

MECHANICAL ENGINEERING | PHYSICS |
PRESERVATION OF THE ARCHITECTURAL
HERITAGE | STRUCTURAL, SEISMIC
AND GEOTECHNICAL ENGINEERING |
URBAN PLANNING, DESIGN AND
POLICY | AEROSPACE ENGINEERING
| ARCHITECTURAL COMPOSITION |
ARCHITECTURE, BUILT ENVIRONMENT
AND CONSTRUCTION ENGINEERING |
ARCHITECTURAL, URBAN AND INTERIOR
DESIGN | BIOENGINEERING | 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



Chair:
Prof. Paola Taroni

DOCTORAL PROGRAM IN PHYSICS

The Doctoral Program in Physics at Politecnico di Milano aims at attracting bright students with good scientific background and clear interest towards development and applications of new ideas and technologies. It offers a wide range of opportunities in the fields of advanced applied physics, such as photonics and optoelectronics (lasers, ultrafast optics), 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 a strong 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), INFN-CNR, IIT-Istituto Italiano di Tecnologia.

At present, the number of students in the three-year course is sixty-five, and sixty-three 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.

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	POSITION*
BERTACCO	RICCARDO	FP
BISCARI	PAOLO	FP
BRAMBILLA	ALBERTO	AP
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	AP
TARONI	PAOLA	FP
TORRICELLI	ALESSANDRO	FP

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

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

TIME-RESOLVED PHOTOLUMINESCENCE IN CONSERVATION SCIENCE: STUDY OF CRYSTAL DEFECTS AS MARKERS OF MODERN SEMICONDUCTOR PIGMENTS AND OF THEIR DEGRADATION

Alessia Artesani - Supervisor: Daniela Comelli

When dealing with the conservation of Cultural Heritage, the development of non-invasive and non-destructive methods to investigate pictorial materials and artworks is highly required for both in-situ (museum and galleries) study campaigns and laboratory analyses. In this context, optical and photonics-based techniques offer unique advantages, thanks to their non-invasiveness, low-cost and simplicity. One of the method that satisfy such prerogatives is based on the detection of the luminescent emission of from artwork surfaces under light excitation. The extension from the qualitative analysis of the color of the emission to quantitative and detailed description of the luminescent parameters, such as the spectrum and the lifetime of the emission, allows the in-depth investigation and characterization of luminescent materials. Here, I discuss the application of such an approach referred to as Time Resolved Photoluminescence (TRPL), with pulsed laser excitation and time-gated detection, for artwork material studies, with particular focus on the study of pigments and paint films (pigments dispersed in an oil medium). This method is applied for both non-invasive identification of artistic

materials of paint surfaces and for probing physical and chemical changes induced on pigments because of the interaction with binder. More specifically, I have studied in detail modern pigments synthetically produced by the beginning of the Second Industrial Revolution. The study of this class of pigments represents a new challenge for conservation scientists and museum curators because of their fast deterioration. In the first part of my thesis work, in order to understand the physical and chemical reactions which induce degradation in modern oil paintings, I have deeply studied one of the most reactive

and problematic pigments of the modern age, which is zinc white (ZnO, n-type semiconductor), started to be used at the beginning of the 19th century. I have characterized the Photo-Luminescence of this pigment and I have investigated on the consequences of its interaction with an oil medium. The TRPL method is highly informative of the micro-environment conditions of ZnO and optimally suited for probing the semiconductor particle surface, since it is sensitive to crystal lattice defects more importantly present at the surface. Moreover, I have evaluated the effect of the pigment-binder

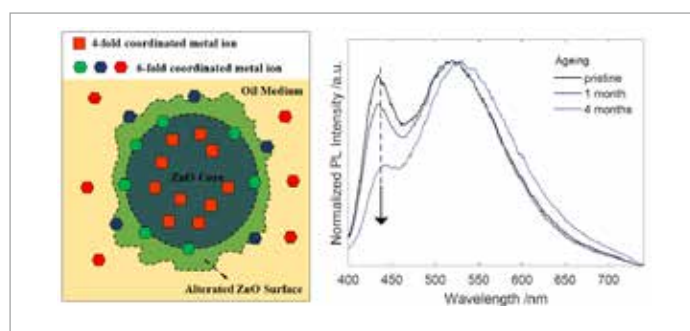


Fig. 1 - (On the left) Simplified scheme of the evolution of the metal ion coordination as a consequence of their migration into the binding oil medium. The EPR results show the co-presence of different metal ion coordination. The 4-fold coordinated metal ions are located in the unaffected ZnO core (orange squares). 6-fold coordinated are located in the altered surface layer (in green), at the ZnO surface (in blue) or leached in the binding oil medium (in red). (On the right) TRPL gated spectra of ZnO dispersed in linseed oil as pristine samples (black line), after 1 month (blue line) and 3 months (light blue line) of artificial ageing. The change in the PL emission is consequence of the pigment-binder interaction.

interaction that comes through the functionalization of ZnO particles made by one the main component of drying oils, the carboxylate groups. I have monitored the changes of ZnO PL emission produced by the surface functionalization of the semiconductor by carboxylic groups and the consequence of the metal ion leaching from the pigment particles to the oil medium. The latter study is conducted through the application of Electron Paramagnetic Resonance (EPR) spectroscopy, a technique sensitive to changes of metal ion coordination. By following the kinetic of ion leaching, I have demonstrated that the phenomenon is mainly important in the first hours after pigment dispersion and is then hindered by the complete passivation of ZnO surface. For completing the scenario, I have detected the changes induced by the metal ion extraction onto the oil medium via Fourier Transform Infrared (FTIR) spectroscopy. The metal ions bond to the fatty acids of the oil medium and form a rigid network. FTIR measurement conducted on artificially and naturally aged samples demonstrated the formation of more complex aggregates, called metal soaps, which clusterize in crystalline forms, reaching

dimensions of order of hundreds of micrometers. In their more advanced status, these aggregates become visible under microscope and represent a serious issue for the painting stratigraphy and surface, since they modify the aspect of the painting itself. Here, I have further evidenced the independence of the PL emission of zinc paint film from the presence zinc soap formation in oil paintings. The second part of the dissertation is focused on the application of a novel multi-analytical approach based on TRPL and Raman spectroscopy for artist material identification. Raman spectroscopy is a widely applied technique in the cultural heritage conservation science and is useful for retrieving chemical information on molecules. In a first case study, I have examined the advantages of this multi-analytical method for the study of a polymorphs pigment: titanium white (TiO₂), used as white pigment in the contemporary age. Titanium dioxide has two stable crystal forms, rutile and anatase, whose presence is dependent on the production method and, as pigment, this corresponds to the transition from an initial and less performant pigment based on anatase to a more suited rutile-based white pigment. The two crystalline phases have

different fingerprints in both luminescence and Raman signal and I have tested the capability of the multi-analytical approach to determine the amount of each phase in powders composed of both phases and in a more complex system as paint film. Finally, for investigating on micro-samples, I have worked at a microscopic approach, conducting the analysis on stratigraphic samples belonging to oil paintings of the Russian avant-garde. I have discriminated between the semiconductor pigments present in these modern paintings through TRPL multi-spectral imaging and the presence of other non-luminescent compounds with Raman spectroscopy. The material complexity of the paint stratigraphy is overcome thanks to the high sensitivity of the two methods to different artistic materials, demonstrating the advantages of this approach for identifying inorganic compounds in modern paintings and thus retrieving the artists' palette.

ACCESSING ANTIFERROMAGNETISM IN THIN FILMS THROUGH ANOMALOUS HALL EFFECT

Marco Asa - Supervisor: Matteo Cantoni

The discovery of the effect presently known as anomalous Hall dates back to 1881 when Edwin H. Hall observed that a current flowing in a perpendicularly magnetized iron slab produces a transverse voltage one order of magnitude larger than in other non-magnetic metals. A proper understanding of this peculiar property of ferromagnets took more than 70 years, and, today, it is well established that the fundamental origin of the anomalous Hall effect comes from the simultaneous presence of spin-orbit coupling in the solid and broken time inversion symmetry coming from the magnetization. Interestingly, recent observations of large anomalous Hall effect have been reported in antiferromagnetic systems, although the magnetization in antiferromagnets is zero by definition. In these systems, like Mn_3Ge or Mn_3Sn , the peculiar non-collinear spin structure introduces a topological term in the transverse conductivity, originating the anomalous Hall effect. These findings were not just important as a fundamental achievement in solid state physics but opened also some possible applications in the emerging field of antiferromagnetic spin-electronics (or spintronics) which

hopes to realize memory devices faster, more scalable and more robust than their ferromagnetic counterpart. In such devices, in fact, the anomalous Hall effect is a potential candidate to probe the state of antiferromagnetic memory cells. Metallic non-collinear antiferromagnets, however, represent a rather specific case, where this anomalous component depends on the precise crystal structure, which is difficult to scale up for applications. The work here presented provides instead a more general approach to engineer **interfaces between antiferromagnetic and non-magnetic** thin films which display a sizeable anomalous Hall effect. What we propose and demonstrate is the possibility to detect electrically the proximity induced magnetization in a non-magnetic layer in contact with the antiferromagnet. The advantage of this method is that it can be exploited independently on the type of ordering (i.e. it works also for collinear antiferromagnets) and is even applicable to insulating antiferromagnets. Here we show a couple of examples which allow to demonstrate how anomalous Hall measurements can be used for a quick and cost-effective way of characterization both in fundamental studies as well as in

actual devices. A first instructive example is provided by the platinum/chromium system. The use of simple elemental compounds as in this case allows for precise *ab-initio* calculations of the electronic and magnetic properties of atoms. By doing so, we found indications that antiferromagnetic chromium induces a net magnetization in platinum. With the idea of electrically detecting this induced magnetization, we grew those elemental compounds as thin films by Molecular Beam Epitaxy on Magnesium Oxide substrates. Very simple structures like the cross in Figure 1 were obtained using conventional lithographic techniques and ion milling, allowing for a comprehensive electrical characterization of the bilayer as a function of temperature and magnetic field. After having assessed a solid antiferromagnetic behavior below 290 K, we demonstrated that an anomalous Hall effect, even if small, can be observed in absence of any external magnetic field. To this scope, we cooled down through the magnetic phase transition in presence of an applied magnetic field to set a defined preferred magnetic orientation of the Pt/Cr interface. Depending on the writing field direction, different states of

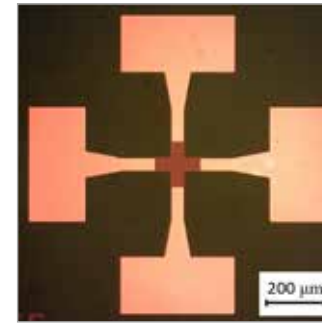


Fig. 1

transverse resistance can be reproducibly set and read-out at remanence up to the transition temperature of 290 K, as can be seen in Figure 2. We demonstrated that the origin of this anomalous transport comes only from the interface, as shown by repeated experiments with various Cr and Pt thickness and verifying the suppression of the effect when a diamagnetic gold interlayer is placed between Cr and Pt. All these results allow to exclude possible competing mechanisms for explaining the observed transport behaviour, and definitely point out a specific role of the proximity induced magnetization in Pt. Even though Pt/Cr is an excellent demonstrator as the origin of this effect could be backed by *ab initio* calculations, the electric signal is extremely small in this case. It requires high-accuracy measurement setup, and the transverse resistance originating from the magnetic state is superimposed to other uncompensated non-magnetic contributions, which determine the offset from zero which is seen in Figure 2. Nevertheless, the principle of

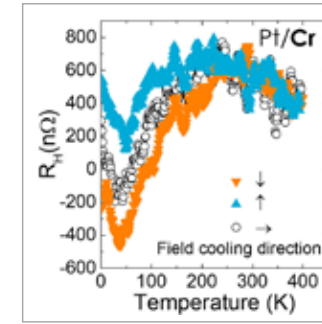


Fig. 2

operation can be extended to antiferromagnetic system other than Cr which provide a larger signal and are thus more suitable for applications. We measured for instance a resistive signal 2 orders of magnitude larger in Pt/TmFeO₃ (the magnetic layer is insulating in this case) and up to 4 orders of magnitude in Ta/IrMn (Figure 3). In this latter case we can see how multiple states can be set using different values of the magnetic field applied out of the plane of the film during the cooling process and read out afterwards at remanence. Moreover, being the state stored in the antiferromagnet, it cannot be erased below the transition temperature by external fields (at least up to 9 T). In conclusion, the interfaces between proper non-magnetic metals and antiferromagnets show peculiar transport properties intimately tied to the magnetic state of the latter, as predicted by *ab-initio* calculations and confirmed by experiments on various material systems. These effects can be used for the characterization of magnetic properties in unknown and new materials as well as in purely

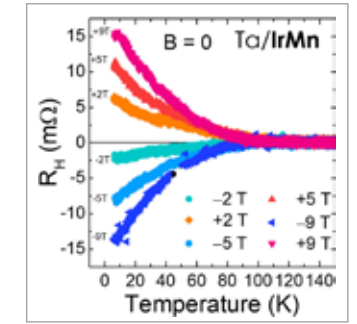


Fig. 3

antiferromagnetic devices built over conventional IrMn alloys, to read-out a magnetic information fully resilient against external fields.

TITLE: MICROFLUIDIC LIGHT SOURCES INTEGRATED IN LAB ON A CHIP PLATFORMS

Silvio Bonfadini - Supervisor: Luigino Criante

As a subclass of MEMS, Lab On Chips (LOCs) take advantage from the miniaturization technology to merge the electro-mechanical and fluidic fields on the same platform. In particular LOCs are microfluidic systems that aspire to integrate on the same chip all the processes that normally take place in a macroscopic laboratory, starting from the preparation and manipulation of the sample up to the detection itself.

In the last thirty years the LOCs devices have widely proven their capability to replicate laboratory operations, and nowadays thanks to the offered advantages, such as the high sensibility and the low costs, they are appearing on the market. Although there are many electro-mechanical processes and LOCs components that are ready for commercialization, the capability to integrate photonic solutions in those platforms, beginning with optical signal generation and detection, could push this technology far beyond the actual potentiality. The applications that could mostly benefit from optofluidic technologies, are in the biological field such a singular specie identification, food quality and environment analysis. Due to its intrinsic properties glass is one of best substrate for biological application, in particular

it is inert and transparent, two important qualities for optofluidic devices. In this substrate a lot of work on the sample manipulation was already done, but just a few preliminary integrated light solutions are offered by the state of art. In this scenario we exploited the femtosecond laser microfabrication assisted by chemical etching for the fabrication of incoherent and coherent light source usable for LOC applications. Fs-microfabrication is a 3D direct writing technique that does not require any mask because the etching procedure removes selectively the material irradiated by the laser, leaving empty zones inside the substrate, thus producing the microfluidic platform.

There are many applications, such as fluorescent dye excitation and photoelectrochemical reactions, that require only incoherent light source. To create a light source that is perfectly integrated in the microfluidic platform and that does not require external energy source we have miniaturized a well know chemical phenomenon as the chemiluminescence. This process uses the energy generated by a chemical reaction to excite a fluorescent specie, which in turn relaxes by emitting photons. Chemiluminescence is known as a fast reaction that expire in few

seconds. However, by reducing the dimensions down to LOCs scale, we have proven that it is possible to control the intensity as well as the duration of the reaction up to several hours. Taking advantage from the flexibility offered by 3D fabrication, different light source geometries (circular, square, triangular) have been created and since it is perfectly integrated in the microfluidic platform it is possible to tune the emission band simply by changing the liquid reagent. The LOC capabilities could be significantly enhanced by the integration of a coherent light source in the microchip, allowing to increase the signal to noise ratio by reducing the coupling and transmission losses. Furthermore, the laser cavity high sensitivity could be used as a sensor to monitor the sample properties. The laser configuration that can be best integrated in the microfluidic platform is a liquid dye laser, a high-gain material that could cover the whole visible region, and that can benefit from the fluidic recirculation to increase the laser life-time. For the fabrication of this microfluidic dye laser we have exploited the combination of fs-micromachining and inkjet printing to create a Fabry-Perot cavity. The microchannel and the 3D structure were micromachined by the laser directly buried in glass

substrate, while inkjet printing allowed to create reflective micromirrors on internal surfaces. As first step we have demonstrated for the first time in literature that the printing of metal ink, based on silver nanoparticles, can be used to create reflective coating with a broad range of transmission, from 0% up to 40%. Taking advantage from these two direct writing techniques the micro-laser cavities were realized with a common basic geometry, shown in fig.1. It is composed by a central microfluidic channel where the active material flows and beside it there are two empty "basins" where the metallic coating can be directly printed (fig.1B). To complete the chip a broadband optical fiber and two microtubes (active medium inlet and outlet) are integrated in order to out-couple the emitted light and connect the chip to the macroscopic world. The working principles was demonstrated by using square basins in order to have two flat mirrors perfectly parallel in the classical Fabry-Perot configuration. The optimization of the chip was performed by exploiting the flexibility of our fabrication technique in the quasi-hemispherical resonator manufacturing, composed by one semi-spherical and one flat mirrors. The possibility to create the spherical mirrors in plane is a peculiarity of the FM fabrication technique that, can guarantee with high precision, the alignment of both mirrors and fiber. The micromirror reflectivity can be precisely controlled by using inkjet printing systems while the construction of a cavity in which the semi-spherical metallic

mirrors are not in contact with the active medium, can help avoiding degradation and contamination phenomena.

A detailed characterization of the laser properties, was performed by using Rhodamine 6G dissolved in ethanol (concentration from 0.5 to $10 \cdot 10^{-3}$ mol/l) as the most studied dye in literature. By pumping the laser with a Nd:YAG laser at 532 nm the emission was detected, as reported in fig.2, with a threshold energy density less than $1.5 \mu\text{J}/\text{mm}^2$ and a linewidth below 0.6 nm. The hemispherical configuration has increased the stability of the emission laser line and decreased the starting

threshold as it manages to confine in 2D the electromagnetic field in the resonator.

In conclusion two new high performance integrated light sources have been developed and they open new and exciting possibilities in the long-term vision of stand-alone optofluidic LOC. More generally, a combination of fabrication processes that is highly flexible, cost-effective and that could be used to expand the capabilities of the lab on a chip platform, has been successfully established.

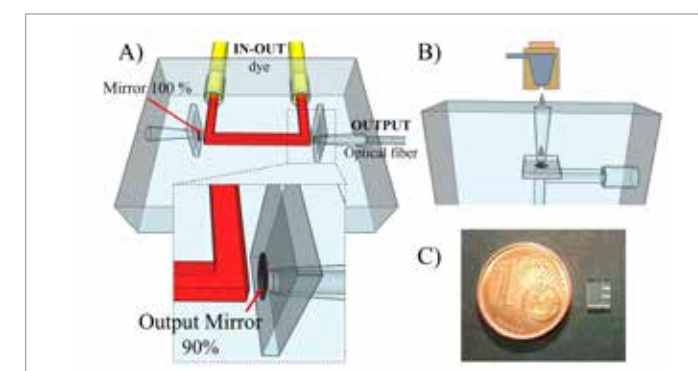


Fig. 1 - Microfluidic dye laser design in glass substrate (A). Metal mirror inkjet printing procedure (B) and glass microfluidic chip after etching (C).

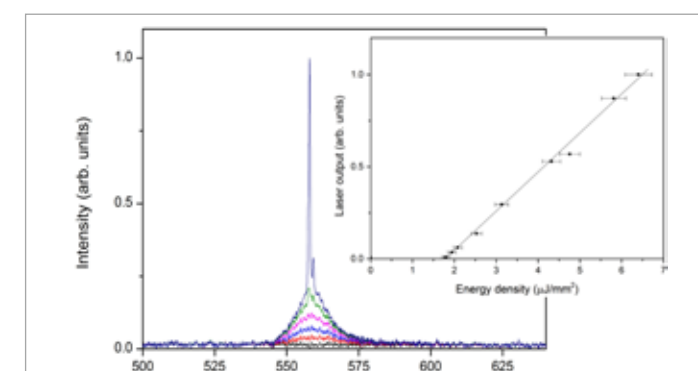


Fig. 2 - Microfluidic laser emission spectrum with Rhodamine 6G 1:10-3 mol/l in ethanol. Typical Narrow emission peak with linewidth below 0.9 nm and threshold energy density at $1.8 \mu\text{J}/\text{mm}^2$ (insertion).

ATTOSECOND TIME-RESOLVED SPECTROSCOPY OF LARGE MOLECULES

Mara Galli - Supervisor: Francesca Calegari

Electron dynamics play a key role in many light-induced processes occurring in biologically relevant molecules, such as bond breaking and formation, which may lead to DNA damage and mutations. Due to the intrinsic evolution time scale of the electronic motion, ranging from few femtoseconds ($1\text{fs}=10^{-15}\text{s}$) down to hundreds of attoseconds ($1\text{as}=10^{-18}\text{s}$), ultrashort laser pulses are needed to investigate such processes. Attosecond science is nowadays capable of providing isolated sub-fs laser pulses, generated via the so called high order harmonic generation (HHG) process, allowing us to perform experiments with the final goal of disclosing the role of the electronic motion in photo-physical and photo-chemical processes occurring in biomolecules. For this purpose, we performed time-resolved spectroscopy experiments in our attosecond laboratories with the conventional XUV-pump NIR-probe scheme: isolated attosecond pulses generated in the extreme ultraviolet (XUV) spectral region are combined in an interferometric setup with sub-5fs near-infrared (NIR) pulses. The XUV attosecond pump pulse is inducing sudden ionization in the molecule under investigation, triggering an ultrafast motion of the residual charge on the

molecular backbone. This process, which is occurring in the first few femtoseconds following the ionization, is named charge migration and it is purely related to electronic motion, since the nuclei are still fixed in their original position. The charge migration process is probed via molecular fragmentation induced by the NIR laser pulse, which is sent to the molecule at a variable delay with respect to the pump pulse. Indeed, the fragmentation pathways the molecules undergo are strongly related to the charge density distribution on the molecular backbone. Therefore, the generation yield of the different

molecular fragments measured as a function of the relative delay between the two pulses is a good observable to retrieve information about the photo-induced electron dynamics. The experimental setup is fully developed in vacuum environment, allowing the propagation of the XUV radiation, and the beamline is providing attosecond stability to perform experiment with the highest temporal resolution. With this approach we performed experiment on biologically relevant molecules, such as amino acids or DNA bases: the molecules are evaporated in the gas phase and delivered to the interaction

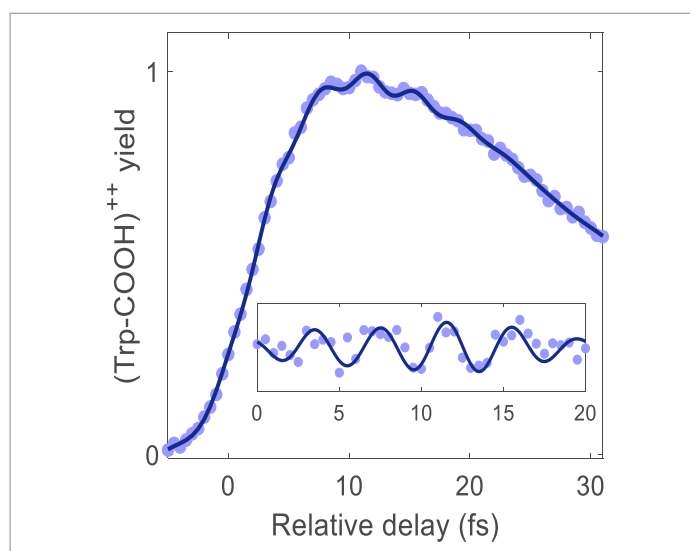


Fig. 1

region by a biomolecular source realized with a piezoelectric pulsed valve coupled with an oven. This experimental technique allowed us to experimentally observe a clear signature of the charge migration process in the amino acids Phenylalanine (PHE) and Tryptophan (TRP). In both the cases an oscillation with a 4fs-periodicity in the generation yield of the molecular immonium dication has been measured (Fig.1 shows experimental data and fitting function for the measurement in TRP): such a short period in the observed oscillatory signal can only be due to electronic dynamics in the molecule. To further improve the experimental technique and to overcome some limitations related to the conventional XUV-pump NIR-probe approach, a new versatile attosecond beamline has been designed, realized and characterized to perform a different pump-probe experiments. Ultrashort pulses in the ultraviolet (UV) spectral range are meant to be used as a pump radiation combined with XUV isolated attosecond probe pulses. Fig.2 shows the new scheme adopted to build our new setup providing several advantages:

- UV pulses are used as a pump non-ionizing radiation: the study of the charge migration process induced in the neutral molecule is now possible
- the energy of the UV radiation is more appropriate to study photo-induced electronic motion in biomolecules from the chemical and biological point of view (it correspond to the most dangerous portion of

- the solar spectrum)
- the combination of UV-pump pulses with XUV-probe attosecond pulses allows to preserve the attosecond temporal resolution in the experiments
- the NIR pulses will still be available: both the conventional and the novel approaches for attosecond time resolved spectroscopy experiments will be available as complementary techniques, ensuring versatility to the setup.

The fundamental and most innovative element of this setup is the generation of sub-2fs UV pulses for the first time to our knowledge: it is performed via third harmonic generation (THG) driven by sub-5fs NIR pulses. Rare gases such as argon or neon are used as nonlinear media: this choice was crucial for achieving the shortest time duration for our UV pulses. Indeed gases, contrary to nonlinear crystals, do not present intrinsic limitations in the maximum bandwidth (and therefore in the minimum time duration) which can be upconverted since neither dispersion effects are present nor

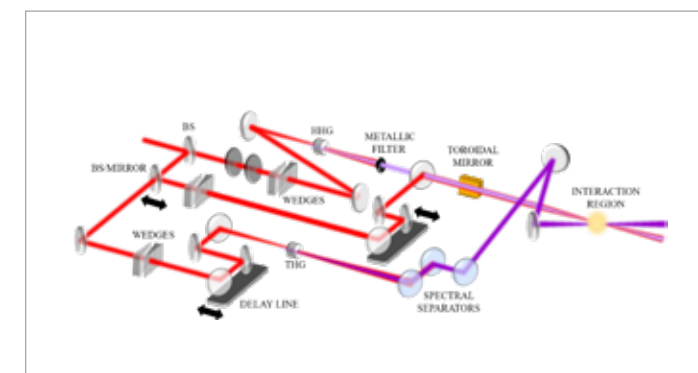


Fig. 2

phase-matching criteria have to be matched. For this reason, a laser-micromachined fused-silica gas cell has been used to perform THG. To handle the significant gas load in high-vacuum environment, a differential pumping system has also been designed and realized together with a gas recirculation system to compensate for the high gas consumption. This technique allowed us to generate and characterize UV pulses with a time duration of 1.9 fs (wavelength ranging from 220nm to 340nm) and 150nJ energy. Such UV pulses represent the ultimate tool to access and investigate the electronic dynamics in biochemically relevant molecules in the deep UV spectral region, allowing the implementation of experiments which have never been performed before with attosecond temporal resolution.

TRACKING PRIMARY PHOTOINDUCED PROCESSES IN BIOMOLECULES BY ULTRAFAST UV SPECTROSCOPY

Lucia Ganzer - Supervisor: Giulio Nicola Cerullo

In the last decades, the study of ultrafast photo-induced processes in biomolecules has attracted a lot of interest due to a variety of applications in medicine, photovoltaics and biophotonics. The molecular processes occurring after light irradiation are very important in living systems since, for example, they can be associated to specific diseases. Thus it is fundamental to shed light on those processes. Ultrafast optical spectroscopy can be exploited to follow the dynamics of photo-induced processes in molecular systems. Among the different spectroscopy techniques, transient absorption (TA) represents one of the most powerful and versatile methods, especially taking into account the relative simplicity of the experimental setup. In this technique, a first pulse, the pump, resonant with a transition of the system under study, brings the molecule to a photo-excited state whose decay mechanisms are tracked by measuring the absorption changes of a second delayed pulse, the probe. Therefore, the pump pulse needs to be tuned in resonance with the absorption, which for many biomolecules, such as DNA and proteins, lies in the ultraviolet (UV) range due to the presence of cyclic aromatic rings. The experimental

temporal resolution, directly related to pump pulse duration, must be sufficient to resolve the decay processes, which are known to occur on an ultrafast timescale. In the visible and near-infrared ranges, the ability to generate pulses with a sub-10-fs duration allows the observation of primary light-induced processes; in the UV region, to obtain ultrashort pulses with duration of the order of 10-20 fs is a technical challenge. As a matter of fact, first in this range there are no broadband optical gain media suitable to generate ultrashort pulses, secondly UV light is strongly dispersed as it travels in materials, meaning that it acquires a frequency chirp which broadens its temporal profile. This thesis describes the development of an ultrafast TA spectroscopy setup in the UV range with sub-20-fs temporal resolution and its application to the study of the ultrafast optical response of biomolecules. Our setup is based on a Ti:Sapphire laser generating 100-fs pulses at 1 kHz repetition rate and 800 nm wavelength. To generate deep UV (250-310 nm) pulses, we double the frequency of a visible pulse generated by a broadband non-collinear optical parametric amplifier (NOPA) by second harmonic generation in a 20- μ m Type I BBO crystal. Thus we obtain

UV light in 260-310 nm range. After compression with a prism pair, the pulse is fully characterized by two-dimensional spectral interferometry (2DSI) and it is found to have sub-20-fs duration. To generate UV light in the near UV (320-360 nm), we perform sum frequency generation between the visible NOPA and a narrowband IR pulse, obtaining also in this case sub-20 fs pulses. The broadband probe pulse is generated through white light continuum by focusing either the fundamental or its second harmonic in a calcium fluoride plate, enabling to cover the 240-700 nm range. In our studies, we combined TA measurements with hybrid quantum mechanics/molecular mechanics (QM/MM) simulations, performed by our computational partners in Bologna, to study the ultrafast relaxation dynamics of several (bio)-molecules: nucleosides, thiobases and *trans*-azobenzene. Nucleosides, which are the building-blocks of nucleic acids (DNA and RNA), are constituted by a nucleobase (uracil, thymine, cytosine, adenine and guanine) and a five-carbon sugar, either ribose or deoxyribose. When nucleic acids absorb UV radiation, the electronic energy acquired by the molecules is converted into vibrational energy on an

ultrafast timescale and with a high efficiency, thus preventing photochemical reactions which might induce mutations or breaks in the nucleic acids strand. In those ultrafast photo-protective mechanisms, conical intersections (CIs) play a crucial role and have been proposed as responsible for sub-picosecond fluorescence lifetimes in nucleobases. During the last years many studies have been performed to unravel photoexcitation dynamics in DNA, but most of them were limited by the temporal resolution (higher than 100 fs). We performed TA measurements on uridine and 5-methyluridine in water solutions upon pumping at 270 nm. Thanks to our sub-20-fs temporal resolution and broad spectral coverage, for the first time it was possible to observe in both nucleosides a stimulated emission (SE) band assigned to the photoexcited $\pi\pi^*$ state. In uridine SE band shows a very fast decay (~90 fs), which is associated to excited state deactivation through a CI. After SE decay, a photoinduced absorption (PA) band appears, assigned to the hot ground state (GS). In 5-methyluridine we measured a slower deactivation pathway. From simulations, we identified the ring puckering as the vibrational mode promoting

the deactivation mechanism in both uridine and 5-methyluridine, excited by the 270-nm pump. The ring deformation is responsible for the sub-100-fs decay timescale in uridine and the heavy methyl group in 5-methyluridine (which is not present in uridine) results in a slow-down of the decay time observed experimentally. If in a nucleobase we replace an exocyclic carbonyl oxygen with a sulfur atom, we obtain a thiobase. With respect to canonical nucleobases, thiobases show a red-shift in the absorption spectra and significant changes in the photophysics, as the major relaxation pathway is via population of long-lived triplet states through intersystem crossing (ISC). Thiobases have very interesting applications as a chemotherapeutic agents or as a cross-linkers between nucleic acids and proteins. Thanks to our temporal resolution, for the first time we provided experimental evidence, supported by simulations, that ISC occurs predominantly via a dark state, of $n\pi^*$ character, intermediately populated on the sub-100 fs timescale from the bright photoexcited $\pi\pi^*$ state, followed by ISC to the triplet state on the 500-fs timescale. Finally, we exploited our temporal resolution to study the

ultrafast photodynamics of *trans*-azobenzene, a photo-chromic molecule which isomerizes if irradiated by light either in the visible or in the UV range. The isomerization takes place on an ultrafast timescale (less than 100 fs) and it involves a conformational change. Some aspects of this process are not clear and the so-called Kasha rule violation (i.e. different photo-isomerization quantum yield depending on irradiation wavelength) has not been explained yet. In our experiments, we could resolve the lifetime of the $\pi\pi^*$ state, the buildup of population in the dark $n\pi^*$ state and the coherent oscillatory dynamics. From simulations, CNN in-plane bendings are found to be active modes in the sub-picosecond photoinduced coherent dynamics out of the $\pi\pi^*$ state. These modes lead *trans*-AB to a high-energy planar $n\pi^*$ /ground state CI, not accessible after direct excitation of the $n\pi^*$ state. Therefore, the CNN-bending channel is considered the main reason behind the violation of the Kasha rule; in fact, *cis*-AB is formed only after intramolecular vibrational redistribution from the bending modes into the torsion on the picosecond time scale.

PHOTOVOLTAGES INVESTIGATED BY REAL-TIME AND ULTRAFAST PUMP-PROBE SCANNING ELECTRON MICROSCOPY

Gabriele Irde - Supervisor: Alberto Tagliaferri

Scanning electron microscopy (SEM) is a consolidated technique to morphologically characterize samples. By scanning the sample under test with a beam of primary electrons (PE), which in turn generates Secondary Electrons (SE), one can reconstruct two-dimensional morphology maps. The intensity of a pixel of those SE maps is determined by the number of collected SE, while the PE beam is focused to that particular sample location. The strength of this far field microscopy technique lies in the reduced De Broglie wavelength of electrons, thus surpassing the light diffraction limit, but also in its applicability to bulk samples. Additionally, the short (few nanometers) escape depth low energy SE, make this technique extremely surface sensitive, and thus suitable to study phenomena of paramount importance in modern technological trends such as nanotechnology: charge presence in nano-sized structures, interface charge accumulation and associated electric patch fields. In this work, we aim to extend the field of information obtained by the SE probe in SEM images to the local electric fields generated upon illumination of semiconductor surfaces and to their dynamics. Pulsed light excitation is exploited as a temporal trigger, allowing

to investigate photo-induced phenomena like temporal evolution of electrical fields and charge transport at sample surfaces, as well as light induced sample modifications and damaging, or nano-mechanical resonant excitations. Given the different nature of these phenomena, it is necessary to monitor samples under test on very different time regimes (from picoseconds to seconds). Different approaches are put in place: either a 'real time' acquisition of several images after a single shot trigger is performed (for dynamical timescales largely exceeding the acquisition time), or alternatively the pump-probe mode is adopted, where each trigger light pulse is synchronized by a single PE probe pulse at a fixed delay time, and the pump-probe process is repeated unvaried many times for each pixel of a single delay time image (Ultrafast scanning electron microscopy). The research activity of this thesis is aimed at the development and application of both approaches, exploiting two experimental apparatuses, where a scanning electron microscope has been coupled with different light sources to investigate photo induced potentials at sample surfaces. The research was carried out on samples such as

Methyl-ammonium lead triiodide perovskite (MAPbI_3) and highly doped Silicon. While the latter is a well-known semiconductor material, exploited in many technological applications, the first is a metal-organic compound, with important applications as a photo-active material, especially in the photovoltaic research and industry. The different nature of these materials and of their electronic properties, ultimately leads to different scientific questions: on one hand I investigated the generation and evolution of patch fields in MAPbI_3 , associated with the motion of charges (both ionic and photo-generated) in the material, characteristic of the microseconds to seconds time regime; on the other hand, I focused on the role of surface states in the recombination of photo-generated carriers in Silicon, a phenomenon occurring in the picoseconds to nanosecond time scale. The investigation of the tiny modulations determined by surface patch fields on the SE signal required first a careful characterization and optimization of the SE image contrast: differential imaging was adopted to remove the leading morphological contribution to SE contrast, while the dependence on the detection geometry

and boundary condition was determined and modeled by ray-tracing simulations. Measurements on MAPbI_3 show a significant impact of light excitation of the sample on the SEM maps, with a time evolution of the SE signal over a time scale range of seconds to tens of hours. A large dynamics of the SE signal is evident both during light exposition and, afterwards, after light removal, presenting also an inversion in gray level contrast between the two phases. Namely, a rapid modification of SE signal response is found upon light excitation, followed by a fast reversal of its contrast after light removal and a much slower – in the range of several hours to tens of hours – recovery of the sample to its pristine state. These findings are consistent with different processes such as electron-hole pair generation and recombination for the fast dynamic, and ions displacement and recovery for the slower one. The surface sensitivity of the SEM strongly suggests – also in accordance with simulations – the presence of an electric field at the sample surface, whose interplay with the measurement geometry determines the changes in SE detection. Measurements on highly p-doped Silicon were performed in a Ultra High Vacuum (UHV)

environment, ensuring a controlled preparation of the sample surface (001) through in situ cleaning and oxidation. The picosecond to nanosecond time regime was accessed thanks to the synchronization between a femtosecond pulsed light source excitation of the sample and a pulsed scanning PE beam. PE pulses were photo-generated by exciting the microscope emitting tip with a femtosecond pulsed ultraviolet light source. Measurements showed a photo-induced dynamic evolving in a few hundred of picoseconds, tentatively attributed to electron-hole recombination mechanisms, mediated by electric fields and states at surface, and diffusion inside the material. Different sample's surface preparations show changes both

in the magnitude and in the time constant of the SE contrast, suggesting a significant role of surface preparation on the density of surface states and on their influence over carrier recombination. The work presented in this thesis confirms the possibility to measure charge transport and evolving photovoltages and to map them in space, and lies the basis to quantitatively interpret SE contrast. Future developments envisage the integration of this technique and data with spectroscopic measurements in situ.

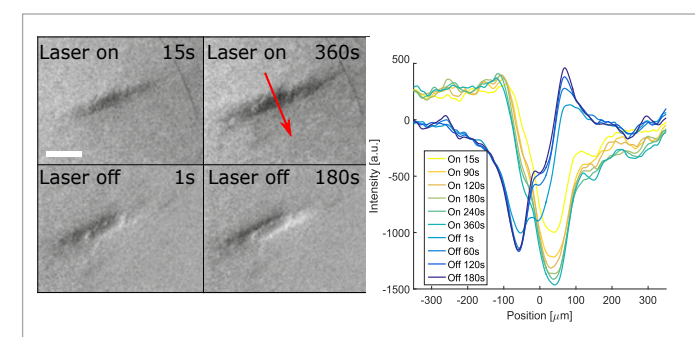


Fig. 1 - Left panel shows selected differential contrast maps on MAPbI_3 . Maps are acquired at different times during laser exposition and afterwards. Scale bar $200\mu\text{m}$. Right panel shows sections along the red arrow for maps acquired at different times.

PRINTED ORGANIC THERMOELECTRIC MICRO-GENERATORS

Matteo Massetti - Supervisor: Mario Caironi

In recent years, the problematics linked to the reduction of fossil fuel reservoirs have reintroduced the importance of the development of renewable sources of energy, especially those environmentally friendly. Among these, thermoelectric generators (TEG) certainly occupy an important place because of their ability to convert heat into electrical energy without the need of any moving part or fuel. These devices exploit the Seebeck effect of appropriately chosen materials, which induces the build-up of an electrical potential in presence of a thermal gradient, to produce a power output.

An interesting alternative to the materials already employed commercially for thermoelectric (TE) applications (e.g. $\text{Bi}_x\text{Sn}_{2-x}\text{Te}_3$ alloys) is represented by organic semiconductors (polymers, oligomers, small molecules). The possibility of processing such materials through solution should allow, in principle, for a drastic reduction of the fabrication costs via their integration with printing techniques. In addition, these functional "inks" can be printed on flexible substrates, in order to obtain devices that could be conformed and adapted to any kind of surface. Therefore, organic based TEG could represent a solution for the realization of low

temperature harvester devices on a commercial scale. These devices could then be employed for low power (1–100 μW) applications such as sensing and powering of wireless networks.

Part of my PhD work has been dedicated to the study of suitable organic materials for thermoelectric applications, in particular to the characterization of both their electrical conductivity and Seebeck coefficient, the so-called power factor ($\text{PF} = \sigma S^2$). The focus has been given mostly to the research of suitable solution processable n-type materials: organic species are generally bound to a strong air instability, due to reactions with oxygen and water, which induces a drastic drop in their electrical conductivity. There are some classes of materials, like metallorganic compounds or doped carbon nanotubes, that show a remarkable stability but are very difficult to be processed through printing techniques. Among the many different materials studied during the PhD activity, we were able to find a fullerene derivative behaving as n-type thermoelectric material, and possessing a good PF, reasonable air stability and soluble in a suitable ink. The effectiveness of the material doping is significantly improved with respect

to standard small molecules: thanks to this a conductivity in the range of 0.1 S/cm and a Seebeck coefficient of $-200 \mu\text{V/K}$ is obtained. In Figure 1, σ and S of the material processed from o-xylene are shown, as a function of temperature, starting from RT to 90°C : the range of application for our devices.

We also conducted some tests on the doping stability and observed that, after 4 hours of exposure to the atmosphere, the electrical conductivity decreased by an order of magnitude, going from 10^{-1} S/cm to 10^{-2} S/cm . This reduction could be partially recovered through an annealing at 120°C in nitrogen atmosphere for at least one hour, indicating that the de-doping effect is, at least, partially reversible. However, the main goal of the PhD has been the realization of a flexible micro-TEG exploiting organic materials for low power applications and using only direct writing techniques. Therefore, once we selected the appropriate materials for our devices, we focused on the integration of these materials into a flexible device. The thermocouples (TC) area were defined on the substrates using a Femtosecond Micromachining Technique, realizing squares with $200\mu\text{m}$ lateral dimension, corresponding to a single

thermoelectric leg. The square area was set to allow for an easy deposition of the thermoelectric materials, but it is well above the minimum resolution of the direct writing techniques employed throughout the process. Even denser device structures can potentially be implemented, by modifying the shape and size of the thermoelectric legs. After the micromachining of the TC, the p and n type materials were printed; as p-type semiconductor a well-known commercial formulation of PEDOT:PSS was employed, while for the n-type area two materials were used. We started to assess the feasibility of the process by realizing devices with the sole PJ700 ink and substituting the n-type semiconductor with a silver nanoparticles-based ink, in order to close the electrical circuit between the device top and bottom contacts. After the validation of the process, we introduced as n-type material the previously optimized fullerene derivative. Then, a thin inkjet-printed PJ700 interlayer was printed, before the silver-based ink deposition, to enhance the adhesion and flexibility of the contacts. The results presented in Figure 2 correspond to a matrix of 128 TCs in an area of 0.36 cm^2 . The device using only a p-type

material obtained a maximum power density of around 3 nW/cm^2 , while the addition of an n-type ink allowed to increase the power extracted by more than a factor of 10, reaching a value above 30 nW/cm^2 . However, by modifying the TC geometry we estimate that we could gain at least another order of magnitude, thus coming even closer to the use of such devices in real-life applications ($1 \mu\text{W/cm}^2$).

RECOMBINATION DYNAMICS IN LEAD HALIDE PEROVSKITE SEMICONDUCTORS AND THE ROLE OF DEFECTS

Silvia G. Motti - Supervisor: Annamaria Petrozza

Lead halide perovskites have been in the spotlight due to the impressive evolution of its application on photovoltaics, that have reached conversion efficiencies over 22%, besides other promising applications such as light emitting diodes, photodetectors and lasers. Some of the main reasons for this success are the high absorption coefficients, long carrier diffusion lengths and long carrier lifetimes, but also to the possibility of low cost solution-based fabrication. However, one of the main challenges for the commercial application of perovskites is the stability of the material, which is greatly affected by migration of ions through the lattice and the high density of defects that is common in solution processed materials.

For both photovoltaic and light emission application, high rates of radiative recombination of carriers are essential for efficient device operation. Such a process competes with the trapping of the carriers at crystal defects. The trap limited recombination is usually investigated by monitoring the quantum yields and dynamics of the photoluminescence (PL). Monitoring the PL quantum yield (PLQY) and dynamics is an interesting approach to investigate intrinsic properties

of perovskites, without the influence of complex interfaces and electrodes. PL quenching and enhancement over time (seconds) can be observed from lead halide perovskite thin films as a result of increase or decrease of defect density, with a dependence on several experimental parameters. To identify the factors driving these transient behaviours in PL, we systematically investigate the luminescence properties of polycrystalline thin films of lead halide perovskites as a function of the excitation density, temperature, excitation conditions and the environment.

We observe a quenching in PL emission of perovskite polycrystalline films under illumination over time in an inert environment. When measuring the PLQY with increasing and decreasing excitation intensities, we observe a hysteresis that suggests a photoinduced increase in trap density, which is supported by increase of the trapping rates obtained from the excitation intensity dependence of the PL decays. We observe this effect on perovskite films of different compositions ($\text{CH}_3\text{NH}_3\text{PbBr}_3$, $\text{CH}_3\text{NH}_3\text{PbI}_3$ and CsPbBr_3) in inert environments. On the other hand, upon exposure to air we observe a strong enhancement of PL emission, combined

with increased PL lifetimes, suggesting decrease in trap density. The transient absorption dynamics also show a decrease in the component assigned to trapped carriers after exposure to air, which further indicates the passivation of defects. By comparing the effects of dry and moist air, we can attribute the passivation effects mostly to oxygen molecules. While water molecules may play a role in the passivation, most of the enhancement is seen in dry air and moisture leads to degradation in a longer time scale. It is worth noting that the enhancement of the PL by oxygen happens also in samples exposed to air prior to the photo-excitation, suggesting a combination of oxygen and photo-excitation for defect passivation, possibly an effect of defect deactivation by the reaction of oxygen molecules with trapped carriers.

To achieve a comprehensive picture of these processes and how they relate to previous reports in literature, we investigate the effect of several experimental parameters on the PL instabilities. We performed measurements under high vacuum to exclude the atmosphere effects and revealed the competition of two opposite effects, which either quench or enhance the PL. By

using a modulated excitation with fixed pulse widths, we observed the PL enhancement at low frequencies and dominant quenching with increasing frequencies. We also investigated the temperature dependence of these effects and found a strong enhancement at lower temperatures, with a simultaneous quenching becoming dominant with increasing temperatures. This indicates the competition of two thermally activated processes with opposite resulting effects. The timescales of these processes are not compatible with electronic effects, so without defect passivation by external factors like the atmosphere, any fluctuation in PL efficiency must be related to intrinsic structural dynamics. Furthermore, we observe a dependence on the illumination geometry, which suggests an important role of the illumination induced gradient in the trap formation.

Based on our observations we propose that the photoinstabilities seen on perovskites are a combination of these distinct processes: self-healing of point defects; trap formation resulting from ion migration; and atmosphere effects that are either the oxygen passivation or moisture degradation on samples exposed to air. The self-healing

has been suggested as the annihilation of Frenkel defects, resulting in enhanced PL. While the self-healing seems to be a local mechanism occurring on a point defect, we found evidence that the photoinduced trap formation is a micrometer scale process that result from ion migration through the film, and therefore is highly dependent on the experiment parameters, such as wavelength and frequency of excitation light, film thickness, spot size and temperature.

In summary, we could disentangle the distinct processes responsible to the photoinstabilities seen in lead halide perovskites, revealing intrinsic structural dynamics and highlighting the fluctuations in photophysical parameters that need to be taken into account in order to acquire reliable information from optical measurements on this material. Besides contributing to the understanding of the material, these results inspire new methods for fabrication and processing, allowing for improved device stability.

EXPLOITING CHEMICAL DOPING FOR HIGH PERFORMANCE ORGANIC ELECTRONIC DEVICES

Diego Nava - Supervisor: Mario Caironi

Recently, a vast amount of basic and applied research has focused on electronic and optoelectronic devices based on organic semiconductors (OSCs), which have several characteristics that offer enhanced performance over the inorganic counterpart. These advantages include mechanical flexibility, light weight, and low-cost, large-area fabrication. Pure semiconductors are known as intrinsic semiconductors and molecular doping of organic semiconductors has proven a powerful strategy to modulate the electronic properties. While for inorganic semiconductors, doping involves substitution of an atom within the crystalline matrix, in OSCs the doping process relies on the addition of sub-stoichiometric amounts of a redox-active species, which donates an electron to the host (n-doping) or accepts an electron from the host, leaving a hole behind (p-doping). Reduction or oxidation of the host are the consequence either of a direct charge-transfer, or of an indirect process, such as for example the transfer of a proton from an acid, or a hydride from a base in case of p-type and n-type doping, respectively.

In this PhD dissertation, the work is divided in two main themes: 1) The investigation of thermoelectric properties of different doped

n-type semiconducting materials, with attention to dopant miscibility and air stability. 2) The exploit of doping in Organic Field Effect Transistors (OFETs) as a tool for the improvement of the charge injection.

The aim of the first theme is the study of the electrical and thermoelectric properties of OSCs, having as final goal the realization of a fully printed Organic Thermoelectric Generator (OTEG). OTEGs are attracting appreciable scientific interest thanks to the possibility to exploit waste heat by converting temperature gradients into electrical energy at reduced cost, in order to supply power to low-consumption electronic devices. The efficiency of the conversion of a heat flux into a current by thermoelectric (TE) materials can be related to the dimensionless material figure of merit zT , defined as:

$$zT = \frac{S^2 \sigma}{\kappa} T$$

where σ is the electrical conductivity, S is the Seebeck coefficient and κ is the thermal conductivity. Since one of the most attractive characteristics of organic semiconductors is their low thermal conductivity (κ), typically below $1 \text{ Wm}^{-1} \text{ K}^{-1}$; a common strategy to improve TE properties

of organic semiconductors is to improve the numerator of zT , namely the power factor [$\text{Wm}^{-1} \text{ K}^{-2}$]. Thus, the tuning of the doping level, namely the modulation of the charge carrier density, is a crucial aspect for optimizing the power factor and zT value.

For the realization of an efficient thermoelectric device, complementary p-type and n-type conducting materials with high PF are needed. While solution processable and printable organic p-type materials having a PF in excess of $100 \mu\text{Wm}^{-1} \text{ K}^{-2}$ have been demonstrated, up to date the major limitations are ascribable to n-type materials, for which examples combining high electrical conductivity and solution processability are very scarce. Several explanations were proposed to clarify limitations in the maximum electrical conductivity of solution processable OSCs; one cause was ascribed to the limited miscibility between molecular dopants and the semiconductor polymeric matrix. In the thesis, I show how the electrical conductivity of electron-accepting polynaphthalenediimide-based (P-NDI) semiconductors could be tuned by the addition of donor molecular species, benzimidazole derivatives, and in which way the backbone design of the OSCs play a crucial

role in the improvement of the dopant miscibility.

A further strong limitation for n-type materials comes from their air instability, which precludes ambient processing of OTEGs and impose severe constraints on devices encapsulation. To overcome this issue, both the dopant and the semiconductor must be air-stable. In this respect, benzimidazole derivatives are chosen as dopant thanks to their peculiar doping mechanism; hydride transfer followed by subsequent electron transfer instead of direct charge transfer scheme. In this dissertation I show how the lowering of the LUMO level of P-NDI, due to a chemical modification, namely a thionation, of the monomer core, leads to a drastically improvement of the ambient stability of the n-type electrical conductivity. The modified P-NDI, when doped with benzimidazole derivatives, shows higher electrical conductivity and an improved power factor with respect to unmodified P-NDI. Importantly, while doped films based on the parent P-NDI copolymer lose several orders of magnitude of electrical conductivity within 200 minutes, reaching almost the pristine film value, thionation results in a decrease of only a factor of two of the electrical conductivity after 16

hours of continuous air exposure of the unprotected doped thin film. Such a pronounced improvement demonstrates that inherent environmental stability of doped n-type polymer conductors can largely be controlled through the proper design of the conjugated semiconductor system, thus opening a path towards the realization of solution-processed and efficient organic micro-thermoelectric generators.

In the second part, the adoption of chemical doping for the improvement of the charge injection in OFETs is reported. In the last years, the widespread research in the field of OSCs has led to remarkable enhancements of OFETs charge carrier mobilities. Despite all the efforts in optimizing OFETs performances, the achievement of efficient charge injection from the electrodes is still an open challenge. At short channel length, the contact resistance becomes not negligible and ultimately hinders the real potential of this technology. As a result, a downscaling of the device size leads typically to a large reduction of the extracted field-effect mobility and other device performance. In this dissertation molecular doping could offer an effective tool to resolve some of these issues, however it has

been proven challenging to implement this approach without affecting structural properties of the materials and operational functionality of devices. Here we present a doping approach involving the employment of multi-layered active layers in bottom-gate top-contact field-effect transistors. An optimal injection from the contacts is obtained by the confinement of the dopant in the bottom layer made by highly doped OSC blended with electrically insulating material, high-density polyethylene (HDPE). The OFET accumulated channel is created in an upper layer of pristine OSC formed on top of the previous, thus exempting the accumulated channel from doping and therefore preserving the typical charge transport of the pristine polymer. In order to achieve such device architecture, solution-based polymer blend systems have been employed; this approach has been proved valid for different type of semiconducting polymers acting as a versatile method to reduce the injection barrier issue in OFETs.

INTEGRATED THREE DIMENSIONAL PHOTONIC DEVICES FABRICATED BY FEMTOSECOND LASER MICROMACHINING

Diogo Pereira Lopes - Supervisor: Roberto Osellame

After the generalization and commercialization of femtosecond pulsed lasers, a new technique surged in the recent years: femtosecond laser direct writing. It provides some unique features that make it a solid alternative to lithographic techniques. For once the absence of need for special facilities such as a clean room. Only temperature/ humidity are needed to control within reasonable parameters. The setup itself is also relatively simple, and in the case of waveguide fabrication it's a single step procedure. But maybe the main differentiating feature is the ability to write in a truly 3D geometry fashion. This has been explored in the past for example in fabricating complex interferometric networks in which the waveguides can cross taking advantage of the 3D capability. Furthermore, the same system can be used with a wide range of transparent materials, from glasses to crystals, but also polymers. In the latter two-photon polymerization occurs only at the focal points and so there is no need to use any mask. Since it involves nonlinear absorption it can be used to create micrometre sized structures. In the case of some materials such as fused silica, it is also possible to exploit the damage created by the laser irradiation to get

selective etching when exposing to a strong acid such as HF or HCl. With this, channels of micrometric dimensions control can be created which is currently being exploited both for microfluidic and micromachining applications.

In this thesis work, femtosecond laser micromachining is used for the fabrication of different kinds of devices, exploring both the ability to directly write waveguides, and the etching of micrometre-sized structures.

In this century of continuous exponential growth of communications worldwide, traditional electrical interconnection is finding increasingly difficult to respond to the bandwidth pressure, and photonic interconnection will most likely be the future standard. The main technique used for the fabrication of optical circuits nowadays is planar lightwave circuit. In the main project of this thesis, we worked together with many industrial and university partners in the European project Teraboard. The objective of this project is to fabricate novel optical interconnection solutions in order to surpass the barrier of terabit per second communication rate. In order to do this, we fabricated

vertical direct written waveguides that bridge the connection between different layers of PLC (planar lightwave circuit) waveguides. Thus, we exploit the best of the PLC technology (high-throughput fabrication and low loss (<0.01 dB/cm)) with the exploration of the third dimension enabled by the vertical direct written waveguides. Even though we can write waveguides with variable depth, writing vertical waveguides is no easy task. Before this thesis only waveguides guiding in red wavelength written by femtosecond laser direct writing were reported in literature. The main obstacle is the spherical aberration that comes from the interface between the writing microscope objective and the sample. In order to reduce these aberrations, we used a water immersion objective. We found that trying to write the core of the waveguide directly only produces waveguides that guide in red wavelength but not at 1550 nm which was our target wavelength for the project. The solution found was to use a higher pulse energy to induce stronger modification, and directly write the cladding instead. With this strategy we managed to write single mode waveguides with low insertion loss

(0.5 dB). We also demonstrated the possibility to write tilt these waveguides up to 6° with marginal increase in the insertion losses, and also possibly curving them from 3° - 6° . These last results are important for our project in particular, since they will be used to couple from a total internal reflection mirror and into a grating coupler, which require different input/output angles.

Lastly, we also demonstrated the possibility to stack two of these samples and couple through two the waveguides written in both samples. The possibility to explore the stacking is crucial in order to increase the density of connections per square meter, that increases with each layer. Currently we are collaborating with writing the waveguides for the different prototypes needed in this project.

The second project, done at the university of Toronto, we explored the possibility to fabricate a polarizer inside glass by using the FLICE technique in fused silica to create air windows that are at Brewster angle with the surface. Due to the micrometre size of these structures, we found that it is possible to explore interference effects and have Fabry Perot cavities with interference both

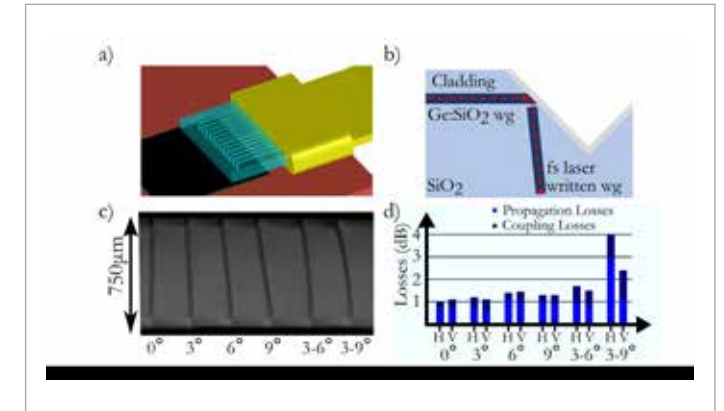


Fig. 1 a) Schematic drawing of an example of a connector. b) Scheme explaining in detail the position of the waveguides. The coupling in this case is done by total internal reflexion. c) Profile picture of directly written waveguides, written with different tilting angles from left to right. The last two start at the bottom with 3° tilt and gradually curve to 6° and 9° , respectively. d) Insertion losses of the waveguides, separated by propagation and coupling losses, and when coupling with light at two different perpendicular linear polarizations.

inside the air gaps and between the different windows. We made some theoretical modelling of the behaviour of these windows and projected a device of 5 windows that should be capable to provide higher than 100 polarization ratio. Unfortunately, it was not possible to fabricate the device, but these limitations are analysed, with the proposal of possible solutions.

The last project presented in this thesis, is the fabrication of glass chips for attosecond pulse generations. Using again the FLICE technique, we fabricated a couple of glasses that are used in the

distribution of Argon gas inside a 400 μm diameter chamber for UV pulse generation step on an attosecond pulse laser. The transparent fused silica provides a good alternative to metal components that were used before and needed to be changed over time due to continuous damage by the laser.

FEMTOSECOND LASER MICROFABRICATION OF 3D PHOTONICS CIRCUITS IN DIAMOND FOR QUANTUM INFORMATION AND MAGNETOMETRY

Carlo Andrea Riccardo Perini - Supervisor: Mario Caironi

The continuously increasing energetic demands, and the need for a reduced usage of fossil fuels, are forcing the urge for greener energy sources and low-energy consumption fabrication processes. With a two-hundred fold increase in installed power capacity in the last fifteen years, photovoltaic promises to be one of the workhorses of the renewable energy generation. Commercially available modules are mostly based on Silicon, which imposes high-temperature fabrication processes and a low design flexibility in order to maintain high throughput in production and to decrease costs. To circumvent such limitations, low-temperature, solution-processable organic materials were proposed as a viable alternative. Such materials can be directly deposited on plastic substrates and offer highly tunable optoelectronic properties, but in most cases are limited by low charge carrier mobilities and power conversion efficiencies (PCE). In less than a decade, Organic-Inorganic Hybrid Perovskite semiconductors gathered the attention of the scientific community, combining the advantages of silicon and organic technologies: up to 23.3 % PCEs in solar cell configurations were reached, altogether with optimal, highly tunable

optoelectronic properties, and with solution processability at low temperature. The fields of application of perovskite materials further expanded, with the realization of photodetectors, light emitting diodes and lasers, were the tunability and low cost of the technology constitutes a significant strength. To fully take advantage of the optimal properties of these compounds, large area deposition methods, green solvent systems and a moisture-robust fabrication must be implemented. Despite significant efforts on the development of techniques able to provide full coverage, high quality films on large area, only marginal attention has been given to high boiling point, toxic solvents as dimethylformamide (DMF) required for perovskite deposition, and to the high sensitivity of the precursors to the presence of oxygen or moisture, which is restraining their fabrication to highly-pure nitrogen environments. Besides, most of the high performing device architectures, include high-temperature processed or evaporated interlayers, that hamper the full exploitation of the strengths given by a solution-based fabrication. The use of evaporation processes is of particular relevance in the field of photodetection,

where evaporation is required to achieve uniform films with minimal thickness. In fact, organic materials with low mobilities are conventionally exploited for the realization of interlayers, and significantly limit the device response speed if thick films are used. The solution deposition of thin layers in turn, leads to inhomogeneities in coverage and to pinhole formation, causing increased leakage currents and power wastage. Leakage currents directly relate to device noise and thus impose decreased device sensitivity. The aim of this contribution is to tackle such criticalities, focusing on the most widely studied methylammonium lead triiodide (MAPbI₃) perovskite as a benchmark. We introduce a novel low-temperature fabrication route for perovskite deposition, stable in air at high moisture levels, and based on acetonitrile (ACN), a greener solvent than the conventionally used DMF. The use of ACN, in which lead iodide (PbI₂) is poorly soluble, is enabled via addition of stoichiometric hydroiodic acid (HI). Upon deposition, we demonstrate the formation of an unreported lead iodide – hydroiodic acid – water (PbI₂-HI-H₂O) intermediate, which can be converted to perovskite either directly, with a methylamine

gas (MA) exposure, or after a short annealing of the deposited film, required to revert it back to PbI₂, exploiting the subsequent reaction with methylammonium iodide. To prove the effectiveness of the proposed fabrication route, we realized a fully solution processed device structure, including the MAPbI₃ film obtained via MA conversion of the PbI₂-HI-H₂O intermediate. We exploit poly(3,4-ethylenedioxythiophene):polystyrene sulfonate (PEDOT:PSS) as hole transporting layer, Phenyl-C61-butyric acid methyl ester (PC₆₁BM) / bathocuproine (BCP) as electron selective and Indium Tin Oxide (ITO) and Silver (Ag) as collecting electrodes. PCEs higher than 7 % are achieved over a wide range of moisture levels, from 50 to 75 % relative humidity (RH), exploiting a spin coating deposition method. Performances peak at 65 % RH, where the highest efficiency of 14 % is obtained. Unoptimized devices, with a blade-coated active layer, reached PCEs of 7.6 %, proving the compatibility of the proposed fabrication route with large area deposition techniques. We extend our investigation further, to the field of photodetection, where we exploit solution processed metal oxides to circumvent the limitations induced by the use of sole organic interlayers. Metal oxides exhibit higher mobilities than conventionally employed small-molecule interlayers, and can be thus deposited in thicker films, to provide effective dark current reduction, without significantly hampering the device response speed. Aiming to maximize the operational

bandwidth of our detector, we optimize a PEDOT:PSS/MAPbI₃/PCBM/aluminum doped zinc oxide (AZO) / Aluminum (Al) stack. The introduction of an AZO layer enhances the hole blocking properties of PC₆₁BM, thanks to the deep HOMO level. As a result, dark currents are reduced to $1.4 \times 10^{-7} \text{ A cm}^{-2}$ at -1 V, and a responsivity higher than 0.1 A W^{-1} over the range 370 - 770 nm is reached, peaking to 0.3 A W^{-1} at 700 nm: values at par with results achieved incorporating vacuum deposited interlayers in the device structure. Most importantly, a fast response time of 100 ns is demonstrated, corresponding to a highest operational frequency of 3.5 MHz. This is, to our knowledge, the fastest response reported for a vertical photodetector exploiting solution processed interlayers: an order of magnitude lower than what typically achieved. To further improve the device sensitivity, we optimize a zinc oxide (ZnO) nanoparticle: Poly[(9,9-bis(3'-(N,N-dimethylamino)propyl)-2,7-fluorene)-alt-2,7-(9,9-dioctylfluorene)] (PFN) polymer blend, and we introduce it in place of the AZO layer. Dark current values are effectively reduced to $2 \times 10^{-8} \text{ A cm}^{-2}$ and charge recombination is hampered, as highlighted by the diode ideality factor approaching the theoretical value of 1 and by an improved responsivity throughout the visible range, peaking at 0.33 A W^{-1} . The device white noise background reaches values below $4 \times 10^{-27} \text{ A}^2 \text{ Hz}^{-1}$ at frequencies higher than 200 Hz, leading to detectivities (a figure of merit representative of the device sensitivity) in the order

of 10^{12} Jones at visible frequencies, which are comparable to performances provided by commercial silicon detectors. In conclusion, we developed a novel fabrication route for perovskite able to overcome two major hurdles of the material deposition: the need of toxic solvents and of a low humidity environment. The use of ACN, a greener solvent with respect to DMF and the formation of a novel PbI₂-HI-H₂O perovskite precursor, enable MAPbI₃ fabrication in environmental conditions, at high relative humidity. The compound can be directly converted to MAPbI₃, upon reaction with MA, or be degraded to PbI₂, to ease the extension of the process to the fabrication of highly performing multi-cation, multi-anion perovskites via sequential deposition. We also demonstrate the possibility of realizing high performance photodetectors exploiting solely solution processed interlayers. We achieved detectivities at par with commercial silicon devices and operational frequencies of up to 3.5 MHz.

DEVELOPMENT OF ULTRAFAST NEAR AND MID – IR SOURCES AND THEIR APPLICATIONS TO HIGH-ORDER HARMONIC GENERATION SPECTROSCOPY

Aditya Pusala - Supervisor: Salvatore Stagira

The motivation of the PhD project has been the development of intense-tunable near-IR (1.3 to 2 μm) and mid-IR pulses (2.7 to 3.7 μm) and their application in generation of high-order harmonics in molecules and solid media for spectroscopy studies. The nonlinear interaction of intense ultrashort laser pulses with atomic and molecular media leads to the emission of High-order harmonics (HH) of the fundamental radiation. The primary features of HH emission can be understood in the framework of semi-classical three-step model: a valence electron of the neutral species tunnels through the potential barrier modified by the intense laser pulses, then is accelerated and driven back to the parent ion by the electric field of the laser pulse and finally may recombine with the parent ion, releasing the excess gained kinetic energy as an attosecond burst of high-energy photons giving rise to a high order harmonic spectrum. HH generation process is not limited to atomic media, it is also possible in solid state media, and the generation process of HH in solids can be understood in a similar way. However, in solids there are two concurrent mechanisms in HHG namely the intra and inter band contributions. The intraband contribution – arising from the

motion of electrons (and holes) in the conduction (and valence) band, produces nonlinear current that subsequently emit high-order harmonics; on the other hand, the interband contribution is due to the polarization buildup between the bands. The nature of HHG allows to obtain spectroscopic information with sub-femtosecond temporal and angstrom level spatial resolutions. In HHG from solid media, it is established that the harmonic cutoff energy scales linearly with the driving fields wavelength and intensity. Therefore, extending harmonic cutoff requires efforts to be focused on using sources of laser pulses at longer wavelengths, which are not commercially available. As the first step towards my motivation, a major part of my PhD was devoted to the development of tunable, intense, near and mid-IR ultrafast optical parametric amplifiers (OPA). In particular, a strong effort was devoted to an OPA operating in the range from 2.7 to 3.7 μm and generating pulses with duration of about 80 fs. The main challenge was in using this sources to generate HH from crystals. In last years, high harmonics from solids is emerging as a frontier of strong-field physics. The availability of intense, ultrashort pulses in the

long wavelength range, allows the investigation of HHG in narrow and wide bandgap materials without damaging the sample. These novel ultrafast tools could be used in studying Floquet states arising from light induced electronic states or imaging valance charge density in bulk materials. In the experimental setup (as shown in fig. 1 (a)), mid-IR pulses having a central wavelength of 3.25 μm with pulse duration of 80 fs at a repetition rate of 10 Hz are focused into a sample (in this case a 5-mm-thick ZnSe (Zinc Selenide) crystal, having a wurtzite structure), and the harmonics generated are recorded in transmission using a spectrometer. We observed harmonics up to the 8th; the spectra showcased an interesting broadening. This broadening of individual harmonics can be related to the electrons born before the peak of the driving electric field subsequently travelling through the lattice of the crystal and recombining at a different lattice point. The non-centrosymmetric property of the material gives rise to the even and odd harmonics seen in fig.1(b). The experiments revealed a dependence of the harmonic intensity as a function of the crystal orientation with respect to the polarization direction of the incoming driving

field. This dependence suggests an important role of the crystal structure in the generation of high-order harmonics. Experiments on high order harmonic generation in materials with wide bandgap and samples of different thickness are underway. In the future, the techniques exploited for the generation by HHG of attosecond pulses in gaseous media such as attosecond lighthouse, polarization gating, amplitude gating could also be extended to solid media, leading to a higher generation efficiency. The thesis work also consists of development of optical parametric amplifiers in the near-IR region, generating high energy tunable pulses from 1.3 μm to 2 μm , with pulse duration as short as 14 fs at a central wavelength 1.45 μm .

As part of secondments during the second half of my PhD, I was involved with Amplitude Technologies in developing a multipass Titanium-Sapphire laser amplifier operating at 1 kHz. The multipass amplifier is a technique exploited to achieve laser gain by geometrical arrangement of the multiple passes of the seed beam in the amplifier cavity. From the technological point of view, the main challenge was to find solutions for alleviating thermal effects due to the high-power pulses focused into the crystal that distort the beam profile, and in parallel to increase the gain output. The thermal effect was dealt by changing the size of the pump laser in the gain medium. The output gain of the IR beam was increased by carefully matching the temporal overlap of seed with respect to the pump. This was

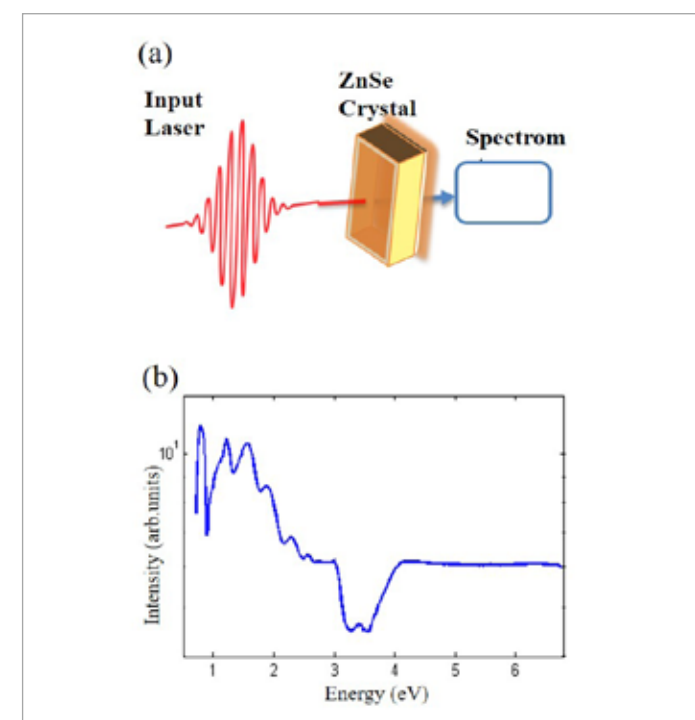


Fig. 1 (a) Generation of High-order harmonics in ZnSe crystal. (b) Representation of harmonic spectra with even and odd harmonics extending upto 8th order.

done by ensuring that the size of the seed was matched with the pump size (to an extent the seed beam was kept slightly smaller compared to pump size, in order to have maximum energy transfer from pump to seed). With five passes of the beam inside the gain medium, we measured an output IR power of 10 W when the amplifier was pumped by a 22.5 W pump laser. The output IR has a broad spectral width of 110 nm corresponding to a pulse duration of 17 fs. My PhD work was performed in the framework of the European H2020 project MEDEA (Molecular Electron Dynamic Investigated by Intense Fields and Attosecond Pulses, grant N.641789); in

particular I am a Marie Curie fellow funded by the MEDEA project. I take this opportunity to express my gratitude to my supervisor and tutor for their effective guidance and in general to the European Union for its role and support.

DIFFUSE OPTICS FOR MONITORING BRAIN HEMODYNAMICS: SIMULATIONS AND EXPERIMENTS IN COMPLEX HETEROGENOUS MEDIA

Lina Qiu - Supervisor: Lorenzo Spinelli

The brain functionality is well known to play an important role in the human health, which is an indicator of the disease diagnosis. In the brain, the blood vessels are linked to the neuronal activity through the process of neurovascular coupling. When facing the external stimulus, the most important responses of the brain include the metabolic response and hemodynamic response. In particular, the hemodynamic response composed of blood flow, blood volume and blood oxygenation is an essential aspect in brain physiology, which are associated with a wide range of neurological diseases. For example, the low arterial oxygen may cause an apnea, the too slow blood flow may induce the ischemic stroke; and the high metabolism of local tissue may imply the cancer. A number of biomedical techniques have been used to measure the brain activity, such as EEG / MEG, PET, SPECT, and fMRI. But these measurement techniques share numerous disadvantages in terms of poor spatial resolution, invasiveness, costs and large instrumentation, which limit their wide application in clinical such as bedside or long-term monitoring. However, diffuse optical method is a relatively compromised method, which can offer a noninvasive, cheap and flexible way to detect the deep hemodynamics by using the near-infrared (NIR) light. Thus, this technique has great

application prospects in studying the brain hemodynamics under different conditions/tasks and clinical diagnosis of brain diseases. Biological tissues (e.g. brain) are optically multiple scattering (turbid) media, which are naturally opaque to the visible light. Photons transport inside the biological tissue usually undergo multiple scattering because of the presence of the static scatterers (e.g., organelles and mitochondria) or absorption due to the absorbers (e.g., hemoglobin, water and lipids); and Doppler shifts when they are scattered from the dynamic scatterers such as moving red blood cells. The characteristics of the tissue (e.g. optical and dynamical properties) can thus obtain from these photon-tissue interactions, which in turn provides important information for clinical applications. Light transports inside the turbid medium usually can be approximated as a diffusive process, which can be described by the Radiative Transport Theory (RTE). Diffusion Equation (DE) and Monte Carlo (MC) method are two most widely used solutions for the RTE. The MC method is a relatively more straightforward and easy-to-program solution that can solve RTE with any desired. The most important breakthrough of optical imaging was happened in 1977 when Jöbsis successfully detected the cerebral hemodynamics in the cat head by using the NIR light (650

-950 nm). This breakthrough paves the way for various optical methods using the NIR light to noninvasively monitor tissue hemodynamics. Since then, NIR light was widely used in optical imaging, especially in diffuse optics. The diffuse optics measurement technologies utilize diffuse NIR light to noninvasively estimate the deep hemodynamics of tissues, including the blood oxygenation and blood flow. Near-infrared spectroscopy (NIRS) and diffuse correlation spectroscopy (DCS) are two most widely used diffuse optics technologies for brain monitor which are sensitive to oxygenation change and blood flow, respectively. There are three types of light sources commonly used in diffuse optics, including the continuous wave (CW), Frequency Domain (FD) and Time Domain (TD). The TD type is related to the FD type via the Fourier transform. They can detect more information of the biological tissue than the CW one, but the complicated principle, clumsy and expensive instrument limit their applications for some special subjects such as freely moving animals. The main aim of my research activity is to examine and prove the ability of diffuse optics (NIRS and DCS) technology for noninvasively monitoring the deep (e.g. cerebral) hemodynamics in the biological tissue, and further demonstrate the possibility to extend their application to clinics, such as

the bedside or operation monitoring and lesion diagnosis. My research work primarily includes three parts: TD-NIRS studies based on MC simulation; TD-DCS studies based on MC simulation; and CW-NIRS experiments in freely moving animals. For the simulation studies, we used a 3D Mesh-based Monte Carlo (MMC) method as the main tool for the photon propagation simulations. In the first part, we first did some simulation to verify the reliability and correctness of MMC. The results showed that the differences between the scattering point coordinates of MMC and the values calculated from analytical expressions are small. Moreover, the comparisons of time-resolved reflectance show that MMC has an excellent agreement with other solvers in homogeneous, perturbation and multi-layer case. Our study has demonstrated that MMC is a correct and reliable solver which can be flexibly applied in modeling various biological media. After that, we applied the MMC to simulate a longitudinal TD-NIR study on the progression of dementia disorders. Such neurodegenerative diseases are often accompanied with progressive brain atrophy that, at late stages, leads to drastically reduced brain dimensions. In this work, we aim to retrieve information concerning the brain-atrophy stage and its evolution, proposing a novel approach based on non-invasive TD-NIRS measurements. For this purpose, we created a set of virtual human-head atlases in which we eroded the brain (i.e. increased amount of cerebral spinal fluid (CSF)) as it would happen in a clinical brain-atrophy progression. The analysis of late photons in the time-resolved reflectance curve –obtained via accurate MMC simulations– exhibited

peculiar slope-changes upon CSF layer increase. The visibility of the effect under several measurement conditions suggested good sensitivity to CSF variation, even in the case of real measurement and under different geometrical models. The robustness of the results might promote the technique as a potential indicator of the dementia progression, relying only on fast and non-invasive optical observations. In the second part, we performed two studies for a novel technique TD-DCS. TD-DCS was recently proposed, which has the unique advantage by simultaneous measurements of optical and dynamical properties in deep tissues. In the first study, analytical models for calculating the time-resolved electric-field autocorrelation function is presented for a multi-layer turbid sample, as well as a semi-infinite medium embedded with a small dynamic heterogeneity. We used MC simulations to verify the analytical models, which demonstrated that the theoretical prediction for the time-resolved autocorrelation function was highly consistent with the MC simulation. Using these analytical models, we also showed that TD-DCS has a higher sensitivity compared to conventional CW-DCS for detecting the deep dynamics. The presented analytical models and simulations can be utilized for quantification of optical and dynamical properties from future TD-DCS experimental data as well as for optimization of the experimental. The second study was aiming to find out the optimal experimental parameters such as S-D separation, gate opening time and width, with which a high contrast measurement on the cortical dynamics can be achieved. In this study, we use a simulation approach

to optimize these parameters based on MMC computations on a realistic human head model. The simulations show that with an acceptable input power of light, the combinations of S-D separation ranging from 0 to 15 mm, gate opening time at 700-800 ps, and gate width of 800 ps are optimal for achieving higher contrast measurement on the cortical dynamics. The simulation approach and results are helpful for the optimization of TD-DCS experimental design focused on brain functional detection. The last part is the CW-NIRS experiments for measuring the cerebral activity in freely moving animals. The main aim of this work is to study the functionally cortical activity of freely moving animals by the noninvasive application of NIRS. A series of behavioral motor and associative tasks such as food reward stimulus, motor task and startling stimulus. During the food reward experiment, we found the sheep showed a cortical activation (an increase in oxy-hemoglobin and a decrease in deoxy-hemoglobin) in both hemispheres, and the right response is greater than the left. In the motor experiment, both hemispheres of the sheep also showed a cortical activation when they are moving with respect to standing still. When the sheep suffering the startling stimulus, they showed a significant cortical activation for about 20s after the stimulus and then restored. These studies can not only demonstrate the ability and flexibility of CW-NIRS to detect the cerebral activity of freely moving animals, but also strengthen knowledge of how animals perceive different environmental situations.

PEROVSKITE BASED INKS FOR OPTOELECTRONIC DEVICES

Roberto Sorrentino - Supervisor: Annamaria Petrozza

Halide perovskite semiconductors have the potential to merge the highly efficient operational principles of conventional inorganic semiconductors with the low-temperature solution processability of emerging organic and hybrid materials. Since the first report on high efficiency, solution processed, solid-state hybrid perovskite based solar cells in 2012, there has been a world-wide explosion of research activities on these materials, with laboratory-scale solar cells power conversion efficiencies recently exceeding 23%.

The growing interest in 3D hybrid perovskite semiconductors has soon expanded their field of application, with proof of concept of electroluminescent and lasing devices, thus potentially impacting optoelectronics under many aspects. In fact, halide perovskite has large absorption coefficients in the visible and UV range and long carrier lifetimes. On top, solution processability would result in a drastic simplification and affordability of the manufacturing processes.

Nowadays, there are a few aspects that currently limit the potential of perovskites and their use for consumer electronics. First of all, the toxicity of

lead-based compounds is probably the most discussed topic. On this side, intense research activities are already going on to develop lead-free materials. Moreover recent studies show the possibility of fully recycle the lead present in exhaust car batteries or in active layer of the optoelectronic devices, thus getting away from the practical and expensive issue of disposal of hazardous materials. The second important aspect regards the organic solvents often used to prepare perovskite precursor solutions, which present health and environmental hazards. Furthermore, typical solvents employed in the processing of lead halide-based perovskites possess high boiling points. These aspects complicate the deployment of energy efficient fabrication processes and increases the environmental impact and the cost of waste handling. Another key aspect is the possibility to control the material's crystallization. In fact the final microstructure, which dominates the optoelectronics properties of the light absorbing layers, depends on how the constituent ions self-assemble during crystallization on the selected substrate. This is a complex function of precursor ratio, solvents, processing additives, substrate roughness and surface energy, atmospheric/

environmental conditions, annealing temperature and treatment time.

Particle-based ink formulations in safer and more environmentally friendly solvents can represent a successful strategy to fully deploy the technology. Various synthetic procedures for lead halide-based perovskite particles have been reported so far in literature. The nanocrystals suspensions are predominantly stabilized by the use of long ligands that are, together with the remnants of high boiling point solvents, difficult to remove. However, all these methodologies still utilize growth controlling capping ligands and/or are hardly scalable and/or involve the use of expensive, high boiling point and often hazardous solvents.

During the Ph.D. period, were developed and optimized two different kind of inks, with the idea to use environmentally friendly solvents and large area compatible deposition techniques to permit the up-scaling of the process for two different applications.

The first ink is thought for light detection applications in the visible range. Light detection is one of the fields where there is large potential for achieving real

applications in a short to medium time-frame with perovskite-based devices. We develop a straightforward and scalable low temperature synthesis of methylammonium lead iodide (MAPbI₃) perovskite particles with tunable dimensions, down to the sub-micrometer range. In contrast to previously reported synthetic procedures, our approach employs only water and isopropanol, which are widely utilized across industrial, medical and household applications and present much lower health hazard and environmental toxicity concerns in comparison to other commonly used organic, toxic and high boiling point solvents. Synthesized particles are formulated into printable inks with isopropanol, without additives. Subsequently they are deposited by a large-area compatible bar coating technique, and coated with a thin [6,6]-phenyl-C61-butyric acid methyl ester fullerene (PCBM) layer, which passivates surface traps, accepts electrons and ensures selective charge circulation of holes. This permits to demonstrate the highest measured specific detectivity in printed light detectors till date, reaching a maximum value of $7.23 \times 10^{13} \text{ cm Hz}^{-0.5} / \text{W}$ in the visible spectrum. This value is even higher than in commercially

available Silicon photodiodes. Moreover, the gain and response time are at least one order of magnitude higher and lower, respectively, than in any other printed perovskite photodetector, demonstrating a good balance between signal amplification and device response speed, two key parameters for photodetector devices.

The second ink is thought to realize tandem solar cells perovskite/perovskite or silicon/perovskite based or outdoor/indoor light harvesting. In these systems, having active materials with tunable band gap is a key aspect. A fast and one-step-injection synthesis is optimized, leading to the formation of stable lead halide perovskite nanocrystals, passivated by short alkyl chains. The synthesis can be done in ambient conditions, at room temperature and can be up-scaled reaching easily liters of inks. Moreover, no post synthetic procedures are needed on the nanocrystals. Here, a fully inorganic cesium lead bromide (CsPbBr₃) perovskite has been used as active material. By using fully inorganic perovskite, it permits to have a better moisture and temperature stability and, since bromide-based compounds

exhibit a wide (2.32 eV) band-gap, these materials can achieve high open-circuit values in the solar cell device. The ink developed permits to disperse nanocrystals in not hazardous and low boiling point solvents. What we focused our attention on, is the optimization of the ink to deeply control the synthesis and we studied the effect of the size and the packing of the nanocrystals to obtain solar cells with large active area by using bar coating as deposition technique. The devices were tested under solar simulator and white LED to exploit outdoor and indoor light harvesting applications. Both synthesis and deposition technique are up-scalable and these up-scalability could open up the door of the optoelectronic market.

BROADBAND AND ULTRAFAST MID-IR LASERS FOR HIGH RESOLUTION

Yuchen Wang - Supervisor: Gianluca Galzerano

Since the experimental researches and theoretical studies of the optical frequency comb have started, this class of devices has attracted attentions of researchers from many fields of study. The equidistant and narrow comb-line structure of a fully-stabilized femtosecond mode-locked laser brings forward the possibility to perform high-resolution and high-precision spectroscopy with absolute frequency calibration. This ground-breaking achievement has been widely recognized as John L. Hall and Theodor W. Hänsch shared one half of the Nobel Prize in Physics of 2005. Behind the success of optical frequency combs, one of the cornerstones is undoubtedly the laser mode-locking technique. While numerous modes of a broadband laser oscillate simultaneously with a well-defined phase interrelation, the laser outputs a train of self-similar ultrashort pulses. Pulses as short as two optical cycle has been demonstrated in a Ti:sapphire laser resonator.

As a tool for spectroscopy, a monolithic source covering the 'molecular fingerprint region' in the mid-infrared (mid-IR) from 3 to 5 μm is of great interest. The versatile ability of the optical frequency combs combined with the intense vibrational transition

features of common gas-phase molecules in this wavelength region could enable sensitive detection of small traces of gas in real-time. In this thesis, the development and characterization of a widely tunable $\text{Cr}^{2+}:\text{CdSe}$ laser at 2.65 μm tunable for more than 900 nm, a mode-locked $\text{Cr}^{2+}:\text{ZnSe}$ laser at 2.4 μm with sub-35-fs pulse duration, and a mode-locked femtosecond (fs) $\text{Dy}^{3+}:\text{fluoride}$ fiber laser at 3.1 μm are reported in detail. The experimental results of amplification and spectral broadening of the $\text{Cr}^{2+}:\text{ZnSe}$ laser are demonstrated.

Based on emission wavelength tuning techniques employing

reflective diffraction gratings, a widely tunable $\text{Cr}:\text{CdSe}$ was developed in collaboration with Bauman Moscow State Technical University in Moscow, Russia. Using mid-IR anti-reflection coating on the crystal surfaces, low intracavity losses were achieved which lead to a high laser slope efficiency of more than 50%. Output powers exceeding 1 Watt in continuous-wave, with a wavelength tunable from 2.2 μm up to 3.1 μm , was demonstrated. The thermal lensing and power scalability were also investigated in this experiment, showing that the current limitation for higher output power is due to the relatively low thermal conductivity

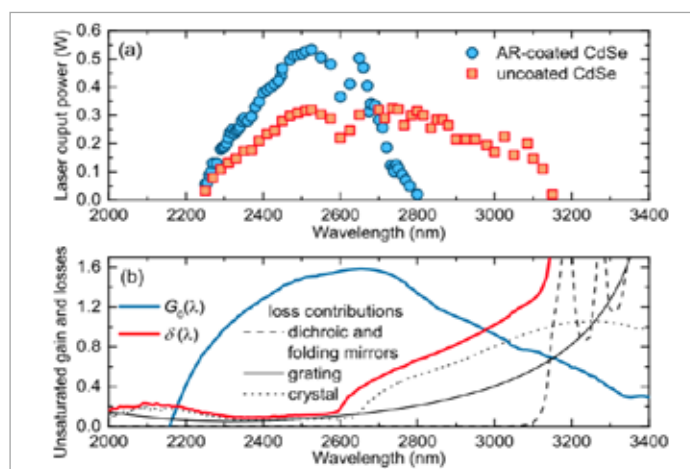


Fig. 1 - Wavelength tunability performance of $\text{Cr}^{2+}:\text{CdSe}$ laser: (a) output power vs emission wavelength at 1.5 W pump power, (b) wavelength dependence of gain and intracavity loss contributions of the AR-coated crystal.

and relatively high thermal lensing coefficient.

In a separate experiment, a thorough investigation of the $\text{Cr}:\text{ZnSe}$ Kerr-lens mode-locked fs laser was demonstrated. Different cavity lengths from 0.5 m to 1 m, hence repetition frequencies from 150 MHz to 300 MHz were tested. Careful tuning and analysis of the cavity dispersion compensation were performed in order to minimize the pulse duration. These efforts have led to a pulse duration of 34 fs (4 optical cycles) with a spectral bandwidth of 220 nm centered at 2.4 μm . The phase noise and relative intensity noise characterizations of the mode-locked laser have proven its good stability for spectroscopic and metrological applications in the mid-IR. Further amplification and supercontinuum generation processes could be implemented for the synthesis of an optical frequency comb directly in the mid-IR.

As another promising candidate for mid-IR femtosecond laser source around 3 μm , a $\text{Dy}:\text{fluoride}$ fiber laser setup was also carefully investigated. During a research internship at Laval University in Quebec (Canada), I have contributed also to researches on this topic. We have successfully demonstrated the first passively mode-locked femtosecond fiber laser beyond 3 μm , providing an solitonic pulse train with pulse duration as short as 830 fs at repetition frequencies from 42 to 60 MHz. The average output power in stable single pulse operation exceeds 200 mW,

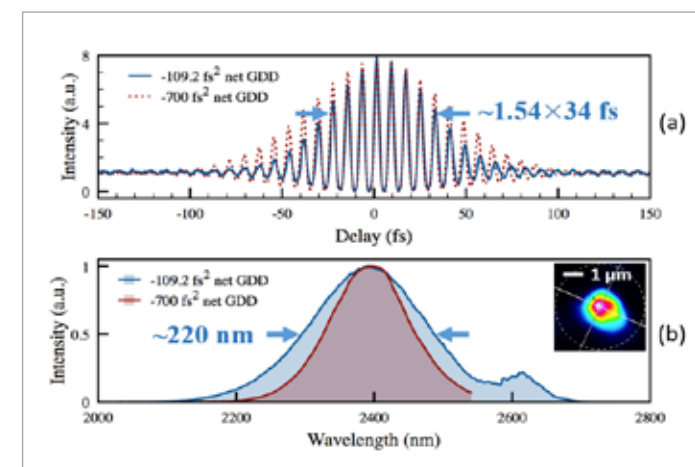


Fig.2 - Pulse train optical spectrum and (b) two-photon absorption interferometric autocorrelation trace. (Inset) laser output beam profile.

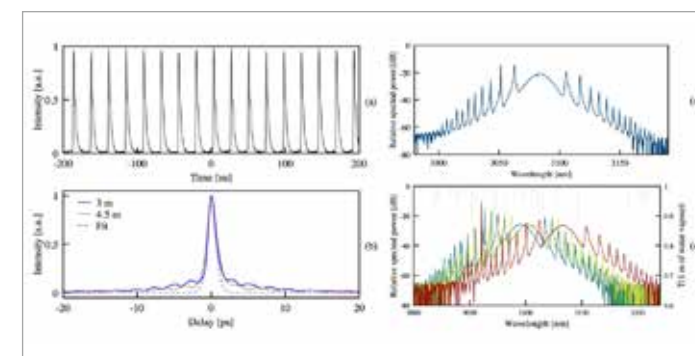


Fig.3 - (a) Pulse train trace of the $\text{Dy}:\text{fluoride}$ fiber laser, (b) pulse autocorrelation trace of the output pulses, (c) optical spectrum with a 4.5 m fiber configuration and (d) wavelength tunability.

which corresponds to a maximum pulse peak power of 4 kW and a maximum pulse energy of 4.8 nJ. This first demonstration of fs mode-locked fiber laser source beyond 3 μm further extends the reach of rare-earth doped fluoride fiber lasers into the mid-IR, opening new possibilities for the direct synthesis of mid-IR frequency comb sources covering the molecular fingerprint region.

These novel developments in the field of mid-IR ultrafast and broadband laser researches should prove helpful for the advance of laser precision spectroscopy techniques and devices. In turn it would greatly broaden the opportunities for frequency metrology, environmental monitoring and industrial gas trace sensing applications.

SPIN-CHARGE INTERCONVERSION IN GE-BASED STRUCTURES

Carlo Zucchetti - Supervisor: Marco Finazzi

Since the time when Brattain, Bardeen and Shockley designed the first transistor (1948) the world of information transport has experienced a revolution. The exploitation of the electron charge as a carrier of information has produced electronic devices with ever increasing performances. In particular, the scalability of the transistor size has gradually allowed integrating a growing number of transistors in the same circuit chip. However, the gate of last generation transistors has reached the (almost critical) dimension of few nanometers. In order to follow the predictions of the Moore law, the industrial technology has now moved to a multi-core technology, which nevertheless appears as a temporary solution. Moreover, the exploitation of the flow of charges involves detrimental issues, like power consumption and capacitive effects, which cannot be solved within the paradigm of common electronics.

Therefore, a great effort has been dedicated to exploring new viable routes to transfer information, which should boost the performances of nowadays electronic devices, holding the promise of a lower power consumption. To realize this goal, spintronics aims at the

active control of the spin degree of freedom of the electrons. Indeed, a pure spin current can be represented as a flow of spin-up electron moving in one direction and spin-down electrons moving in the opposite one. Since no net flow of charges is associated, the exploitation of pure spin currents should result in a drastic decrease of the power consumption. A key point in future development is the integrability with the nowadays mainstream silicon technology. In this context semiconductors appear as the most natural hosting material for spintronic studies. However, due to the fact that they are non-magnetic materials, the lack of a net spin population at equilibrium is the first goal to address. Several techniques of spin injection have been already exploited in the literature. Among all of them, during my Ph.D. activity I have used the so called "optical orientation": by shining a semiconductor with circularly polarized light, it is possible to generate a net spin population in the conduction band of the material, with a spin polarization up to 50%. This guarantees high efficiencies of spin injection and represents a great tool to investigate spin-related properties, since the kinetic energy of the spin-population can be easily tuned by selecting the wavelength

of impinging photons.

Germanium is the material of choice in this field. Indeed, the efficiency of the spin injection in Ge is up to the 50%, and, notably, this value is obtained when the photon energy is tuned at the direct gap of Ge, which perfectly matches the most exploited telecommunication window (1550 nm). Moreover, the 4% lattice mismatch between Ge and Si is small enough to allow for the easy integration with a Si platform. Thus, Ge can be viewed as an ideal material for the coupled exploitation of the functionalities of electronics, spintronics, and photonics.

Beyond the generation, the investigation of spin-related properties of materials involves the possibility of driving and detecting the non-equilibrium spin population. To drive for a long distance a spin-polarized population of electrons, the material should have a low spin-orbit coupling, since otherwise after very few scattering events the spin-character of the population would completely be lost. On the contrary, in order to detect a spin population one can exploit the so called spin-charge interconversion phenomena. These effects allow for the conversion of a charge

current into a spin current, or vice versa. This represents a great tool for spintronic studies, since a spin current (which cannot be easily measured) can be converted in a detectable charge current. The ultimate ingredient for spin-charge interconversion phenomena is a large spin-orbit coupling. Thus, the study of spin transfer between materials with different strength of spin-orbit coupling is another key point for the spintronic development.

By growing a thin Pt layer on the top of a semiconductor we investigate the injection of spins in Ge and their transfer into the Pt layer. Indeed, Pt is a heavy metal with a large spin-orbit coupling, which makes it a good platform to investigate the spin-charge interconversion. Once the spin current is injected from Ge to Pt, it undergoes to the conversion in a detectable charge current, from which we can infer key spin-related properties of the materials. In this sense we observe that a thin Pt layer grown on the top of Ge works as a spin detector.

By moving to a nonlocal spin injection/detection scheme, we can investigate the transport of the spin in the germanium substrate. Indeed, by substituting the flat Pt film with a small Pt pad grown on the top of semiconductor, we locally detect the spins reaching the position of the Pt detector. We inject spin-polarized electrons populations at increasing distances from the detection Pt pad. We experimentally demonstrate that if the spins are injected close to the detection

point most of them are detected, while if the injection is tens of micrometers far from the detector, most of the spins lose their spin-character, thus decreasing the detected signal. From this, we estimate the typical lengths for a spin population to depolarize, which results to be around 10 μm in Ge at room temperature. It is worth mentioning that this value is larger than the common sizes of electronic devices.

In order to properly investigate the spin-related properties of Ge we have probed the spin-to-charge and the charge-to-spin conversion phenomena in the Ge itself. From this, we have inferred a small efficiency for spin-charge interconversion in the case of quasi-thermalized electrons, while the efficiency of the conversion is drastically enhanced as the kinetic energy of the spin-polarized carriers is increased and the spin-charge interconversion is mediated by collisions with phonons instead of impurities.

At this point, we have exploited the suitability of Ge as a substrate for the epitaxial growth of several materials. Thus, we have studied the spin-related properties of thin Bi films grown on Ge, as a function of Bi thickness. With spin- and angle-resolved photoemission spectroscopy we have detected the presence of spin-polarized surface states in Bi, fingerprint of spin-charge interconversion localized at the Bi surfaces or interfaces. It is worth mentioning that the spin-charge interconversion in a single surface could be more efficient than a bulk

one, while the opposite surfaces of a layer give opposite contribution to spin-charge interconversion, thus canceling the overall spin-charge interconversion signal. By means of scanning tunneling microscopy we have observed the presence of nano-islands in the early stages of growth of Bi. This produces the opening of a gap in the bulk of the Bi nano-islands, which electrically disentangles, at least partially, the two Bi surfaces, favoring the spin-charge interconversion from the Bi/Ge interface with respect to the one occurring at the Bi/air surface. Indeed, by injecting spin-polarized electrons in Ge by means of optical orientation it was possible to detect a spin-charge interconversion signal in the region where the Bi nano-islands are present. As the quantity of Bi deposited on Ge surfaces is increased, the islands start to merge and the gap is closed: in this region a negligible spin-related signal is detected. This study paves the way to the exploitation of the confinement as a tool to control and tune the spin-charge interconversion.

All the investigations I carry on during my Ph.D. point towards the exploitation of Ge as a platform to generate, transport, detect or eventually inject in other materials a spin-population: a key step in the exploitation of spintronics for either a new generation of electronic devices or memory storage.