POLITECNICO DI MILANO

PhD Yearbook | 2007

PHYSICS

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PHYSICS

Chair:
Prof. Franco Ciccacci

DOCTORAL PROGRAM IN PHYSICS

The Doctoral Program in Physics at Politecnico di Milano aims to attract bright students with good scientific background and marked 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 make use of 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 an Advisory Board, 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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FIELD ENHANCEMENT AND CONFINEMENT AT OPTICAL WAVELENGTHS: NONLINEAR NEAR-FIELD MICROSCOPY AND RESONANT METAL NANOPARTICLES

Paolo Biagioni

In the application of optics to nanotechnologies, one of the most remarkable consequences of the wave nature of light is the difficulty to squeeze it into volumes smaller than the wavelength: this is a fundamental limit encountered both in high-resolution optical imaging (where it gives rise to the so-called diffraction limit) and in the engineering of mesoscopic optical circuits and devices. The field of nano-optics, which has been gaining increasing attention over the last decade, deals with two strongly related phenomena: the confinement of light into sub-wavelength volumes and the interaction of light with single emitters, typically single molecules or quantum dots. On the one hand, light confinement is one of the obvious requirements in the development of high-resolution microscopy techniques, which resulted more than twenty years ago in the first demonstration of a scanning near-field optical microscope (SNOM). In aperture-SNOM the sample is imaged by shining light through, or collecting light from, a subwavelength aperture which is brought in close proximity to the sample, thus ensuring an optical resolution basically of the order of the aperture diameter (typically, 50-100 nm). On the other hand, light confinement by resonant metal nanostructures is becoming a basic ingredient in spectroscopic studies of single emitters, where the field enhancement which accompanies the confinement is used in order to locally provide the power needed to efficiently excite the emitter. Typically, localized surface plasmon resonances (i.e. collective oscillations of the conduction electrons) are exploited by a proper choice of the material and shape of metal nanoparticles, which can be structured on a substrate or on a tip.

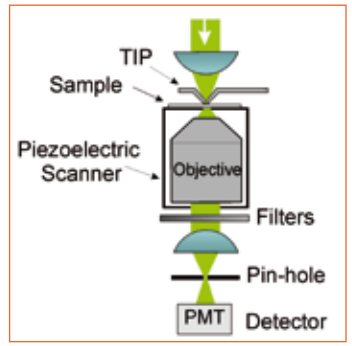
The possibility to perform highly-sensitive single-emitter spectroscopies is a key step towards their application, e.g. in fluorescence imaging, new generation laser systems, optical nano-devices or single-photon sources for quantum computing. In this frame, an important issue is the ability of the metal system to efficiently link far-field propagation and near-field localization, which can be seen, borrowing the language from antenna design, as the problem of matching the optical impedance of the emitter with that of the free space where the exciting and the emitted waves must propagate. The design of the best metal nanostructure to locally excite an emitter and efficiently re-radiate its emission is in fact the problem of building an efficient resonant antenna working at visible wavelengths.

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 both on the development of an efficient experimental probe to address local field distributions at metal nanostructures and on the design of a new class of resonant optical antennas. The scanning-probe microscopy laboratory of the group is based on a commercial apparatus featuring an atomic force microscope, a scanning confocal optical microscope, and a scanning near-field optical microscope [Fig. 1].

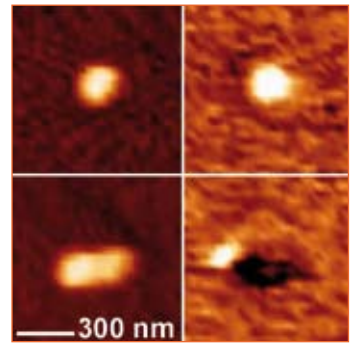
First, I worked on the characterization of light polarization at the aperture of the SNOM probes (in our case, hollow-pyramid tips): a complete control over light polarization is indeed a fundamental prerequisite for any SNOM application aiming at the excitation of resonant nanostructures. By means of a thin dichroic fluorescent polymer, we succeeded in characterizing the transverse polarization state of light in the proximity of the aperture of hollow-pyramid tips, and found that this is extremely well preserved. A future perspective of this work will be the development of polarization-contrast techniques on the SNOM setup, with a special focus on magneto-optical imaging.

Most of my Ph.D. has then been spent in a collaboration with the group of G. Cerullo, S. De Silvestri, and O. Svelto at our Department, working on nonlinear SNOM imaging by coupling ultra-short pulses from a home-made cavity into a SNOM apparatus. The use of nonlinear SNOM microscopy is very challenging, but also extremely effective to study local-field distributions at resonant metal nanostructures, given the intrinsic improvements in terms of sensitivity and contrast provided by nonlinear optical effects. We performed near-field second harmonic generation (SHG) to study periodic arrays of Au nanoellipses, developed as substrates for surface-enhanced spectroscopies by the group of J. Grand, P.-M. Adam, and P. Royer in Troyes, which constitutes to my knowledge the first example of SHG from single resonant metal nanoparticles excited with a near-field microscope. The results clearly reveal that SHG combined with SNOM is a powerful tool to image local field distributions at metal nanostructures, with high sensitivity and sub-100 nm resolution. It allows for a way to visualize the strong field enhancement which accompanies surface plasmon resonances and to relate localized field hot-spots to the particle topography [Fig. 2]. Moreover, polarization analysis of SHG shows that new peculiar emission channels, which are forbidden under plane-wave illumination, become accessible thanks to the local near-field excitation, an issue which might have important consequences for SNOM-based spectroscopies. The nonlinear SNOM setup has also been used to locally excite two-photon photoluminescence from poly(9,9-dioctylfluorene), a blue-emitting organic semiconductor widely used in organic light emitting diodes. This collaboration with the group of prof. G. Lanzani at our Department resulted in the discovery that two-photon excitation selectively addresses oxidized chains, thus providing a novel super-resolved diagnostics for degradation in organic devices.

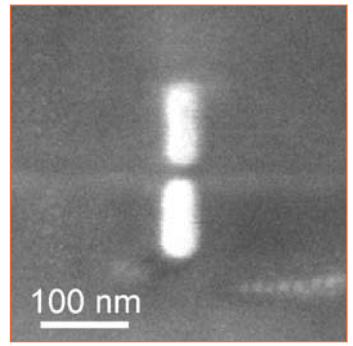
During my third year, finally, I worked on resonant optical antennas in the group of B. Hecht and D. Pohl at the University of Basel. I produced and fully characterized a sample of gold optical dipole antennas on a substrate [Fig.3], which has been the subject of a nonlinear SNOM study later on in Milan. I then explored the possibility to build a tunable dipole antenna, where one arm of the dipole is structured on a tip and the other one lays on a glass substrate, so that the effective length of the antenna can be tuned by scanning the tip over the sample. Promising preliminary results show that this system, though not completely reliable yet, might be a valid solution, possibly allowing for an easier way to place a single emitter in the gap of the antenna and always get a fine tuning of the antenna itself.



1. Sketch of the SNOM setup



2. Upper row: topography (left) and SHG (right) of a particle showing a plasmon resonance; lower row: topography (left) and SHG (right) of a particle showing a localized field hot spot

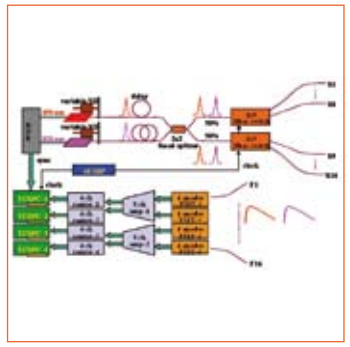


3. Scanning electron microscopy image of a gold dipole antenna on a glass substrate

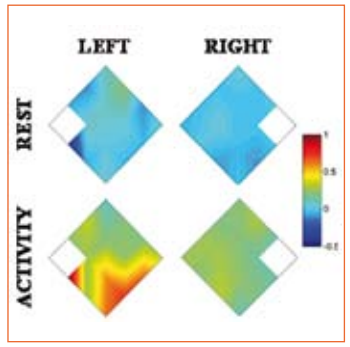
TIME-RESOLVED FUNCTIONAL NEAR INFRARED SPECTROSCOPY FOR NEUROSCIENCE

Davide Contini

The monitoring of cerebral activity in response to some stimuli (motor, visual, etc.) can help in the study of cognitive processes, diagnosis of mental diseases and localisation of brain injuries. This field was fostered by the capabilities offered by magnetic resonance imaging (MRI), positron emission tomography (PET), electroencephalography (EEG) and magnetoencephalography (MEG). Functional Near Infrared Spectroscopy (fNIRS) is a new emerging non invasively tool to monitor brain activity that exploit near infrared light (600-1000 nm) as the probing radiation. Multiple scattering is the dominant effect for light propagation in tissues. This implies that photons are scattered many times before being absorbed or re-emitted from the medium, thus it is impossible to know with precision the path performed by the photon in the medium (Photon Migration). For decades it was believed that scattering prevented the possibilities of probing tissues in depth. Instead 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 fact, in this spectral region biological tissues are rather transparent and penetration depth is relatively high, allowing for the non-invasive investigation of deep tissues. Furthermore, main tissue constituents like water, lipid, and in particular oxygenated and deoxygenated haemoglobin, exhibit distinct spectral features, which may help to discriminate them and to derive their concentrations measuring the absorption coefficient at different wavelengths.



1. Instrument Layout



2. Oxygen saturation maps (6x6cm) during activity of the left motor cortex

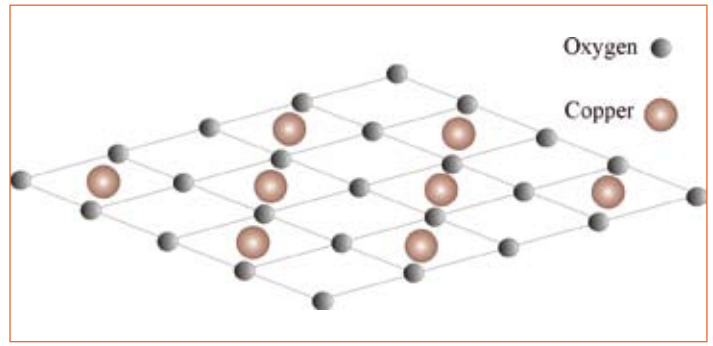
The aim of fNIRS is to localise and identify brain cortex activity exploiting the link between cerebral activity and hemodynamic response. In fact, after brain activation, following a stimulus, the involved neurons need a supply of oxygen because of the increased consumption. The vascular response to this request gives as result a local increase in the concentration of oxygenated haemoglobin and a contextual decrease in the concentration of deoxygenated haemoglobin. Thus brain cortex activity can be identified and localised by monitoring the concentrations of these two chromophores.
To measure the optical parameters of tissues and thus the concentration of oxy- and deoxy-haemoglobin there are mainly three approaches, that are different one from the other for the type of light sources employed: continuos wave light, amplitude-modulated light and pulsed light.
Time-resolved (TR) methods should be preferred to frequency-domain or continuos-wave approaches because time-resolved techniques rely on the possibility to derive absolute values for the hemodynamic parameters, and on an easier approach to the problem of depth sensitivity. In fact in time-domain measurements depth sensitivity can be improved by simply exploiting the temporal information.
In the context outlined in the previous paragraphs, my work, performed in the Biomedical Optics group at the department of Physics (Politecnico di Milano) leaded by Prof. R. Cubeddu, has been mainly focused on four main aspects:

- development and characterisation of a functional time-resolved near infrared spectroscopy system for the assessment of the brain hemodynamic parameters.
  The instrument [Fig. 1] designed, realised and characterised is a compact time-resolved functional near infrared spectroscopy imager based on pulsed semiconductor lasers, fast compact multi-anode photomultipliers (PMT) and time correlated single photon counting (TCSPC) acquisition scheme. The system has been designed to operate like two parallel, independent systems, for instance, for the measurements of the right and left brain hemispheres at the same time. It has 16 independent injection channels (S1-S16) and 16 parallel detection channels (F1-F16) for a maximum number of measured points of 36. The instrument was extensively characterized showing an optimum linearity both in the absorption and scattering coefficient estimation, a good reproducibility and a discrete stability;
- optimisation and definition of analysis strategies in order to exploit depth information encoded in time-resolved measurements.
  The main idea is to exploit the depth information intrinsically encoded in TR data: photons collected at early time (early photons) have a very low probability to reach deeper layers, while photons collected at late time (late photons) carry information not only on the superficial layer, but also on the deep one. In this Ph.D. work it was developed a novel method, with lower implementation cost, to improve depth selectivity for fNIRS of the brain by means of a straightforward exploitation of the depth information encoded in time-domain contrast functions. The aim of this model is to separate systemic hemodynamic changes, occurring in particular in the scalp, from functional changes related to brain activation. The method has been tested with numerical simulation and, during in-vivo measurements, it effectively discriminates brain cortex activation from hemodynamic changes associated to systemic effects in the scalp;
- application of TR-fNIRS technique to Neuroscience.
  Both the instrument and the analysis method are successfully applied to in-vivo. These experiments have the aim to verify the applicability of the proposed instrumentation and analysis method in the research field of Neuroscience. We focused our attention on the sensory-motor cortex and used its activation as test-bed to study the characteristics of our instrument in terms of imaging capability, spatial resolution, sensitivity and specificity [for instance see Fig. 2]. The performed experiments verified that the proposed hardware and the theoretical apparatus fulfill the specifications to be a useful tool in the field of Neuroscience. Recent studies have combined functional magnetic resonance imaging (fMRI) with functional near infrared spectroscopy. This multi-modality approach is interesting for the complementary characteristics of these two techniques.
  Up to now only continuous wave or frequency-domain fNIRS/fMRI studies have been reported. As explained before the use of a time-domain fNIRS system would allow a better depth-discrimination and possibly a more robust assessment of absolute changes in the hemodynamic parameters. To this aim we demonstrated, for the first time, that TD-fNIRS can be used coupled with fMRI for brain functional studies;
- application to fNIRS of the novel photon migration approach based on null inter-fiber distance.
  Recently the Biomedical Optics group at the Department of Physics of the Politecnico di Milano (Italy) theoretically demonstrated the advantages, in terms of signal-to-noise ratio, spatial resolution and achievable contrast, obtained with time-resolved measurements performed at null inter fiber distance. We experimentally demonstrate, for the first time, the feasibility of this kind of measurements both on tissue phantoms than during in-vivo tests of functional brain activation.

ELECTRONIC EXCITATIONS IN STRONGLY CORRELATED ELECTRON SYSTEMS MEASURED WITH RESONANT INELASTIC X-RAY SCATTERING

Francesca Luciana Fracassi

The aim of the work is the study of the electronic structure of transition metal compounds, which are strongly correlated electron systems. A complete model describing the electronic properties of these systems has not yet been found because of the competition between electron localization and delocalization. For this study the Resonant Inelastic X-ray Scattering (RIXS) spectroscopy with linearly polarised incident radiation is used. The electronic structure of NiO and MnO are investigated. These compounds are the prototypical transition metal monoxides and in the 1930's their insulating behaviour instigated the study of electron correlations. The knowledge of monoxides electronic structure can also help in the understanding of the electronic properties of more complex compounds like magneto-resistive manganites and high-T_c superconductive cuprates.
We measured NiO and MnO electronic excitations up to about 10 eV energy, with a particular interest in *dd* excitations: they allow to know the 3*d* levels splitting of transition metal ions due to the anisotropic electric field produced by the ligands. The measured excitations were already observed by optical and electron energy loss spectroscopy (EELS). In respect to the former the RIXS technique measures more intense *dd* excitations: they are forbidden by electric-dipole selection rules so they have low intensity with optical spectroscopy, whereas they are allowed in the second order RIXS process. In comparison with surface-sensitive EELS, RIXS has the advantage to be bulk sensitive (this characteristic is necessary for the study of bulk properties like high-Tc superconductivity). NiO and MnO RIXS data and calculations are compared. Our spectra have a good agreement with the calculations and show that a part of RIXS measurements can be interpreted by the simple and easy to handle ionic model. This test is very important to study the potentialities of RIXS spectroscopy, whose energy resolution has a continuous improvement with the new generation synchrotron radiation devices. The data interpretation has allowed to find important physical parameters of NiO and MnO.
We took absorption and RIXS spectra of the high-T_c superconductive superlattices $[BaCuO_{2+x}]_2/[CaCuO_2]_{n=2,6}$, of the superlattice $[BaCuO_{2+x}]_2/[CaCuO_2]_{12}$ and of the two infinite layers $BaCuO_{2+x}$ and $CaCuO_2$. The aim was the study of the copper 3*d* levels at room temperature.
These orbitals are strongly hybridised with the O 2*p* orbitals and this seems to play a fundamental role in high-T_c superconductivity mechanism, which is considered to be linked to the presence of bound couples formed by a copper 3*d* hole and an oxygen 2*p* hole. $[BaCuO_{2+x}]_m/[CaCuO_2]_n$ superlattices are perovskite-like superconductive cuprates. The structure of these cuprates is characterized by the presence of CuO_2 planes separated by blocks of various composition. Along these planes the superconductive current flows and the charge carriers seem to be holes occupying the O 2*p* orbitals. We studied the electronic energy levels of CuO_2 planes.
Many RIXS measurements investigated the oxygen 2_p levels. RIXS spectra of the copper 3*d* levels were taken on other perovskite-like cuprates, our measurements are the first on the $[BaCuO_{2+x}]_2/[CaCuO_2]_n$ superlattices. We measured dd and charge-transfer excitations (charge transfer excitations give information about the hybridisation of Cu 3*d* and O 2*p* orbitals).
Our absorption spectra and the charge-transfer excitations we measured indicate that the doping-induced holes are provided by the $BaCuO_{2+x}$ block. We assigned the observed *dd* excitations. We observe a structure at 0.5 eV whose interpretation is very debated in literature. It was measured by optical spectroscopy only for incident light linearly polarised along the CuO_2 planes. Our energy resolution allows to observe it with RIXS for the first time. Calculations show that this structure can be a dd excitation or a magnetic excitation. Our measurements on the $CaCuO_2$ infinite layer show this feature only for polarisation along the CuO_2 planes and with weak intensity, whereas the data of the superlattices $[BaCuO_{2+x}]_2/[CaCuO_2]_{n=2,6,12}$ and the $BaCuO_{2+x}$ infinite layer present it for polarisation both parallel and perpendicular to those planes and with strong intensity. The presence of the structure seems to have a correlation with the coppers local structure: it is measured only for along CuO_2 planes polarisation when no coppers have apical oxygens, it is observed for both polarisations when some coppers have apical oxygens. This difference could be due to a different nature of the feature: it could correspond to a magnetic excitation or to a dd excitation. We did also measurements on the optimally doped $[BaCuO_{2+x}]_2/[CaCuO_2]_2$ under T_c. Their comparison with the spectra taken at room temperature seems to indicate a more delocalized



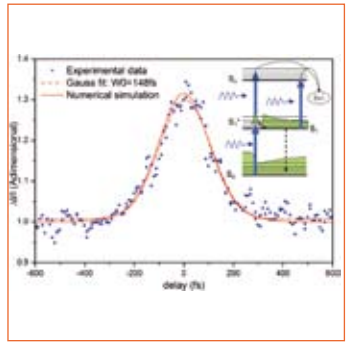
1. CuO_2 planes, along these planes the superconductive current flows. We studied their electronic structure

character of the intermediate state of the RIXS process in the superconductive state, with the consequent more efficient screening effect of the core hole. Perovskite-like cuprates have a very complex electronic structure, still not described in a complete way by a model. The study of the copper 3*d* levels and their hybridisation with oxygen 2*p* orbitals can help to understand their role in the mechanism of high-T_c superconductivity, still far to be completely explained.

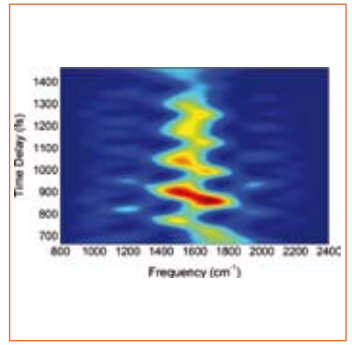
FEMTOSECOND CHARACTERIZATION OF π-CONJUGATED MATERIALS AND DEVICES FOR OPTOELECTRONICS

Alessio Gambetta

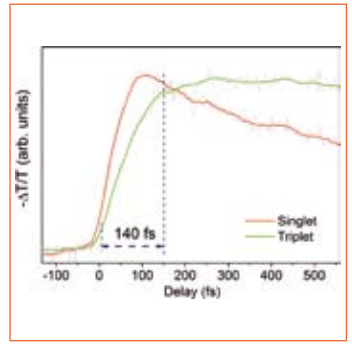
The research activity has been focused mainly on the study of organic devices and nano-materials for optoelectronic applications. In order to achieve the time resolution and wavelength tunability needed to investigate the electronic processes occurring in these materials a wide variety of Ti: Sapphire based laser systems for time resolved spectroscopy has been used: these systems, exploiting different nonlinear optical processes, are capable of generating ultrashort laser pulses with a time duration down to 10 fs (ten millionth of billionth of second) and, combined together, allow to span over a very wide range of frequencies from medium infrared to near UV.
A first research line has concerned the realization of thin film polymeric optoelectronic devices and the investigation of the charge generation mechanism which are still widely under debate in this kind of materials. In the particular case of PFO, poly(9,9-dioctylfluorene) polymer, cross correlation photoconductivity measurements show how the main mechanism for charge generation is the sequential absorption of two or more photons to higher energy excited states: taking advantage of this non linear mechanism the device has been employed as an autocorrelator that allows the characterization, with around 100fs time resolution, of laser pulses generated by sources in the near UV. The device has been patented and an international extension is actually under consideration. Mathematical analysis and modeling of the electronic levels of the material has also been exploited in order to evaluate important parameters like the linear and non linear excited states absorption cross-sections and vibrational relaxation time constants.
Recently the discover of Single Walled Carbon Nanotubes (SWCNT) has aroused great interest in optoelectronics because of the peculiar electronic and structural characteristics of these nano-materials: depending on the chirality (a structural parameter) each tube behaves either like an ideal one dimensional semiconductor or a metallic nano-wire. Using a laser system consisting of two synchronized non collinear optical parametric amplifiers it has been possible to observe dynamics of energy relaxation process with time resolution of the order of few tenths of femtoseconds and to assign a time decay constant of 40 fs from the second excitonic level to the first one in SWCNT with semiconductor characteristics. The strong coupling between electronic



1. Autocorrelation of UV (λ=390nm) laser pulses made with a PFO non-linear photodiode. Red lines are numerical simulations of the device response. Inset: model of the electronic states of the material and the sequential mechanism for charge generation



2. Frequency modulation of the Carbon-Carbon stretching mode: the frequency oscillates periodically in time around the center frequency with a period equal to the inverse of the radial breathing mode oscillation frequency



3. Singlet (red line) and triplet (green line) early times dynamics in platinum doped polymers: triplet states are generated within 140 fs after photoexcitation.

and vibrational levels (vibronic coupling) existing in this materials allows also to exploit optical spectroscopy techniques in order to study their vibrational motion: two main vibrational modes have been observed (252cm^{-1} and 1588cm^{-1}) and by means of comparison with Raman spectroscopy measurements they have been assigned respectively to the total-symmetric oscillation of the tube diameter (Radial Breathing Mode) and to the stretching of the carbon double bonds (Carbon-Carbon Stretching Mode). A time-frequency hybrid analysis has finally allowed to observe a frequency modulation of the 1588cm^{-1} mode, assigned to an anharonic coupling between the two oscillation modes.
In semiconducting polymers and carbon nanotubes the primary photoexcitations are singlet states which consists in a coulombically bound electron-hole pair with antiparallel spin configuration. Triplet states (with parallel spin orientation) can also be subsequently generated and they play a very important role in organic based optoelectronic devices: the generation of these states inside the material strongly limits the electroluminescence quantum efficiency in organic Light Emitting Devices (LED) and more in general reduces the lifetime of organic devices because of the strong interaction with oxygen present in the atmosphere.
Various continuous-wave and ultrafast spectroscopy techniques (among which the use of an Optical Parametric Oscillator, tunable from near to mid infrared and pulse duration of around 150 fs) have been used in order to study the generation mechanisms of such states in platinum chemically doped polymers: the presence of an heavy metal atom along the polymer chain greatly enhances the chance of directly generating triplets and allows them to be studied by optical means. A preliminary study on materials with different average distance between adjacent platinum atoms has been performed and a record generation time of 140fs has been recorded for the material with the shortest metal-metal inter-distance.

NONLINEAR EFFECTS AND OPTICAL QUANTUM ANALOGIES IN LITHIUM NIOBATE AND TANTALATE GUIDING STRUCTURES

Mirko Lobino

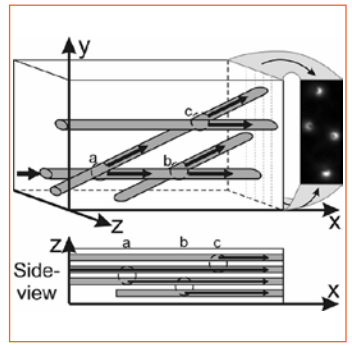
The thesis work is focused on the design, realization and characterization of single channel waveguides and more complex optical guiding structures in congruent lithium niobate (CLN) and stoichiometric lithium tantalate (SLT), for nonlinear applications like second harmonic generation (SHG), third harmonic generation (THG) at telecom wavelengths, and linear application related to light propagation in waveguide arrays for visualization of solid state physics predicted phenomena in an optical frame. Among the materials used in this work, lithium niobate is a well known crystal, commonly used in several optical applications because of its wide range of transparency and the availability of large optical quality single crystal wafers grown by the Czochralski technique. Every year several tons of lithium niobate are produced in order to satisfy the request of high-tech companies where it is employed as substrate for the realization of high repetition rate electro-optical modulators. Recently, periodically-poled (PP) crystals have been proposed for the realization of prototype integrated nonlinear optical devices, showing extremely interesting performance. Wavelength converters, optical diodes and other nonlinear devices have been successfully implemented on lithium niobate waveguides realized by annealing-proton-exchange (APE), reverse-proton-exchange (RPE) or titanium in diffusion (in:Ti). These devices were shown to be able to improve the performance of TLC optical network by all-optical signal processing scheme, that overcomes the bottleneck created by the opto-electronic signal conversions; nevertheless they did not succeed in a breakthrough in the industrial world yet. The main reason for this missed chance is the low optical damage threshold of LN crystal, that even for coupled power of few tens of mW, manifests photorefractive effect and a strong reduction of nonlinear conversion efficiency. Optical damage can be avoided only by raising the working temperature above 80 °C by an external oven, but this drawback makes such devices not commercially convenient because of increased maintenance charges and a reduction of their reliability. Oxide magnesium doped stoichiometric lithium tantalate (Mg:SLT) is a new material with the same crystalline structure of LN, with a lower nonlinearity but with a much higher optical damage threshold. Good quality substrate of Mg:SLT have been produced only recently by a modified Czochralski technique and are now commercially available. The technology of periodic poling, which is essential in order to obtain phase-matched nonlinear interaction in guided geometry, can be implemented on Mg: SLT with an excellent quality of the grating due to its low coercive field. Furthermore the doping with magnesium oxide increases considerably the optical damage threshold of the crystal, thus enabling nonlinear waveguides to operate at room temperature. Some of the first nonlinear optics experimental results ever obtained on Mg: SLT substrate will be presented in this thesis, using a buried optical waveguide configuration realized by the reverse-proton-exchange technique. The use of this new material required a preliminary modeling of all fabrication stages in order to achieve an optimized waveguide design. Subsequently second harmonic radiation, at telecom wavelength, was generated in optical waveguides of periodically poled Mg:SLT with good value of normalized conversion efficiency, while optical damage resistance was checked with a coupled power of more then 300 mW. Two different refractive index profile configurations have been analyzed: one enhancing the nonlinearity of the waveguide, and thus the overlap integral of interacting modes, and the second one optimizing the linear properties of the device in terms of coupling and propagation losses. The potentiality of this new crystal and the capability of operating in a real network are experimentally demonstrated. A second nonlinear interaction, in a more complex scheme than pure second harmonic generation (SHG), has also been studied. Triple frequency was produced in APE lithium niobate waveguide by a cascaded process of second harmonic generation and sum frequency generation (SFG) leading to third harmonic generation (THG). First order quasi-phase-matching (QPM) is used for SHG and third order QPM for SFG. A simultaneous phase-matching is obtained for the two processes through a suitable choice of interacting modes, an optimized design of the waveguide optical parameters, and by adjusting the working temperature that is kept above 80 °C so as to avoid photorefractive effects. Lithium niobate was preferred to SLT for its higher nonlinearity in virtue of the fourth power dependence of THG efficiency on nonlinear susceptibility. The highest value to date of THG conversion efficiency was obtained at telecom wavelength in the double quasi-phase-matching regime. This device has been developed as the main tool of a laser frequency stabilization scheme that locks the third harmonic of a 1.55 μm laser to one of the absorption lines of iodine or rubidium in the green region ($\lambda \sim 515$ nm).
The consolidated expertise in the fabrication of APE waveguides has been then applied to the realization of optical guiding structures used to visualize linear effects. Annealed proton-exchanged waveguide arrays were fabricate on lithium niobate substrate for the visualization of quantum optical analogies and solid-state-physics predicted phenomena in an optical frame. This work is based on the formal analogy between paraxial wave-equation and Sch\"{o}dinger equation that will be explained in detail in the thesis and to the correspondence of array bending with an external electric field effects. A theoretical and experimental analysis is given, mostly concerning sinusoidally curved waveguide arrays of evanescently coupled waveguides that permitted the first experimental visualization of dynamic localization. Multiband effects have been also studied in both straight and curved arrays. Experimental results showed a very good agreement with theory, proving the quality of our arrays and the potentiality of this experimental environment.

FEMTOSECOND LASER FABRICATION OF OPTICAL WAVEGUIDES AND MICROFLUIDIC CHANNELS

Valeria Maselli

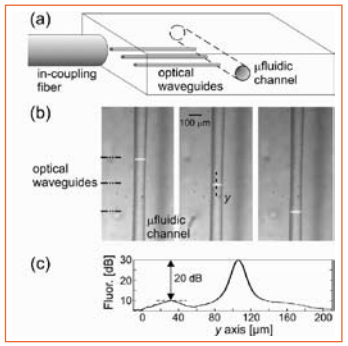
The scientific activity was dedicated to the development of new techniques of micro-fabrication in glass substrates, by means of femtosecond laser systems. These techniques are based on nonlinear absorption of laser radiation focused inside a transparent material, thus modifying the material properties. This modification can result in a refractive index change, which can be used to create waveguides, or in a higher etching rate of the exposed material in hydrofluoric (HF) acid solutions with respect to the pristine material, which permits to realize microchannels. The first research line concerned the fabrication of waveguides and photonic devices, for applications in the fields of optical telecommunications and optical sensing of biomolecules. Two different femtosecond laser systems were used, the first one with low pulse repetition rate (1 kHz) and high energy (1-5 μJ), the second one with high repetition rate (25 MHz) and low energy (20 nJ). In the first case, a particular astigmatic focusing technique was used which allowed to realize waveguides with symmetrical cross-section in fused silica glasses. These waveguides show good characteristics (single-mode, low losses) in the visible and are promising for sensing applications. The high repetition system was used to produce waveguides with good optical properties at the wavelength of interest for telecommunications (1.5 μm). These waveguides were combined, exploiting the peculiar capabilities of the femtosecond fabrication technique, to obtain three-dimensional photonic devices [Fig. 1], such as splitters and WDMs, realized in the Corning 0211 and Schott IOG-10 glasses. A second research line concerned the realization of microchannels in SiO2 substrates, by means of femtosecond exposure followed by chemical etching in hydrofluoric acid. Thank to the astigmatic focusing technique, to the use of ultrasounds and to the process parameters optimization, it was possible to fabricate microchannels with circular cross-section and length greater than 3 mm, value up to now never obtained in literature. To overcome the problem of the limited length of the microfluidic channels a new iterative method, in which several chemical etching steps in HF are conducted after femtosecond pulses irradiation of the sample, was tried. It was found that the length of the microfluidic channels increases by almost 500 μm per hour. A third laser system (an Ytterbium:glass diode-pumped cavity-dumped oscillator) with repetition rate and pulse energy values intermediate between those of the amplifier (low frequency regime) and the long-cavity oscillator (high frequency regime), was used to reduce the microchannels fabrication time, since the oscillator allows to translate samples with a higher speed [Fig. 2].

Moreover, it was demonstrated the possibility to fabricate, in the same substrate and with the same laser system, both microfluidic channels and optical waveguides. Waveguides were used to verify the selective optical excitation of molecules present inside the channels [Fig. 3]. This result opens innovative and interesting perspectives toward integration of optical functionalities on microfluidic devices, in particular the lab-on-chips, used for biomolecules sensing.



1. Schematic of the 1x4 splitter (top and side view), with an experimental near field of the output face at 1550 nm

2. On the right: microfluidic channel fabricated with the diode-pumped cavity-dumped oscillator. On the left: corresponding circular cross-section



3. (a) Schematic of the waveguides crossing the microfluidic channel; (b) microscope image of the microfluidic channel with the fluorescence excited by the optical waveguides, which are not visible due to the low refractive index change and scattering losses; (c) intensity profile acquired in the middle of the microchannel (y axis in previous panel) across one of the fluorescent filaments.

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