



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:

- 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.
- 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, INFN-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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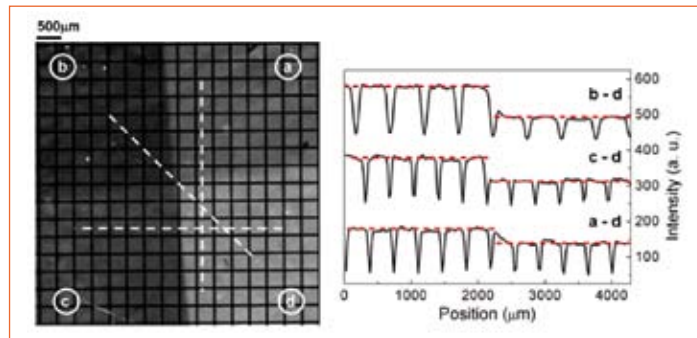
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# SOFT X-RAY GENERATION FOR APPLICATIONS IN NANO-FILMS IMAGING AND MOLECULAR SPECTROSCOPY

Francesca Calegari

The extremely nonlinear interaction of high-power femtosecond laser pulses with solid and gas targets has been investigated extensively in the last decade. This strong laser-matter interaction allows one to produce extreme ultraviolet (XUV) and soft X radiation with a more cost effective and compact design compared to synchrotrons. This emission can be exploited in a wide range of advanced scientific and technological applications such as soft X-ray microscopy, nano-lithography, organic in-vivo imaging and time resolved inner-shell spectroscopy. Focusing a high-peak power laser ( $I \sim 10^{11}$ - $10^{19}$  W/cm<sup>2</sup>) onto a solid target allows the creation of a plasma. The laser-plasma interaction efficiently converts the impinging laser energy into soft X radiation. This emission is incoherent and characterized by a pulse duration of several picoseconds. Conversely, the interaction of an intense laser pulse ( $I \sim 10^{13}$ - $10^{14}$  W/cm<sup>2</sup>) with a gaseous medium allows the generation of high order harmonics of the fundamental laser frequency. Due to the nature of the process, the emitted harmonic radiation is coherent and characterized by a very short time-duration ranging from the femtosecond to the attosecond scale. Owing to the high soft X

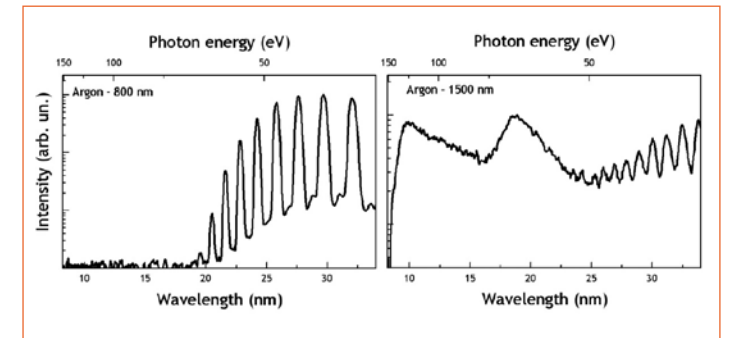


1. Left panel: soft X-ray imaging of 0 (d), 20 (a), 40 (c) and 60 (b) nm thick Al layers. Right panel: experimental (solid lines) and calculated (dashed lines) image profiles along white traces

photon flux and to the strong absorption in this spectral region of many atomic species, Laser-Produced Plasma (LPP) sources can be successfully used in the context of contact imaging. In the first part of this work we demonstrate that the use of a LPP source combined with a color center detector (LiF crystal) is a reliable technique to perform imaging of thin films with a very compact setup, a wide field of view and a high spatial resolution. Soft-X radiation was generated by focusing intense laser pulses from a Ti:Sapphire system (800 nm, 60 fs, 120 mJ, 10 Hz repetition rate) on a Teflon target. Samples were exposed to soft-X rays at 30 cm from the plasma source; the transmitted radiation impinged on a LiF plated kept in contact with the sample. The acquired image was obtained recording the

fluorescence pattern emitted by LiF color centers under exposure to 450 nm light. Left panel of Figure 1 shows the absorption image of a four-quadrant sample obtained evaporating 0, 20, 40 and 60 nm thick Al layers on a parylene substrate. As can be seen from the figure, a strong difference in absorption is observed for increasing aluminum thickness. In right panel, we report experimental (black solid line) and calculated (red dashed line) image profiles. The predicted intensity values are in excellent agreement with the experimental results. We performed a similar experiment with a four-quadrant sample obtained evaporating respectively Al, Cu, Ag and Au layers on the parylene substrate. Experimental results shows that soft X-ray imaging is also

strongly affected by sample composition. High-order Harmonic Generation (HHG) is a powerful table-top tool for a time resolved spectroscopy in the attosecond domain. Up to now, isolated attosecond pulses have been extracted in the XUV spectral region, whereas single attosecond pulse production in the soft X region is still an important challenge. A possible approach to extend the harmonic emission in the soft X is to use longer wavelengths for the driving pulse. Owing to the larger harmonic cutoff they provide compared to conventional Ti:Sapphire laser sources, parametric sources operating in the near IR have been proposed as a way to generate isolated attosecond pulses exceeding 100 eV photon energy. The characterization of a parametric source operating in the near IR with passive carrier-envelope phase stabilization is included as a part of this work. This source has been developed starting from the amplified Ti:Sapphire laser system described above. A broadband supercontinuum is generated by filamentation in a gas cell and a phase stable seed is then produced by difference frequency (DF) of the supercontinuum spectral components. This seed is then amplified through a two-stage



2. High-order harmonic spectra generated by 0.8  $\mu\text{m}$  (left panel) and 1.5  $\mu\text{m}$  (right panel) driving pulses in argon

near-IR optical parametric amplifier (OPA) up to 1.2 mJ. The overall tuning range of the amplified pulse is between 1.4 and 1.9  $\mu\text{m}$ . For generating high-order harmonic radiation we focused the driving pulses on a synchronized gas jet operating at 10 Hz. The harmonics have been detected by a soft X-ray spectrometer and a micro-channel plate coupled to a phosphor screen and a CCD camera. Figure 2 shows a comparison between the harmonic spectrum generated by the 1.5  $\mu\text{m}$  DF source (right panel) and by the 0.8  $\mu\text{m}$  Ti:Sapphire laser source (left panel) at comparable intensities in argon. A noticeable spectral extension in the soft X was measured for the 1.5  $\mu\text{m}$  driving pulses with respect to the 0.8  $\mu\text{m}$  source. It is worth noting

that the cutoff photon energy for the 1.5  $\mu\text{m}$  source represents the instrumental limit of our spectrometer. Additionally, we performed HHG in a two-color configuration. Indeed, it has been theoretically demonstrated that a temporal gate of the harmonic emission can be obtained when the driving electric field is the superposition of two pulses, one at frequency  $\omega_0$  and another at frequency  $\omega_1$  slightly detuned from the second harmonic. Experimental results shows that 1.45  $\mu\text{m}$ +0.8  $\mu\text{m}$  driving pulses give rise to a continuous emission which is the signature of single attosecond pulse production. This preliminary results opens new and encouraging perspectives for the extension of attosecond physics in the soft X spectral region.

# CARRIER-ENVELOPE PHASE STABLE, FEW-OPTICAL-CYCLE PULSES TUNABLE FROM THE VISIBLE TO THE MID-IR AND THEIR APPLICATION TO TIME-RESOLVED SPECTROSCOPY

Giovanni Cirmi

## Introduction

Ultrashort optical pulses have become a major research topic in the last decades. In this work many sources have been developed covering the whole spectral range from the visible to the mid-IR, and have been applied to spectroscopy and coherent control.

## 1. Ultrafast nonlinear optics

Nonlinear optics deals with frequency conversion of photons. It is possible to generate high energy ultrashort pulses with duration of few femtoseconds, that is few optical cycles in the visible and infrared, by using nonlinear processes like white light generation and Optical Parametric Amplification (OPA).

OPA is a nonlinear optical process where a weak seed (signal) is amplified by a strong pump at higher frequency, with the production of a third beam, at the difference frequency (DF), called idler, so that the energy is conserved among photons. The phase matching condition among pump, signal and idler corresponds to momentum conservation among photons. It can be achieved in birefringent or periodically poled crystals and allows high efficiencies in the parametric amplification. When there is group velocity matching between signal and idler it is possible to obtain huge

phase-matching bandwidths, so as to produce pulses with bandwidths compatible with durations of few fs in the visible and infrared (two-three cycles of the carrier frequency). A typical OPA setup consists of a seed generation part, typically white light generation in a suitable material, and a delay line for the synchronization with the pump pulse.

It is also possible to amplify ultrashort signals with much longer pumps, for example a ps pump. In this case it is necessary to stretch the signal before amplification and compress it after (Optical Parametric Chirped Pulse Amplification). Many methods have been developed to control the spectral dispersion and obtain the shortest pulses compatible with the bandwidth, based on chirped mirrors, prisms, gratings and deformable mirrors. By using these methods it is possible to compensate the spectral phase and therefore obtain ultrashort pulses. Once ultrashort pulses have been produced, they have to be characterized in spectrum and time, with some autocorrelation techniques, like interferometric autocorrelation or Frequency Resolved Optical Gating. An important feature of ultrashort pulses is the Carrier-Envelope Phase (CEP): when

it is stable from a pulse to the next one, together with the spectrum, the intensity and the spectral phase, the electric field is constant, allowing for the generation of as pulses. The CEP stability can be measured with f-2f techniques, by which the CEP of the pulse is compared to the CEP of its second harmonic.

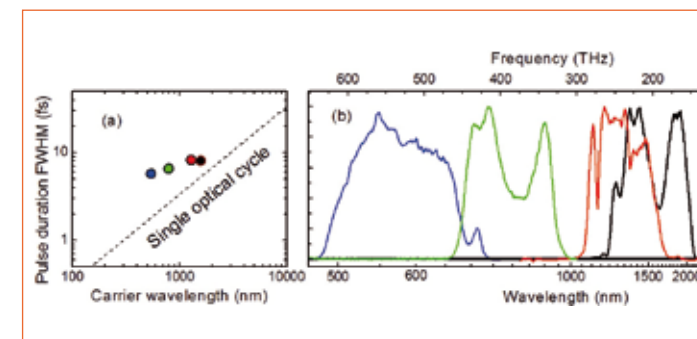
## 2. Tunable few-optical-cycle pulses from optical parametric amplifiers

During this work many OPAs have been developed producing optical pulses with few-optical-cycle duration. To achieve broad amplification bandwidths it is possible either to work at degeneracy, when signal and idler have the same frequency, or with a noncollinear geometry (NOPA).

Visible NOPAs are a workhorse for the generation of ultrashort pulses in the visible. They start from a Ti:sapphire laser, at 800 nm. A small amount of energy is focused in a sapphire plate, where white light is generated. Most energy is frequency doubled, to 400 nm, and used as a pump to amplify the white seed in a  $\beta$ -barium borate (BBO) crystal. After compression these pulses have durations down to 6 fs. BBO does not have the same broadband phase matching in the near infrared (except at degeneracy), but other crystals,

like PPSLT, work well in this region. We were able to produce pulses with 8.5 fs duration around 1.3  $\mu\text{m}$  with a NOPA with PPSLT, and around 1.6  $\mu\text{m}$  with BBO at degeneracy. With these sources we have been able to cover the whole range from the visible to the

control on the pump intensity, passive stabilization is all optical, and it relies on the fact that the idler of an OPA, the DF between pump and signal, has the difference CEP between pump and signal. Therefore, if pump and signal both come from the same source, the idler has a



1. The figure shows in the right panel the spectra produced, with measured durations of two-three optical cycles, covering the whole spectral range from the visible to the near-IR. The left panel shows the duration of the pulses, compared to the single optical cycle limit

near-IR with pulses comprising two-three optical cycles of the carrier frequency, as shown in the figure. With the same crystals mentioned before, e.g. PPSLT, it is possible to produce idler pulses in the mid-IR, from 3 to 5  $\mu\text{m}$ , that are compressible with bulk materials to 20-30 fs.

## 3. Few-optical-cycle pulses with Carrier-Envelope Phase stabilization

An important feature of few-optical-cycle pulses is the Carrier-Envelope Phase (CEP): when it is stable from pulse to pulse it is possible to drive experiments of high harmonic generation and as pulse production. The CEP can be stabilized either actively or passively: active stabilization relies on electronic feedback

stable CEP. Passive stabilization can be achieved with an intrapulse geometry, producing the DF between the long and short wavelengths of one pulse: with this technique we produced high energy CEP stable pulses at 1.5  $\mu\text{m}$ . Passive stabilization can be done also interpulse, producing the DF between two different pulses: with this technique we produced CEP stable pulses in the visible. This OPA is made up of two stages: the first one is narrowband in the near-IR, and the CEP stable idler is used to produce a white that is amplified by a pump at 400 nm in the second stage. We therefore produced CEP stable pulses with 6-fs duration compressed with chirped mirrors. We also produced 7-fs pulses at 800 nm with the same technique.

## 4. Applications of few-optical-cycle pulses to time resolved spectroscopy

Such few-optical-cycle pulses can be used for fs time resolved spectroscopy, to study extremely fast molecular dynamics. The most important technique is called pump-probe, where a first strong pulse, the pump, excites the sample under study; a second pulse, the probe, is measured. The probe variations due to the pump are measured and compared to the probe without pumping. This is repeated for different pump-probe delays and different probe wavelengths.

Visible fs pulses were used for an experiment of coherent control on quinque thiophene photoluminescence: in this experiment two visible pulses are used to excite (pump) and deexcite (dump) a sample of this molecule, and the time and spectrally integrated photoluminescence is measured as a function of the pump-dump delay. In this way it was possible to control the population of the excited state without any pulse shaping. Another experiment with visible pulses was used to study the planarization dynamics of hepta (9,9-dihexylfluorene), a pump-push-probe experiment with which it was possible to study the ultrafast planarization dynamics of this molecule.

# BROADBAND DIFFUSE OPTICAL SPECTROSCOPY BY TIME-RESOLVED TECHNIQUES

Andrea Farina

Research presented here mainly concerns the interaction between light and diffusive media, such as that associated with biological tissues. These media are constituted by chromophores and scattering centers: the first are responsible of light absorption, the second deviate the direction of light propagation without energy loss. The capability of a tissue to absorb and scatter light is quantified by two coefficients: the absorption ( $\mu_a$ ) and the scattering ( $\mu_s$ ) coefficients (called "optical properties"). Optical properties recorded over a wide spectral range provide important information about the composition and the morphology of the sample. Due to the low attenuation of VIS/NIR radiation caused by the main chromophores constituting a tissue (water, lipid, collagen, oxy- and deoxy- hemoglobin), diffuse optical spectroscopy is typically performed in the 600-1100 nm spectral range. In the last years, there has been increased an interest for the non-invasive characterization of biological tissues by means of optical techniques. Several techniques have been implemented for the optical properties characterization over a broad spectral range, such as Continuous Wave (CW), Time-Resolved (TR), Frequency-Domain (FD) and Modulated Imaging (MI).

In this work a TR approach has been used. A monochromatic laser pulse is injected into a sample: due to scattering and absorption the pulse is broadened and attenuated when detected at a certain distance from the injection point. By means of a suitable theoretical model it is possible to estimate the absorption and scattering of the sample.

This work focuses on this subject and deals with three main topics:

- Theoretical models,
- Instrumentation development,
- Industrial and biological applications.

In the following text these topics are summarized.

## Theoretical models

In this work a new model for the light propagation in a semi-infinite medium has been formulated and validated. Starting from an exact solution of the Radiative Transfer Equation (RTE) for an infinite medium with isotropic scattering, approximated boundary conditions have been applied to derive a Green's function for a semi-infinite medium. The accuracy of the new model in retrieving optical properties has been tested by fitting the model to Monte Carlo simulations. A further comparison with the generally used theoretical model, based

on the Diffusion Equation (DE), has been performed. Results suggest that the model based on RTE improves the accuracy of the retrieved absorption coefficient with respect to the DE.

## TR instrumentation development

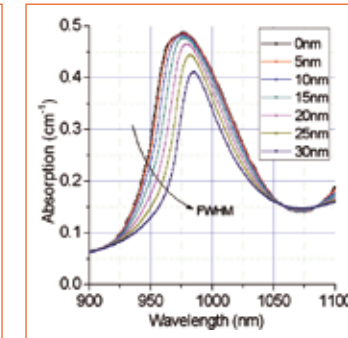
A time-resolved spectroscopy (TRS) system for diffusive media is made of a tunable light source providing pulses on the picoseconds scale and of a fast detector. The implementation of a system like this is challenging due to the tunability requirement over a broad spectral band. A considerably part of this work has been devoted to the development of a compact system for TR spectroscopy in the range 600-1100 nm. The system takes advantage of new technologies in the field of fiber lasers and fast detectors. *In-vivo* measurements on breast, wrist and triceps have been performed with good results. The compactness and the ease-to-use make the system suitable for the clinical environment. The optical system for wavelength selection, conceived during the development phase, has been implemented with the aim to have enough power to the sample without excessively broaden the spectral width. Due to the source power spectral density and to the dispersive element used (a prism) this

trade-off has not been obtained for all wavelengths. Because of this issue, the evaluated absorption spectrum can be distorted, leading to a non accurate estimation of the chromophore concentrations of the sample. The problem has been discussed for the first time for TR diffuse



1. Compact TRS system

optical spectroscopy of small tissue samples, with attention to bone tissue. The motivation of this work is that some *in-vivo* and *ex-vivo* experimental situations like the investigation of fingers and teeth involve small volumes whose dimensions can affect data analysis. The theoretical model generally used to analyze TR profiles assumes a laterally-infinite diffusive slab. If this model is applied to analyze data obtained by TR measurements on a small volume, it can lead to an overestimation of the absorption coefficient due to photon exiting the lateral boundary. Thus, a theoretical model describing the light diffusion inside a parallelepiped has been tested by Monte Carlo simulations and by experimental measurements on bone samples. Results suggest that the parallelepiped model improves both the absorption estimation of thin samples and the estimation of water, collagen, lipids and hemoglobin contents.



2. Water absorption spectra simulated for different bandpasses (from 0 to 30 nm)

spectroscopy. In particular, the estimated absorption spectrum is modified in amplitude, width and also in peak position if the absorption is asymmetric (Fig. 2). This investigation has been carried out theoretically, by simulations and experimentally. Finally a spectrally constrained data fit capable to compensate the distortions has been proposed and validated.

## Industrial and biological applications

The broadband spectroscopy of diffusive media started as an investigation tool for biological tissues. Nonetheless other industrial applications take advantage of diffuse optical spectroscopy, for example application in the analysis of fruit and pharmaceutical tablet. To test the system for some applications, the optical

material mainly constituted by cellulose, lignin and water that are the main responsible of light absorption in the material. A first phase of the work has been dedicated to the optical properties investigation of cellulose and lignin. Subsequently, a characterization of dry, wet and degraded samples of soft and hard wood has been carried out. Water content can be estimated by the change of the absorption spectrum from dry to wet wood. This last feature has inspired investigations in the possibility of assessing the MC variations in wood in equilibrium with a controlled humidity environment. Results are that, by TR diffuse optical spectroscopy, it is possible to detect MC variations of about 1%. The second experimental work has been dedicated to the

optical spectroscopy of small tissue samples, with attention to bone tissue. The motivation of this work is that some *in-vivo* and *ex-vivo* experimental situations like the investigation of fingers and teeth involve small volumes whose dimensions can affect data analysis. The theoretical model generally used to analyze TR profiles assumes a laterally-infinite diffusive slab. If this model is applied to analyze data obtained by TR measurements on a small volume, it can lead to an overestimation of the absorption coefficient due to photon exiting the lateral boundary. Thus, a theoretical model describing the light diffusion inside a parallelepiped has been tested by Monte Carlo simulations and by experimental measurements on bone samples. Results suggest that the parallelepiped model improves both the absorption estimation of thin samples and the estimation of water, collagen, lipids and hemoglobin contents.

# SINGLE-CHANNEL NANOELECTRONIC AND NANOFUIDIC DEVICES IN TWO-DIMENSIONAL SIGE HETEROSTRUCTURES

Alessio Miranda

SiGe heterostructures have played an extremely important role in up-to-date nanoelectronics. Their high mobility together with the low cost of material make them to be considered as the evolution of the Si CMOS (Complementary Metal Oxide Semiconductor) technology, which occupies a dominant position in the field of microelectronics because of its low energy dissipation, high integration levels and low production costs (0.01 USD per  $\text{mm}^2$  with respect to 2 USD of GaAs epitaxy in 2005). However, because of the low mobilities of electrons and holes in bulk silicon, these technologies are limited to applications operating at relatively low frequency, leaving the role of leader materials in fields, such as communications technology, to III-V semiconductors, such as GaAs. Among the many attempts to overcome this limitation, MODFET (Modulation Doped Field Effect Transistor) devices, based on strained Si and Ge heterostructures with high mobility represent one of the most significant methods to improve the performances of devices based on Si technology. The hole mobility in particular is usually much lower than the electron mobility both in bulk and heterostructure systems. This is due to the

fact that its mass is bigger than that of electrons, hence it would be advantageous if the mobilities of electrons and holes were matched, and increased. This would facilitate higher operational frequencies or low-power operation, depending on the requirements of the application. The research performed on SiGe heterostructures at the L-NESS (Laboratorio per Nanostrutture Epitassiali su Silicio e per Spintronica, laboratory for epitaxial nanostructures on silicon and for spintronics) at the Como campus of the Politecnico di Milano, aims to fill this gap. The heterostructures were grown by low-energy plasma-enhanced chemical vapor deposition (LEPECVD), an innovative system of deposition developed by Prof. von Känel and collaborators, which permits a very high-purity epitaxial deposition on Si substrate and at high growth rate. One of the heterostructures grown with this method recorded the highest reported value of mobility for p-carriers in a Ge channel heterostructure (more than  $120000 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ ) making this heterostructure extremely interesting for high-speed applications and as a tool to obtain more insights into quantum and mesoscopic transport and low-dimensional physics. With the aim of

exploiting and study better the physical properties and the applications of this material, an EBL system was installed in Politecnico di Milano.

The work was based at the very beginning on the calibration and optimization of the EBL system in order to get the highest possible resolution. Several tests were carried out and a wide range of experiments has been performed. The experience with lithographic and lift off techniques was used in the cooperation with other research centers in which we participated in the fabrication of nanostructures to be used in applied and base research. Afterwards attention was focused on using the EBL system to pattern nanodevices based on the SiGe heterostructures grown in house. Hereafter, concentration was focused on the design, fabrication and characterization of novel nanoelectronic and nanofluidic devices based on the SiGe heterostructures grown in house.

The first experiment was to fabricate a quantum point contact in order to observe conductance quantization for p-carriers in a Ge channel in SiGe heterostructures, that was never observed before in such structures and carriers.

The structure was optimized in order to reduce leakage currents and measurements were performed at the lowest possible temperature available with our cryostat (1.6K) and with the support of lock-in amplifiers. The same structure was used to propose a new multifunction logic gate concept which is based on a single Hall bar technology and exploit the physical features of the split gate. The device has the great advantage of performing a logic operation with just a single electronic component while several components are required with other technologies (e.g. CMOS). Furthermore the device is based on a simple quantum point contact fabricated in a split gate configuration, which means that another functionality to this long studied device has been implemented.

After these tasks were successfully accomplished, the attention was focused on the realization of two externally gate controlled rectifiers in which the rectification is induced by an asymmetric Schottky depletion originated from a nonequipotential gate. The main advantage of the device is that the asymmetric potential barrier, which cause rectification can be externally controlled. Hence these devices can be tailored by the user for specific applications. The method presented here is suitable to any homogeneous material exhibiting the field effect. A rectification ratio of more than four orders of magnitude proved the validity of the concept. A variant of the method based on an equipotential gate offers

an advantage with respect to the previous concept since the gate does not dissipate power, the external control however is strongly reduced, proposals for further studies and possible applications are also introduced.

During the nanofabrication process of the heterostructures for the previously discussed devices it was noted that a thin layer of Ge, which constitutes the channel, was etched with a much higher rate than the rest of the heterostructure which has a higher Si content. This phenomenon was studied very thoroughly and exploited to fabricate sealed nanochannels to be used to develop a new method for fabricating nanochannels without the use of advanced lithography, stacked multichannel fluid conductance was demonstrated and the advantages of the method with respect to the existing ones is described. The great advantage of the process is the precision with which the nanochannels are created, the possibility of fabricating them in multiple array, and the compatibility with Si-technology which is an asset for the fabrication of lab-on-a-chip devices.

An alternative way for creating (sub-)microchannels involving the relaxation of the internal stress in evaporated material after selective etching of the underlying polymer and corresponding rolled off in evaporated material was described. Rolled up micro and submicrotubes of tunable diameter and controlled position were reproducibly fabricated with this method.

All the subjects presented in this thesis open the way to further studies and wide number of applications. Some examples of them were described in the single chapters and briefly summarized.

In particular the rectifying methods are thought to be implemented for the realization of an externally gate-controlled transistor, exploiting the series of two rectifiers fabricated with the presented technology and an aperture for the base. The main advantage of these new transistors would be the possibility of controlling externally the performance of the device, by applying different potentials on the gates of the diodes which constitute the transistor. Nanochannels for nanofluidic find a huge range of applications both in medicine and for sorting and control of molecules and biochemistry. Any collaboration with a biological or medicine group can take advantage of the highly reproducible and precise method to fabricate lab-on-chip or pure fluidic devices or for basic studies on the property of chemistry and molecules in constrained environments. Rolled up microchannels would found an application in spintronics and transport of magnetic beads. These are only few examples of the many applications of SiGe heterostructure in both basic and applied physics. Several other devices can be conceived with these high mobility and low cost heterostructures.

## VACANCY-SOLUTE INTERACTION IN MG-RARE EARTH ALLOYS

Fabio Moia

Positron spectroscopy is a technique ideal for the investigation of open-space defects. This work is about positron annihilation spectroscopy and it is divided in two parts: (i) analysis of Mg-rare earth alloys by positron techniques and small angle X-ray spectroscopy; (ii) characterization and optimization of a slow positron beam.

In recent years there has been an increasing interest in the weight reduction in aeronautical industry. This demand can be satisfied developing low-weight, high strength Mg alloys for elevated temperature applications. The addition of rare earth elements improve mechanical properties via precipitation hardening. The development of new Mg alloys is possible only understanding the sequence of precipitation and the precipitates' formation kinetics. This work is about clarifying this second point in different Mg-based alloys. Three techniques have been used: (i) positron lifetime spectroscopy (LT); (ii) positron coincidence Doppler spectroscopy (CDB) and (iii) small angle x-ray spectroscopy. (i) The positron lifetime is the measure of the time between the emission of a positron by a radioactive source and its annihilation in a material. This time depends on the local chemical composition

around the annihilation site and on the presence and density of vacancies. In fact vacancies can work as trapping site for positrons and once trapped positrons' lifetime is longer than that of the positrons free inside the material. (ii) The spectrum of the annihilation photons, detected by two solid state detectors in coincidence, is broadened by the Doppler shift due to the longitudinal momentum of the positron-electron pairs. Since the positron injected in a material thermalize in few psec, the CDB annihilation spectrum provides direct information on the momentum distribution of the electrons encountered by positrons in the sample. The high momentum part of this spectrum gives information on inner core electrons, that retain their atomic character even inside a solid. As a consequence CDB can give information on the chemical environment of the annihilation site. (iii) Information on the dimensions and the density of particles present in a sample can be obtained by SAXS spectra. This technique is mostly useful when the particles are aggregates of few atoms, being difficult to detect with other techniques. Positron lifetime spectroscopy and positron coincidence Doppler broadening spectroscopy have been used

to investigate the role of vacancies during ageing at 250°C in a Mg-Y-Nd system alloy designated as WE54. The weak positron trapping in the initial state, after solution treatment, testifies a practical dissolution of the population of vacancies formed during the solubilization treatment, explaining the absence in Mg-RE alloys of natural ageing. In order to accelerate the hardening process, cold work was applied prior to artificial ageing. It was demonstrated that the better hardening response comes from a residual population of vacancies formed during deformation and not annealed in the first minutes of heating. Nevertheless the ageing response of Mg alloys is not as effective as that of Al alloys. The addition of a few weight percent of Ag in Mg-RE alloys improves mechanical properties. In this work a MgNdAgZr (QE22) alloy is considered and the sequence of precipitates occurring at different temperatures is characterized according to the presence of vacancy-like defects or misfit interfaces. In the initial state the measured LT so near to that of annihilation in Mg bulk and the CDB results showing positron annihilating in a high Mg environment and the existence of a fraction of positron annihilating in solute atoms are consistent with a high

density of vacancy-like defects coherent with the matrix and linked to GP zones. During ageing at 150°C CDB positron traps are the same as in the WQ case. The peak-age hardening is reached after 16 h ageing at 204°C (T6). The increase in LT and the ratio between the coefficients of Mg and solute contributions are consistent with the formation of new phases and positron trapping in the precipitate solute/matrix interfaces.

The early ageing stages of another Mg-RE alloy (EV31) are considered. From SAXS results it was possible to suggest a precipitation mechanism. Two temperatures were considered, 150°C and 200°C. The evolution at the latter temperature is faster, but the mechanism is the same in both cases. The initial rapid fall of the number density of precipitates shows that the dense initial distribution of very small clusters dissolve rapidly and contribute to the growth of larger particles (Ostwald ripening process). Then the main precipitation mechanism can be summarized in three steps: i) rapid nucleation at the beginning of artificial ageing; ii) the particles grow by Ostwald ripening process combined with the solute aggregation from the matrix; iii) the formed particles reach a stable thermodynamic condition and continue to grow



1. Inside this vacuum chamber an electrostatic optics collects the positrons emitted by a radioactive source (on the right in the photography, just behind the lead shields) and focalizes them on a target (on the left in the photography)

by means of solute aggregation from the matrix, which explains that the number of precipitates tends to a constant. During the last two mentioned steps, particularly at 200°C, the growth of larger particles is more energetically favoured than the nucleation of new particles. The second part of this work is about a slow positron beam. Positrons emitted by a radioactive source are implanted in the bulk of a sample. In order to obtain a depth profiling of a sample, positrons must be slowed down and accelerated to different kinetic energy of few keV. Tests with electrons were made to optimize the potentials given to the electrodes of the electrostatic lenses in order to focalize the beam in a spot about 2 mm large. The annihilation Doppler broadening

spectra of those positrons emitted by a  $^{22}\text{Na}$  source and focalized on a sample were obtained by a hyper-pure Ge detector. First measures of a multi-layer sample showing the electron pulse induced resistance effect (EPIR) are compatible with considering this effect due to vacancy-like defects' different localization in the layers.

## ORGANIC DEVICES FOR MOLECULAR PHOTONICS AND ELECTRONICS

**Stefano Perissinotto**

Since electrical conduction was discovered in plastics, conjugated polymers (CP) gathered interest from many people working in electronics, telecommunication and solar energy. Indeed commercial OLED displays are now available, though yet expensive, and commercialization of organic solar cells seems to be close in time thanks to companies like Konarka. Organic materials can efficiently work as emitters, photodiodes, transistors and lasers. Following a resurgence of interest in photonics and the commercialization of cheap plastic optical fibers, which transmit in the visible range, it is natural to think about organic visible emitting lasers. Among existent cavities and structures, Distributed Feedback (DFB) lasers show the best performance and lower thresholds.

In this work we studied optical properties of organic DFB lasers and we explored novel modulation techniques for future all optical telecommunications. Not only optical properties of organic materials were explored: a new technology for self assembled monolayers upscaling and integration is presented, being the most advanced technology for molecular electronics at present.

We studied temporal dynamics of polymer lasers via ultrafast

time-resolved spectroscopy, describing the mechanism that rules laser emission in these devices. Experimental data are supported by a rate equations model, that allowed us to carefully describe the nature of lossy processes. Indeed one of the main culprits for losses in organic DFB is charge photogeneration via two-photon sequential absorption. This is also one of the main problems for electrical injection in such devices. In the characterization we also explored the influence of the fabrication process on DFB optical performance, discovering that lower quality replicas of Electron Beam Lithography made devices can show lower thresholds and steeper in-out characteristic, thanks to higher optical contrast. Moreover an investigation over three all-optical modulation techniques was carried on, concerning the use of a gate pulse to control losses, two photon pumping for conversion of infrared signal to visible range and the employment of a photochromic material to implement a chemical switch by activating energy transfer and absorption processes via an external pulse.

In gate pulse modulation we pumped an emitting polymer with a blue pulse and then switched off its emission via

a second pulse, falling in the red region of the spectrum. Indeed red pulse further excites population in the excited state, thus not allowing inversion of population and lasing. But removal of population from excited state is not sufficient to switch off emission, due to fast relaxation of higher lying excited states, which re-populate the high laser level in few tens of femtoseconds. Indeed once further excited, a fraction of the population auto-ionizes into charged pairs, with long lifetimes. This mechanism allowed us to control losses in the polymer, thus modulating laser emission with extreme precision.

The use of two photon two colour modulation concerns the use of two pulses, one in the visible and one in the near infrared, namely resonant with II telecommunications window at 1300 nm. None of the pulses has sufficient energy itself to be absorbed by the emitting polymer, but if they are sent together onto the pulse, they are able to achieve inversion of population and thus laser emission from the polymer via two photon absorption. Once the infrared pulse is removed, emission is quenched. In this way it is possible to directly convert signal from telecommunications fibers to the visible range, which better

suits Plastic Optical Fibers transmission windows. Finally photochromic modulation employs an emitting polymer and a photochromic material (C4), which can absorb UV or yellow light, according to its configuration. Moreover when absorbing UV light it switches to yellow absorbing configuration and vice versa. We used photochromism to modulate emission of a polymer. We continuously pumped a blend of the two materials with a blue pulse and then used a modulated UV beam. When absorbing UV, C4 switches to yellow absorbing configuration, thus giving rise to an energy transfer from the yellow emitting polymer, resulting in a quenching of emission. By absorbing polymer emission, C4 switches back to UV absorbing structure, thus allowing the gaining material to emit, in absence of the UV pulse. In this way we implemented a NOT logical port, driven by a UV pulse.

This three novel techniques offer new possibilities for optical communications. Moreover DFB lasers can be employed in a number of applications, ranging from emitters to sensors, like stress sensors or for analytes detectors. In this particular field they could be used because of their high sensitivity due to their

highly non-linear response to excitation. Concerning molecular electronics, at Philips Research Labs Eindhoven we developed a new technology for patterning, upscaling and integration of low cost molecular electronic devices. We concentrated our efforts on large area molecular junctions (ranging from 1  $\mu\text{m}$  to 100  $\mu\text{m}$ ). This approach was chosen, instead of break-junction approach, because it allows reproducibility of results and better fulfils industrial requirements. Wafers with up to 20.000 junctions and integration of up to 200 junctions in series were realized. The single junction consists of Gold-Alkanethiol-Pedot-Gold layers. The Pedot layer serves as a conductive barrier between Gold electrodes, thus increasing fabrication yield from previous 1% to actual  $\sim$  100%. A deep investigation over the role of Pedot layer was also carried on. The work is completed by a description of electrical conduction in such devices. Large area molecular junctions may be used in matrixes and displays. Indeed high degree of reproducibility was reached, but high rectifications are still to be achieved to exploit their potential commercial value.