DESIGN AND TECHNOLOGIES FOR CULTURAL HERITAGES | ELECTRICAL ENGINEERING | ENERGY | GEOMATICS AND INFRASTRUCTURES | INDUSTRIAL CHEMISTRY AND CHEMICAL ENGINEERING | INDUSTRIAL DESIGN AND MULTIMEDIA COMMUNICATION | INFORMATION TECHNOLOGY | INTERIOR DESIGN | MANAGEMENT, ECONOMICS AND INDUSTRIAL ENGINEERING | MANUFACTURING AND PRODUCTION SYSTEMS | MATERIALS ENGINEERING | MATHEMATICAL MODELS AND METHODS IN ENGINEERING | MECHANICAL SYSTEMS ENGINEERING | **PHYSICS** | PRESERVATION OF ARCHITECTURAL HERITAGE | PROGRAMMING, MAINTENANCE, REHABILITATION OF THE BUILDING AND URBAN SYSTEMS | RADIATION SCIENCE AND TECHNOLOGY | ROTARY WING AIRCRAFT | SANITARY - ENVIRONMENTAL ENGINEERING | STRUCTURAL SEISMIC AND GEOTECHNICAL ENGINEERING | TECHNOLOGY AND DESIGN FOR ENVIRONMENTAL QUALITY IN BUILDINGS AND URBAN CONTEXT | TERRITORIAL DESIGN AND GOVERNEMENT | URBAN AND ARCHITECTURAL DESIGN | VIRTUAL PROTOTYPES AND REAL PRODUCTS | WATER ENGINEERING | AEROSPACE ENGINEERING | ARCHITECTURAL COMPOSITION | ARCHITECTURE, URBAN DESIGN, CONSERVATION OF HOUSING AND LANDSCAPE | BIOENGINEERING | BUILDING ENGINEERING

PhD Yearbook | 2010

Chair:
Prof. Franco Ciccacci

DOCTORAL PROGRAM IN PHYSICS

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

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

The contents of the doctoral program are strictly related to the research activities carried out in the laboratories at the Department of Physics. They can be divided into two main areas:

a. Condensed Matter Physics, including photoemission; spin-resolved electronic spectroscopy; magneto-optics; X ray diffraction; magnetic nanostructures for spintronics; synchrotron radiation spectroscopy, positron spectroscopy, semiconductor nanostructures.
b. Optics and Quantum Electronics, including biomedical applications of lasers, laser applications in optical communications; diagnostics for works of art; time-resolved optical spectroscopy; ultrashort light pulse generation and applications; UV and X optical harmonics generation.
All these research activities rely on advanced experimental laboratories located at Politecnico di Milano (Milano-Leonardo Campus and Como Campus) and are performed in collaboration with several international Institutions. Besides the experimental research, a consistent effort is devoted to the design and development of novel instrumentation.

As for the educational program, it can be divided into four parts: 1) Laboratory of Basic Physics, implying that the students join full time different experimental laboratories, guided by their tutor as well as other colleagues at the Department of Physics; 2) Main courses specifically designed for the PhD program; 3) activities pertaining more specific disciplines which will constitute the basis of the research work to be carried out during the Doctoral Thesis; 4) Doctoral Thesis.
The thesis work (which constitutes the most relevant part of the program) has a marked experimental character and will be carried out in one or more laboratories at the Department of Physics. Based on the scientific collaborations of the Department, the students are encouraged to perform their thesis work also in laboratories of other national or foreign Institutions.
Numerous collaborations, which the PhD students may be involved in, are presently active with several national and international Institutions, such as: ETH-Zürich, EPL-Lausanne, Lund Institute of Technology, University of Paris-sud, Ecole Polytechnique-Paris, University of Barcelona, University of Berkeley, Technical University of Wien, University of Bordeaux, MIT-Cambridge, INFM-CNR, IIT–Istituto Italiano di Tecnologia, European Space Agency, ENEA, Elettra–Ts, PSI-Villigen, Agenzia Spaziale Italiana, European Synchrotron Radiation Facility (ESRF-Grenoble).
The mean number of fellowship-grants for students entering the PhD program is around eight per year, while the mean number of available positions is sixteen per year. At present the overall number of students in the three-years course is thirty.
Teaching and research activities of the Doctoral Program are controlled and organized by a number of Faculty members large enough to cover a wide spectrum of research fields.
All members are highly qualified and active researchers. This ensures a continuous updating of the PhD program and guarantees that the students are involved in innovative work.
The Doctoral Program relies also upon a Steering Committee, formed by distinguished experts (see table below) coming from R&D industries or Research Labs, taking care that the goals of the PhD program conform with the needs of non academic world.

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LOCAL AND COLLECTIVE EXCITATIONS IN CUPRATES INVESTIGATED BY HIGH RESOLUTION RESONANT INELASTIC X-RAY SCATTERING

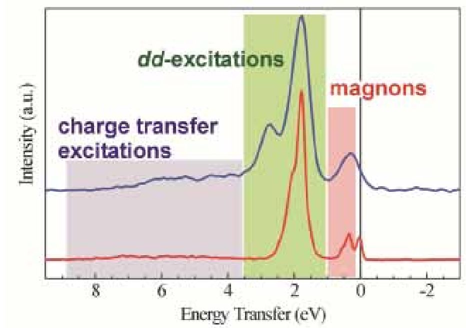
Valentina Bisogni

The thesis is an experimental work dedicated to the study of the electronic and magnetic properties of the cuprate compounds, superconducting materials at high temperature (high-T_c), by means of Resonant Inelastic X-ray Scattering. Thanks to the properties of synchrotron radiation sources, which produce high brilliance and high intensity X-ray beams, and to recent improvements in the instrumentation, Resonant Inelastic X-ray Scattering (also called RIXS) has been established as a very powerful technique for the study of strongly correlated electron systems. This is due to the enormous progress in energy resolution in the soft X-ray range achieved first at the European Synchrotron Radiation Facility (ESRF) in Grenoble and later with further progress at the Swiss Light Source (SLS) in Villigen. This happened in 2007 and after; thus high resolution RIXS can be regarded as a new emerging field. In the thesis is presented one of the first applications to the doped high-T_c superconductors and to their undoped parent compounds (insulators).
Most of the experimental work has been done at the soft X-ray beamline of the ESRF, ID08, using the AXES spectrometer (see Fig. 1). The instrument has a dedicated monochromator situated before the sample and

1. The AXES spectrometer at the ID08 beamline of the ESRF

it is characterised essentially by two elements, a dispersive optics - a grating - to analyse in energy the photons emitted by the sample and a detector – a CCD camera – which records the intensity of the photons. AXES has been realised fifteen years ago by the group of Prof. L. Braicovich from the Physics Department of the Politecnico di Milano (the reaserch group I have been working with) and it has been continuously upgraded during the years. Further soft X-ray RIXS measurements have been done at the ADRESS beamline of the SLS with the SAXES spectrometer, realised by the same the group with the same optical layout and operational since 2007. We added also hard X-rays RIXS measurements at the ID16 beamline of the ESRF by using the new spectrometer developed by the ID16 staff (S. Huotari and G. Monaco *et al.*).
The Resonant Inelastic X-ray scattering technique is a *photon in - photon out* process of the second order which first excites the sample on resonance by using the X-rays and then detects the energy losses of the X-rays emitted during the relaxation process and corresponding to neutral excitations of the system. The technique is presented in the thesis by explaining its physical mechanism starting from the electron-matter interaction and by showing the importance of the energy resolution in the study of the low energy scale excitations. The RIXS instrumentation used at the ID08 beamline is illustrated together with a recent intervention done on the AXES spectrometer which was part of my thesis work: a refocusing mirror introduced between the spectrometer itself

and the monochromator to improve the optical matching and a new CCD camera to improve the energy resolution.
The systems under study, the cuprates, are strongly correlated materials with anomalous properties both in the undoped case (two dimensional



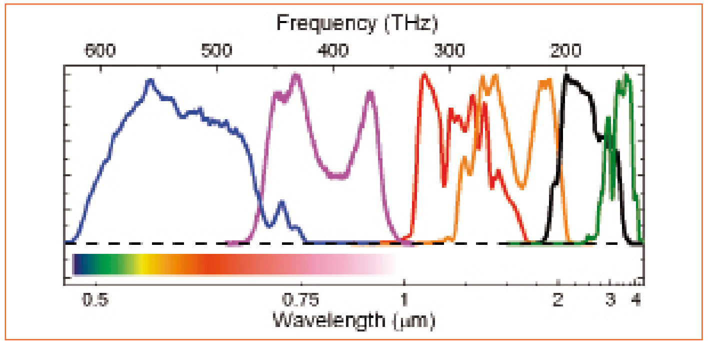
2. RIXS spectra of $CaCuO_2$ (blue) measured with the AXES spectrometer and La_2CuO_4 (red) measured vwith the SAXES spectrometer

antiferromagnetic insulator) and in the doped one (still unexplained superconducting behaviour). The periodic crystal structure characterised by the presence of a CuO_2 plane is described in the thesis within a general presentation of these materials and together with their intriguing electronic and magnetic properties.
During the time of the thesis original results on these materials have been obtained thanks to the high resolution RIXS study. Two kinds of excitations have been investigated having the same orbital character, Cu *3d*, but with completely different behaviour: local for the *dd*-excitations and collective for the magnetic excitations (see Fig. 2).
The *dd*-excitations correspond to transitions between *3d* orbitals of different symmetry so that their energy can be considered equivalent to the energy separation between the concerned levels; therefore *dd*-excitations give information on the energy structure of the cuprates valence band. The measurement of such excitations is quite difficult with one step techniques (as the optical absorption) because *dd*-excitations are forbidden by the dipole selection rules; however Cu-L_3 RIXS presents a very high sensitivity to these features being a two steps process and chemically selective.
Cu-L_3 RIXS has been applied to several undoped cuprates, like La_2CuO_4, $CaCuO_2$ and $BaCuO_2$, to study the dependence of the *dd*-excitations with the scattering geometry and the momentum transfer. The local behaviour of these excitations we have found experimentally is interpreted with a single ion model based on the Cu^{2+} and elaborated within the research group I have been working with: the good agreement between theory and experiment confirms the excitonic character of the *dd*-excitations and gives the possibility to assign the energy and the symmetry to the *3d* states representing a good starting point for more complicated models.
Magnetic excitations in the undoped cuprates are magnons, quanta of the spin waves, which propagate in the antiferromagnetic CuO_2 plane. These excitations, at lower energy than the *dd* ones, have been accessed by high resolution soft X-ray RIXS for the first time in 2007 at the ESRF during this thesis work. Further results at very high resolution allowed different contributions to be distinguished in the undoped La_2CuO_4: the single magnon, as measured with Cu-L_3 RIXS at SLS, and the bimagnon, as measured with RIXS at different edges, the Cu-L_3 (at SLS) and the O-K (at ESRF). Also data on bimagnon seen with hard X-rays at the Cu-K edge are presented; the data were taken at ID16 of the ESRF.
The most relevant result on parent compound is probably that the RIXS data are in perfect agreement with the neutron work; this allows a great extension of work to tiny samples that cannot be studied with neutrons.
The data analysis is supported by a theory of magnetic excitations in RIXS due to J. van den Brink, L. Ament *et al*; this theory is summarised in the thesis.
Finally, magnetic excitations in the underdoped $La_{2-x}Sr_xCuO_4$ have been recently measured by means of Cu-L_3 RIXS (at SLS) and discussed by comparing them to the case of the La_2CuO_4 parent compound. We present data suggesting phase separation of spin and charge in underdoped $La_{2-x}Sr_xCuO_4$; of course this is a work in progress.

PROBING PRIMARY PHOTOINDUCED PROCESSES WITH BROADLY TUNABLE FEW-OPTICAL CYCLE PULSES

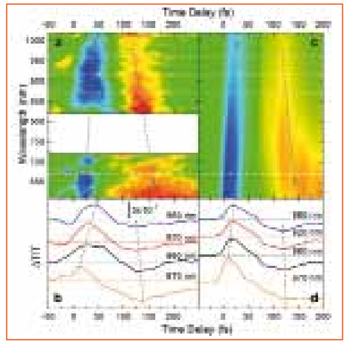
Daniele Brida

Many events in nature occur on so fast timescales that they have been traditionally considered as instantaneous. For centuries, in fact, physical processes could be observed only by eye in combination with low resolution time-keeping devices: Galileo, for example, used his own heartbeat to study the motion of objects. With the development of technology, and in particular with the invention of photography in late ’800, it became possible to study in detail fast motions, like the horse gallop captured by Muybridge in 1878, that could not be fully perceived by the human eye. Since the invention of photography and with later improvements in electronics, the scientific community succeeded in observing natural phenomena occurring in faster and faster timescales. But it was only with the invention of lasers and the generation of ultrashort optical pulses that it was possible to observe physical events taking place in the femtosecond timescale. Nowadays, it is possible to follow photoinduced processes with unprecedented temporal resolution and in some cases it is possible to go down to few attoseconds. The observation of ultrafast phenomena it is crucial for several reasons; first of all, many fundamental and ubiquitous physical processes are extremely fast, and a deep understanding of such phenomena would expand our knowledge of the underlying mechanisms on which the nature is established. Second, but equally important, a fast event can often display an extremely high efficiency that, if completely understood, can be transferred into technology; as an example we can notice that the light harvesting capabilities of plants and bacteria are much higher than the one that can be obtained in solar cells for energy production.
Ultrashort optical pulses are the tools typically used to trigger and track ultrafast phenomena. In fact, the possibility to investigate primary processes on extremely short timescales relies on the generation of ultrashort pulses with of widely tunable carrier frequency, from ultraviolet to mid-infrared. The minimum pulses durations that can be obtained approaches the single-optical-cycle, i.e. a single oscillation of the carrier wavelength in the pulse envelope. Ti:sapphire laser, operating in mode locking regime and then amplified, are perfect for short pulse generation and their high peak pulse power allow us to exploit nonlinear optics techniques to reach the needed tunability with the possibility to obtain pulses with extremely short temporal durations.
The first part of this thesis deals with the generation of near- and mid-infrared pulses in the so-called Optical Parametric Amplifiers. Lot of efforts were spent in order to extend the few-optical-pulse generation concepts successfully applied in the visible spectral range where nowadays sub-5-fs pulses are routinely generated in few laboratories around the world.

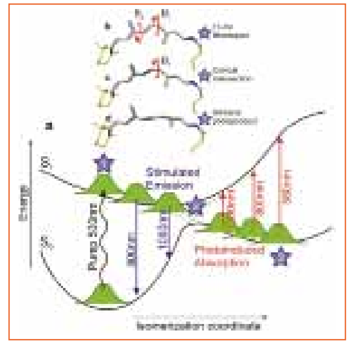


1. Series of ultrabroadband spectra covering the whole visible to mid-IR spectral range

The main reason of this activity is related to the fact that several processes can be observed only in the infrared spectral window, where few-optical-cycle were so far lacking. We succeeded in generating sub-two-optical-cycles pulses by means of new different parametric amplification geometries and now we are able to cover a broad spectral region from 600 nm up to 5 μm.
These pulses, alone or synchronized with other sources already available such as the sub-5-fs visible pulse, allow to study a wide range of primary photoinduced processes occurring in the femtosecond timescale.
In the second part of the thesis, we introduce the experimental technique that by means of ultrashort pulses allows us to observe in real time the evolution of an optically excited sample: pump-probe. In particular, a new theory about the temporal resolution that can be achieved in an pump-probe will be presented with the astonishing result that the resolution is not only related to the instrumental setup but also depends on the sample itself in a non-trivial way. To conclude and highlight how powerful ultrashort optical pulses can be, we present the studies about two primary processes that occur in nature upon photo-excitation. The first one is the first event that that triggers vision in our eyes: the photo-isomerization of Rhodopsin. Rhodopsin is the pigment in our retina that is responsible for the highly efficient night vision; upon excitation it photoisomerizes starting an avalanche of processes that leads to vision.
We were able to observe in detail the first fast step of this chain by observing that the isomerization process is driven by a conical intersection crossing that happen within 100 fs. The second ultrafast phenomenon investigated is the Mott-gap collapse that takes place in a 1D organic Mott insulator. We observed the quantum interference between the optical excitation pathways in the first femtoseconds after photo-doping. Both these two studies would not have been possible without the broadly tunable few-optical-cycle pulses presented in this thesis.



2. Wavepacket dynamics through the rhodopsin conical intersection

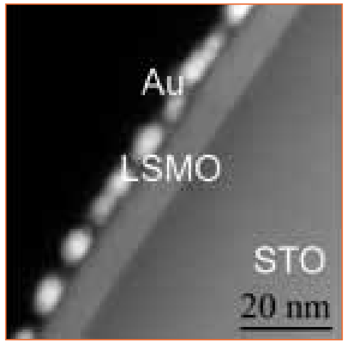


3. Isomerization potential energy surfaces of rhodopsin

MAGNETOELECTRIC EFFECTS AT METAL-OXIDE INTERFACES

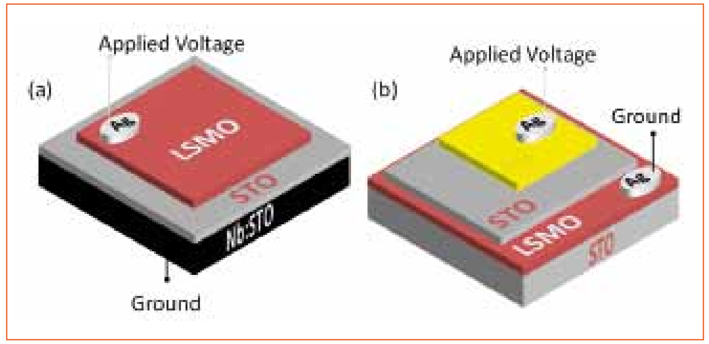
Stefano Brivio

Magnetoelectric coupling is an attractive issue, above all for its possible application in magnetic devices, so that in recent years it has given rise to increasing research in material science and engineering.
In this context the interaction between a gold film and a mixed valence manganite, like $La_{0.67}Sr_{0.33}MnO_3$ (LSMO), has been studied. Such an interface, besides being a prototype of interface for electrical contacts in possible magnetic devices, becomes more meaningful in view of many interfacial effect displayed by manganites. Indeed the peculiar features of manganites are sensitive to many kind of perturbations as strain, charge injection or simply screening. Our experimental work revealed a huge deterioration of the interface properties of $La_{0.67}Sr_{0.33}MnO_3$ when covered by thin gold films. The reduction of the Curie temperature by hundreds of K and an increase of resistivity by four orders of magnitude have been measured. Various techniques were needed to completely understand the details of the interface problem. An essential ingredient is the cluster growth mode of Au on oxides.
Figure 1 displays a transmission electron microscopy image of a sample of 6 nm LSMO grown on $SrTiO_3$ (STO) single crystal substrate covered with 2nm of gold. Gold organizes in nanometric particles and this conformation dramatically increases its reactivity. The migration of oxygen from the manganites towards the Au nanoparticles was finally recognized as the main agent influencing the properties of LSMO in terms of an enhancement of the phase separation towards a more insulating and non magnetic behaviour.
Field effect devices based on LSMO were also produced in order both to have a clear indication of the importance of charge injection in the abovementioned phenomena and to study a reference device for the electric control of the magnetic properties of a ferromagnetic film. Two kinds of structures were conceived and developed, as shown in figure 2. The structure depicted in panel (a) uses a Nb-doped STO substrate and allows the application of an electric field to the bottom part of the LSMO film whereas in the structure of panel (b) the electric field is applied to the top interface of the LSMO film. In both cases the electric field is applied through an STO insulating barrier. It was found that only the latter geometry allows, to some extent, the manipulation of the ferromagnetic properties

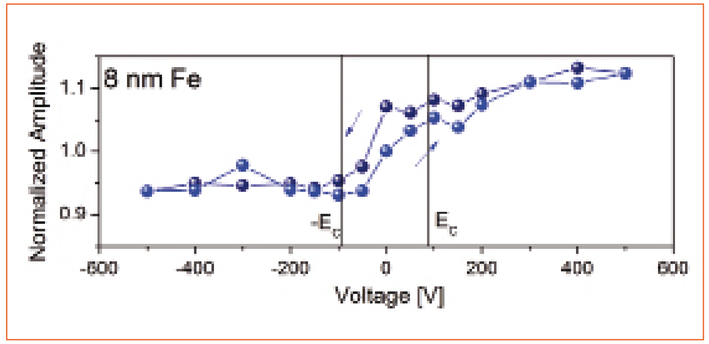


1. TEM image of the sample 2 nm Au/6 nm LSMO/STO substrate. The gold layer forms nanoparticles

through an electric field in agreement with the fact that that the former structure acts on the so called *dead layer* of the LSMO film, where the magnetic properties are depressed. The measured magnetoelectric effects consist only in a limited variation of the Curie temperature of the LSMO film upon electric field application, which is in agreement with reported studies on similar structures. The picture arising as a whole is then that field effect devices based on ultrathin manganite layers are not really promising in view of practical applications.
In this sense another direction has been explored, much more promising in terms of reliability, entity of the magnetoelectric coupling and compatibility with devices operating at room temperature. A preliminary study of the $Fe/BaTiO_3$ interface has been performed, motivated by rapid succession of theoretical works predicting interesting magnetoelectric coupling at this interface, while detailed experimental studies on this interface are still lacking. Fe is a prototypical of ferromagnet and $BaTiO_3$ (BTO) is one of the best known ferroelectric materials, which displays a remnant electric polarization. Fe films with different thicknesses have been grown on $BaTiO_3$ crystals and a magnetic analysis was performed by MOKE at different temperatures and BTO polarization states. Significant variations of the coercive field and, more interesting, Kerr amplitude (proportional to the magnetization) have been recorded.
In figure 3 the variation of the Kerr amplitude as a function of the voltage is shown: the Kerr amplitude switches hysteretically between two states. While the variation of coercive field can be primarily attributed to a strain interaction, we suggest that the modulation of the Kerr variation arises essentially from the spin dependent screening of BTO surface polarization charges in the Fe/BTO interface. Additional work is needed for a full understanding of this phenomenon but the results presented in this thesis are very promising and pave the way to the realization of spintronic devices with electric control of the magnetization.



2. Field effect structures based on LSMO. The structure of panel (a) applies the electric field from the bottom, the one of panel (b) from the top

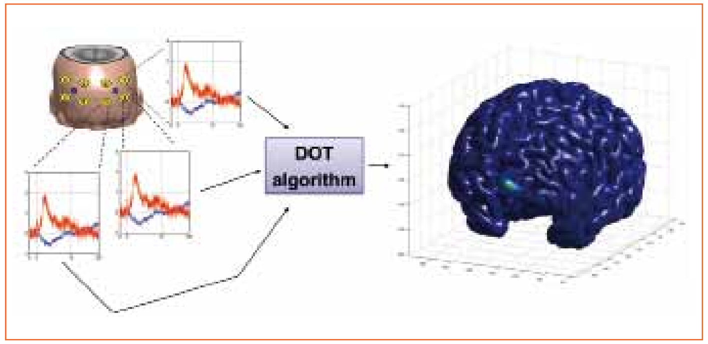


3. Kerr amplitude versus voltage applied to the BTO substrate. The signal switches hysteretically between two distinct states

DIFFUSE OPTICAL TOMOGRAPHY
Development and Validation of a Medical Device and of Physical Models for Brain Activation Studies

Matteo Caffini

Diffuse Optical Tomography (DOT) is an emerging technique to non-invasively perform *in vivo* studies of tissue oxygenation. My principal interest is the study of brain activity in response to specific stimuli and DOT is a powerful tool to perform scientific and clinical investigations in this field. The study of brain activity has been carried out through the years by physicians, physiologists, psychologists and even by some physicist. Many things have been discovered, but many others haven't been understood, yet. The brain controls almost every system of the body, by activating muscles, by causing secretion of chemicals and in many other fascinating ways. This centralized control allows rapid and coordinated responses to changes in the surrounding environment.
Standard neuroimaging techniques, such as Computed Tomography (CT) and Magnetic Resonance Imaging (MRI), dramatically improved the *in vivo* anatomical imaging of the brain features. Since the birth of functional imaging, Positron Emission Tomography (PET) and Single Photon Emission Computed Tomography (SPECT) have become standard medical support, especially in tumors localization, while Electroencephalography (EEG) and Magnetoencephalography (MEG) arose as fundamental techniques to measure and monitor the electrical activity of the brain. Moreover, in the last decade, functional Magnetic Resonance Imaging (fMRI), has given new vigor to functional imaging of the brain activity. More recently, DOT is rising in academic research and as possible future standard in bedside monitoring of the brain activity.
DOT is based on Near InfraRed Spectroscopy (NIRS), that is the measurement of light absorption in living tissues in the frequency range between 700 nm and 1200 nm. Infrared absorption strongly depends on tissue oxygenation, because when oxygen binds to hemoglobin, it changes hemoglobin absorption spectrum. Hemoglobin is a protein whose function is to bind oxygen and carry it, through the blood flow, to every tissue in the body where oxygen and other nutrients are withdrawn from the blood. Thus, the measurement of hemoglobin and oxygenated hemoglobin concentrations is a method to estimate the oxygenation status of a tissue. Moreover, we can think to interpret the oxygenation status to study whether a living tissue is `working' or not and, even more, to study how much it is working (Fig. 1).
Jobsis, in 1977, demonstrated that the oxygenation status of brain cortex tissue could be evaluated from measurement of the absorption coefficient at the near infrared wavelengths. In this spectral region biological tissues are transparent enough to allow relatively high penetration, and thus non-invasive investigation of deep tissues is possible.
The simplest way to perform NIRS studies is the Continuous Wave (CW) approach that uses light with constant intensity to measure variations in hemoglobin and oxyhemoglobin concentrations. Because of the diffusive nature of biological tissues, absolute concentrations measurements are not possible. Depth sensitivity in CW-NIRS is only possible by multi-distance source-detectors approach and thus increasing the system complexity. However CW-NIRS instrumentation is relatively cheap and provides excellent signal to noise ratio.
Using pulsed light from a laser source, Time-Resolved (TR) NIRS adds temporal information to the measurements. TR-NIRS, in principle, allows absolute concentration measurements and, moreover, temporal information intrinsically shows depth sensitivity. Models of photon migration in turbid media are necessary to describe the light propagation in tissues and calculate oxy- and deoxy-hemoglobin concentrations.
An even different approach is Frequency Domain (FD) NIRS, in which intensity modulated light is used to probe absorption properties of living tissues. Absolute concentration can be obtained measuring dephasing and amplitude of the re-emitted light.
My dissertation is focused on three aspects: instrumentation, clinical studies and data analysis models.
In Chapter 1 an extended review of NIRS and DOT techniques is presented. Starting from a physiological description of brain activity, functional imaging is introduced. Absorption spectroscopy and NIRS principles are thus explained in detail, together with the different NIRS techniques (CW, TR, FD). In order to better describe the TR-NIRS approach, the photon migration physical model known as Radiative Transfer Equation (RTE) is also presented.
Chapter 2 describes the TR-NIRS instrumentation developed at Physics Dept. in Politecnico di Milano and the data analysis techniques used to process the NIRS data. The 1st generation oximeter is presented, together with the upgrade of the instrumentation (2nd generation oximeter). Data analysis in NIRS studies can be an issue, thus particular attention is given to standard analysis and to more complicated statistical analysis, such as the General Linear Model theory.



1. Diffuse Optical Tomography is the most promising technique for non-invasive investigation of the brain activity

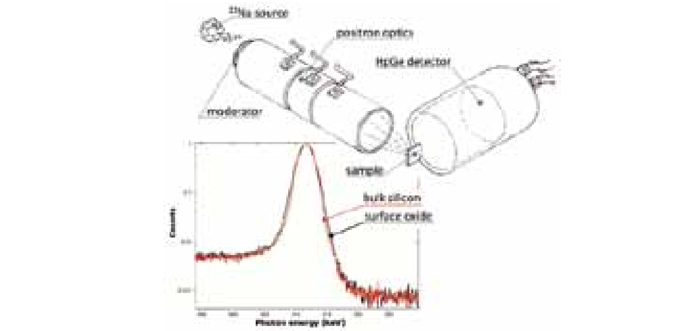
In Chapter 3 two clinical studies are reported. The first application is a cognitive study of sustained attention. NIRS data have been collected in frontal areas on 19 healthy volunteers, during a psychological test (CPT) that selectively activated the frontal areas of the brain cortex. The second is a working memory study in which NIRS data have been collected from the same frontal zones, during a working memory protocol on 19 healthy volunteers. Both studies have been carried out with the instrumentation and the data analysis methods described in Chapter 2.
Chapter 4 reports a MRI-based approach to DOT reconstruction. Being DOT spatial resolution intrinsically poor because of light scattering in biological tissues, the use of *a priori* information is often exploited to add spatial resolution to NIRS data and thus obtaining a 3D tomographic approach to NIRS data reconstruction. In the first section a general algorithm for activation localization is exposed. In the second section a MRI-free method is described. Making use of a brain atlas a reconstruction method and its validation are proposed. I carried out this research activity in the Photon Migration Imaging group at the Martinos Center for Biomedical Imaging in Charlestown, MA.
Being DOT systems made of little more than a fiber-optic probe, a light source, light detectors and a laptop computer, I believe DOT is ideally suited for both clinical applications and high-level academic research. Thus, looking into the next future, DOT can really become a brain monitoring standard technique.

POSITRON BEAM SPECTROSCOPY OF THIN LAYERS AND POROUS MATERIALS

Alberto Calloni

Positron is the antiparticle of the electron, has the same mass and spin, but different charge and magnetic moment. Positrons are produced by the radioactive decay of a ^{22}Na source; they have an extremely high kinetic energy (the endpoint energy of positron emission from ^{22}Na is 546keV) and are usually implanted into bulk samples.

However, fast positrons can also be “moderated”: a moderator is a piece of material in which fast positrons from a radioactive source are implanted and thermalize. An appropriate moderator material then reemits positrons from the surface with a well defined energy and preferentially normal to the moderator surface. The moderated positrons have a kinetic energy in a range that allows to guide them by means of conventional electrostatic or magnetic optics.



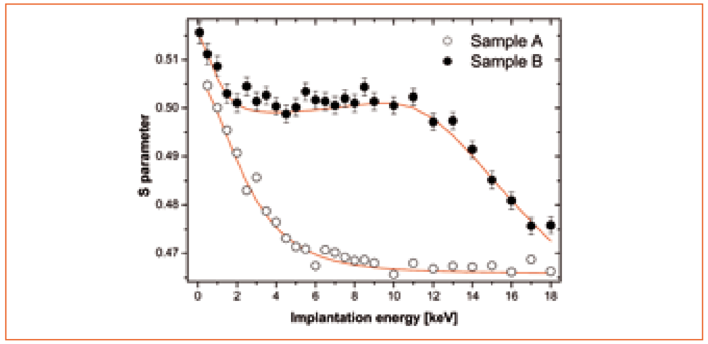
1. Pictorial representation of the positron beam. Positrons are produced by the radioactive source, they are moderated and then accelerated on the target. The graph shows the shape of the annihilation peak as recorded by the gamma ray detector placed nearby the sample when positrons are implanted into two different chemical elements: silicon (high implantation depth) and silicon oxide (low implantation depth), present on the surface of any silicon sample

Since the beginning of 2008, a positron beam has been operated at the L-NESS lab in Como. The beam can accelerate positrons up to 20keV, implant them into the sample and probe thin layers on the surface (the implantation depth ranges from the sample surface down to ~1µm, in particularly soft samples). Due to their nature of positively charged particles, positrons are repelled by ion cores and localize into open space defects and at negatively charged impurities, very often related to reticular defects in crystalline layers or to defect sites at the interfaces: that is why the positron technique is often labeled as a defect characterization tool.

Three problems were studied: the first one is related to the estimation of the density of gallium vacancies in thin films of gallium nitride (GaN) grown by the newly developed technique LEPEVPE (Low Energy Plasma Enhanced Vapor Phase Epitaxy). The vacancy concentration information was used to address the problem of substrate damage during growth under intense substrate bombardment by the plasma ions.

The first result of the study was to confirm that the new technique can produce GaN layers with a quality comparable to standard industrial substrates. A clear change with respect to the literature values was found in the positron parameters, indicating vacancy decoration with hydrogen in the growing layers.

Positron were then used to investigate the structure of a multilayer sample made of a thin silicon film over silicon oxide (SOI). After a morphological characterization, a thin layer of SiGe alloy was grown on top of the SOI structure, in order to study the process of relaxation of the SiGe/Si bilayer. The SiGe layer (50nm thick) is compressively strained on Si; however, the extremely low thickness of the substrate (10nm) floating over an amorphous layer of oxide should allow for strain sharing between the two materials, possibly without the formation of strain relieving dislocations, detrimental for any microelectronic circuit grown on the strained layer. Our technique shows that defects are indeed introduced when the structure is allowed to relax from its meta-stable state by heating at high temperature (750°C for 30min), and that trapped positrons annihilate preferentially with germanium electrons.



2. Example outcome of a positron beam experiment. The lineshape parameter S is reported as a function of the positron implantation energy (related to the implantation depth by a power law). Sample A) GaN sample with low defectivity. Sample B) thin GaN layer (650nm) grown on sapphire. The high level of the S parameter relative to the surface GaN layer (implantation energies from 0 to ≈12keV) is symptomatic of an high defect concentration

The third problem is related to the characterization of porous samples for the production of positronium, a bound state between an electron and a positron which exists in two forms: ortho positronium (o-Ps, triplet state) and para positronium (p-Ps, singlet state). The o-Ps long mean lifetime of 142ns allows for positronium atoms manipulation.

In porous insulators, positronium can be usually formed with high efficiency. In the most efficient sample we analyzed, a piece of silica Xerogel of very low density (0.85mg/cm3), positronium is formed by positrons implanted into the silica grains, it is emitted into the pores with an energy in the order of 1eV and is then allowed to cool by collisions with the pore walls. The presence of an open porosity allows for the formed o-Ps (p-Ps decay is too fast) to be emitted into vacuum: this is one (the other is the possibility of a partial o-Ps thermalization when it is inside the sample) of the characteristics which make the silica Xerogel an optimum candidate to be used as positronium converter in the AEGIS experiment at Cern.

AEGIS (Antimatter Experiment: Gravity, Interferometry, Spectroscopy) has the ambitious goal of measuring for the first time the gravitational acceleration of antimatter. In order to create an antimatter neutral object (less influenced by experimental disturbances like stray electric fields in the experimental area) cold positronium is made to react with anti protons in order to obtain cold antihydrogen atoms (charge exchange reaction).

PHOTOPHYSICS OF CHIRAL ENRICHED SINGLE-WALLED CARBON NANOTUBES STUDIED WITH FEMTOSECOND PUMP-PROBE SPECTROSCOPY

Sajjad Hoseinkhani Asl

Single-walled carbon nanotubes (SWNTs) are quasi-one-dimensional structures consisting of rolled-up graphene sheets. Depending on their "chirality" (roll-up vector that controls their chiral properties), they behave as semiconductors or metals. Owing to their size and their unique mechanical, chemical and electronic properties, SWNTs attract growing attention in fundamental and variety of nanometer-sized electronic and optical applications.

The advent of ultrafast pulsed lasers opened a way to study the structure and dynamical details of materials. Ultrafast optical spectroscopy, in particular pump-probe spectroscopy, is a unique tool for the study of fast relaxation dynamics in molecular systems. The ultrafast technique has enabled us to observe elementary processes such as charge carrier, exciton formation and mobility, coherent oscillations, and intersubband decay of exciton resonances. Knowledge of excited-state dynamics in carbon nanotubes is determinant for their prospective use in optoelectronic applications.

In semiconducting CNTs, the lowest-lying photoexcitations are strongly bound one-dimensional excitons with binding energies, depending on chirality and diameter, of up to about 0.5 eV. Such excitations are described as bound electron-hole pairs with two characteristic coordinates, the centre-of-mass position (RCM) and the relative electron-hole distance or correlation length (). The latter is directly linked to the electronic structure of the material and its physical properties, such as screening, Coulomb attraction, binding energy, exchange interaction and confinement of wavefunctions. For this reason, is the key figure of merit for a better understanding of optical, optoelectronic and photonic properties and also for validation of existing theories on excitonic effects in CNTs. Specifically, if is comparable to the lattice constant, then the exciton is of the tightly bound Frenkel type, typical of molecular solids. In contrast, a value of much larger than the lattice constant supports the Wannier-Mott picture, typical of covalent semiconductors. Exciton size corresponds to a finite volume in the phase space. This volume can be directly measured by nonlinear spectroscopy provided the time resolution is short enough for probing before population relaxation.

In this thesis, we report on the experimental determination of exciton size and mobility in (6, 5) carbon nanotubes. The samples are sodium cholate suspensions of nanotubes (produced by the CoMoCat method) obtained by density-gradient ultracentrifugation. According to the phase space filling (PSF) model, the measured reduction in oscillator strength can be directly related to the exciton size, By using sub-15 fs near-infrared pulses to measure the nascent bleach of the lowest exciton resonance, we estimate the exciton size to be . Exciton–exciton annihilation in our samples is found to be rather inefficient so that many excitons can coexist on a single nanotube. In addition, we use the experimentally determined exciton densities to quantify exciton annihilation kinetics which in turn yield the exciton diffusion constant and diffusion length. The diffusion constant that we obtain is, in the same order of magnitude as the value obtained by fluorescence quenching. The exciton diffusion length as given by, where is the non-radiative decay time, is found to be . Our estimate on the exciton annihilation rate in isolated tubes suggests that higher values observed before arise from inter-tube interactions. Since many frontier applications of carbon nanotubes, e.g. in molecular electronics and nanomedicine, deal with single carbon nanotubes, our characterization provides the proper background for describing their performance. The mobility of the exciton along the tube is indeed crucial for bio-sensors, and our results suggest the right length-scale for surface quenching of optical properties is below 10 nm. We also study coherent phonons in polymer-carbon nanotubes composites by sub 10 fs pump-probe spectroscopy. We find that coherent phonons in the polymer network modulate the exciton resonance of the wrapped nanotube. We propose a model of dynamic environmental coupling in which the polymer vibration affects the carbon nanotubes exciton energy by virtue of the modulation of its dielectric screening. Carbon nanotubes act as antenna for the local environment and highlight small changes in the dielectric constant. This shows the extreme sensitivity of carbon nanotubes to their surrounding, a property essential for sensing applications and crucial for understanding composite materials.

It is common sense that near future applications of CNT are in networks or composite materials. As a practical advantage, composites do not require fancy nano-probes for testing or exploitation and their preparation is suitable for large scale industrial production. A proper engineering of these composites requires however a deep understanding of the environmental influence on CNT properties which is at present still missing. In this thesis we report a study on CoMoCat CNT wrapped into two kinds of conjugated polymers with largely different optical gap and phonon energy: namely poly(9,9-dioctylfluorenyl-2,7-diyl) ("PFO", optical gap ca. 3.0 eV and main C=C stretching frequency of 1600 cm^{-1}), and regioregular poly-(3-hexylthiophene-2,5 diyl) ("P3HT", optical gap ca. 1.9 eV and C=C stretching frequency about 1450 cm^{-1}). Such conjugated polymers form an ordered arrangement around some tubes of proper chirality, according to patterns not fully known yet. We use steady state and transient absorption spectroscopy for investigating our samples, and detect coherent phonon spectra which bring a wealth of information about the vibronic dynamics. We find that the effect of polymer wrapping can be clearly seen in the optical resonances. In particular the nanotubes influence the polymer network morphology while the polymer affects the excitonic resonances of the nanotubes. Dielectric screening however is not just a static effect, but can be modulated at THz frequency by coherent phonons which represents collective, in phase vibration of the carbon atoms in the polymer chains.

In conclusion, we reported transient CNT exciton resonance modulation in polymer-CNT composite for two quite different systems. We propose this be due to the transient modulation of the polymer matrix dielectric function induced by the coherent phonon (Raman Effect). We assume that the exciton in the CNT follows adiabatically this modulation, resulting in a non-stationary screening of the e-h interaction.

Knowledge of the interplay of charged and neutral photoexcitations in carbon nanotubes (CNTs) is indispensable for their prospective use in optoelectronics. Elementary events like exciton breaking and charge trapping have been suggested to occur on a subpicosecond scale, where only optical probes can be used for real-time tracing. In the last Part of this thesis, we demonstrate by a combined spectroscopic-theoretical approach that excitonic and charged excitations in semiconducting CNTs exhibit well distinct optical probes in the E_{22} and E_{11} spectral regions, which is conveniently accessible in a standard pump-probe experiment. We show that the charge carrier yield depends strongly on the bundling and on the photon excess energy. In bundles, inter-tube charge transfer and stabilization by trapping occurs on a time scale of a few hundred femtoseconds.

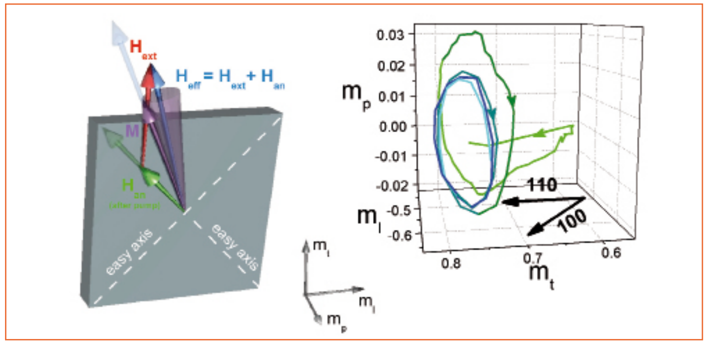
ULTRAFAST ELECTRONIC AND MAGNETIC DYNAMICS IN FE THIN FILMS

Eduardo Mancini

In this work we illustrated the results obtained exploiting the powerful *pump and probe* technique for the investigation of the ultrafast electronic and magnetic dynamics mainly in iron thin films.
In the pump and probe scheme a femtosecond laser pulse locally excites the sample and a subsequent femtosecond pulse probes the excitation. The effect induced by the pump can be probed by measuring, among others, a reflectivity change or a photoemission signal (if probe photons have enough energy to overcome the sample work function). For the optical measurements we exploited the time-resolved magneto-optical Kerr effect (TR-MOKE) i.e. the polarization changes induced by the magnetization on the reflected probe beam on a femtosecond timescale. For the photoemission experiments, we measured the changes in the photoemission yield for different delays between pump and probe (time-resolved photoemission, TR-PES).
During this thesis in order to perform these experiments we developed both an optical setup and a Time-Of-Flight (TOF) analyzer. The optical setup was designed to multiply the fundamental photon energy of the laser (1.55 eV) up to the fourth harmonic (6.2 eV). The home built time-of-flight analyzer served for the detection of the electrons in the photoemission experiments.

We start from the discussion of the TR-MOKE experiments. These experiments addressed the sub-picosecond and the hundreds of picosecond timescales on epitaxial iron thin films grown on magnesium-oxide substrates.
On the short timescale the pump excitation creates a hot non-equilibrium electronic distribution. Comparing the reflectivity and MOKE measurements we determined some important timescales. The electrons thermalize to a hot Fermi Dirac distribution via electron-electron scattering taking place on a timescale < 30 fs. The electrons then lower their energy by electron-phonon scattering with a time constant of 240 fs. The magnetic response shows an ultrafast decrease (< 100 fs) that can be explained in terms of electron-magnon scattering. The hot electronic distribution triggers the magnons, efficiently reducing the magnetization. This process is mediated by the spin-orbit interaction which allows the transfer of angular momentum from the spin degree of freedom to the orbital angular momentum that is eventually absorbed by the lattice. The recovery of the magnetization is instead associated with the Elliot-Yafet scattering with a time constant of 800 fs. The validity of these findings is not limited to iron but extends to other ferromagnets.
In a different set of magneto-optical measurements we focused on the magnetization dynamics on the hundreds of picoseconds timescale. We showed that in Fe thin films, after the initial drop following the pump laser pulse, the magnetization starts to precess (see figure 1) with a period of 120 ps.
In order to detect the precessional dynamics we developed an experimental method that allowed us to extract all three components of the magnetization vector in real space. Knowing the three components of the magnetization we could verify experimentally that the precessional dynamics takes place around an effective time dependent field, given by the vector summation of the magneto-crystalline anisotropy field (function of the pump probe delay) and the external magnetic field (constant in time). The time-dependence of the anisotropy field relies on the local time-dependent temperature variation induced by the pump. The pump creates a local heating of the sample. Both the magnetization and the anisotropy field decrease as the temperature increase. The corresponding misalignment between the magnetization and the anisotropy field causes the magnetization to start precessing (because of the angular momentum associated to the magnetization) with an amplitude depending on the external field (see figure 1). The time variation of the anisotropy field is related to the evolution of the magneto-crystalline anisotropy constant. We extracted the values of the magneto-crystalline anisotropy as a function of time, and therefore of the local temperature. The observed decrease yields the mechanism driving the precessional dynamics of the magnetization. Our experiment provides a clear and direct experimental evidence of the magnetization precession and it represents a simple and widely applicable way to study the ultrafast evolution of the spin order in magnetic structures.
For the photoemission measurements, in order to check the performances of this apparatus we carried out a set of photoemission experiments on bulk crystals. In particular, from static photoemission spectra on a Cu(100) crystal, we extracted the experimental energy resolution depending on the electron kinetic energy, showing that it ranges from 90 meV for electron kinetic energies of 2.7 eV to 58 meV at 1.7 eV. We also explored the possibility of angle resolved photoemission (ARPES) experiments analyzing the dispersion of the surface state on Ag(111) and obtaining results in agreement with the data reported in literature. We concluded our performance measurements with a time resolved two photon photoemission (TR-2PPE) experiment on a Cu(111) surface. In this case we proved the possibility to retrieve the lifetime of an image potential state (10 fs) using femtosecond pulses with cross correlation of 115 fs. Finally we reported the first time resolved one photon photoemission (TR-1PPE) experiments on Fe thin films. These preliminary measurements have been carried out both at low temperature (80 K) and at room temperature. The data showed interesting effects related to the different dynamics of electrons and holes above and below the Fermi level in the two temperature regimes. We attributed these differences to a temperature dependent phonon contribution.

As future perspectives we plan to apply the developed magneto-optical setup to study the spin dynamics on other ferromagnets, thinking of the possibility to make ultrafast writing of magnetic supports a viable solution for not so far in time technological applications. This application could exploit an ultrafast variation of the anisotropy field to control the precessional dynamics. On the other hand our now fully tested and operative time-resolved photoemission setup offers the possibility to gain direct access (namely not optically mediated information) on the femtosecond electronic processes.

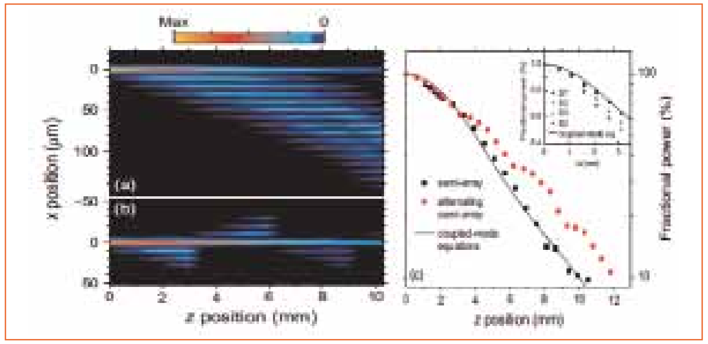


1. (Left) Schematic diagram showing the angular relation between M and the effective filed H_{eff} given by sum of the anisotropy field H_{an} and the external field H_{ext}. The greyed arrows indicate the static condition before the pump arrival while the dark arrows represent the situation after the pump. (Right) Real space trajectory of the magnetization M (for H_{ext}=75 Oe). Various portions of the motion have been marked with different colors for a better visualization. (Center) Coordinate system for the three components of the magnetization (longitudinal, polar and transverse) with respect to the sample

QUANTUM OPTICAL ANALOGIES WITH WAVEGUIDE-BASED OPTICAL STRUCTURES

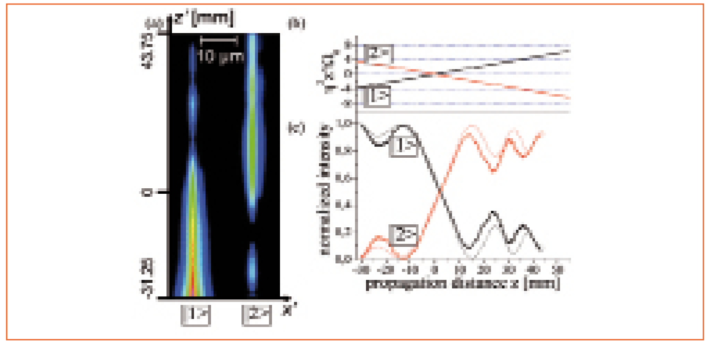
Marco Ornigotti

Analogy is a basic concept for understanding nature, since it analyses and connects different phenomena linked by common properties or similar behavior. In particular, analogy can to some extent apply to specific quantum phenomena and their corresponding classical effects, although quantum physics differs from classical physics in both formalism and fundamental concepts. The main motivation on studying quantum optical analogies rely on the fact that analogies between different fields of physics have proven themselves extremely fruitful in understanding the basic physical concepts and the limits of applicability of different theories; in particular, the analogies between classical physical theories and quantum phenomena reveal the fact that similar mathematical formalisms apply to phenomena that cannot be related at first glance and are a priori conceptually different. The role of mathematics is crucial, because the essence of the analogy resides in the fact that completely different systems can be modeled by similar mathematical equations, unveiling a hidden unity in Nature, beyond its apparent diversity. Among quantum-classical analogies, those concerning wave optics and wave mechanics are perhaps the most familiar ones. The research for analogies between optics and quantum mechanics is rather flourishing, and enables to transfer new ideas, concepts and methods among apparently unrelated fields of physics. Some of the most evident analogies can be found by observing that the time-independent Schrödinger equation has the same mathematical form as the Helmholtz equation, or that there is an uncertainty relation in optics that is very similar to the Heisenberg uncertainty principle. Moreover, from the early days of quantum mechanics, similarities between wave optics and wave mechanics have been highlighted on many occasions; the analogy between geometric optics and newtonian mechanics (expressed by the formal similarity between the Fermat's principle of ray optics and the least action principle of mechanics) was in fact the guiding line to the born of the wave mechanics after de Broglie published in 1923 his hypothesis on the wavy properties of material particles. As compared to a quantum system, using a quantum-classical analogue offers several advantages, such as the possibility of a direct visualization in space of typical ultrafast time evolutions of quantum states, or the possibility to explore coherent dynamical effects not yet accessible in a real quantum system: light propagation in optical waveguide structures offer a high degree of coherence, and no other effects compete to prevent this coherence. Another important advantage relies on the possibility to mimic light-matter interactions by simple geometric bending or twisting of the guiding photonic structures. In the wide scenario provided by the vast literature appeared in the past decades on quantum optical analogies, here the attention is focused on optical analogs of non relativistic quantum physics, which can be easily classified in three categories.



1. Experimental visualization of the optical analogue of the Quantum Zeno Effect

The first category relates to some general issues of quantum mechanics and quantum information and include Aharonov-Bohm and Berry phase, wave mechanics in non-Hermitian quantum systems with parity-time symmetry, spin Hall effect and classical simulators of quantum entanglement, quantum teleportation and quantum random walks. The first two chapters of this thesis fit into this category, dealing with the problem of quantum collapses and revival phenomena and the control of quantum mechanical decay and Zeno dynamics.
The second category of optical analogues mimics coherent effects of atoms or molecules driven by laser fields, such as Rabi oscillations and adiabatic passage and stabilization of atoms in ultra-strong laser fields. To this category belong chapters 3 and 4, that deal with the interaction of two level systems and many level systems with external driving fields. Chapter 4 deals also with the problem of adiabatic passage and to its exploitation for finding new ways of controlling the flow of light in a waveguide optical system.
Finally, the third category deals with problems related to solid-state physics like Bloch oscillations, Zener tunneling, Anderson localization, dynamical localization, and surface physics, to name a few; although these topics are not subject of this thesis, their importance in the developing quantum-optical analogies makes them necessary to be mentioned here.
Finally, it is worth pointing out that very recently analogies have allowed to mimic, in either classical or quantum systems, some key dynamical aspects reported in the relativistic quantum theory and quantum electrodynamics, which are still inaccessible in relativistic quantum mechanics, like Klein Tunneling or Zitterbewegung.

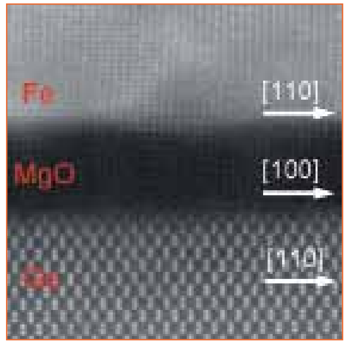


2. Visualization of Landau-Zener tunneling in optical coupplers

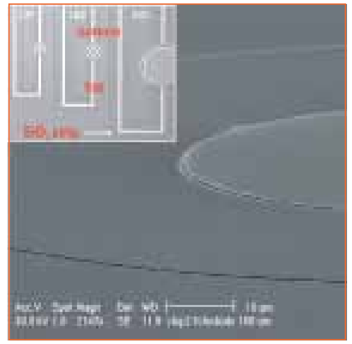
SPIN DEPENDENT TRANSPORT IN FE/MGO/GE(001) HETEROSTRUCTURES

Daniela Petti

During the last two decades, the spin electron degree of freedom has moved into the world of electronics and has yielded new devices, now well-established in the industrial world under the name "magnetoelectronics" (e.g. magnetic random access memories MRAMs). They consist of a combination of magnetic and nonmagnetic metals and rely on the giant, colossal, or tunnelling magnetoresistance. The basic requirement to exploit the intrinsically bistable magnetization states of ferromagnet into a digital electronic device is to be able to interrogate the ferromagnetic element F and 'read' the magnetization state non-destructively. This can be done considering that electrons near the Fermi surface of F are spin polarized, so that itinerant carriers can be used to interrogate the magnetization state of F.
In this picture, the injection of spin-polarized electrons from a ferromagnetic electrode into non-magnetic materials, above all semiconductors (SC), has been a topic of growing importance during the last years. The employ of semiconductors opens the possibility to couple magnetism and traditional electronics, giving rise to the so-called "spintronics".
A fundamental obstacle to the spin filtering at interface F/SC is the conductivity mismatch between the two materials, responsible for the current depolarization and the decrease of spin injection efficiency. This problem can be overcome by inserting a potential barrier between F and SC; an example of potential barrier is an epitaxial MgO tunnelling barrier, which represents also an effective spin filter if coupled with transition metal like Fe, FeCo or Co.
In this scenario, the aim of this thesis is the study and the realization of a heterostructure for spin transport measurements. The work has been realized in the Center L-NESS (Laboratory for Nanometric Epitaxial structures on Silicon and Spintronics) of the Politecnico di Milano located in Como.
This study is focalized on the Fe/MgO/Ge heterostructure. While the use of Fe and MgO is justified by the motivations mentioned above, Ge was chosen for the high mobility of its carriers, for the possibility of creating a spin polarized current through optical pumping and the possibility of spin manipulation through spin-orbit coupling.
The first step of the research activity was the optimization of the heterostructure growth by means of molecular beam epitaxy (MBE). In particular, regarding the MgO/Ge interface, three issues were addressed for the optimization of the oxide deposition: (i) Ge surface preparation and termination; (ii) growth temperature, (iii) post-annealing treatments. Both the interfaces Fe/MgO and MgO/Ge were characterized in situ, chemically by means of X-Ray photoelectron spectroscopy (XPS), structurally by means of low energy electron diffraction (LEED), reflected high energy electron diffraction (RHEED) and X-Ray photoelectron diffraction (XPD); ex situ and morphologically by atomic force microscopy (AFM) and scanning transmission electron microscopy (STEM). In optimized conditions, the samples present low roughness (above 0.3 nm, the same roughness of the substrate), sharp interfaces and good epitaxy, satisfying the fundamental requirements for effective spin dependent transport. The epitaxial relationship found in the heterostructures is Fe[100]||MgO[110]||Ge[100](100), different from that of very similar systems (e.g. cube on cube growth of MgO/GaAs). In fig. 1, a high resolution Annular Dark Field image (z contrast) from a STEM performed in the Oak Ridge National Laboratory by J. Gazquez and M. Varela is presented. The image shows that the heterostructure is fully epitaxial with some dislocations at the Fe/MgO interface; although some defects are present, no interdiffusion occurs.
The second step of research was the optimization of the optolithographic process for the production of tunnel junctions (of dimensions ranging from 4 µm^2 to 600 µm^2) and of photodiodes (ranging from 80 µm to 1000 µm of diameter) to be employed in experiments of optical spin injection in Ge and spin dependent detection across Fe/MgO/Ge interface. In fig. 2 a Scanning Electron Microscopy (SEM) image of a particular of the photodiode active area and mesa area is shown. The dimension of the active area is 80 µm; in the inset an optical image of the whole photodiode structure is presented.
Tunnel junctions on substrates with different doping were fabricated and characterized, in order to verify that the prevalent transport mechanism was tunnelling through MgO barrier and to measure the Schottky barrier between Fe and Ge. These data were interpreted also on the basis of XPS measurements of electron bands alignment at the interfaces Fe/MgO and MgO/Ge. All the samples show a parabolic differential conductance, reflecting the typical behaviour of tunnelling junctions. In particular, very good results have been obtained for light n-doped Ge substrates ($N_D = 10^{15}$ cm^{-3}) in terms of resistance-area product and Schottky barrier: the values are about 10^{-1} Ωcm^2 and 0.3 eV respectively. The RA product is optimized for achieving high spin polarization at interface, while the Schottky barrier, which can give rise to a depolarization of spin current, is strongly reduced respect to the value in Fe/Ge interfaces (0.6 eV). This is a confirmation that the MgO barrier is effective in the modulation of the Schottky barrier, thus in the overcoming of the conductivity mismatch.
Preliminary transport measurements have been subsequently performed employing photodiodes. This experiment is based on the optical pumping of spin in Ge by illuminating the photodiode with a circularly polarized light; using the Fe layer as analyzer, it is possible to detect the spin transport across the heterostructure as an electrical response.
The measurements reveal that a spin filter effect is detectable at room temperature, thus spin polarization seems conserved across the interface, although deeper investigation is required.



1. ADF high resolution STEM (z contrast) image; the heterostructure is fully epitaxial, with sharp interfaces, although some defects are present



2. High magnification SEM image of the photodiode active area and mesa. In the inset: optical images of three photodiodes; the numbers correspond to the dimension of the outer diameters (in µm)

CW-SPECTROSCOPY AND MATERIAL PROCESSING OF Π-CONJUGATED SYSTEMS

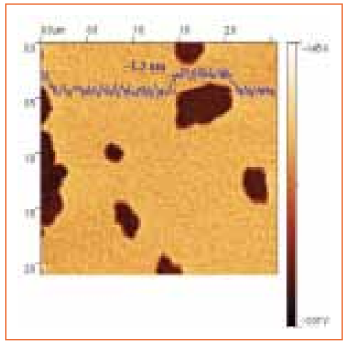
Calogero Sciascia

Π-conjugated systems are a broad class of organic functional materials of great technological and fundamental relevance. In the thesis three main families are treated: Single Wall Carbon Nanotubes (SWNTs), Graphene and Phthalocyanine molecules. The work spans from material production, purification, device fabrication to characterization. Among others, we emphasize cw-spectroscopy (photo-induced absorption, PIA, and electro-reflectance, ER) as useful and effective tool for probing photo-physics on millisecond timescale. PIA (ER) relies on variation of optical transmission (reflection) upon the effect of quasi-continuous laser (electrical) excitation.

Graphene is the "youngest" known carbon allotrope and it is, strictly speaking, a two-dimensional crystal. A current issue is the availability of reliable and affordable methods for graphene production. Starting from a water-surfactant solution, in which graphite is dispersed and exfoliated through a mild sonication, here we propose density gradient ultracentrifugation (DGU) as a novel method for high yield sorting of mono-layers graphene (about 2% in weight of starting material results in graphene mono-layer). The basic idea in DGU is to create a medium with non-constant (typically linear) density in which, as effect of centrifugal force provided during the ultra-centrifugation process, dispersed material is forced to reach its isopycnic point (the point where buoyant density of the object matches density of the environment). The sorted material is characterized through atomic force microscopy (fig. 1), Raman spectroscopy, optical microscopy and optical absorption spectroscopy.

SWNTs are quasi one-dimensional objects, entirely made of carbon atoms, with intriguing physical properties strictly depending from their diameter. Unfortunately, growth methods are still characterized by large poly-dispersivity which affects geometrical as well as optoelectronic homogeneity. Part of the PhD work was devoted in developing an efficient purification strategy based on DGU (see fig. 2). After the same standard characterizations used for graphene, enriched nanotubes sample is used for spectroscopic study. In particular we performed PIA in order to understand intrinsic long-lived phenomena occurring in SWNTs. On the basis of our measurements we speculate photo-generated electrons are trapped onto nanotubes surface with consequently SWNT local expansion.

Finally we used a confocal microscope, coupled with an ER

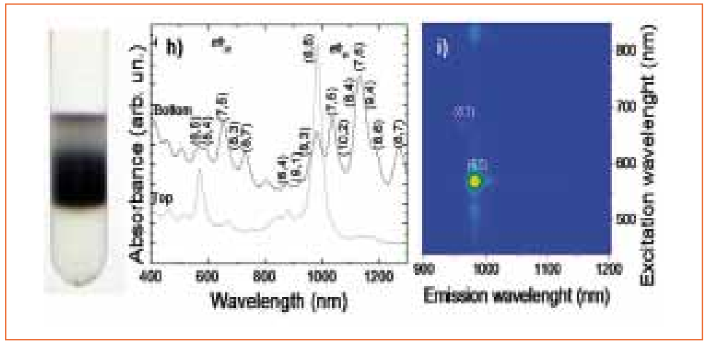


1.Tapping mode atomic force microscopy picture of graphene (dark flakes) deposited on silicon oxide substrate (yellowish background). Here is reported a phase map (sensitive to mechanical differences between substrate and graphene) with superposed the topological height curve (blue line). The measured graphene height is about 1.3 nm, compatible with previous measurements performed on single layer graphene

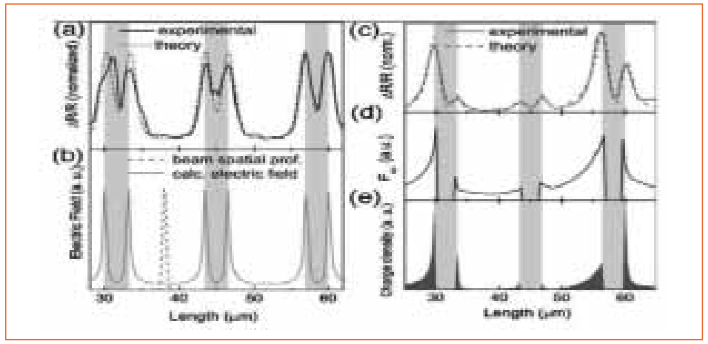
set-up, for measuring the field distribution on a Phthalocyanine-based diode under working conditions. This measurement strategy, introduced by our group, joints spectroscopy sensitivity with sub-micrometric spatial resolution.

Phthalocyanine, a small organic molecule, was firstly employed as organic pigment but became interesting electronic material since its cupper-fluorinated derivative, the CuPcF16, showed high n-type conductivity under air atmosphere. In order to obtain a non linear device, nominally a diode, we evaporated it on top of a couple of interdigitated gold electrodes. Comparing empirical data with mathematical model, we argue large fluctuations in electric field amplitude and charge density exist, even between nominally identical electrodes.

Space charge distributions have therefore a huge effect on the electric field structure and not much can be predicted on their location a priori (fig. 3). In this context, it appears clear the importance of the proposed diagnostic tool.



2. SC bile salts-encapsulated SWNTs solution. On the left-side there is a picture of the tube after ultracentrifugation. The top fractions (light grey lines) shows the enrichment of the (6,5) tubes while in the bottom fractions (dark grey lines) there are tubes of larger diameter such us (7,6), (8,6) (8,7). In the middle panel is reported the optical absorption of top and bottom fractions, the presence of a single sharp peak at 980nm is univocally associated to the presence of a single chiral species. On the right panel, the Photo-Luminescent Excitation map of the topmost fraction confirms the high percentage of (6,5) tubes



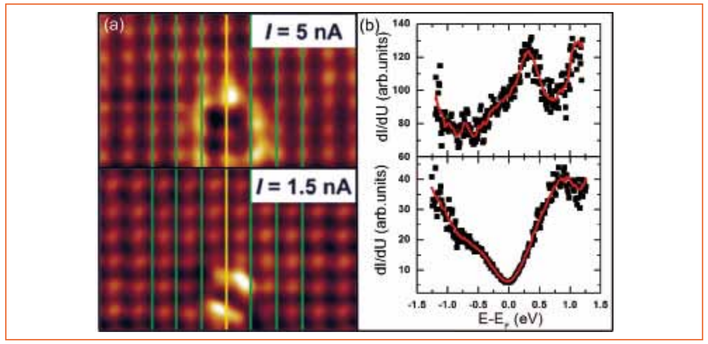
3. Comparison between ΔR/R at 4300 Hz (solid line) and ΔR/R simulated with symmetric electric field (dotted line). b) Symmetric electric field obtained as solution of the Poisson equation assuming zero charge density inside the interdigitated channel. The response of the confocal microscope is provided as a dashed line. c) Comparison between ΔR/R at 143 Hz (solid line) and ΔR/R simulated using a superposition of symmetric electric field with a space charge electric field (dotted line). d) Proposed space charge electric field module and e) charge distribution inside the channel obtained as the first derivative of the space charge electric field

SCANNING TUNNELING MICROSCOPY OF MAGNETIC SURFACES: OXYGEN INDUCED MODIFICATIONS AT THE FE(001) SURFACE AND ANTIFERROMAGNETISM IN MN/W(110) NANOSTRUCTURES

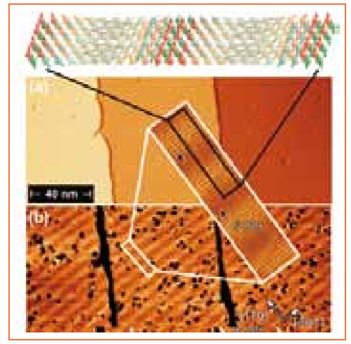
Paolo Sessi

Driven by applications which range from medicine to information technology, the new field of nanotechnology has attracted an increasing interest in recent years. Many new fascinating phenomena have been found to occur in systems of reduced dimensionality and their understaning could give rise to significant technological innovations. Nevertheless, the detailed investigation of nanosize objects requires nanometer scale characterization techniques. I spent most of the three years of my PhD program studying the structural, electronic and magnetic properties of thin films and nanostructures by means of Scanning Tunneling Microscopy (STM), a technique which allows to study structural, chemical, electronic and magnetic properties of nanostructures with atomic scale resolution. In particular, my attention has been focused on two systems: the so-called Fe(001)-*p*(1 × 1)O surface and Mn nanostructures grown on W(110).

The Fe(001)-*p*(1 × 1)O surface, characterized by one oxygen monolayer adsorbed on the clean Fe(001) surface in a well-ordered fashion, has been widely studied by means of spatially averaging techniques. Previous results demonstrated that at the origin of the Fe(001)-*p*(1 × 1) O surface properties there is a strong interplay between a number of elements, including structural modifications, chemical interactions, electronic and magnetic effects. To gain a further insight into the Fe(001)-*p*(1 × 1)O surface properties, I performed an investigation on a microscopic scale. In particular, I used the STM for obtaining topographic and spectroscopic information which, compared with ab-initio calculations, helped to shed light on the role of the atomic interactions in determining the macroscopic properties of this interesting system.
Analyzing large scale (hundreds of nm) STM images, it has been demonstrated that oxygen adsorption induces step–bunching at the Fe(001) surface, an effect that could have interesting implications in the growth of thin films of other materials. When going to the atomic scale, it has been shown that the resolution of sub-nm features becomes more easily achieved after oxygen exposure. The formation of atomically resolved STM images has been studied.
In particular, the occurrence of corrugation reversal between oxygen and iron atoms as a function of the tip-sample distance has been demonstrated [see Figure 1 (a)]. Such an effect, that makes the correct assignment of atomic sites non–trivial, has been explained in terms of the interplay between the geometrical and the electronic structure of the surface.
Finally, by performing Scanning Tunneling Spectroscopy (STS) measurements, it has been demonstrated that oxygen adsorption leads to a dramatic change in the Fe(001) surface electronic structure [see Figure 1 (b)].
In Mn nanostructures grown on W(110), the ability of the STM to investigate electronic and magnetic properties of surfaces with high spatial resolution has been applied to explore the limits of antiferromagnetism, measuring the temperature required to support antiferromagnetic order as the dimensions of the structures are reduced.
While these boundaries are well understood in ferromagnetic materials, antiferromagnetic materials, where neighboring magnetic moments cancel rather than add together, have proven more challenging to unravel.
Measurements have been acquired during a period I spent as a visitor at the Argonne National Laboratory and exploit the unique properties of manganese spin spirals on tungsten (see Figure 2) to correlate spin-sensitive scanning tunneling microscopy techniques on the atomic scale with electronic signatures.
The results showed that the ordering temperature for the antiferromagnetic structure depends both on its size and its orientation with respect to the crystal lattice.



1. (a) STM atomically resolved images of the Fe(001)-*p*(1 × 1)O surface. The vertical lines are guides to the eye for highlighting the corrugation reversal. All images are centered around the same defect used as reference position. (b) STS spectra taken on clean (upper panel) and oxidized (bottom panel) Fe(001) surface. The *dI/dU* signal is proportional, to a first order approximation, to the surface density of states

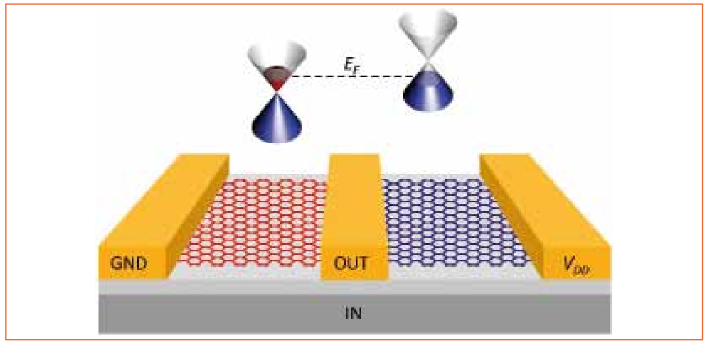


2. (Top) Schematic of the spin structure of the Mn monolayer on W(110). (a) Topography and (b) differential conductance at 40 K. (Inset) High-resolution topographic data taken with a spin-sensitive tip; stripe contrast is related to the degree of antiferromagnetic order

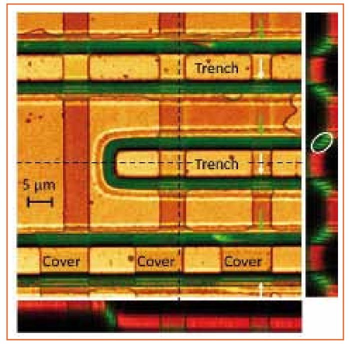
FABRICATION AND CHARACTERIZATION OF NANOELECTRONIC AND NANOFLUIDIC DEVICES IN TWO DIMENSIONAL SYSTEMS

Floriano Traversi

Two different subjects are discussed in this PhD thesis: graphene nanoelectronic and nanomechanical devices, and nanofluidic devices made from SiGe heterostructures. However both subjects have in common nanofabrication in the field of two dimensional (2D) systems. SiGe heterostructures have been the starting point of the development of several 2D electronic devices, but here they are used to fabricate nanofluidic channels. On the other hand, graphene is a real 2D material, with charge carriers confined in a single layer of sp^2 hybridized carbon atoms laying on an isolating substrate.
Nanoelectronic devices based on carbon nanostructures, such as carbon nanotubes (CNTs) and graphene, are a promising alternative to Si-based devices due to their small size and extraordinary properties. CNTs have not been successfully implemented in large-scale integration electronics mainly due to a difficulty in their precise positioning on a chip. Graphene, if epitaxially grown, transfer printed, or deposited from a solution on a large wafer, does not suffer from this limitation as it can be patterned by Si-compatible lithographic techniques. The high mobility of carriers in graphene could allow fabrication of transistors operational in a sub-10 nm regime in which the ultimate limits of Si technology would probably be reached.
However, intrinsic graphene is a semimetal, implying a very small current ON / OFF ratio of graphene transistors. This means that if graphene devices were to replace conventional Si devices, new approaches in bandgap engineering or circuit design would be needed, with the most attractive possibility being to implement the same functionality with fewer transistors. Here the implementation of four basic logic gates with just one graphene transistor is presented. This has been obtained by exploiting the existence of a maximum in the transfer resistance of a graphene transistor. Most of the fabricated logic gates require at least four conventional FETs.
Afterword, the operation of the first graphene integrated electronic circuit, consisting of two graphene FETs of opposite type (Fig. 1), is presented. The transistors are fabricated on the same sheet of monolayer graphene and comprise an integrated digital logic inverter (NOT gate), the main building block of Si complementary metal-oxide semiconductor digital electronics.
Graphene has attracted great interest during the past few years due also to its remarkable mechanical properties, that make it ideal as a main building block of advanced nanoelectromechanical systems (NEMS). Here a method for fabricating multiple free-standing structures on the same sheet of graphene is presented. Graphene sheets were sandwiched between two layers of polymethyl methacrylate. Suspended areas were defined by e-beam exposure allowing precise control over their shape and position. Mechanical characterization of suspended graphene sheets was then performed by nanoindentation with an atomic force microscopy tip. The obtained built-in tensions are significantly lower than those in suspended graphene exfoliated on an SiO_2 substrate and therefore permit access to the intrinsic properties of this material system.
In the field of Nanofluidics, a novel method for the production of arrays of nanofluidic channels with nanoscale cross-sectional dimensions is presented. Lab-on-a chip devices based on such nanofluidic channels show promise for achieving absolute single molecule sensitivity combined with high selectivity along with the advantages of high throughput, low access times, and extremely small sample volumes (pL to fL range). Alternative technologies have recently been developed in order



1. A schematic of the fabricated graphene inverter. Three electrodes patterned on the same flake of monolayer graphene define two FETs. The part of the flake between the two leftmost electrodes (depicted in red) is an n-type FET. The other part of the flake (depicted in blue) is a p-type FET. The flake is electrically insulated from the input (highly doped Si depicted in dark gray) by a layer of SiO2 (depicted in bright gray)



2. Overlay (reflection and fluorescence) confocal images of a three nanochannel structure filled with fluorescent dye. The fluorescence signal is mapped onto a green colour scale, while the reflection signal is plotted using a golden colour map. Trench depth is about 2 µm. The vertical section profiles along the dashed lines are plotted on the right and at the bottom.

to fabricate nanofluidic channels without expensive top-down nanolithography. However, these technologies lack the ability to integrate nanofluidic channels in a vertical arrangement without significant increase in fabrication complexity.
Here a simple conventional process technology capable of producing 3D arrays of nanofluidic channels is demonstrated. Vertical arrays of nanofluidic channels, in which both cross sectional dimensions are controllable down to 10 nm, were fabricated by selective side etching of a SiGe heterostructure comprised of layers of alternating Ge fraction and were subsequently sealed by deposition of material by evaporation. The present fabrication process is compatible with standard semiconductor technology enabling simple integration with conventional electronic and fluidic devices for fast on-chip processing.
The suitability of the fabricated Nanochannels for nanofluidic applications is demonstrated by observing the flow of a fluorescent dye solution through the nanochannels with the help of a confocal laser scanning microscope (Fig. 2).
The potential utility of the nanochannels in biologically relevant applications - e.g., size-based separation of biomolecules - is demonstrated by imaging aggregates of amyloid beta (Aβ). The size of the Aβ aggregate that can enter a nanochannel is found to be dependent on the channel cross-section.