



## DOCTORAL PROGRAM IN MATERIALS ENGINEERING

Chair:  
**Prof. Chiara Castiglioni**

The courses of the Doctoral Program provide Ph.D students in Materials Engineering with a common, basic knowledge on Materials Science and Technology, followed by a specialized training in specific fields. The objective is to combine the theoretical knowledge with the skills required by technology in order to form qualified researchers who can manage the design, manufacturing and use of traditional and/or new materials.

### Contents of the Doctoral Program

The Doctoral Course covers the following areas:

*Polymers and composites*

*Cements and ceramics*

*Metals*

*Biomaterials and materials for biomedical applications*

*Processing and characterization of advanced metallic alloys*

*Corrosion and durability of materials*

*Innovative materials for civil and industrial engineering*

*Materials Characterization (Microscopies, Scattering, Spectroscopy)*

*Modelling and theoretical approaches to the study of materials structure and properties*

*Micro and nanostructured materials*

*Functional materials for applications in photonic, electronic and sensors*

*Surface engineering and advanced coatings*

*Materials for industrial design*

*Meta-materials*

*Transformation of materials*

*Material for Cultural Heritage*

The courses face immediately advanced issues both in the main and elective courses. Different curricula are offered, which will be activated on the basis of the decisions of the faculty. The Doctoral program is characterised by high flexibility, in order to satisfy the needs of students that have to develop their research activity in different thematic areas. For this reason each student submit to the Faculty a "Curriculum" to be approved. The Courses offered deal with theoretical, experimental and modelling aspects. Several Courses comprise workshops and seminars, with the participation of invited internationally celebrated speakers. Students can use the most modern facilities for materials synthesis, processing and characterization available at the Politecnico di Milano or in other research laboratories. The research activities related to the Ph.D. theses develop, full time,

along the three years of the Ph.D. courses. Stages in industries or in national laboratories in Italy or abroad are offered. Each Ph.D. student are supervised by a professor of the faculty: the faculty evaluates the progress of his research activity and at the end of each year expresses a judgement on the continuation of the work for the subsequent year. At the end of the third year the Ph.D. student presents and defends, in a public hearing, his thesis work with a jury formed by three experts.

The Ph.D. student is strongly encouraged to attend at national and international meetings and present papers in his specific field. The Ph.D. student is also assigned to give seminars on topical issues and/or to lecture on the specific fields of his research or on the cultural aspects related to his thesis.

The Doctoral School requires the acquisition of 180 credits (in 3 years) :

- at least 30 credits must be obtained through attendance at Doctoral Courses (with positive evaluation in the examinations); in addition, attendance at National and International Schools are strongly encouraged.
- the remaining credits will be assigned on the basis of the research activity necessary to the development of the Thesis project.

### Faculty:

The faculty is constituted by Professors from several Departments of Politecnico di Milano:

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#### Professional skills achieved by PhD in Material Engineering:

The industrial world depends necessarily on a great variety of materials. Nowadays, it is easy to outline two industrial needs: i) development and innovation in the production, processing, application and conservation of traditional materials; ii) development of innovative materials for the production of new manufactured goods or devices to cope with the growing demands of modern technologies. Since these two kinds of industrial needs require specialized people a few specialized curricula are offered. On the other hand, the capabilities acquired through the courses, the research work and the teaching activity assure an adequate preparation to the academic career.

# CONTROLLED SYNTHESIS OF NOBLE METAL NANOPARTICLE ARRAYS AND THEIR BEHAVIOR AS SERS SUBSTRATES AS BIOMEDICAL SENSORS

Nisha Rani Agarwal - Supervisors: Paolo M. Ossi, Matteo Tommasini

Nanostructured Au substrates for Surface Enhanced Raman Spectroscopy (SERS). Synthesis of gold nanoparticle (NP) arrays was done using Pulsed Laser Deposition (PLD) in controlled conditions (collaboration with Dr. S. Trusso – CNR-IPCF, Messina). These substrates were characterized using SEM and TEM. Furthermore, theoretical analysis of plume dynamics was carried out by fast imaging and values obtained were introduced to a mixed propagation model to estimate NP sizes. The substrates were tested for SERS using a standard (rhodamine 6G) and a pharmaceutical drug (apomorphine) at low concentrations. The suitable wavelength to excite the localized surface plasmon was chosen after UV-Visible measurements. Detection limits were reached proving a high degree of sensitivity, reproducibility, stability and uniformity of these substrates. These substrates were able to give SERS for aromatic thiols which covalently bind to the substrate. Hence, the substrates are suited to exhibit SERS based on the commonly reported mechanisms: charge transfer on adsorption and covalent bonding. SEM image analysis was performed on two batches of substrates fabricated

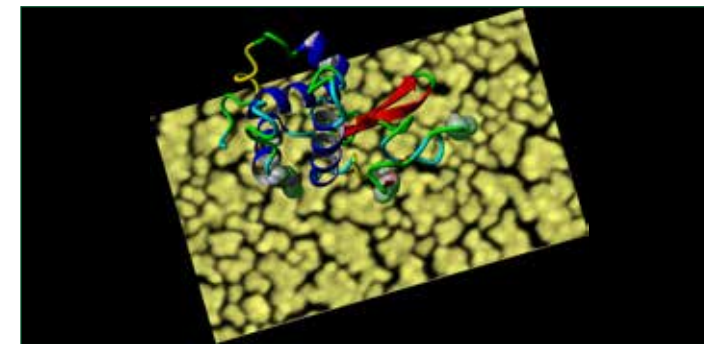
by changing PLD process parameters. The analysis was carried out to understand why the two batches of substrates are different in their SERS behavior despite the morphologies being similar. Detailed interpretations revealed that surface coverage and regularity in spatial distances give a boost to SERS enhancements. To utilize these substrates in biomedical applications, we focus on label-free detection of lysozyme with the PLD produced substrates in comparison with SERS with Ag colloids. Assignment of Raman and SERS peaks has been done proposing a binding site of lysozyme. SERS was achieved for lysozyme which is difficult especially for a solid substrate which lacks NP mobility as colloids.

## Raman and IR spectroscopy of $\pi$ -conjugated systems

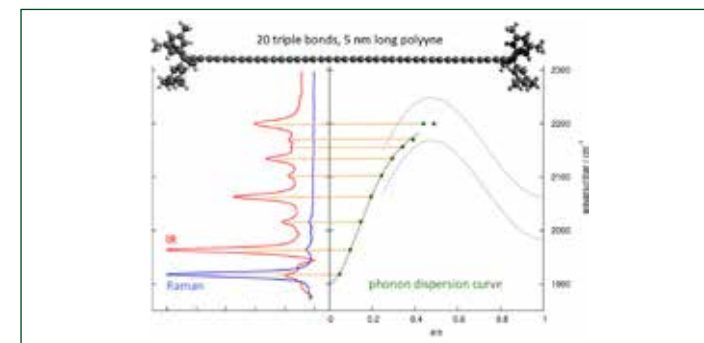
Symmetric and asymmetric trityl end capped polyynes with increasing lengths of the sp carbon chain were studied. Polyynes are interesting systems since they are the ultimate one-dimension atomic wires consisting of sp conjugated carbons. Their presence in interstellar space, as intermediates in production of nanostructured forms of carbon, their good electronic and optical properties and

their availability in laboratories, thanks to a collaboration (Prof. R.R. Tykwinski, University of Erlangen) further motivates to explore their behavior. Vibrational assignment of peaks observed in experimental IR and Raman spectra of polyynes end-capped with bulky groups were possible by comparison with DFT calculations and by analysis of vibrational displacements. For symmetric polyynes vibrational spectroscopy provides clear evidence of the presence of a chain bending effect with increasing chain length. An additional effect was observed for asymmetric polyynes induced by polarization of the sp carbon chain due to asymmetric capping. As a 1D system, these systems prove to be useful non-linear optical materials compared to other sp<sup>2</sup>  $\pi$ -conjugated systems. Detailed analysis was carried out to evaluate the vibrational component of molecular hyperpolarizability ( $\gamma$ ) for both the symmetric and asymmetric polyynes. Through collaboration with Prof. S. Abbate (University of Brescia), Dr. E. Blanch (University of Manchester) and Prof. F. Fontana (University of Bergamo) spectroscopic study of helicenes dealing with the intriguing chiro-optical properties of these compounds have been performed. In addition, they are also  $\pi$ -conjugated molecules.

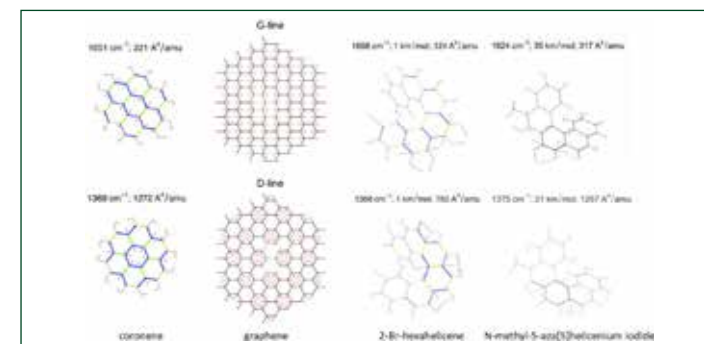
The detailed understanding of their vibrational structure through Raman and IR spectroscopy was carried out with assignment of strong peaks based on a comparison with strong modes (G and D bands) of coronene and graphene. Thus, giving a complete explanation of these vibrations in the helicenes and explaining slight deviations due to the presence of the Br and nitrogen-methyl moiety in 2-Br-hexahelicene and N-methyl-5-aza[5]helicene iodide respectively. They have demonstrated to be promising biosensors, since suitably functionalized helicenes have been shown to bind selectively to DNA in cells.



1. Schematic representation of lysozyme lying flat on the Au substrate with indications of the binding position. The scale lengths of the substrate and lysozyme protein are unproportional



2. Correlation between Raman and IR spectra of SP[20] polyyne and its phonon dispersion curve



3. Sketches of molecular vibrations of G and D bands of graphene and coronene correlated with strong modes of 2-Br-hexahelicene and N-methyl-5-aza[5]helicene iodide

## PHOTOCHROMIC SWITCHES AS TOOLS FOR CONCEPT DEVICES

Rossella Castagna - Supervisor: Chiara Bertarelli

The research activity within this Ph.D program aims at developing new concept devices based on photoactive molecular switches, starting from the material design up to the device testing. Switches which reversibly trigger physical and chemical properties with light have found in photochromic materials and, in particular, in diarylethenes a promising candidate. Thanks to their good fatigue resistance, they have been widely proposed to be applied in optics and optoelectronics. In photochromic systems colour is the peculiar property that reversibly changes by irradiation with light of suitable wavelength as a result of an isomerization that converts the species in a stable or metastable photoproduct. Even more intriguing, the two isomeric states differ for many other properties. In this framework starting from the macroscopic feature that switches in the desired device, the general method implies that a light-triggered modulation of the related molecular property has to be addressed and maximized through a suitable molecular design. Accordingly, a deep investigation on the correlation between structure and properties is necessary to perform a challenging material design. Some study cases have been faced in this work and herein reported. The modulation of the transmittance in the UV visible region has been exploited to realize photoactive mask in Absorbance Modulation Optical Lithography (AMOL). This is a new technique

that can overcome most of the existing resolution limits in optical lithography. The system architecture is very simple thus enhancing resolution with a technology less expensive than electron beam or ultra UV technology. A kinetic model which describes the photoconversion through the volume of a photochromic layer was applied to the case of the AMOL. For sake of clarity the developed model has a general validity for AB(1 $\Phi$ ) systems and contributes to the understanding of the behaviour of photochromic systems at the solid state under complex illumination conditions, thus mimicking what occurs during the writing step of a photochromic device. In this background, the photochromism of diarylethene-based system has been studied in solution and at the solid state, by this mathematical model. Of great relevance, the model offers also the possibility to quantify the photoreaction quantum yield at the solid state, which is no longer reported in the literature due to the intrinsic difficulty in the experimental method. Aimed at allowing multiple time exposure, AMOL has been recently upgraded to POST (Patterning via Optical Saturable Transition), a procedure that combines photo- and electrochemical switching of stable photochromic isomers. The technique combines AMOL with a blocking step that gets the first impressed pattern fixed, thus enabling a new writing run. This

multisteps route can be repeated many times to give a dense final pattern of dark and bright areas. Moreover when large transmittance contrast between the two photochromic states is desired in optical devices based on the change in colour, especially for demanding optical elements for astronomy such as focal plane mask and computer generated holograms, materials have to fulfil strict requirements such as high surface flatness, bulk homogeneity and low scattering. Photochromic polyesters and polyurethanes (PUs) containing 1,2-diarylethenes in the main chain, successfully combine highly sensitive response, an improved homogeneity and high optical quality. These systems are very versatile since the properties of the final material can be tailored acting on the molecular design of the monomer dye. The use of a photochromic polyester was in this thesis proposed as light-triggered microcavity in Bragg's reflectors dielectric mirrors. This application was ruled by the change in refractive index that results from the photochromic reaction. Moreover, we refer to one of the less applied light-triggered properties of photochromic materials, namely the change in dipole moment. and we applied such type of switches to a new concept device which converts photon energy into electric current, but free from the charge carrier transport issue that is a main limit of the third generation photovoltaic devices. The system

is a photochromic electret which exploits the modulation of the permanent field polarization in a capacitor, which takes place as a result of a change in molecular dipole moment induced by the photochromic reaction. Such a change in polarization causes a charge flow in the external circuit to balance the charges on the capacitor plates. Therefore, a current signal is generated by light, exploiting the reversible and repeatable photochromic reaction that occurs in the dielectric photoactive layer. Since the benchmarks for this device are the change in dipole moment between the two photochromic isomers and their orientation, the latter was previously tested by aligning the chromophores by means of corona poling and light switching the second order non linear optical (NLO) properties of the poled materials. This photochromic electret demonstrates an unprecedented mechanism for light energy harvesting and conversion. Analysis of the parameters that contribute to the efficiency and device performances gives space to improvements acting on material design and device fabrication. Regarding materials, an amphiphilic diarylethene was synthesized to form a Langmuir-Blodgett photoactive non-centrosymmetric coating, as the first building block of an alternated anisotropic multilayer. Beyond colour change, another property of great relevance that can be switched upon irradiation

of a photochromic material is conductivity. The concept is on the basis of the development of optoelectronic devices and this goal has been pursued in different ways. In this background we followed the approach which consists in modifying, upon irradiation, the properties of a molecular component coupled with the photochromic matrix. Specifically we combined photochromism with the peculiar electronic properties of carbon nanotubes (CNTs). Therefore, a photochromic polyester has been synthesized to be used as switching polymer matrix coupled to a network of CNTs. Irradiation of the polymer/CNTs blend results into a light-triggered and reversible conductance switching device with an overall resistance modulation of the blend up to 300% . This conductance switching can be repeated many times with full reversibility. I hope that the general approach I followed in these selected studies, which moves from molecules towards devices, will give a contribution to spread new concept applications of photochromic diarylethenes.

# CRITICAL CONDITIONS FOR THE INITIATION OF CHLORIDE-INDUCED CORROSION OF STEEL IN CONCRETE

Andrea Della Pergola - Supervisor: Luca Bertolini

During the last decades, models, aimed at predicting the service life of reinforced concrete structures subject to reinforcement corrosion, have been proposed. The service life could be predicted as a function of the environmental loads (for instance the presence of chlorides) and of the properties of the materials (for instance the resistance to the penetration of chloride for concrete and to the initiation of corrosion for steel bars). Although some accelerated tests have been proposed to predict the resistance of the concrete to the penetration of chloride, up to now no tests are available to predict the "critical" chloride content that causes the initiation of corrosion. Although the chloride threshold level is being studied by an international research group organised by Rilem, many open issues still exist, mainly because the value of this parameter depends on many variables, whose role has not been completely defined yet. One of the main variables that affect the chloride threshold is the electrochemical potential of reinforcing steel and, in some particular conditions, the initiation of corrosion cannot be simply described through a chloride threshold value, since also the potential plays a major role in the definition of the critical conditions for

corrosion initiation. In these cases a "critical combination" of the two parameters should be considered, as first proposed by Pietro Pedeferra in describing the principles of the technique of cathodic prevention. The aims of this thesis are: to study the particular conditions in which the potential promotes or prevents the initiation of corrosion (e.g. the presence of a macrocell or of a cathodic prevention system); to develop a test method aimed at determining the critical combination of chloride content and potential that causes the initiation of corrosion of reinforcing steel in concrete; to create a diagram that shows the active or passive behaviour of reinforcing steel in concrete, as a function of the parameters that affect it.

Conditions in which the potential of reinforcing steel may have a significant influence on the initiation of corrosion have been studied through numerical simulations. In order to study the different macrocells that may develop in reinforced concrete structures, a FEM model has been considered: it shows a structure with a bottom part submerged in seawater and a top part emerging from seawater (thus exposed to the atmosphere); furthermore, the structure is hollow and has an

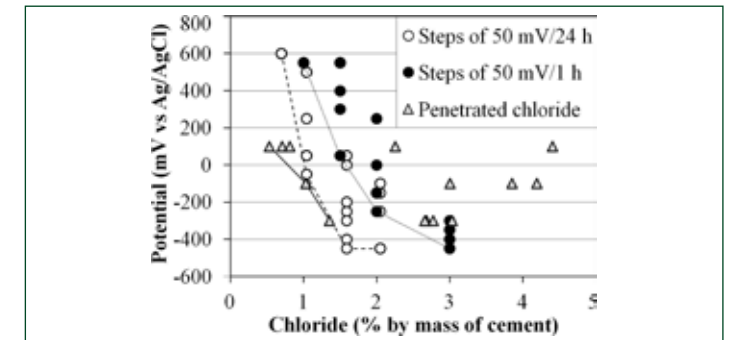
aerated internal part. The model showed that the macrocell among the different portions of the structure causes an increase in the potential of the reinforcement in the portions exposed to the submerged, tidal and spray zones. As a consequence, the macrocell promotes the initiation of corrosion in the parts of the structure where the lack of oxygen usually prevents it. Further models showed that, in such structures, sacrificial anodes placed in seawater are an effective system to contrast the negative effects of macrocells and to lower the potential of the reinforcement, thus delaying corrosion initiation.

In order to study the consequences of potential changes on the initiation of corrosion in different parts of a marine structure, a test procedure should be implemented which is able to evaluate the critical combination of potential and chloride content. Most of the test methods presented in the literature that are aimed at measuring the chloride threshold level, cannot be applied to determine the influence of the steel potential; hence, a new test method has been developed. The method proposed in this thesis is based on three major steps: 1) the addition of chloride

into fresh concrete (mixed-in chloride); 2) the cathodic polarisation of reinforcing steel during the curing period (pre-polarisation), to avoid the initiation of corrosion in this phase; 3) the stepwise increase of steel potential until the occurrence of the initiation of corrosion. Results obtained by the application of the proposed method have been compared to results obtained by a "traditional" method with penetrated chloride. A series of specific tests have been performed in order to verify the feasibility of the proposed technique. Through these tests it was determined that:

- the addition of up to 3% chloride by mass of cement into fresh concrete has a negligible effect on the properties of hardened concrete (i.e. resistance, density, sorptivity, water absorption);
- a galvanostatic pre-polarisation with a cathodic current density of  $100 \text{ mA/m}^2$  is an effective way to prevent the initiation of corrosion and it does not cause a significant migration of chlorides (hence, the pre-polarisation does not cause a variation of the chloride content on the surface of reinforcing steel).

The proposed method has been applied to different sets of specimens, that have been cast with different chloride contents mixed-in the concrete. Fig.1 shows the diagram, obtained by the application of the proposed method, that relates the initiation of corrosion to the critical combination of potential and chloride content. The figure shows that the result of the test depends on the duration of the potential



1. Comparison among the test with penetrated chloride and the tests with mixed-in chloride with steps of 50 mV per hour and per 24 hours

steps: the critical combination determined through steps of 50 mV/24 h is similar to the critical combination determined through the "traditional" (time-consuming) test with penetrated chloride, especially for potentials lower than  $-100 \text{ mV vs Ag/AgCl}$  (i.e. properly for the potentials that could be difficultly studied through traditional methods). However, the test with steps of 24 h have two disadvantages: first, the duration of this test may be longer than one month; second, if (for practical purposes) during the test the specimens are immersed in a saturated calcium hydroxide solution, a long duration of the steps may cause a significant leaching of chloride into the solution and the chloride content in the moment of the initiation of corrosion is not known *a priori*, but it have to be estimated at the end of the test.

The test with steps of 50 mV/h has a lower duration (i.e. less than one week) and during this period the leaching of chloride is negligible at the steel surface. However, as shown in Fig.1, this test shows a higher resistance of steel to the initiation of pitting corrosion and the result of this test needs to be calibrated in order to take this aspect into account.

In conclusion, the potential determined through numerical simulations and the diagram obtained by the application of the test method can be applied to determine the chloride threshold in the different portion of the structures. This piece of information could be used as input data for the model codes for the design of durability of reinforced concrete structures.



# DEVELOPMENT OF ANTIBACTERIAL SURFACE MODIFICATION TREATMENTS FOR TITANIUM TO IMPROVE THE OSTEOINTEGRATION

Cinzia Della Valle - Supervisor: Roberto Chiesa

Titanium and titanium alloys have replaced over the years other commonly employed metals in different implantable devices and represent the first choice in hard tissue applications, especially for dental implants and joint replacements. Due to the presence of a passive titanium oxide layer, titanium and titanium alloys possess optimal biocompatibility when implanted in the human body, but some surface modification techniques are necessary to enhance specific biological properties to enhance their clinical performance. In particular, as regards bone contact applications, surface modifications are mainly needed to promote and speed up osseointegration process favoring osteoblast adhesion, proliferation and differentiation, increasing the anchoring to the bone and possibly improving the functional implant lifetime. Unfortunately one of the main serious complications related to implantable biomaterials is represented by the infection which leads, in many cases, to implant failure and need for revision, increasing also the social and health costs. One possible smart strategy to contrast the bacterial infection is to inhibit or avoid the microbial adhesion and/or to limit the bacteria proliferation.

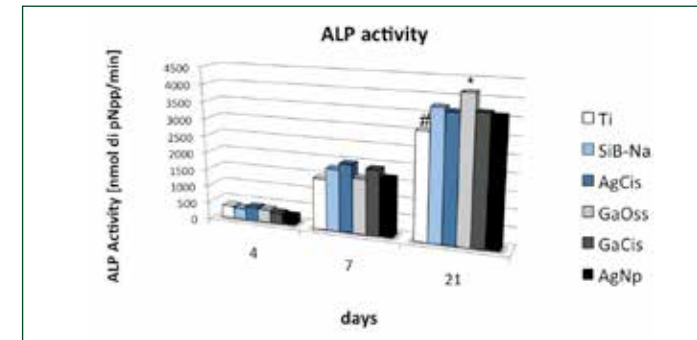
## Aim of the work

The aim of the work was to develop new biomimetic treatments for titanium and titanium alloys characterized by antibacterial properties maintaining high osteointegrative potential; more specifically the researched treatments had to prove cytotoxic effect for prokaryotic cell without any adverse effect on eukaryotic cell and on the mineralization process. The technique chosen to reach this goal was Anodic Spark Deposition (ASD), an electrochemical technique which allows to homogeneously modify titanium oxide surfaces characterized by microporous and nanorough topography with a modified surface chemical composition enriched by the elements present in the treatment electrolytic solution. Silver and gallium compounds were considered as antimicrobial agents, whose are known for their bactericidal properties and for the absence of bacterial resistance, while Ca, P, Si and Na were considered for their bone affinity. By ASD, titanium oxide was properly enriched with different chemical elements to provide antibacterial effect while, at the same time, to improve osseointegration. Among many developed different ASD electrolytic solutions, four of them were particularly studied

(AgCis, GaOss, GaCis and AgNPs): electrical variables were researched to properly modify chemical and physical properties of the obtained oxide films. Untreated titanium and a previously developed osteointegrative ASD coating nowadays used in clinical practice in dental field (called SiB-Na) were used as controls.

## Characterization of the developed coatings

The physical characterization of the developed materials was performed using SEM, TF-XRD, laser profilometry (LP), optical contact angle measurements (OCA). The chemical properties of the developed coatings were analyzed using EDS, XPS and GDOES. Additionally the antibacterial agents release from the coating was quantified with ICP-OES up to 21 days. The mechanical characterization of the developed materials was performed using micro-indentation to define the hardness and the elastic modulus while scratch test and delamination test were considered to analyze the coatings adhesion. The direct cytocompatibility of the coating was investigated with osteoblast Saos2 cell line up to 21 days and primary human gingival fibroblasts (HGFs) up to 7 days. The cell viability was studied respectively with Alamar Blue assay and MTT assay, while



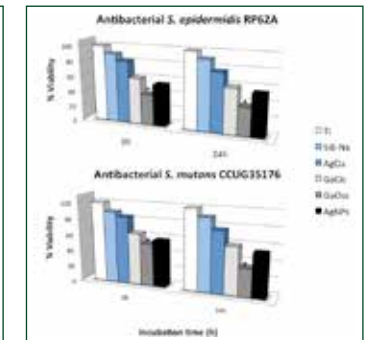
1. ALP production by the Saos2 cells cultured on different ASD samples up to 21 days. The data are reported as mean values  $\pm$  standard deviation. (\* higher ALP production than the other treatments  $p < 0.05$ ) (# lower ALP production than the other treatments  $p < 0.05$ )

cell morphology and spreading was investigated by SEM and from the actin and tubulin staining (for Saos2). Additional Alkaline Phosphatase (ALP) production of Saos2 cell was quantified after 21 days of cells culture on samples. The indirect cytotoxicity was evaluated using Saos2 cell cultured with the supernatants conditioned up to 21 days, on primary human gingival fibroblasts (HGFs) and periodontal ligament fibroblasts (hPDLs). Antimicrobial characterization was performed on both gram positive and gram negative bacteria strains: *S. epidermidis*, *S. mutans* and *E. coli* which are commonly infections. In particular the bacteria viability after 3h and 24h of incubation was studied and the anti-adhesion properties

of the coating was investigated after 3h of incubation in bacterial solution. Moreover, the antibacterial activity of the coatings was also assessed on the samples after 21 days of antibacterial agent release in D-PBS to test the long-lasting antibacterial activity. Finally the *S. mutans*, *S. epidermidis* and *A. baumannii* (an operating theatre weeds agent) biofilm formation was investigated after 24 and 72h of incubation.

## Results

The ASD biomimetic treatments developed allowed to obtain stable, reproducible, and homogeneous coatings characterized by microrough and porous topography with a completely modified surface chemistry capable to stimulate the osteointegration process and to possess (Figure 1), at the



2. Antibacterial activity to untreated and surface modified titanium samples at the indicated time points. Data are expressed as the percentage of bacterial survivability after 3 h and 24 h of incubation time. Data are representative of three replicate experiments with similar results (\*  $p < 0.05$  than all the others)

same time, antibacterial activity on both gram positive and gram negative bacteria strains: these treatments were found effective against bacteria adhesion and bacteria proliferation (Figure 2). Furthermore they interfere with the biofilm formation in all of the bacterial biofilm producer strains investigated. Finally the experimented coatings showed a long-lasting antibacterial activity, probably due to the stable presence of the antibacterial agents in the oxide layer.

# NANOTUBULAR TITANIA ELECTRODES - PREPARATION AND PROPERTIES

Alice Mazzarolo - Supervisor: Antonello Vicenzo

Nanotubular (NT) structures are a class of materials providing a unique opportunity to enhance specific material properties –thanks to the availability of high surface area– and to tune their behavior thanks to the modification of the nanoscale geometry. Recently, a strong worldwide research activity has focused on the synthesis of NT oxides from metallic substrates –notably the so called valve metals. Among all transition metal oxides, titanium oxide, has been one of the most investigated, due to its versatility and properties, making it suitable for a variety of uses in diverse application areas, from photocatalysis to bioengineering. What makes this material so attractive is in particular its semiconductor nature with a wide band gap of  $\sim 3$  eV and band-edge position suitable for solar light absorption/conversion. Following this research direction, the present work was conceived as a wide range investigation on the synthesis, characterization and application of NT anodic titanium oxide,  $\text{TiO}_2$ . The anodic growth of  $\text{TiO}_2$  was studied by combining electrochemical and microstructural analysis to gain insight on key processes involved in the formation of barrier-type and NT oxide on Ti, in fluoride free and containing environment,

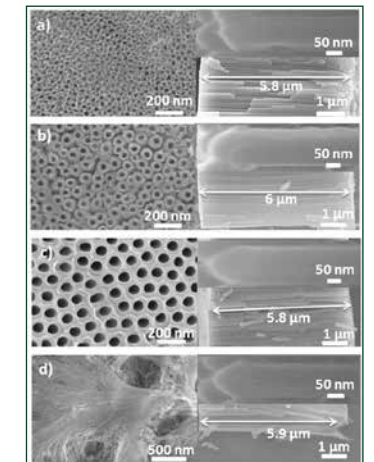
respectively. The synthesis of a  $\text{TiO}_2$  barrier oxide layer was studied using potentiodynamic and potentiostatic polarization techniques accompanied by electrochemical impedance measurements, Transmission Electron Microscopy (TEM) and Scanning Electron Microscopy (SEM) analysis. The investigation on fundamental aspects of  $\text{TiO}_2$  growth, was continued by looking at the effect of fluoride and process time on the electrochemical behavior and the formation of NT oxide in aqueous electrolytes. The NT oxide formation process was studied by electrochemical methods (potentiodynamic polarization and chronoamperometry) and by microstructure and surface characterization techniques (XRD, X-Ray Diffraction, SEM, Glow Discharge Optical Emission Spectroscopy, GDOES). A further aim of the latter investigation was to analyze the potentiodynamic behavior during NT oxide formation, in connection with the usual practice of applying the anodizing potential by ramping up to the desired value and maintaining it for the time required. During potentiodynamic anodizing in the absence of fluoride, an amorphous to crystalline transformation was revealed, that was apparently suppressed

under conditions leading to the formation of NT oxide, i.e. in the presence of fluoride. In this respect, while it is usually believed that the amorphous structure of the oxide favors the incorporation of fluoride, it may also be suggested that the fast and early incorporation of fluorides prevents the amorphous to crystalline transformation of the oxide. Moreover, potential ramping before potentiostatic polarization is suggested to allow for the formation of a relatively stable passivation layer preparing the NT initiation growth stage and preventing early breakdown. Turning to the application side, the preparation of NT oxide array was performed using highly efficient organic electrolyte, in the presence of small amount of water, and particularly studied to shed light on the correlation between morphology and performance of NT array in  $\text{H}_2\text{O}$ -splitting and photocatalysis application. Several studies have been performed on the influence of tube geometry –in terms of NT length, pore diameter and tube type– as well as crystal structure (anatase vs. rutile) on properties and performance of NT arrays. The tube top morphology is another distinct oxide feature dependent on the specific anodic growth

conditions: tubes may show different top morphologies, depending mainly on electrolyte composition and anodization time. Changing the anodization solution, operating parameters have to be set properly in terms of potential ramp, if any, steady state potential and anodization time. The type of electrolyte has a major effect on the oxide morphology, while the anodization duration determined the thickness of the NT array. Substantial work was devoted to the selection of electrolyte composition and operating conditions for the synthesis of different NT oxide with tailored morphology. To this purpose, electrolytes belonging to different “generation” were chosen and tested, namely: an aqueous electrolyte (1 M  $\text{Na}_2\text{SO}_4$  + 0.133 M NaF); a glycerol-water electrolyte (50:50vol% and 60:40vol% + 0.27 M  $\text{NH}_4\text{F}$ ); an ethylene glycol electrolyte (with 0.1 M  $\text{NH}_4\text{F}$  and 1 M  $\text{H}_2\text{O}$ ). Following electrolyte evaluation, the ethylene glycol (EG) solution was adopted and further studied. A careful optimization of the anodization conditions allowed the obtainment of NT oxide of different morphology with the same thickness as shown in the figure. For photocatalysis and photoelectrochemical water splitting, the thickness should not exceed 10  $\mu\text{m}$ ; for this reason, in the present work, it was fixed at 6  $\mu\text{m}$ . The different morphology were named as follow: initiation layer (IN), open tubes (OT), double anodized (DA) and grassy tubes (GT). They were formed respectively: at 60 V for 15 min (IN) and at 55 V controlling the charge and using a photoresist positive mask (OT) in EG + 0.1

M  $\text{NH}_4\text{F}$  + 1 M  $\text{H}_2\text{O}$ ; in EG + 0.5 wt %  $\text{NH}_4\text{F}$  + 3 vol %  $\text{H}_2\text{O}$  at 60 V using a two-step anodization (DA); and in EG + 0.2 M HF + 0.5 M  $\text{H}_2\text{O}$  at 120 V for 70 min (GT). Oxide electrodes were thoroughly characterized, in particular by investigating their behavior in photocatalysis and bias assisted water splitting under illumination. As a result of this work, it was shown that the performance of NT  $\text{TiO}_2$  arrays is dependent not only on the usual geometric parameters –i.e. tube length and diameter– but also, and to a large extent, on the tube top morphology. Particularly the grass presence is found to be highly detrimental for both open circuit degradation experiments and photoelectrochemical solar light water splitting. As a further research direction, different modification strategies were probed in the attempt to enhance the performance of NT  $\text{TiO}_2$  arrays in water splitting application, performing an extensive experimental work in different directions, and also conceiving and demonstrating new processing routes. In particular, the possibility to form a N-doped oxide by direct anodizing of titanium nitride based thin films was explored and demonstrated; metal decoration of the oxide was investigated in view of an enhancement of the photocatalytic behavior; the fabrication of titanium oxide transparent electrode was achieved and their performance in water photosplitting was characterized. The investigation and development of these processes provided interesting and promising results that,

however, require further and more focused work.



1. SEM micrographs of the surface (left) and cross section (right) of different NT oxide types: (a) initiation layer; (b) open tubes; (c) double anodization; (d) grass

## ORGANIC-INORGANIC HYBRID COATINGS THROUGH SOL-GEL PROCESSES

Francesca Piccinini - Supervisor: Stefano Turri

The general aim of the research is the synthesis and characterization of high performance (scratch and chemical resistance, durability, cleanability...) organic/inorganic hybrid coatings prepared through sol-gel process by combining a silanized organic binder with an alkoxisilane and/or a metal alkoxide.

Organic/inorganic hybrids are characterized by a high homogeneity of phase at the nanometric level and show interesting characteristics that are not found in the organic polymer or inorganic material independently since they result from the combination of the properties of the two moieties. The high homogeneity of phase at the nanometric level is the reason of the high transparency of these materials. The most intriguing advantage of hybrid materials is their wide field of application as multifunctional materials, due to the many possible combinations of organic and inorganic components. The desired properties of such materials can be tuned by modulating the composition at the molecular level.

It is known that  $\text{TiO}_2$ , especially in its anatase form shows photoinduced properties (photoinduced superhydrophilicity, PCA and

photocatalysis, PSH) upon UV exposure. The two properties have a common ground but they are substantially different phenomena. The combination of the two properties leads to the self-cleaning effect: PCA and PSH work in a synergetic way to promote and maintain this functionality.

The first part of the research was focused on the development and characterization of a class of polyester- $\text{SiO}_2$  hybrid coatings. The properties were studied as a function of the increasing inorganic (silica) content. Good optical, mechanical and morphological properties were found out.

The main objective of the second year was the development of a new class of sol-gel  $\text{SiO}_2$ - $\text{TiO}_2$  hybrid coatings, exhibiting photoinduced properties (PSH and PCA). To this purpose, the easily UV-degradable polyester binder was substituted by a fluorocarbon polymer belonging to the class of chlorotrifluoroethylvinylether copolymers, selected for the availability of OH functionalities, the relatively high surface tension (due to the presence of polar bonds) and the excellent weatherability and outdoor durability. The  $\text{SiO}_2$  inorganic network was modified with the addition of amorphous  $\text{TiO}_2$ .

The presence of an organic binder limited the synthesis of crystalline  $\text{TiO}_2$  due to the fact that the too high processing temperatures required for such purpose could not be withstood by the polymer. The optical (homogeneity and transparency), mechanical (scratch hardness, chemical resistance), thermal (DSC) and morphological properties (AFM topography and phase and XRD analysis) were studied. Wettability was evaluated by means of contact angle measurements. The coatings photoinduced properties (PSH and PCA) were studied as a function of the  $\text{TiO}_2$  amount.

The third-year activity was oriented towards two targets. The first one was to further characterize the fluoropolymer based  $\text{SiO}_2/\text{TiO}_2$  hybrid coatings (prepared during the second year) by calculating their scratch hardness and Young's modulus (by means of AFM nanoscratch and nanoindentation) and carrying out XPS analysis in order to provide an insight of the surface elemental composition. Furthermore the photoinduced properties of pure crystalline titania were investigated by preparing nanocrystalline  $\text{TiO}_2$  through a low temperature process (non-hydrolytic sol-gel) and compared with the ones observed in the hybrid materials

containing only amorphous phase. The second aim, performed during the six-month internship at the Fraunhofer Institute (Würzburg), was to develop different sol-gel/UV-curable and waterborne organic/inorganic hybrid coatings with potential antifogging properties, starting from a silanized polyol combined with different dual cure (UV-curable and sol-gel functionalities) oligomers. The mechanical properties (hardness and abrasion resistance) of the hybrid materials were improved by the introduction of TEOS into the formulation.



# SPECTROSCOPIC INVESTIGATION OF STRUCTURE-PROPERTY RELATIONSHIPS IN ORGANIC MOLECULAR AND POLYMERIC CRYSTALS FROM FIRST-PRINCIPLE METHODS

**Claudio Quarti** - Supervisor: **Mirella Del Zoppo**

Organic materials present a unique combination of features that make them suitable for a large variety of applications. However, the development and the optimization of these materials requires an in-deep knowledge of the structure-property relationships. In the last two decades, quantum chemical methods for electronic structure calculations have proven to be useful tools in the study of structure-property relationships but their application to extended, complex systems such as organic molecular crystals and polymeric materials, whose properties are dictated by both intra- and inter-molecular interactions, has been quite limited. In this thesis we apply state-of-the-art quantum chemical methods to study the structure, the electronic properties and the spectroscopic response of some molecular and polymeric crystals. In the first part of the thesis, we have investigated the exciton properties of molecular crystals. The Frenkel exciton Hamiltonian has been used to model excitons in crystals and the main parameters of this Hamiltonian, the exciton couplings, have been calculated by using quantum chemical simulations. We have tested our methodology to a test case, the crystal of para-nitro-aniline, and then we have studied the exciton properties

of some molecular crystals of technological interest, acenes and their derivatives. In this case in particular, we were interested in finding useful guidelines for the design of materials which show efficient Triplet-Triplet Annihilation (TTA). Through this study we highlighted the effect of the chemical substitution on the exciton mobility in these crystals and we have addressed some of the molecular requirements necessary to obtain materials with efficient TTA. In the second part of the thesis, we have studied the structure and the InfraRed (IR) spectroscopic response of polymeric crystals. The structure and the IR spectrum of the  $\alpha$  form of nylon 6,6 and of the  $\alpha$  and  $\gamma$  forms of nylon 6 have been calculated. For the first time these calculations have been carried out on 3-D periodic models, instead of on infinite chains or on oligomeric models. The good agreement between theoretical and experimental spectra demonstrates that quantum chemical methods are nowadays suitable to study complex systems such as polymeric crystals. On the basis of the theoretical calculations, we have revised the interpretation of the IR spectra of these polymers, solving the ambiguities and the controversial assignments found in the literature.

A thorough study has been carried out to revise the interpretation of the IR spectrum of crystalline poly(tetrafluoroethylene), PTFE, in particular on the assignment of the doublet at 626-638  $\text{cm}^{-1}$ . On the basis of quantum chemical calculations we were able to address the contributions to the IR spectrum from the ordered phase, from conformational defects and from the amorphous phase. In addition, we have assigned the low frequency component of the 626-638  $\text{cm}^{-1}$  doublet to the formation of helical-reversal defects. Finally, we present the results of some DFT and TD-DFT calculations aimed to explain the optical properties of an organic dye, the 4-hexylamino-7-nitro-2,1,3-benzoxadiazoles in solution. UV-Vis and photoluminescence spectroscopies have showed that this chromophore presents a non monotonic shift of both the absorption and emission energy with the solvent's polarity.

## SURFACE INTERACTIONS IN MICRO AND NANO DEVICES

Anahit Raygani - Supervisor: Luca Magagnin

The reliability of Micro and Nano Electromechanical Systems (MEMS and NEMS), such as sensors, is often limited by surface interactions and modification between parts which should maintain the capability of relative motion. This research project is aimed to understand and predict the interaction between surfaces of silicon in MEMS in different applications particularly biosensors.

**A biosensor is an analytical device that incorporates a biological recognition element associated with a physical-chemical signal transducer. The way in which the biological component is immobilized should never be underestimated, as it can generate phenomena of inactivation of the processes.**

The first year of research activities focused on developing innovative processes for the production of hybrid materials to be easily integrated into electrochemical biosensors in order to improve the selectivity, detection and the response time of sensors themselves. Metal nanostructures are especially promising in biosensing applications.

There are several microelectronic processes which are based on gold due to its unique physical and chemical properties. Adhesion of gold

films which are deposited by galvanic displacement is investigated by micro hardness measurement. In this study, load-displacement tests are performed on gold nanostructures which are deposited on mono and polycrystalline silicon 100 in sulfite solutions. Composite hardness model for soft film on hard substrate is used to analyze the results. Gold films growth and composite Vickers microhardness are influenced by the adhesion of the gold film to silicon, as a function of different electrolytes and silicon substrates. The higher composite hardness and more extended deformation zone at the film/substrate lead to stronger adhesion. For the same film thickness, the composite hardness of films which are deposited onto mono silicon is higher than films on poly silicon. The effect of cysteine as an additive on adhesion and microhardness measurements is emphasized.

Study the adhesion phenomena in poly-silicon Micro-Electro-Mechanical Systems (MEMS) by means of experimental characterization and numerical simulation was another purpose of this research. In the experimental part, the adhesion energy is measured on-chip by means of laboratory designed and fabricated

devices; moreover, the surface roughness was characterized through the atomic force microscope. For the numerical part, a specific method has been developed in order to simulate the process of adhesion.

Finally, we investigated the possibility to deposit metal nanoparticles on a silicon surface starting from a fluoride-free solution. Six different solutions have been used; five based on a copper salt and the last based on a silver salt. The copper solutions differ in the copper salt used or in the pH of the solution. In all of the cases a concentration of 2mM salt has been used. The main goal of the deposition was to reduce the stiction phenomena of MEMS devices by increasing the roughness and modifying the surface energy. The surfaces have been analyzed by an Atomic Force Microscope, an X-Ray Diffractometer, Lateral Force measurements, and the water contact angle. Surface activation was performed by dipping the samples in diluted hydrofluoric acid (10%) for 2 minutes, right after the samples were immersed in the deposition bath for different times. Further treatments, such as thermal oxidation and application of a self-assembled Monolayer, have been applied to improve the property of the

surface. The relative humidity has been monitored during the test to obtain more comparable results and to check the dependency of the adhesion on its level. Moreover, the above results will be compared with those obtained from a cantilever beam arrays test after surface modification by galvanic displacement.

During the third year of Ph.D. activity, in conjunction with the above research, **Indium Phosphide deposition as a Low Cost III-V Solar Material** project was investigated. Indium Phosphide (InP), which is a semiconductor material with a band gap of 1.35 eV, has gained important applications in MEMS substrate and in particular as thin-film photovoltaic solar cells. This work reports electrochemical process for obtaining InP films. The experimental part for investigating InP was studied with three different methods. First method was direct deposition of Indium phosphide; the second one was ECD of Indium, phosphorization and then annealing and the third method was co-deposition of Indium and red phosphorous particles. The samples were characterized before and after annealing with XRD, EDX, Photoluminescence and Time-Resolved Photoluminescence (TRPL), which are important

techniques for measuring the purity and crystalline quality of InP semiconductor, together with its PV properties.

# PULSED LASER DEPOSITION OF SILICON NANOSTRUCTURES FOR PHOTOVOLTAIC APPLICATIONS

**Tushar Somanath Salve** - Supervisor: **Andrea Li Bassi**

The research activity was dedicated to synthesis of new nanostructured inorganic materials in view of their application in third generation photovoltaics (PV), in particular semiconductor (Si) quantum dots (QD) for QD – based PV (e.g. heterojunctions or QD sensitized solar cell).

The aim was to synthesize Si quantum dots (QDs) with controlled structural and electronic/optical properties using Pulsed Laser Deposition (PLD) technique in a background (inert and reactive) atmosphere as in literature, the systematic study of Si nanostructures in different matrices, role of low and high annealing temperatures and their relative photoluminescence (PL) mechanism is still under debate. Synthesis of Si nanoparticles at Room Temperature withstanding its optical properties have always been a problem as they get oxidized easily when exposed to air therefore it is one of the goals to prevent the as-deposited Si nanocrystals from ex-situ oxidation. The PLD was chosen for present study due to its versatility in control of deposited structures. I've explored the role of various PLD parameters i.e. different fluence and wavelength of the laser, different target-to-substrate distance and partial pressures of inert and reactive gases and

effect of different annealing temperatures on growth of Si nanostructures. With optimized parameters of PLD, the research activities led to following conclusions. The nanoscale morphology was varied from compact to open porous by varying the pressure from 1-60 Pa as observed by Scanning Electron Microscopy (SEM). The results obtained from photoluminescence characterization show a very interesting blueshift trend in PL energy bands (1.6 - 2.1 eV) while increasing the partial pressures (from 1 to 60 Pa) of both inert and reactive gases. The high energy component shifts with pressure and we attribute it to quantum confinement in Si nanoparticles. This suggests potential for bandgap engineering for PV application. Annealing in vacuum at 400 °C, results in increment of PL intensity, which further increases at 1000 °C, accompanied by a redshift in PL energy bands. This suggests defect reduction after annealing. Raman scattering measurements show amorphous phase in compact films while no crystalline Si signal was detected in porous films and in 1000 °C annealed films. TEM analysis shows the presence of nanocrystals only after annealing the samples at high temperature i.e. 1000 °C. We believe that

the Raman signal was missing due to oxidation of the films as porous Si films are oxidation-prone which also makes the PL discussion very complicated. To prevent our films from oxidation was the next challenge. To be sure that the synthesized silicon nanoparticles do not undergo ex-situ oxidation or to be prevented from oxidation, a thin, compact capping Si layer was deposited on the top of the porous (60-150 Pa of Ar and 100-500 Pa of He) films. Raman spectra indicate the contribution of both amorphous and crystalline Si in this case. The Raman shift ranging from 516.3 to 518.5  $\text{cm}^{-1}$  for the crystalline Si peak (whose position in bulk Si is 521  $\text{cm}^{-1}$ ) corresponds to particle size 4 to 6 nm. The presence of Si nanocrystals was confirmed by High Resolution TEM micrographs showing a mixed aSi-SiNPs i.e. Si nanoparticles embedded in amorphous matrix and the nanocrystal size was good in agreement with the size calculated from Raman shift. The Si/O atomic content found by EDS via Scanning TEM was 3/5, suggests that the films were not completely prevented from oxidation. The contribution of different components in PL spectra at 1.64, 1.78 and 1.85 eV was observed. A set of four-layered films with different pressures of

Ar and He was also deposited and presence of size distributed Si nanocrystals was realized by Raman and PL results. Therefore the compact capping layer was able to reduce oxidation thus making the presence of nanoparticles at room temperature clearly traceable. These observations also confirm the possibility of tailoring the structural and optical properties of nanocrystalline thin films for multi-layer, solar cell structure. The room temperature deposition of Si QDs on temperature sensitive substrates like plastic will add an advantage in case of hybrid solar cells. In future perspective, the superlattice of Si nanocrystals embedded in oxide, carbide or nitride matrix with different size of Si nanocrystals in each layer would be suggested using optimized PLD parameters.