit heterostructures are marking a turning point for the implementation of more efficient neural networks' architectures. These approaches share a common ground. The computing capability is enhanced by exploiting materials with new functionalities, e.g. ferroelectricity, phase-change effect for RRAM or spin-orbit coupling effects as Rashba or topological states in the case of Spin-Orbitronics. These new variables allow to relax the complexity of the network, which is transferred to the fundamental physics of the materials.

From this perspective, FErroelectric Rashba SemiConductors (FERSC) stand out with their intrinsic multi-functional nature. FERSC combine ferroelectricity, Rashba effect in a unique semiconductor and they could bridge resistive memory and Spin-Orbitronics to a new approach of in-memory computing.

The discovery of FERSC dates to 2013, when Density Functional Theory (DFT) calculations by S. Picozzi *et al.* of the electronic bands structure of Germanium Telluride disclosed a giant bulk Rashba effect at room temperature intrinsically related to ferroelectricity. The essential concept of FERSC is depicted in **Figure 1**. The ferroelectric material can host different polarization states without an external electric field. The non-volatility is the key ingredient of a memory device. The ferroelectric distortion is owed to a breaking of the symmetry of the crystal below a critical transition temperature, which at the same time generates a bulk Rashba momentum- and spin-dependent splitting of the electronic bands as result of a large spin-orbit coupling. This translates into a link between ferroelectricity and the electronic spin up and spin down populations. Noteworthy, the spin direction in each spin dependent sub-band is predicted to be reversed by switching the polarization vector. Spin-Orbitronics makes wide used of the Rashba effect for low-power spin-based computing applications, for the generation of dissipation-less spin currents from unpolarized charge currents and vice-versa in non-magnetic platforms. Spin-charge interconversion in two dimensional Rashba surface or interfaces can be tuned in amplitude and sign by means of an external electric field that modulates the Rashba splitting and the spin texture of the electronic bands, as for example in $LaAlO_3$/$SrTiO_3$. Noteworthy, the electric field must be kept on all the times to induce the Rashba effect. In a FERSC material instead, the spin texture is nonvolatile and locked to the internal displacement field associated to a specific ferroelectric state. This would eventually lead to spin-charge conversion with remanence and tunable with ferroelectricity. Finally, ferroelectric dependent spin-charge conversion would be achievable in a CMOS compatible semiconductor, opening the route towards low-power transistors combining memory (ferroelectric polarization) and computing (spin-charge conversion).

The main purpose of this thesis is to convey the theoretical predictions of GeTe to an experimental implementation. We achieved the ferroelectric switching of the *p*-degenerate semiconductor GeTe by means of a micrometric gate, despite the common belief that high density of free carriers would simply make the material show a polar surface not switchable by an external field. We developed an innovative current-voltage method to switch and monitor the ferroelectric state, based on the modulation of the resistance of the GeTe/gate interface with the polarization orientation (ferroelectric bipolar resistive switching). While the polarization is set by voltage pulses between metallic electrodes, the remnant state is read out in non-destructive way monitoring the resistance. Moreover, we demonstrated that the modulation of the interface resistance is correlated to the nucleation and propagation of ferroelectric domains, measured by Piezoresponse Force Microscopy. We can explain our results based on energy arguments: a semiconductor can react to an external electric field and minimize the electrostatic energy, both by switching its polarization state and by moving free carriers. This demonstration opens the route to the exploitation of ferroelectric semiconductors in devices.

Fig.1 - The essential concept of FERSC.

Ferroelectricity in GeTe is connected to its spin physics. By Spin- and Angle-Resolved PhotoEmission Spectroscopy (SARPES), we demonstrated the inversion of the spin texture of the bulk Rashba electronic bands with the polarization vector and we studied the implications of the ferroelectric dependent Rashba effect on the spin-charge interconversion. By spin pumping experiments and theoretical DFT calculations we achieved a remnant spin-to-charge conversion. The sign of the conversion efficiency is reversed by controlling the ferroelectric state with a gate, resembling the behavior of the spin texture. Remarkably, tunable spin-charge conversion can be operated up to room temperature, a head start on other electrically tuned systems as 2DEG and topological materials. GeTe-based devices could represent an innovative concept of spintronics operating without ferromagnets which exploits the ferroelectric states as memory variable. The remnant electric gating of the spin-charge interconversion could represent the missing link towards tunable spin torque applications such as memories, oscillators or magnonic circuits, as well as advanced spin orbit logic like the MESO-device architecture proposed by Intel, thus removing the need for technological scaling and high-density memories.

CLINICAL TIME-RESOLVED NEAR INFRARED SPECTROSCOPY

Marta Zanoletti - Supervisor: Davide Contini

Diffuse optics exploits radiation in the near infrared region (700-1000 nm, the so called “optical window”) that can penetrate biological tissues for several centimetres. In this window tissue chromophores, such as oxy-haemoglobin, deoxy-haemoglobin, total haemoglobin etc, can be accessed. In particular, in Time Resolved Near Infrared Spectroscopy (TR-NIRS), laser pulses at different wavelengths is injected into a biological tissue where photons undergo many scattering and absorption events. The light pulse exiting the tissue encodes in its shape information about optical properties of the medium and thus the concentration of its main constituents.
The starting point of this work is the application of this technique in real clinical scenario by exploiting an old generation device, which is made out of commercially available components but with the main disadvantages of being rather bulky and expensive.
With the final aim of utilizing TR-NIRS as a successful long-term monitoring tool in clinical settings, a step forward to cost-effective, compact and devices with better performances, have been made. In fact, latest advancements in laser and detection technologies let us design and develop a new TR-NIRS device with reduced costs and performances competitive with traditional and commercial systems.
Furthermore, reducing the size of the instrument let us couple TR-NIRS with Diffuse Correlation Spectroscopy (DCS) and Ultra Sound (US) to provide better results and diagnosis. This work can be then divided into two sections:

Application of TD-NIRS: a clinical study on ischemic stroke events in the acute phase.

Acute ischemic event in the brain is an extremely common and sever condition that arises from a complete or a partial occlusion of a blood vessel. Hemodynamic consequences of acute ischemic stroke may affect the microcirculation and the metabolism of ischemic and normal cerebral regions. The week immediately after the occurrence of this event is considered as acute phase in which monitoring at the bed-side of the patient is crucial for long term wellbeing. Traditional techniques, such as Computed Tomography or Magnetic Resonance Imaging, give accurate information about the state of the patient’s brain but are not suitable for bed-side and long term monitoring due to radiation exposure and bulky systems. Exploiting Time Domain Near Infrared Spectroscopy it is possible to monitor non-invasively the dynamics and heterogeneity of an ischemic event occurring in the outer layers of the brain, by recovering absolute values of deoxy-haemoglobin and oxy-haemoglobin.
Since very, few studies have reported reference values on NIRS measurements, a clinical study involving healthy subjects and ischemic-stroke affected patients was carried out in collaboration with the Neurology Department of the Scientific Institute San Raffaele. All the TD-NIRS data were acquired by means of a medical device that was independently developed at the Department of Physics of Politecnico di Milano in the Stroke Unit of San Raffaele Hospital. The device was fully characterized by means of well-established protocols developed within previous EU projects.
This study has two important aims, namely: 1) Analyse the reproducibility of cerebral TD-NIRS measurements and report normal values of cerebral optical properties and haemoglobin species from different head regions of adult healthy controls; and the 2) Comparison between patients’ data with age matched controls.
For the first step, a large cohort of 88 subjects with no neurological pathologies were enrolled. Evidences of reproducibility of cerebral TD-NIRS data were extracted along with normal values of cerebral optical properties, haemoglobin species and saturation. In particular saturation shows the smallest range of variability across brain regions and between subjects.
As for the second step, 47 ischemic stroke patients were enrolled within 24 hours from the onset of acute ischemic stroke symptoms. Furthermore, all the patients were monitored closely at the bed-side in the first week after onset of the symptoms. It has been found that patients had significantly different TD-NIRS features compared to controls as well as according to their cerebrovascular status, in particular suggesting the saturation of oxygen to be a marker of the activity of brain tissue.

Spectroscopic Time Resolved system for thyroid cancer screening.

Thyroid nodule is a growing problem in society, which makes it important to distinguish thyroid cancer from thyroid nodules in order to avoid unnecessary surgical intervention. Nowadays the screening steps of thyroid cancer nodules involve ultrasounds and fine needle biopsy, which have insufficient specificity and sensitivity, leading to false positives and thus to unnecessary surgeries. This makes the characterization of the nodules themselves of fundamental importance. Furthermore, the thyroid can be accessed by diffuse optics since it is generally found less than one-centimetre-deep in the tissue and has a very different structure compared to its surrounding tissues.
Within this framework, the European project LUCA (Laser and Ultrasound Co-Analyzer) aims to develop a low cost, non-invasive device based on a multimodal approach, combining diffuse optics techniques such as Diffuse Correlation Spectroscopy DCS and Time Resolved Spectroscopy TRS, along with ultrasounds US. This could lead to more specific results, better diagnosis and to socio-economic impact. This work mainly focused on the development and the preliminary characterization of the Time Resolved discrete spectroscopic system, featuring 8 pulsed diode laser sources emitting at different wavelengths in the near-infrared spectral region ranging from 635 to 1040 nm, and two detection channels (short and long distance) based on Silicon Photomultipliers (SiPM) and Time Correlated Single Photon Counting (TCSPC) based Time to Digital Converters.
In order to meet the challenging requirements of compactness, low cost and resolution of the integrated final device, each component of the sub-system was characterized and optimized to make it comparable with state-of-art systems. The characterization was carried out by following the guidelines of already available protocols for performance assessment of diffuse optics devices (MEDPHOT and BIP). The experimental characterization proved that the average laser power was suitable for measurements on biological tissues at all wavelengths. The stability over time and with ambient temperature for several hours of operation was verified. It is also possible to exploit the system for a broad range of applications where pulsed laser sources and TCSPC technique are needed, while guaranteeing real-time data acquisition.

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