





Chair:  
**Prof. Chiara Bertarelli**

## DOCTORAL PROGRAM IN MATERIALS ENGINEERING

The Ph.D. Programme in Materials Engineering provides high educational opportunities to young talents and executives who intend to become proactive professionals and researchers skilled in the design, production and application of both traditional and innovative materials, their optimization for specific applications, the prediction and assessment of their performance, and in developing new concepts and technologies in any materials-related fields.

Highlights of the Ph.D. Programme in Materials Engineering are:

- a rigorous scientific approach to address outstanding research
- an effective interdisciplinary approach
- connection with international leading scientific and technical communities
- a strong integration with the Doctorate School of Politecnico di Milano to increase knowledge with transversal courses, to gain soft skill and to join stimulating activities.

### PHD CONTENTS and PROGRAM STRUCTURE

Materials Engineering involves the investigation of correlation among materials structure, processing and functional and structural properties, and the knowledge management from materials design to final applications.

The Programme includes advanced research and training on:

- Research and development in traditional materials (*polymers metals, ceramics, concretes, composites*) and related technologies.
- Specific application areas: *materials for energy, materials for environment, materials for electronics, optoelectronics and photonics, materials for cultural heritage, materials for product design, materials for packaging, biomaterials.*
- *Smart, responsive and self-healing materials, nanostructured materials.*
- *Materials corrosion and durability, life cycle assessment, coating and surface functionalization*

The achievement of the Ph.D. title in Materials Engineering requires a full-time study and research activity of at least three years which is completed by the development and defense of the Ph.D. thesis.

The Ph.D. students give an original contribution to increase knowledge in a material-related research field, and they acquire a problem-solving capability in complex contexts, including the ability of performing deep problem analysis, identifying original solutions, and evaluating their applicability in practical contexts. Students can use modern facilities for materials synthesis, processing and characterization available at the Politecnico di Milano or in other research laboratories.

The Ph.D. Programmes and the Ph.D. School activate courses, seminars, project workshops and laboratories. Teaching activities cover both basic research topics (problems, theories, methods) and specialistic topics related to the subjects developed in the theses. Ph.D. students are also encouraged to attend national and international Conferences Workshops and Schools and to plan a research period abroad.

### PROFESSIONAL OPPORTUNITIES AND THE JOB MARKET

The Ph.D. Programme in Materials Engineering aims at training Ph.D. laureates having a common background and specialized qualifications in advanced research areas. The knowledge and skills of a Ph.D. in Materials Engineering enable graduates to pursue their career in the Manufacturing industry, given its quest for innovation in the production, processing, application and conservation of traditional materials, and for the development of innovative materials allowing radically new, currently unforeseeable applications.

Moreover, the background deriving from full-time activity both in research and in education also qualifies the Ph.D. graduates for an academic career. Several graduates from the Materials Engineering Programme have been able to secure post-doctoral research positions at high-ranking universities and research Institutes.

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# APPLICATION OF NUMERICAL SIMULATION TO THE STUDY OF MACROCELL CORROSION AND CATHODIC PROTECTION MECHANISMS

Mehdi Attarchi - Supervisors: Andrea Brenna, Marco Ormellese

Tutor: MariaPia Pedefferri

In this work, the finite element method (FEM) was used to overcome the complexity and non-linearity of the study of macrocell corrosion and cathodic protection (CP) systems. In the present study, FEM simulation was used for three main sections: macrocell corrosion, optimizing some practical cathodic protection design, and DC interference in the presence of CP.

FEM can provide precious information on the corrosion rate in the macro-cell corrosion system, such as galvanic coupling and pitting corrosion. Potential and current distribution equations obtained by FEM were then extended to macro-cell corrosion systems. Typical examples are pitting corrosion of stainless steels and galvanic coupling, which cover the major causes of corrosion degradation of industrial equipment. Pitting corrosion of stainless steel in the presence of chlorides has been modelled by FEM using the secondary current distribution for a wide range of variables, including geometry, resistivity, oxygen content, and water velocity. FEM model gives an opportunity to develop new criteria based on the passive current density, which is not possible to measure directly. Based on the new criteria, a new equation for corrosion rate calculation was proposed and approved by laboratory tests. In practical FEM modelling of CP systems, three cases were studied. In

the first case, linear anode alongside the pipe has been modelled. Primary current distribution analysis (which does not consider the overvoltages at the electrodes) was initially adopted by solving general equations that are valid in a stationary electric field with five variables: anode-pipe distance, pipe diameter, anode current output, electrolyte resistivity, and maximum allowable potential range of the pipe. The outcome was a new equation useful for finding the minimum linear anode pipe distance in a different electrolyte (soil) and pipe diameter. After primary current distribution analysis, secondary current distribution with five different scenarios and complex boundary conditions were studied by FEM. Overvoltages at the metal-to-electrolyte surface have been implemented in the FEM software, by using the Butler-Volmer equation, which correlates local electrochemical potential and current density at the metal surface. Pipe coating degradation was also considered, supposing: (a) a uniform coating degradation (i.e. the whole pipe surface absorbs the protection current); (b) a high-quality coating with two defects that absorb all the protection current. The performed simulations showed that besides solution resistivity, oxygen diffusion rate has a crucial role in the polarization of the cathode. The results of the simulation were proved

by laboratory tests.

The second practical CP system was a buried vessel protected by a linear anode. Linear anodes are placed in a loop shape around the vessel. The main challenge is the limited available space for anode installation, besides all mentioned complexity in the linear anode-pipe system. As for the first system, electrochemical and physical variables were considered in the model. The number of anode loops and anode-to-vessel distance were considered, too. The mentioned CP system for buried vessel is optimized by FEM.

In the third practical studied CP system, a grounded pipe protected by a CP system has been modelled with a wide range of variables and possible scenarios. The studied model included the different patterns and locations for coating defects on the pipe, anode and earthing arrangement, polarization behaviour, and

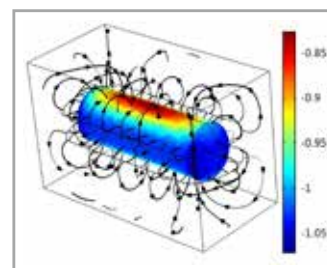


Fig.1 - Secondary current distribution of buried vessel

environmental factors. As a result, a modification factor for the estimation of the protection current is proposed. Laboratory tests have been used for confirming the simulation results. In the last part of the thesis, DC interference effect on the corrosion of the cathodically protected structure has been studied. Two test modes, i.e. constant potential and constant current mode, and different intensity and frequency of interference were applied. Corrosion rate and current/potential data were extracted and elaborated. The results, referred to more than seven months of testing, confirm the advantage of CP to reduce the corrosion rate of carbon steel under anodic DC interference. Moreover, it has been shown the short time potential measurement is misleading, and current density analysis is crucial for the evaluation of corrosion protection state in the presence of DC interference. The advantage of CP was linked to the increase of pH at the cathode surface, so a new test arrangement was built to do the measurement of pH at the vicinity of the sample (40-100  $\mu\text{m}$ ). This integrated sample-pH meter was used in both pH analysis of protection and DC interference. pH measurements during different DC interference have been done. The results of pH measurement were in alignment with the previous long-term interference test and expected corrosion rate.

A FEM model including electrochemical reactions, oxygen diffusion, moving of ions under concentration and potential gradients, and water stability reaction was built to analyse cathodic protection of carbon steel in simulated soil solution. A model was analysed as a time transient model. Two main electrochemical parts of this model are diffusion polarization of oxygen reduction reaction and steel corrosion. In this work, these two essential parts were considered dynamic and linked to some other parameters. Oxygen reduction reaction polarization was linked to the oxygen diffusion and its availability at the cathode surface. Iron anodic polarization was linked to the pH at the surface of the electrode, e.g., in high pH, the anodic slope was increased to the order of Volts/decade. Cathodic polarization of the integrated sample-pH meter, including both electrochemical parameters and pH measurement, was used as the experimental boundary condition of the FEM model. After analysing the FEM model and its pros and cons, it was used to predict the long-term response of carbon steel under cathodic protection.

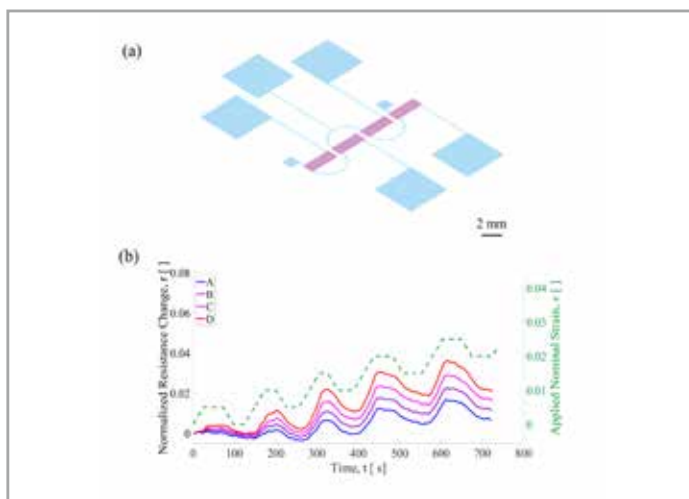
## INKJET-PRINTING TECHNIQUE FOR DEFORMABLE STRAIN SENSORS

Martina Costa Angeli - Supervisor: Pasquale Vena

Printing technologies are modifying the burgeoning field of deformable sensors and electronics by providing cost-effective routes for processing new electronic materials. Inkjet-printing has been established in extensive research work as a low-cost, prototyping technique able to pattern conductive material on a polymeric substrate without the need for a mask. Despite these established advantages, inkjet-printing is still a fairly young technology, therefore the reliability of both the fabrication process and the fabricated material systems is still a key point to achieve competitive devices. This project was devoted to evaluating inkjet-printing technology as a fabrication technique for the realization of deformable strain sensors. Strain sensors are devices capable of measuring strain by transducing mechanical deformations into measurable, usually electrical, signals. Ranging from civil to biomedical field, strain gauges allow deformation measurement on the surface, which is of great interest for numerous applications. With the aim of developing a fully inkjet-printed deformable strain sensor the first step was to understand the reliability of the inkjet-printed process itself. Thus, process parameters and their effect on the performances of printed devices were evaluated by realizing and electro-mechanical characterizing inkjet-printed

deformable silver nanoparticles electrical interconnections of different geometries, linear and serpentine, on polyethylen-terephthalate (PET) and polydimethylsiloxane (PDMS) substrates. Inkjet-printing on PET surface is a well-established practice; however, it is fundamental a deep knowledge of the printing procedure to realize high-quality devices. Results showed the relevance of an accurate design of the geometrical layout that should be considered during the design phase. Indeed, even if inkjet-printing allows for printing

versatile patterns directly from CAD drawings, the geometrical layout strongly affects the printing quality. This aspect particularly affects narrow and complex geometries, such as the serpentine interconnects. Therefore, the successfully reliable fabrication of serpentine interconnections is possible only after an accurate optimization of the printing parameters; in particular, drop spacing turned out to be one of the most important parameters to be tuned. Moreover, the electromechanical results confirmed that the geometrical



**Fig.1 - (a) Scheme of the uniaxial strain sensors array made of four inkjet-printed carbon nanotubes sensitive elements. (b) Normalized resistance vs time of each sensor (A-D) in customized loading-unloading experiments in the non-homogeneous configuration for sensors array. The four sensors were subjected to a tensile strain whose amplitude increases from sensor A (less stretched) to sensors D (most stretched, sensors B and C were subjected to intermediate values). Sensor D showed the highest resistance change and the electro-mechanical response decreases from sensors D to A, accordingly to the applied local strain.**

layout strongly affects the reliability of printed interconnects: serpentine interconnections exhibited higher electro-mechanical reliability than linear ones.

Subsequently, the ability of the inkjet-printing technique of the realization of a reliable fully-inkjet-printed uniaxial resistive strain mapping array on PET substrate was assessed. A carbon nanotubes matrix was selected as strain-sensing material and its sensing ability initially was characterized and optimized through in-situ electro-mechanical tests on single strain sensors. After the single strain sensor optimization, a fully inkjet-printed strain sensors array was designed and realized. The array was characterized through a confined electromechanical tensile test in which non-homogeneous strain states were applied. Results showed the mapping capability of a fully-inkjet-printed deformable sensors array that was able to measure different local strains on the substrate surface, paving the way for using inkjet-printing technique for the realization of sensors with a larger number of interesting applications.

A different sensing mechanism was exploited for the realization of inkjet-printed deformable wireless strain sensors. Thus, an inductive inkjet-printed strain-sensitive coil characterized by a serpentine-shaped geometry was designed. The serpentine-shaped geometry has a

dual function: guaranteeing adequate stretchability and simultaneously strain-sensitivity. Indeed, serpentine-shape is fundamental to ensure a wider strain-working range and good wireless performances during its functioning. Based on these considerations it is clear that in the design of a deformable serpentine shape strain-sensor inductor is fundamental to understand the correlation between inductance and coil geometry. This analysis allows evaluating the parameters that can influence the design of the inductor and its sensing performance. Hence, a numerical analysis, through the use of COMSOL Multiphysics software, was performed in order to evaluate the effect of the geometrical parameters on the nominal inductance of the coil and thus the inductor strain-sensitivity. Results showed that coil arrangement is a crucial aspect for the realization of an inductive strain sensor. Particularly, for the proposed serpentine-shape inductor it was found that to increase strain sensitivity the serpentine inductor should have a more compact shape (lower meander radius), although this entails a lower inductance value.

# MOLECULAR DYNAMICS SIMULATION OF THE MECHANICAL PROPERTIES OF BUTADIENE RUBBER AND ITS SILICA NANOCOMPOSITES

Alessio David - Supervisor: Guido Raos

Tutor: Valdo Stefano Meille

Polymer composites are a class of materials in which a micrometre-sized filler is dispersed into a polymeric matrix. They have outstanding mechanical properties, because they incorporate the flexibility of the matrix and the reinforcement properties of the filler. Polymer nanocomposites (PNCs), which have been consistently used from the 90s, incorporate nanometre-sized filler. For classical composite, the outcome properties coming from the mixing of the constituents is predictable by using micromechanical models. For PNCs, those equations are broken by the huge extension of filler surface that induces structural modifications to the polymer at the surface of the particles. Given the surface extension, the majority of the matrix is considered interfacial polymer, which explains the exotic properties at even low filler load. Typical nano-fillers are cheap and easy to produce. Carbon black, silica and clay are example of ecological filler, but also more complex constituents, such as fullerenes and nanotubes are used. Improved properties span from electrical conductivity, to thermal and fire isolation, to mechanical reinforcement.

## The reinforcement mechanism

The mechanism behind the outstanding mechanical reinforcement of PNCs is currently not completely understood. Since a consistent mathematical formalism does not

yet exist, predictions are case-related and limited. The mechanical models used to describe these materials contain parameters that are not directly connected with their molecular structure, failing to build a link between the desired properties and the molecular structure. The reason why the models based on continuum equations cannot grasp the mechanical behaviour stands in the molecular origin of the reinforcement, that must be investigated at the nanometre level. The lack of a model describing the reinforcement reflects onto the controversy in describing the reinforcement drop under some moderate deformation conditions, which represents a critical industrial issue. When PNCs are cyclically deformed above a critical threshold, their properties drop to the ones observed in classical composites, therefore losing the exotic reinforcement. The origin of this phenomenon, called Payne effect, is still to be clarified and only some empirical attempts have been made to control and minimise it.

## Silica/butadiene rubber

The specific material we investigate is silica/butadiene rubber, vastly utilised in the automotive tire industry. The particles used have size of tens of nanometres, are mesoporous and tend to aggregate forming a percolating structure that gives strength to the material. Rubber nanocomposites have been known and exploited for

a long time in automotive tires and other rubber goods, well before the 'nano' keyword came into fashion. Right from their early production, tires blend has been mixed with carbon black, a high-surface paracrystalline carbon coming from incomplete combustion of petroleum derivatives, that gives reinforcement to the tire. Introduction of silica nanoparticles (NPs) has become popular in the 90s, when it was discovered that silica NPs that are grafted and chemically linked to the rubber network, significantly improve the performance and lower the consumes. Indeed, the introduction of silica lower the rolling resistance, while improving the grip, even in wet conditions. Rolling resistance is due to the elliptical deformation of the tire during motion and it experimentally manifests in the heat loss (hysteresis) experienced at low-frequency deformation. The

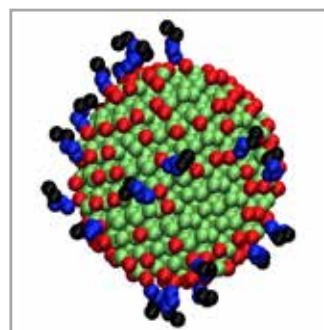


Fig. 1 - Snapshot of a coarse-grained silica nanoparticle with Si-69 grafting units.

origin of grip is part of an on-going discussion in the field of tribology. Its contributions come from adhesion forces and high-frequency deformation, that is the capacity of the material to deform coherently with the asperities of the road. Tires with silica particles have shown large hysteresis at high-frequency deformation and they also guarantee grip in wet conditions, thanks to improved adhesion.

## Molecular Dynamics simulation

Simulation represents a cheap and fast way to explore the space of structural parameters affecting mechanical properties. For this reason, we built a semi-automatic method to explore the property landscape of this specific material. Molecular Dynamics is not meant to substitute experiments, but can shortlist the systems to be

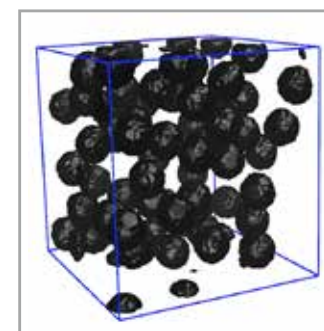


Fig. 2 - Snapshot of the final system composed of 11% vol. silica nanoparticles represented as black spheres (hidden matrix surrounding the particles).

experimentally characterised and guide the experimental research to interesting and promising paths. The thesis is structured as a route to the simulation of silica/butadiene rubber. In the first chapter, we designed an algorithm for the vulcanisation of united atom polybutadiene, a level of coarse graining where hydrogen atoms are suppressed. We tested basic theories of rubber elasticity and characterised the topology and mechanical properties of the networks obtained. In literature there exist many works testing the basic concepts of polymer physics on bead-and-spring models. The effect of introducing bending and torsional constraints is less investigated and imposes a higher level of complexity to the design of a vulcanisation algorithm.

The second chapter is dedicated to the parametrisation of a force field for coarse-grained silica. We built the slimmest model possible, maintaining the level of detail required to observe the characteristic phenomena. The force field was built by matching the density fluctuations of the polymer sandwiched between reference atomistic and coarse-grained silica walls. The sandwich conformation was also used to address the origin of the Payne effect in conditions where silica is grafted or chemically decoupled to the polymer.

The last chapter is dedicated to the ultimate mechanical properties of

silica/butadiene rubber and combines the simulation protocols investigated in the previous chapters. The simulations include the possibility of bond breaking, in order to simulate failure. We applied a material design exploration that is typical of the industrial mindset. By changing one parameter of the system at a time, we optimised the material by maximising some target properties.

# SMART MATERIALS FROM REVERSIBLE POLYMER NETWORKS

Giovanni Fortunato - Supervisor: Stefano Turri

Reversible or dynamic covalent polymer networks (DPNs) have been recently proposed as a sustainable alternative to conventional thermosetting polymers. Their dynamic character, arising from the reversibility of specific chemical bonds, results in stress relaxation and flow in the presence of a suitable external stimulus. Thus, the integration of dynamic covalent chemistries into polymer networks provides them with properties like self-repair, better recyclability, reprocessability and enhanced degradation. In particular, self-healing ability allows to extend the lifespan of a plastic object, while reprocessability permits a closed loop recycling, which is of pivotal interest in the view of sustainable management of thermoset composite wastes. Based on these two aspects, the work described in this PhD thesis is focused on the implementation of DPN concept to obtain fully recyclable fibre-reinforced thermosets and self-healing coatings for optical applications. DPNs were designed on the base of two cycloaddition reactions: the Diels-Alder (DA) addition between furan and maleimide, thermally reversible and the photo-induced [2+2] coumarin dimerization, photo-reversible. In the first part of the thesis a new approach to fully recyclable thermoset composites was introduced, based on the thermal reversibility of an

epoxy-based polymer network, crosslinked through DA chemistry. Carbon fibre composites, fabricated by compression moulding, were efficiently recycled through a simple solvolysis procedure in common solvents, under mild conditions. The purity of the reclaimed fibres was very high and allowed direct reprocessing into second generation composites. Furthermore, the dissolved matrix residues were directly reprocessed into smart, thermally healable, coatings owing to their reversible character. The second part of the work dealt with the development of coatings which combine high transparency with self-healing ability. First, reversible polymers networks were obtained by reacting a series of linear copolymers of furfuryl methacrylate with aliphatic bismaleimides through DA reaction between furan and maleimide moieties. As expected, the obtained coatings exhibited high thermal reversibility and thermal remendability of recovery of manually damaged surfaces. The outstanding transparency and absence of colour, due to the intrinsic properties of the selected precursors, combined with a pronounced hydrophobic behaviour and an excellent adhesive strength on glass substrates, indicated their suitability for optical applications. Thus, a judiciously selected formulation was proposed as host matrix for luminescent solar

concentrator (LSC). A careful tuning of the concentration of a commercial perylene-based luminophore allowed to obtain optical efficiency and maximum electrical power conversion efficiency comparable to commercial plastic matrices. These properties were fully recovered after thermal treatment for the healing of mechanically-induced surface damages. Aimed at widening and facilitating the application of the presented transparent coatings, a novel aliphatic bismaleimide linker, allowing high solubility in common industrial solvents. Furthermore, the effect of increasing furan/maleimide functionality on healing, mechanical properties, adhesive strength and surface properties was systematically studied. Additionally, healing and weathering were studied on these novel coatings pigmented with titania, providing important information about durability of these systems. Lastly, the DA matrix was embedded with silica



Fig. 1 - Recycling scheme of a composite based on a reversible polymer network. Solvolysis allows for the efficient separation of both reusable fiber and resin component.

nanoparticles, in order to improve the surface hardness. The final part of the thesis was focused on the development of a photo-responsive polyurethane network based on the photo-reversible dimerization of coumarin groups under UV irradiation. Firstly, a novel, photo-active macromer, obtained by a one-step modification of a commercial aliphatic polyisocyanate was crosslinked under UVA radiation. Once studied the kinetics and the efficiency of crosslinking/decrosslinking, scratched coatings were subjected to UVC/ UVA healing cycle which resulting in complete visual repair and recovery of fluorescence. The neat coatings possessed excellent high transparency and stability and thus, similarly to the thermo-responsive polyacrylate studied in

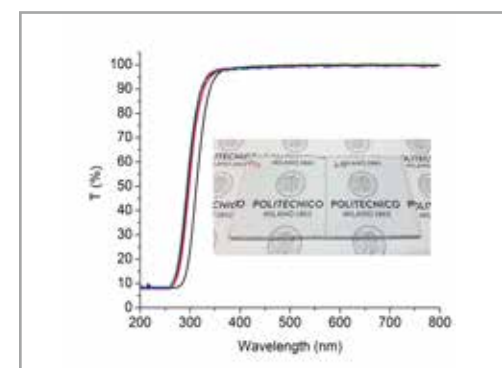


Fig. 2 - Outstanding transparency of coatings based on reversible polymer networks from UV-Vis transmittance spectra. Inset: picture of coated glass slabs.

the previous part, was tested as host matrix for thin film LSCs. Therefore, two standard luminophores were embedded in the matrix and the obtained coatings were characterized from the optical point of view. The presence of the dyes did not affect the efficacy of the healing process and the devices efficiencies, were found to be comparable to host commodity plastic matrices and fully recoverable after scratch damages and photo-healing treatment. Overall, as the innovative approach of DPNs gains importance in the view of a circular economy of crosslinked polymers, more application-oriented studies are needed. The work presented in this thesis aims to respond to this issue by showing how the versatility of few known dynamic reactions allows to impart interesting (smart) properties to

variety of matrices for very different applications.

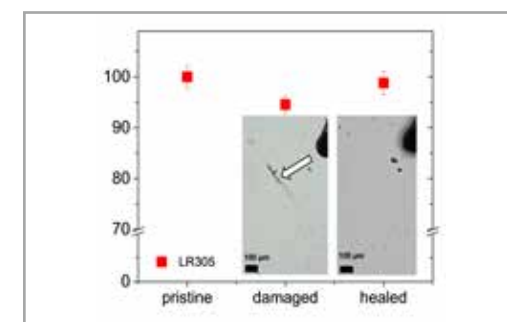


Fig. 3 - Power conversion efficiency (%) of a luminescent solar concentrator based on a reversible polymer network as the host matrix. Healing treatment allows for complete aesthetic and functional recovery. Inset: micrographs of the cut and healed film.

# INNOVATIVE POLYMERIC SYSTEMS FOR VOLUME HOLOGRAPHY

Paola Galli - Supervisor: Andrea Bianco

Tutor: Chiara Bertarelli

Volume phase Holographic Optical Elements (VHOE) are innovative diffractive optical devices that find application in different industrial fields. Volume Phase Holographic Gratings (VPHGs) are of particular interest as dispersing elements for astronomical instrumentation thanks to the very high diffraction efficiency that they can achieve. Light dispersion in VPHGs is due to a periodical change of the refractive index in the volume of the material (Figure 1). The efficiency of such elements depends on their thickness and on the refractive index modulation ( $\Delta n$ ). The optimization of the latter property is crucial to obtain reliable and effective devices. Among the different existing classes of materials for holography, photopolymers probably represent the most promising one, but the  $\Delta n$  achievable should be increased to extend their applicability range and cover the different spectroscopic needs. In this framework, the goal of this work is the design of new photopolymer materials based on innovative monomers, the application of available photopolymer systems in the manufacturing of VPHGs for astronomical instruments and finally the study of new reactions/molecules that can be the base for innovative photosensitive systems for volume holography.

The photopolymer system presented is based on cyclic allylic sulfide (CAS) monomers, which

polymerize through a free-radical ring-opening mechanism (Figure 2) that does not suffer from large polymerization-induced shrinkage contrary to common free-radical polymerizations. This allows for a very precise pattern transfer with a limited material distortion. The addition of multifunctional thiols to the formulation changes the reaction to a thiol-ene polymerization, which turns into a high monomer conversion and allows exploiting almost all the potential dynamic range of the mixture. Moreover, a thermal treatment after the holographic writing promotes a further rearrangement of the formed polymer chains in the grating, leading to an important increase of  $\Delta n$  that reaches values above 0.03. In order to maximize the index contrast and improve the performances of the photopolymer system, new high-index CAS monomers showing high polarizable groups are designed and synthesized.

The use of known photopolymer systems (Bayfol® HX) for the manufacturing of astronomical dispersing elements (Figure 3) is also reported, covering different case studies and showing the versatility of these materials. As for the new materials and reactions for volume holography, materials undergoing the photo-Fries reaction and triazenes were selected, synthesized and characterized.

The first system consists in the photoinduced rearrangement of an aromatic ester into a hydroxy ketone, while the second one leads to the release of volatile nitrogen during light irradiation. Both systems are characterized in terms of reaction in solution and the behavior of triazenes in thin films is studied. The results are interesting and pave the way for further development of such holographic systems.

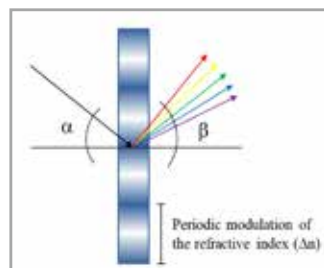


Fig. 1 - Mechanism of light dispersion in VPHGs.

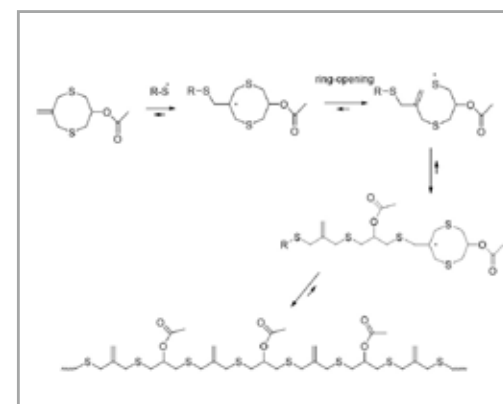


Fig. 2 - Free-radical ring-opening mechanism of cyclic allylic sulfides.

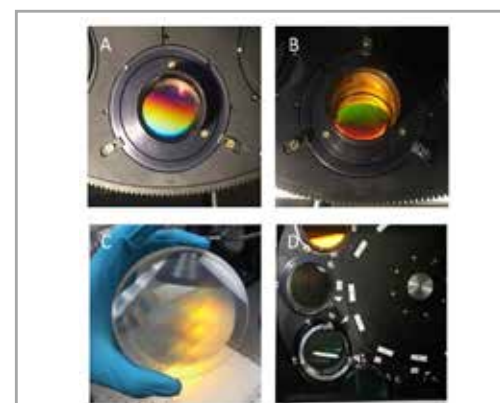


Fig. 3 - Photopolymer-based dispersing elements manufactured for astronomical spectrographs.

# ELECTRODEPOSITION FOR WAFER BONDING

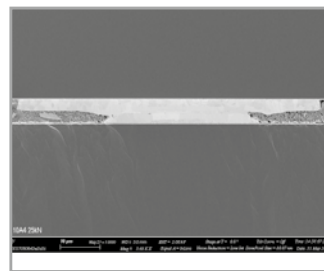
**Mattia Pallaro - Supervisor: Luca Magagnin**

**Tutor: MariaPia Pedferri**

Since their commercialization in the eighties, microelectromechanical systems (MEMS) became more and more important in microelectronic industry. The MEMS market is growing almost at 20% over the period 2018-2023 (according to Yole Développement), with a big share in the consumer market. MEMS are usually made up of a processor part that is the brain of the device, and some parts that interact with the surroundings. They cover a wide range of applications, like the inertial sensors for automotive (e.g. airbag deployment or electronic stability control) or for consumer electronics such as game controllers and smartphones, blood pressure sensors, micromirrors for digital light processing and inkjet printers. Most of these devices have to operate in controlled environments, therefore are encapsulated during production. Wafer bonding is a packaging technique that confers protection to sensitive parts of the MEMS from the external factors that can compromise their functionality. It also assumes a key role in the miniaturization of devices, because it enables three-dimensional integration. It can be done by joining two wafers directly, or by coating one wafer with a material that will act as junction by a proper treatment. Electrodeposition, also known as electroplating or electrochemical deposition (ECD), is a wet deposition method that is well

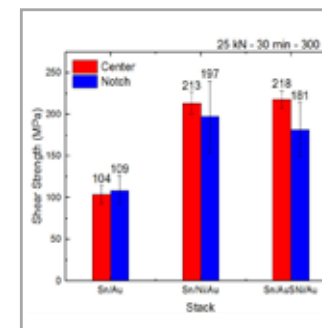
established in electronics industry. In this work, tin and tin-copper alloy electroplating have been carried out respectively from a commercial bath and from a non aqueous solution created in laboratory to obtain metal layers suitable for metallic wafer bonding. In the first part tin electrodeposition was optimized by varying deposition current density. The deposits were observed at optical microscope and scanning electron microscope (SEM) to check the quality at a first glance and to observe the evolution of the microstructure with the different parameters. Stylus profilometry was performed to measure the thickness of the layers and check the uniformity of the deposition over the whole area of the substrate. Atomic force microscope (AFM) provided an analysis about the topography of the films and their roughness. Few attempts were made with pulsed deposition and the same characterization of the films was performed. In the case of tin-copper co-deposition, ethylene glycol solutions containing copper(II) and tin(II) chloride salts were characterized electrochemically by means of cyclic voltammetry (CV) and linear sweep voltammetry (LSV). Deposition was performed both under direct (DC) and pulsed (PC) current conditions and the advantages of the latter were observed, also in terms of surface morphology as observed by SEM. Samples with plated tin over

copper showed whiskers growth after deposition: their presence was monitored in time and for different plating conditions with SEM. As a whiskers mitigation strategy, the introduction of a Ni underlayer was adopted. The interaction at room temperature between tin and gold was studied. Energy dispersive X-ray spectroscopy (EDX) was useful in the evaluation of the interaction. Sn/Ni/Au and Sn/AuSnNi/Au (AuS stands for "gold strike", a very thin layer of gold deposited at high current) stack was proposed as an alternative, to hinder gold rapid diffusion into tin. The final goal of the work was to prove the feasibility of the Au-Sn and Cu-Sn metallic wafer bonding with the electrodeposited structures characterized through the life of the project. Samples with Sn/Au, Sn/Cu, CuSn/Cu, Sn/Ni/Au and Sn/AuSnNi/Au plated stacks onto patterned wafer were bonded and characterized. Process parameters such as bonding



**Fig. 1 - SEM cross section image of a Sn/Au sample bonded at 25 kN, 300 °C for 30 min.**

temperature, time and pressure were varied and the junction was successfully obtained. Bonding was characterized with SEM and EDX analysis of the obtained structures. The reliability of the metallic bonding was studied with shear test of 3 x 3 mm dies cutted from the wafers. Fracture surfaces were then analyzed by SEM and EDX, and an assessment of the phases at the fracture surfaces of the dies was given by Auger electron spectroscopy (AES).



**Fig. 2 - Shear strength of Sn/Au, Sn/Ni/Au, Sn/AuSnNi/Au stacks bonded at 25 kN, 300 °C, for 30 min. In red are shown the values for dies taken from the center of the wafer, in blue values for samples cut from the outside area.**



## METHODOLOGIES FOR THE CONSERVATION AND NON-INVASIVE STUDY OF METALLIC WORKS OF ART

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The research activity of this PhD was focused on the conservation and non-invasive characterisation and monitoring of metallic cultural heritage. The main degradation process that affects the metallic works of art is by far corrosion. It is an electrochemical process that occurs spontaneously on the metallic surfaces, and its mechanism can significantly vary according to the specific environment to which the artefacts are exposed. Upon corrosion, the formation of the so-called natural patina is observed: a series of mineral compounds are formed as a consequence of the interaction of the metals with the substances and pollutants present in the environment (e.g. atmosphere, soil, seawater). During this PhD thesis four main topics related to the conservation of the metallic artefacts have been investigated: i) study and characterisation of copper-based works of art; ii) study and production of artificial patinas; iii) optimisation and development of electrochemical and electrical techniques for corrosion monitoring and diagnostic; iv) setup and optimization of sustainable conservation methodologies. The presence of natural patinas and corrosion layers is a fundamental feature of the metallic artefacts of the cultural heritage, that very seldom present polished and uncorroded surfaces. In fact, they are commonly

exposed to environment for long periods (years or even centuries), during which natural patinas are formed. The exposure environment dramatically influence their composition, which in turn affects their corrosion behaviour. During this work different case studies have been studied and characterised with the purpose of carefully evaluating their overall conservation conditions and their corrosion behaviour, in relation to their exposure environment. In particular, six bronze artworks from the *Cimitero Monumentale* of Milan have been studied to consider the effects of several decades of exposure in polluted urban environment. Then the bronze *Monumento ai Caduti* of the city on Lecco, on the shores of the Como Lake, was studied, to consider a less polluted urban environment characterised by the proximity to the lake. Finally, an extensive diagnostic campaign was carried out on the Colossus of San Carlo of Arona, a monumental statue exposed to rural environment for three centuries and built by a peculiar construction technique. It is in fact constituted by a skin of embossed copper sheets fixed on a structure of iron bars, supported by a central stone pillar. Therefore, the diagnostic activity on such artwork provided the opportunity of studying a large variety of patinas, both on copper and iron elements, formed in different exposure conditions: sheltered and unsheltered surfaces,

internal and external ones have been investigated. On such artefact, in order to better understand the apparently scarce presence of galvanic coupling corrosion between copper and iron elements, their microstructure and composition were investigated. Besides the natural patinas, it is common practice to realise artistic artificial patinas on metallic artworks. They have been widely employed in sculpture since ancient time to provide the desired appearance to the surfaces. When they are present, therefore, they should be properly preserved as they are an integrating part of the works of art. To this purpose, therefore, a good knowledge of their composition and corrosion behaviour is fundamental. Therefore, during this PhD thesis a series of patinas realised by an artistic foundry have been characterised both from the aesthetical and corrosion point of view. It was demonstrated that their presence could be a criticality in terms of preservation, and thus it was highlighted the need for specific conservative procedures. In addition, artificial patinas are also important in the conservation science, as they are often produced in laboratory tests by means of artificial ageing or by chemical or electrochemical procedures to reproduce natural corrosion products. Such patinas are used as model systems for the investigation of

corrosion processes or for the testing of new conservative treatments such as cleaning methodologies or protective systems like coatings or inhibitors. In this context it is therefore fundamental to be able to reproduce the natural corrosion products. In this PhD thesis a series of chemical methodologies have been applied for the reproduction of the most common natural corrosion products formed upon atmospheric corrosion. A selection of such methodologies have been then adopted for the pre-corrosion of electric resistance based sensors for the monitoring of environmental corrosivity. The effective monitoring of corrosion rate of metallic surfaces can be performed following two main approaches: on one side periodical electrochemical analysis can be performed directly on the artworks surfaces, while on the other environmental corrosivity can be evaluated on material reproduction of the examined artefacts. Environmental corrosivity probes, in particular, can be adopted for the realisation of sensors for the remote and real time monitoring. Both such approaches present advantages and drawbacks: the former allows investigating directly the artefacts surfaces, which often present complex stratigraphies of corrosion and degradation products, that are often difficult to reproduce by laboratory procedure. However,

in this case a real-time monitoring can hardly be performed. The employment of material reproductions allows instead to perform a real time monitoring, even by means of destructive techniques, but requires the employment of representative probes of the real surface conditions of the artefacts, that are sometimes difficult to reproduce. During this PhD thesis both these approaches have been considered and adopted. Linear Polarisation Resistance (LPR) and Electrochemical Impedance Spectroscopy (EIS) for the *in situ* monitoring of corrosion rate have been employed, and the influence of a series of experimental parameters on the obtained results have been assessed. As a result, an optimised protocol for on-site LPR and EIS have been proposed. Moreover, a new kind of customised electric resistance (ER) based corrosivity sensors have been designed and realised for the monitoring of copper-based surfaces. As regards the preservation of the cultural heritage artefacts, two main phases of the conservative interventions have been considered: cleaning and the application of protective coatings and inhibitors. In this PhD two relevant aspects in this context have been considered. On one side the long-term effects of five different cleaning methodologies, from the corrosion point of view have been investigated. Cleaning procedures, in particular, should be

aimed at selectively removing the deposit layers and the unstable, incoherent and hygroscopic corrosion products that may undermine the aesthetical perception of the works of art and their conservation. However, cleaning may also cause the undesired partial removal of more protective layers that could cause an instantaneous increase of the reactivity of the surfaces. Therefore, a proper evaluation of this phenomenon would be a powerful tool for the selection of the optimal cleaning procedure for each specific case. In addition, the performances of a series of “green” inhibitors for the protection of copper-based surfaces have been evaluated. Nowadays the most diffused corrosion inhibitors for copper-based surfaces in cultural heritage field is BTA. However, since its harmfulness for environment and humans health have been proven, the identification of environmental friendly alternatives to BTA, which could provide a satisfactory protection to the surfaces have acquired great importance. In particular, the performances of eight green inhibitors on polished and pre-corroded copper and bronze surfaces have been analysed, along with a naturally aged bronze artefact from the *Cimitero Monumentale* of Milan.