Chair:
Prof. Franco Ciccacci

DOCTORAL PROGRAM IN PHYSICS

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

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

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

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

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

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

The mean number of fellowship-grants for students entering the PhD program is around eight per year, while the mean number of available positions is sixteen per year. At present the overall number of students in the three-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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FABRICATION AND CHARACTERIZATION OF METAL NANO-STRUCTURES

Thin film, Nanowires and Nanoparticles

Laura Cattaneo

The research work developed in this Ph.D. thesis is entirely in the area of Nanotechnology; in fact it is dedicated to the synthesis and characterization of metal nano-structured materials. The three main studies reported in this thesis treat not only of the specific properties of the formed nanostructures, in view of their potential application in the new era of Nanomaterials, but also look into the early phases of nucleation and growth, when the atoms start to organize themselves: the crucial steps to control the entire structure. In detail:

Chapter 1-The influence of nucleation on the growth and morphological stability of (00.1) textured electrodeposited cobalt

The electrochemical nucleation and growth of cobalt onto sputtered [111] Cu film on a silicon wafer substrate was studied. Cobalt was electrodeposited from sulphamate solution at pH slightly above 6, in conditions previously shown to give rise to the growth of highly textured (00.1) cobalt layer with a field-oriented columnar microstructure, so called cellular cobalt. The nucleation mechanism was qualitatively probed by comparing experimental current transients to theoretical transients according to the Sharifker et Hills model and undoubtedly recognized as instantaneous in nature. Hetero-epitaxy of the (00.1) cobalt on (111) copper was confirmed by transmission electron microscopy (TEM), thus demonstrating the implication of two-dimensional nucleation preceding the instantaneous formation of three-dimensional nuclei. The nucleation layer was found to consist of highly faulted crystals, about 30 nm wide and an aspect ratio (height/width) of 1, having a high density of stacking faults running parallel to the film-substrate interface. The cellular cobalt growth become unstable at an aspect ratio of about 2 (crystal width of 40-60 nm), following the loss of planarity of the crystallization front, which evolves, through an abrupt transition, into a coarse island growth morphology by extensive bunching of growth layers.

Chapter 2-Nanowires (NWs)

2.1-Co NWs

Nucleation and growth of Co NWs embedded into three different pore sizes (D_p= 27, 51 and 244 nm) Anodic aluminum Oxide (AAO) membranes were deeply investigated by means of electrochemical techniques and direct observation by SEM analysis. SEM investigation revealed that the shape of the cathodic current transients are closely related to the formation, at the beginning, of a Co thin film at the Au/AAO side, followed by the growth of NTs at the pore basements and their gradual thickening, until they seal completely the channel section so that the current rapidly decreases because of the abrupt reduction of the effective cathodic area.
From TEM characterization it was possible to conclude that NWs with diameters <30 nm are actually single crystal and their growth seems to proceed irrespective of the initial nucleation of the Co film at the Au sputtered side membrane, which however is not the case in the intermediate-diameter NWs, where sporadically grain boundaries appear mainly localized in the lower part, where Co film nucleation took place; and especially in the larger diameter NWs that maintain a polycrystalline structure all through their growth. AGFM measurements were performed at room temperature on Co NWs embedded in AAO membranes, both in parallel and perpendicular field. The comparison between XRD/HR-TEM and AGFM analysis confirm that there is a strong correlation between the crystallographic orientation of the magnetic material and the corresponding magnetic anisotropic behaviour.
Finally, from MFM measurements the domain structure of ordered arrays of Co columns (average diameter of 50 nm) is labyrinth like. Each magnetic pillar acts as a single domain magnetic particle, magnetized perpendicular to the template surface. Due to the high coercivity field and quite high squareness (almost 60%), by improving the order of the AAO template it may be expected that each Co NW can switch independently of nearest neighbours, storing its magnetization direction.

2.2-Au NWs

At the nanometric scale, electronic, mechanical and thermal properties are size-dependent. Gold NWs, due to their nanometric size (diameter) can be an interesting material to investigate this size-dependence. Melting point depression of Au NWs embedded in AAO membranes has been measured by DSC measurements and compared with the calculated values according with the Qi's model. Moreover, the AAO embedded Au NWs was thermally treated above the bulk melting point in order to cause their fragmentation and the formation of gold nanorods and particles having the diameter of pores of the AAO templates.

2.3-Switching mechanisms in NW Metal-Oxide-Metal (MOM) heterostructures

The aim of this third work is to synthesize NW heterojunctions (metal-oxide-metal) into AAO templates and to study the NWs array resistive switching, to use them as basic building blocks for the next-generation ReRAM (Resistive switching Random ss non-volatile Memory). Single component and multilayered NWs were prepared by electrochemical deposition in AAO templates. The heterojunction MOM NWs were than obtained by selective thermal oxidation of Ni NWs and of metallic multilayered Au/Ni/Au NWs. Single element Ni and Au NWs ECD into AAO membranes was carried out to develop an experimental procedure to get a uniform deposition within the matrix, and to determine the kinetics of growth in galvanostatic conditions. AFM, EFM and C-AFM measurements proved the possibility to use scanning probe techniques to characterize arrays of NWs or single NW, clearly decoupling the topographic signal from the electrostatic (EFM) or flowing current (C-AFM) one. It was finally demonstrated through TEM analysis, the ability to synthesize heterostructures NiO/Ni and Au/NiO/Au NWs by thermal oxidation of Ni and Au/Ni/Au NWs still embedded in the AAO matrix.

Chapter 3-Synthesis of Ag nanoparticles (NPs) into SiO2 layers by ultra low energy ion implantation (ULE-II) for plasmonic application

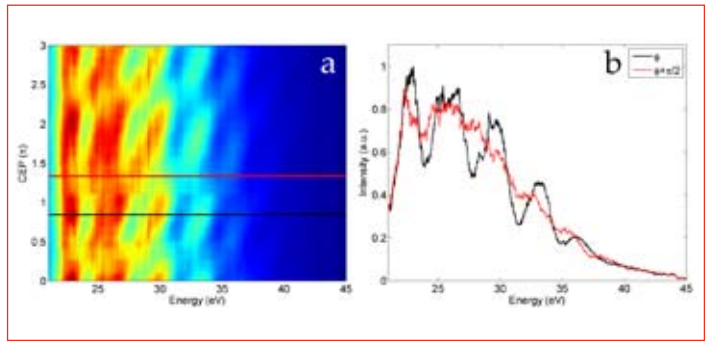
Recently it has been shown that ultra low energy ion implantation (ULE-II) can be a promising technique for the wafer-scale fabrication of Ag NPs planar arrays embedded in a silica layer (SiO_2) thermally grown on silicon substrate. The advantage of this method is the direct embedding of the nanoparticles in a transparent dielectric matrix, which does avoid their dissemination and their alteration, while preserving their plasmonic properties. The aim of this research is to reach a complete control in spatial organization of silver nanoclusters stabilized in silica matrices, in detail density, size and position playing with ion implantation energy (3-20 KeV), ion dose (ions cm^{-2}) and fluence (current-temperature). The target is to obtain a 2D layer of closed-packed silver particles at a defined nanometric distance respect to the surface in order to build SERS usable substrates. These layers are studied by TEM in both Bright Field and HREM conditions.
To improve the optical spectroscopy response of such systems, it has been also demonstrated how to extend to 3D structure the patterning of such Ag NPs assembly by implanting Ag^+ ions through a patterned stencil mask in close contact with the SiO_2 surface (lines or dots arrays or gratings). Finally, the Ag NPs stability with time was investigated demonstrating the possibility to prevent any form of oxidation by post implantation annealing. The heat treatment will have only the function of stabilizing the composite because in our system Ag nanocrystals nucleate already during the implantation process and no post-annealing procedure is required to form them. XPS and HREM analysis were performed to investigate the possible causes of the loss of optical signals in no-annealed samples with time and both techniques revealed the presence of Ag_2O NPs in aged samples and metallic Silver NPs in annealed samples.

HIGH-ENERGY ISOLATED ATTOSECOND PULSES BY SUB-CYCLE IONIZATION DYNAMICS

Federico Ferrari

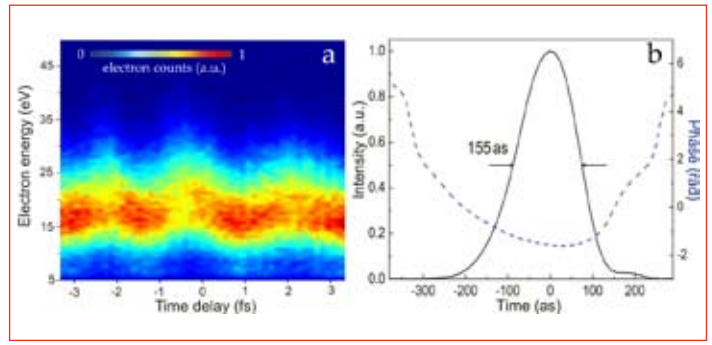
After a decade from the first experimental demonstration of the generation of isolated attosecond (1 as = 10^{18} s) pulses, attosecond physics has become a well established branch of ultrafast science, with important technological and scientific breakthroughs. Since the first demonstration of the generation of isolated sub-femtosecond pulses, various techniques have been proposed and implemented for the production of isolated attosecond pulses. So far, these techniques rely on the selection of a portion of the spectrum of the emitted XUV radiation or/ and on the confinement in the time domain of the emission to a single burst, by acting on the key elements that influence the emission efficiency.

A critical aspect in the generation of such isolated pulses is the photon flux: indeed, at present isolated attosecond pulses are characterized by a very low energy, usually in the picojoule range. While such an energy is already sufficient to perform some experiments, a higher photon flux would allow to probe nonlinear effects in the XUV region and to perform attosecond-pump/ attosecond-probe experiments. For this reason, great effort is being currently devoted, both theoretically and experimentally, to the development of schemes for the generation of high-energy isolated attosecond pulses (that is, with an energy higher than 1 nJ).



1. XUV spectra generated in xenon by 5-fs pulses. Panel (a) shows a complete scan over a 3π shift of the CEP of the driving pulses, while panel (b) presents a comparison between two particularly significant spectra, marked in panel (a) with a line of the corresponding color.

The research activity described in this thesis work is related to this last topic: the goal was to develop a technique capable of generating isolated attosecond pulses with higher energy with respect to what is currently achieved. In order to do this, ultrashort laser pulses with high peak-intensity were used in the generation process. As a first step, an analysis of the generated XUV photon spectra was performed, for different experimental configurations and different gases. Figure 1 shows a scan over a shift of the carrier-envelope phase (CEP) of the driving field of 3π of the radiation emitted from xenon atoms, at a static pressure of ~ 2.5 torr. The laser pulses were 5-fs long, with a peak intensity $I = (2.3 \pm 0.3)\times10^{15}$ W/cm^2. One can clearly see well resolved harmonic peaks, whose position changes with π periodicity, while, for some CEP values, the spectrum becomes continuous. This is a strong evidence that, in the temporal domain, by controlling the CEP of the driving pulses it is possible to confine the XUV generation process to a single event. Since no spectral selection was needed to obtain the photon spectra of figure 1 (apart from the contribution of an aluminum filter, which only blocks the low order harmonics and the fundamental radiation) the isolated attosecond pulses generated have a very high photon flux, which corresponds, on target, to about 2.1 nJ (the target position indicates the area where attosecond experiments are performed). Such an energy is from one to three orders of magnitude higher than what has been currently achieved by other techniques.



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

In order to measure the temporal characteristics of the attosecond pulses, the frequency resolved optical gating (FROG CRAB) technique was used. The XUV pulses transmitted by the aluminum filter were focused onto an argon gas jet, where they ionize the gas atoms in the presence of an infrared (IR) pulse. By measuring the photoelectron spectra as a function of the delay between the XUV and IR pulses it is possible to retrieve the temporal characteristics of the attosecond pulse. Figure 2 (a) shows a portion of the FROG CRAB trace measured for XUV pulses generated in xenon by 5-fs pulses with a CEP value leading to the production of a continuous spectrum. The reconstructed temporal intensity profile of the XUV pulses, reported in figure 2 (b), confirmed the generation of an isolated attosecond pulse, with a duration of 155 as and a small residual chirp. This corresponds to only 1.1 optical cycles of the carrier frequency.

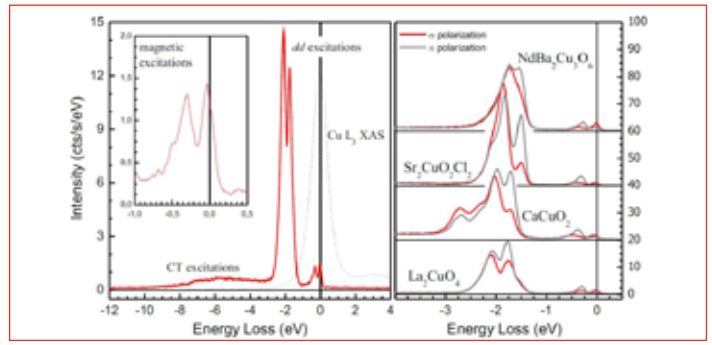
The physical mechanism at the basis of the generation of an isolated attosecond pulse is related to the ionization dynamics in the generating medium. If the driving laser pulses have an intensity above the saturation intensity of the gas, complete depletion of the neutral atom population is achieved on the leading edge of the laser pulse, thus preventing the generation of other attosecond pulses. Numerical simulations were performed to gain a deeper physical insight on such a generation process: both single atom calculations and three-dimensional (3D) propagation simulations confirmed the generation, for certain CEP values, of isolated attosecond pulses when the laser intensity is higher than the saturation intensity of the gas. In addition, the 3D model showed that the spatial characteristics of the XUV radiation are strongly influenced by the CEP. In the case of continuous spectra the XUV emission is predominantly on-axis, thus confirming the excellent spatial characteristics of the generated attosecond pulses.

The energy of the attosecond pulses reported in this work was limited by the energy of the few-cycle driving pulses. With an appropriate choice of the interaction geometry (for example, by loose focusing of the excitation pulses) numerical calculations performed with the 3D propagation model show that this technique could be scaled to higher energies, to generate pulses in the microjoule range. The availability of attosecond sources with such an energy would open new avenues for studies with attosecond temporal resolution of electronic processes in atomic and molecular physics.

MAGNETIC AND ORBITAL RESONANT INELASTIC SOFT X-RAY SCATTERING

Marco Moretti

This thesis deals with the resonant inelastic soft x-ray scattering activity I carried out within the group of Prof. G. Ghiringhelli and Prof. L. Braicovich at the Politecnico di Milano (Italy). The group has a long tradition in synchrotron-based spectroscopies for the study of magnetic properties and the electronic structure of transition-metal and rare earth compounds. In the last 15 years, the activity of the group has been concentrated in soft x-ray emission pectroscopies and resonant inelastic x-ray scattering (RIXS), in particular. Both on the instrumentation and the scientific side, the group contributed and still contributes substantially to develop this technique.
In the last three years, results of fundamental interest and importance have been obtained, some of which are presented in this work.
The largest effort regards the study of 3*d* transition-metal compounds, with special emphasis to insulating and superconducting layered cuprates, by means of Cu L_3 edge RIXS. RIXS is shown to probe both orbital and magnetic excitations in these compounds, with the possibility of sampling different regions of the reciprocal space (finite transferred momentum, **q**).
The presence of 2D CuO_2 planes of Cu^{2+} alternated to O^{2-} ions is a common feature to all layered cuprates. Cu^{2+} ions ($3d^9$, one-hole system) have one unpaired spin-1/2 per site, which are antiferromagnetically coupled via super-exchange interaction. The strong hybridization with neighboring oxygen ions is such that super-exchange interactions are exceptionally high, i.e. with coupling constants larger than 100 meV. These CuO_2 planes with antiferromagnetic order constitute the background in which doped holes in the superconducting compounds have to move. Cu-O hybridization and pure crystal field effects give rise to the removal of the Cu-3*d* state degeneracy. The hole is thus characterized by its orbital and spin degrees of freedom. The lowest energy state, the ground state, is known to be the one with the hole in an orbital with x^2-y^2 symmetry. Transitions of the hole to orbitals having different symmetries, possibly accompanied by spin-flip processes, are allowed and are called crystal field, or *dd*, excitations.
The investigation of these excitations by means of Cu L_3 edge RIXS is here demonstrated to be very effective.
Thus, crystal field (*dd*) excitations were studied in several undoped layered cuprates, parent compounds of high-T_c superconductors, as a function of the scattering geometry and incoming polarization and are demonstrated to be local excitations with no or little dispersion with respect to the transferred momentum, **q**.
A single ion model was introduced to evaluate the RIXS cross-section of such excitations and to fit the experimental trends. It was possible to unambiguously determine the energy and symmetry of Cu-3*d* states in La_2CuO_4, $Sr_2CuO_2Cl_2$, $NdBa_2Cu_3O_7$, $Sr_{0.5}Ca_{0.5}CuO_2$ and $CaCuO_2$. *dd* excitations in superconducting systems, on the other hand, show a very little dependence on polarization and scattering geometry and the features that are remarkably well separated in the insulating compounds merge into a unique asymmetric peak, of triangular shape. Note that, however, the energy of such *dd* excitation peak is always larger than 1 eV, resolving speculations made in the literature about a possible role of $3z^2$-r^2 states lying as close as 0.5 eV to the x^2-y^2 ground state. The absence of dd excitations in the mid-infrared spectral region greatly supports the hypothesis that magnetic excitations (up to about 400 meV) play a major role in Cooper pairing in cuprate superconductors.
Moreover, one of the major outcome of the single ion model calculations is that, beside orbital excitations, Cu $L_{2,3}$ edge RIXS is found to be able to probe single magnon excitations in undoped layered cuprates. Spin-flip can be seen as a special case of *dd* excitations, the one having the hole in a final state with the same symmetry as in the ground state (x^2-y^2), but with opposite spin. Spin-flips perturb the antiferromagnetic order and trigger spin-waves within the CuO_2 planes. Of fundamental importance is the theoretical demonstration and experimental evidence that such spin-flip processes are allowed in Cu $L_{2,3}$ edge RIXS. Therefore, RIXS can be exploited to probe the dispersion of magnetic excitations, for instance magnons, of layered cuprates, both insulating and superconducting. These findings put RIXS as a technique on the same footing as inelastic neutron scattering (INS) in this field of research. Application of Cu L_3 edge RIXS to superconducting systems showed that magnetic excitations survive in both the normal and the superconducting state. By studying magnetic excitations it was possible to support that underdoped $La_{2-x}Sr_xCuO_4$ (with p=0.08) is in an inhomogeneous magnetic state, with two magnetic branches separated by about 100 meV. Optimally doped $La_{2-x}Sr_xCuO_4$ (x = 0.16), instead, does not present any clear evidence of phase separation.
Finally, orbital excitations were studied in orbitally ordered systems, such as $RTiO_3$ and RVO_3 compounds, displaying novel elementary low-energy excitations, called orbitons. RIXS was in this case applied to the study of these excitations at finite momentum (**q**) in reciprocal space, in order to determine their local or collective nature. Orbitons are shown to have an appreciable dispersion in selected compounds, although an interpretation in terms of a local model cannot be safely ruled out. With the present thesis, then, soft x-ray RIXS is demonstrated to be a powerful probe of the electronic structure and magnetic properties of 3*d* transitino-metal compounds. It is defined magnetic and orbital resonant inelastic soft x-ray scattering in the sense that it is here shown to effectively probe the orbital and spin degrees of freedom of electrons in solids.

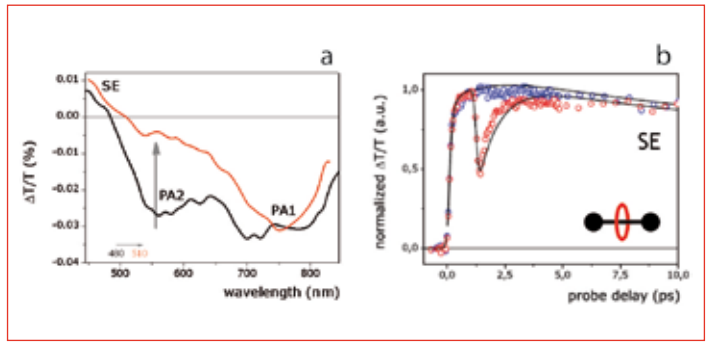


1. (Left panel) Example of Cu L_3 absorption (dashed) and RIXS (solid) spectra of La_2CuO_4 with σ polarization. One can immediately recognize charge transfer (CT), *dd* and magnetic excitations at different energy ranges. A closer look of the mid-infrared energy region is given in the inset. (Right panel) RIXS spectra of *dd* excitations in La_2CuO_4, $Sr_2CuO_2Cl_2$, $NdBa_2Cu_3O_7$, and $CaCuO_2$ both with σ and π polarization.

PHOTOPHYSICS AND APPLICATION IN PHOTONICS OF CONJUGATED POLYMERS

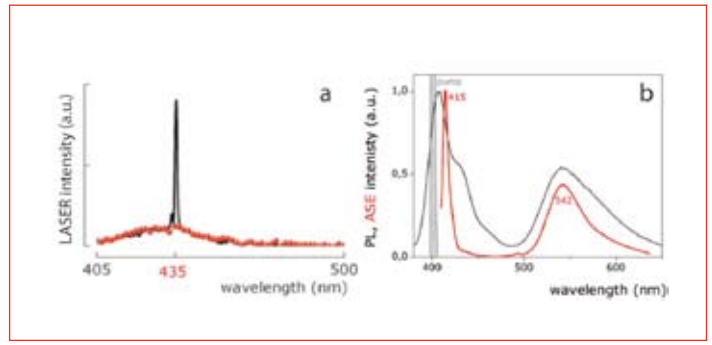
Marta Magdalena Mróz

Polymer semiconductors are usually depicted as bundles of loosely bound chains of conjugated carbon atoms. Interchain interactions are far from negligible in their photophysics and separating inter-chain from intra-chain contribution is an important issue in organic photonics research area. This research activity was focused on the study of the photophysics of conjugated polymers (CPs) through ultrafast spectroscopy, which allows to investigate the primary excitation taking place in the system. The study was focused on the class of CPs threaded with sugar macrocycles (polyrotaxanes), concentrating on the two main classes of the emitting polymers: polyfluorenes and polyvinylenes.
Fundamental studies regarded the elementary photoexcitations and their dynamics in polymer network with different degrees of inter-chain coupling. Applied studies regarded optical gain, lasing and all-optical switching in polymer based media. Basic science mainly concerned low dimensional physics of π-electrons, because an isolated polymer chain is a natural quantum wire with extreme confinement, and inter-chain interaction. These issues were directly coupled to applications. In technologies such as OLED, amplifiers and LASERs, aggregation can be detrimental for quantum efficiency, pointing out chain separation as a possible route towards solid state high yield emitters.
The dynamics of the excited state confined on isolated conjugated segments is relevant to all-optical switching.
We demonstrated that supramolecular chemistry is a reliable tool for controlling chain interactions, to yield effective control of the secondary interactions between CPs chains and to inhibit the generation of charges in the threaded CPs backbone under optical excitation. This isolation allowed good inter-chain separation even in densely packed solid-state samples, thus preserving characteristics of the material for applications, and introducing new functionalities.

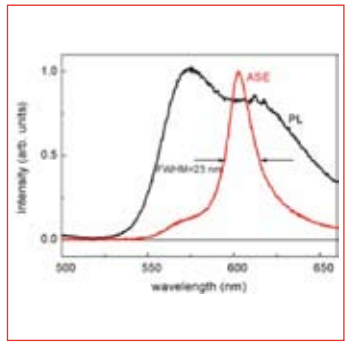


1. Normalized (a) pump-probe spectra at 2 ps time delay for pristine (black line) and threaded (red line) PFBP chain (b) kinetics of stimulated emission (@460 nm) of PDV⊂β–CD chain with (red) and without (black) re-excitation

In order to implement supramoleculary isolated CPs into processable electronic technologies their complex photophysical properties must be understood. Note, that the surrounding structure provides full separation of long conjugated segments, leaving only small fractions of the chain exposed to possible interactions with neighbouring chains.
Optical properties bear the clear signature of this modification. First, charge photogeneration in the isolated chain was investigated. The process shown peculiar intra-chain phenomena due to chain separation: long-lived inter-chain charges are suppressed while intra-chain charges photo-generated in the insulated systems recombined on a ultrafast time scale. This feature has been exploited to develop all optical switching devices. Moreover, an interesting phenomenon of multi-colour ASE in a polymer blend of this materials was reported.



1. Laser and ASE action. (a) Laser emission for PFBP⊂β.CD (black) and emission when the gate pulse reaches the sample (red) - laser action is totally shut down, (b) simultaneous ASE from the blend of PFBP⊂β.CD:F8BT (red line) deposited onto the DFB substrate using just one excitation @390 nm together with the photoluminescence spectrum (black). The filled area shows the pump pulse.



3. ASE under CW pumping. Emission spectra bellow (black line) and above (red value) the pump value where the narrowing occurs.

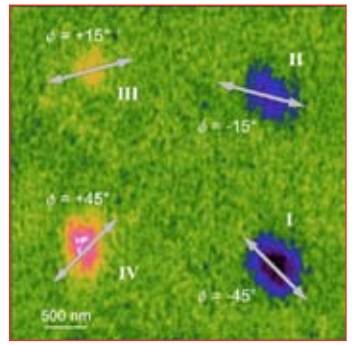
The second branch of the research activity was focused onto the studies of CPs with the goal of obtaining emissive device working in continuous wave (CW) pumping regime. the field of organics photonics there is a big interest in CW pumping and electrically driven organics lasers, such devices will have a great opportunity to apply the organics materials in industry. Here, ASE action under CW pumping in a pristine MEH-PPV film was demonstrated. This unusual and of great importance result was carefully studied and characterized. We found out that this material shows particularly long-lived emissive state (us time scale). This result suggests that it is possible to obtain optical gain in organic materials simply using a CW pumping laser thus paving the way to cheap and more simple pumping schemes for organic lasers and taking out a limitation for many industrial applications such as automotive or LAN amplifiers, where the pulse operating mode is an obstacle to actual implementation.
All our findings point out the potential role of plastics materials in photonics and shed positive light to long standing challenges such as the electrically pumped organic laser or the all-optical logic devices.

LIGHT POLARIZATION IN STRONGLY CONFINED FIELDS

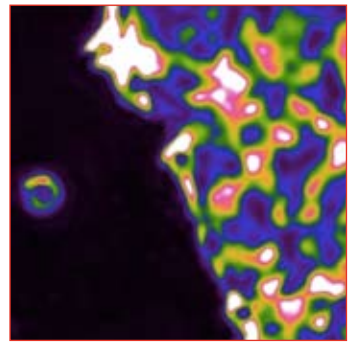
Characterization and applications of confined polarized light

Matteo Savoini

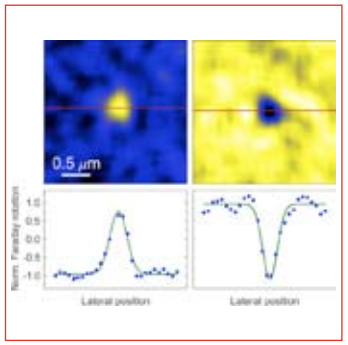
Light polarization has been extensively studied since the beginning of 1800s; since then, a lot of different applications have been found dealing with differently polarized states of light; ranging for example from magneto-optic effects, to polymeric science, and to LCD screens. All these possible different applications have been extensively exploited in a range of dimensions far from the smallest diffraction-limit areas attainable. Usually, in fact, the general implementation is with the use of collimated laser beams or by weak focusing through lenses. Thus, typical dimensions can range from millimeters down to few hundreds of microns.
With the development of nanotechnology, strong interest has been devoted in the confinement of light beams in order to have higher and higher resolving power, thus the possibility to study light-matter interaction on an extremely small scale.
So techniques like conventional optical microscopy nowadays employ objective lens with high focusing power (defined by the numerical aperture, NA), allowing resolutions down to few hundreds nanometer, with visible illumination light. Better resolution can be attained by less conventional techniques; like scanning near-field microscopy (SNOM), where typically we have resolution of 100 nm. Even further improvement in the resolution can be obtained with plasmonic nanoantennas, where the electric field can be confined to dimensions down to 10/20 nm.
In the field of optical microscopy employing high NA objectives, Török and coworkers have provided an extensive characterization of the polarization characteristic in strongly focused beams. His work, published in the '90s, showed that the light polarization can be strongly influenced by high numerical aperture objectives, making elliptical a perfect linear polarization.
For SNOM and plasmonic antennas, instead, a lot of efforts have been devoted to obtain an always-improving resolution, but little work has been done in the characterization of the polarization properties for these techniques. Especially for plasmonic antennas the non-polarization preserving behavior is well known. With their pioneering work at the beginning of this millennium, Biagioni and coworkers have demonstrated that also near-field microscopy and plasmonic antennas can effectively present a polarization sensitive behavior; they have, in fact, demonstrated that linearly polarized light can be transmitted to the sample by a particular type of SNOM probes; moreover they have also proposed a new design for a polarization preserving plasmonic nanoantennas.
I spent most of the three years of my Ph.D. in the Surface Physics Group at the Department of Physics, Politecnico di Milano, under the supervision of M. Finazzi, L. Duò, and F. Ciccacci.
My research project focused on the study of possible applications for linearly and circularly polarized light, especially devoted in the practical demonstration of feasibility of all-optical nanoscale memories, with the use of confocal and near-field microscopy.
Firstly, I have demonstrated all-optical polarization-encoded information storage onto polymeric substrates exploiting the linear polarization preserving behavior of SNOM probes.
In particular, by inducing reorientation (thus birefringence) in photosensitive azo-polymer thin films, five-level bits are created by associating different bit values to the different directions of linearly polarized near-field illumination.
The reading routine is then performed by implementing polarization-modulation techniques on the same SNOM apparatus in order to measure the encoded birefringence direction. Typical bit dimensions of 250 nm are demonstrated [Fig. 1].
Another activity in my PhD studies was devoted to the study of circularly polarized light at the nanoscale. Within collaboration with Prof. Meskers, Technical University of Eindhoven, and Prof. Hecht's group, University of Würzburg, we demonstrate that a high degree of circular polarization can be delivered to the near field at the apex of hollow-pyramid SNOM probes. This result is achieved by analyzing the dichroic properties of a chiral polyfluorene [Fig. 2].
We also prove that the degree of circular polarization does not depend in a significant way on the shape of the aperture, at variance with the far-field behavior. Moreover, we exploit the behavior of an asymmetric cross antenna structure, constituted of two perpendicular dipole antennas with different lengths, sharing the same feed gap, in order to shape the local polarization state. As an application of this concept, we propose a λ/4 nano waveplate, able to shape and confine linearly polarized propagating waves into circularly polarized fields localized in the feed gap.
The last year of my PhD, was mainly devoted to the study of the interaction of polarized light with magnetic media. Within this field of study, we modify a confocal microscopy setup in order to make it able to record magneto-optical hysteresis cycles separating the magnetization components. Within the last year, I spent a considerable period in Prof. Theo Rasing's group, Radboud University, where I could learn the basics of opto-magnetism, i.e. the use of polarized light as a tool to manipulate the magnetization vector in magnetic media. In particular, the focus of my research activity was the study of Inverse Faraday effect on a ferrimagnetic TbFeCo sample, i.e. the use of illumination through microscope objectives with short pulses in order to induce a change (namely, the switching) of the magnetization vector and subsequently record the induced effect with the use of linearly polarized near fields. Although this is still a work-in-progress, at the present stage we were able to induce the switching in areas of 250 nm of diameter, reducing the dimensions of 2 orders of magnitude compared to previous experiments [Fig. 3].



1. Mapping of 4 different pentabits induced in the sample



2. Mapping of the circular dichroism of chiral polyflourene with hollow pyramid SNOM probes

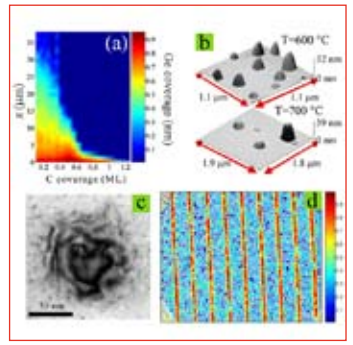


3. Near-field mapping of the magnetization reversal induced by focusing a single femtosecond pulse

INVESTIGATION OF GE SURFACE DIFFUSION AND SIGE NANOSTRUCTURES BY SPECTRO-MICROSCOPY TECHNIQUES

Giovanni Maria Vanacore

SiGe nanostructures on crystalline Si substrates with (001) orientation are among the most studied system in condensed matter physics and nanoscience. This interest has been mainly driven by the important potential applications in opto and nano-electronic devices thanks to the improvement of the optical and electronic properties compared to bulk systems. These features come essentially from the possibility of engineering the strain field within the nanostructures using the lattice mismatch of ~ 4 % between Ge and Si and from the spatial confinement, capable of modifying the electronic band structure leading to an increase of the charge carrier mobility.
It is obvious that these applications largely depend on the control of surface processes during the growth of the nanostructures, and their performance are strongly dependent on strain relaxation and dislocation injection.
Besides the technological interest, the SiGe/Si(001) system has received much attention since it is also a model for understanding the fundamental processes occurring during 3D island formation and self-organization phenomena. In fact, the lattice mismatch between Ge and Si introduces a stress field which has dramatic effects on the growth process and is responsible for a number of structural and electronic phenomena.
In particular, the stored elastic energy can be partially relieved by spontaneous formation of 3D objects of nanometric size on top of a pseudomorphic SiGe wetting layer. This growth mode, called Stranski-Krastanov (SK), is a way of easily forming self-assembled nanostructures, which can be used to obtain quantum confinement of charge carriers in nanoelectronics device applications.
In recent years, considerable efforts have been devoted to the growth of hetero-epitaxial SiGe nanostructures with well controlled size, shape and positioning, and with defined stoichiometry and strain state. However, some aspects still need to be addressed for a complete understanding of this system, including: (i) the competition between kinetic and thermodynamic factors for island formation, (ii) the mechanisms governing the relative growth of individual nanostructures, (iii) the interplay between SiGe intermixing and strain relaxation mechanisms.
In the present work, we carry out an experimental investigation of the relationship between morphology, elemental composition, strain state and electronic structure of self-assembled and lithographically defined SiGe nanostructures by means of several spectro-microscopy techniques. The Si and Ge diffusion dynamics and the self-organization phenomena during the growth of SiGe islands have been studied by Scanning Auger Microscopy (SAM) and Atomic Force Microscopy (AFM). Micro-Raman, SAM and Scanning Transmission Electron Microscopy coupled with Electron Energy Loss Spectroscopy (STEM-EELS) techniques have been used for the investigation of the interplay between strain relaxation mechanisms and SiGe intermixing in self-assembled islands.
The effects of strain and composition on the electronic band structure in lithographically defined SiGe nanostructures, in layout very close to those used in prototype devices, have been characterized with nanoscale spatial resolution joining information from Tip Enhanced Raman Spectroscopy (TERS), nanofocused X-Ray Diffraction (XRD) and Energy-Filtered PhotoElectron Emission Microscopy (PEEM).
The thesis is conceptually divided in two main parts: the first, to which belong Chapters 1, 2 and 3, deals with the experimental investigation of the Ge surface diffusion and of the self-organization phenomena of SiGe islands grown in a bottom-up approach; the second, including Chapters 4 and 5, is based on the experimental characterization of the strain state and of the strain-induced effects on the electronic band structure of lithographically defined SiGe nanostructures obtained in a top-down approach



1. (a) Ge diffusion profiles measured by SAM analysis for different pre-existing C coverage. (b) 3D AFM image of self-assembled SiGe islands. (c) Plan view TEM image of a single dislocation-free SiGe island. (d) Ge concetration map of the SiGe nano-stripes obtained by PEEM analysis.

Chapter 1 presents an overview on the basic processes occurring during hetero-epitaxial growth of thin solid films.
In the **Chapter 2** the surface diffusion of Ge on a clean and C covered Si(001) surface promoted by annealing at high temperatures in UHV of pure Ge stripes is experimentally investigated by means of *in-situ* Scanning Auger Microscopy.
The influence of a controlled carbon coverage on the Ge surface diffusion is quantitatively studied, showing that the diffusion coefficient presents a strong dependence on carbon coverage (see Fig. 1(a)).
Chapter 3 deals with the experimental investigation of the growth process of self-assembled SiGe islands on Si(001) (see Fig. 1(b)). From the size and density evolution exhibited by the nucleated islands, we propose a scenario where the island growth is essentially driven by kinetic factors within a diffusion limited regime. Finally, we investigated the interplay among SiGe intermixing and plastic relaxation, showing that the surface thermal diffusion growth method leads to the formation of coherent islands (dislocation-free), as shown in Fig. 1(c), larger than those attainable by MBE and CVD.
Chapter 4 presents the mapping with nanoscale resolution of strain, composition, local work function and valence band structure of lithographically defined SiGe *embedded* nano-stripes using TERS and Energy-Filtered PEEM (see Fig. 1(d) showing the Ge concentration mapping of the nano-stripes as obtained by PEEM analysis).
In **Chapter 5** are presented the first results of a *direct* characterization of the strain state of lithographically defined SiGe nano-ridges using the recently developed nanofocused XRD technique.
The work presented in this thesis is the outcome of an experimental PhD research project developed at the Politecnico di Milano (Milano, Italy) in co-tutorship with the École Polytechnique (Paris, France) and the French Atomic Energy Commission (CEA-Saclay, France). SAM and AFM have been performed at Department of Physics of the Politecnico di Milano.
Micro-Raman Spectroscopy has been carried out at the Materials Science Department of the Università Milano-Bicocca.
PEEM measurements have been realized at CEA and during two standard experimental runs at the TEMPO beamline of SOLEIL Synchrotron (France). TERS and preliminary TEM analysis have been performed at the École Polytechnique, while more extensive TEM and STEM-EELS measurements have been developed at IMM-CNR in Catania. The nano-XRD experiment has been carried out during a standard experimental run at ID13 beamline of the European Synchrotron Radiation Facility (ESRF). The close collaboration with the laboratory L-NESS in Como made available the set of the lithographically-defined investigated samples.
The experimental results have been exploited in close collaboration with a theory group at the Materials Science Department of the Università Milano-Bicocca for a deeper insight into the atomic level mechanisms during island growth process.