Final Report Summary - NAS-ERA (Reinforcing Nanostructured material research cooperation between the Unité de Développement de la Technologie du Silicium (UDTS) and the European Research Area (ERA))

Executive Summary:
The Algerian Centre de Recherche en Technologie des Semi-conducteurs pour l'Energétique (CRTSE) aims to become a major actor for nano-structured materials research. The three year project NaS-ERA supported CRTSE in performing better research in its three strongest research topics:
A) Production of functional nanostructures,
B) Development of new detection methods, and
C) Design and development of new sensors.

The NaS-ERA project built upon CRTSE’s existing strengths as a high-quality research institution via capacity building activities with the following four excellent European research and innovation organisations:
1. CNRS – Laboratoire de Physique de la Matière Condensée,
2. National Institute of Metrological Research,
3. Fraunhofer Institute for Mechanics of Materials, and
4. Intelligentsia Consultants.

The capacity building activities consisted in the following:
• Twinning activities consisting in exchanging knowledge and setting up joint experiments on the Research Topics A, B and C.
• Training of CRTSE’s staff on the Research Topics A, B and C during workshops, conference and staff exchange.
• Implementing a Promotion and Dissemination plan to increase the visibility of CRTSE in Europe and promote the scientific results obtained with the European partners.
• Organisation of three (3) workshops in Algeria on the Research Topics A, B and C.
• Organisation of an international conference in Algeria.
• Assessment of CRTSE’s research excellence using a detailed evaluation methodology and preparation of a tailored strategy plan for CRTSE.

CRTSE and the European partners worked hard on twinning activities and as a results, the Algerian centre published a significant number of papers in the framework of the NaS-ERA project (e.g. 10 scientific publications, 1 chapter of a book and 1 scientific paper in an international proceeding). They also participate to numerous events in Algeria, Europe and worldwide to promote the NaS-ERA project and the results obtained.

Project Context and Objectives:
The overall aim of the NaS-ERA project is to integrate the Centre de Recherche en Technologie des Semi-conducteurs pour l’Energétique (CRTSE) into the European Research Area (ERA), by developing cooperation with European research and innovation organisations in its three strongest ICT research topics: A) Production of functional nanostructures, B) Development of new detection methods, and C) Design and development of new sensors. These are also research topics highly relevant to
The FP7 ICT and NMP work programmes.

CRTSE is the only Algerian Research Centre working in all application domains based on silicon technologies: energy with photovoltaic technology, medical and biotechnologies, information and communication technologies but also in the field of detection mainly used for industrial and environmental issues. CRTSE’s researchers regularly publish international papers and present their results at international conferences in these research topics.

The NaS-ERA project will involve expanding CRTSE’s capacities and scientific expertise through strategic collaboration with the following four excellent European research and innovation organisations: CNRS Laboratoire de la Physique de la Matière Condensée (CNRS-PMC), National Institute of Metrological Research (INRIM), Fraunhofer Institute for Mechanics of Materials (Fraunhofer-IWM) and Intelligentsia Consultants Sàrl (Intelligentsia). By making a major contribution towards research cooperation in the production of functional nanostructures, the development of new detection methods, and the design and development of new sensors, the NaS-ERA project will enable CRTSE to participate and contribute to several FP7 thematic priorities.

Project Results:

Twinning between CRTSE and CNRS

1/ The various activities performed with CNRS are listed below:

• Learning the techniques of sample preparation (e.g.: cutting, cleaning)
• Training on the use of electrochemical tools (e.g.: AUTOLAB, electrochemical cell)
• Coupling of ferrocene on the flat surfaces of silicon Si (111).
• Quantitatively interpretation of the recorded data and derivation of surface concentration
• Quantifying the electrochemical redox couple ferrocene coupled to the silicon surface and in solution using cyclic voltammetry. Determination of the redox couple of ferrocene.
• Quantifying redox ferrocenes elements using the software driver AUTOLAB: OPUS.
• Characterization by FTIR spectroscopy (Fourier Transform Infrared) in te ATR mode in order to verify the presence of ferrocene on the silicon surface through chemical bonds produced following the coupling of the different stages.
• Grafting ferrocene moieties to a silicon surface,
• Electrochemical recording of electrochemical response of electro active groups at the surface,
• Performing a useful set of measurements in order to check the validity of the recorded response.

The twinning experiments have been performed on well-controlled, atomically flat silicon surfaces. Nevertheless, the acquired skills will be of direct interest for the PhD project of Ms Amina KERMAD which deals with the use of enzyme-functionalized porous silicon for the electrochemical detection of phenol derivatives. In the framework of twinning activities, numerous discussions and working meetings have been organized for helping Ms Amina KERMAD to define better the requirements and conditions for setting the first assays in the framework of her project.

The purpose of quantification electrochemical redox couple ferrocene is to determine the rate of ferrocenes hung on the silicon surface, we are interested in studying the ferrocene as a redox system is simple and allows us to study of another redox system namely the enzymes in order to produce biosensors for the detection and quantification of pollutants in aqueous media.

The redox coupling elements on the flat surfaces of silicon has certain limitations i.e. a low specific surface area which makes it difficult to attach a high rate of redox elements and subsequently, a low electrochemical response. The use of porous silicon is an attractive solution for gripping and trapping a high level of functional elements.

2/ The various activities performed with CNRS are listed below:

• Recording IR spectra in ATR geometry with s- or p-polarized infrared radiation,
• Recording several reference spectra and combine them for minimizing perturbation associated with atmospheric interferences in the spectra,
• Performing calibration experiments in the liquid phase, in view of a quantitative analysis,
• Measuring the actual number of reflections in an ATR experiment for a given prism,
• Fitting experimental data to a combination of several peaks, and drive the fitting procedure to obtain reliable results,
• Obtaining quantitative surface concentration from the results of the fits,
• Learning the techniques of sample preparation (e.g.: cutting, cleaning),
Training on the use of any tool electrochemical (e.g.: AUTOLAB, electrochemical cell),
• Training on the use of infrared spectroscopy (FTIR) in the ATR geometry (Ex and in-situ) and using its software driver AUTOLAB: OPUS,
• Sample Characterizations: The chemically modified surfaces were characterized by infrared spectroscopy (FTIR) in the ATR geometry. The surface concentrations of grafted carboxydecyl and succinimidyl ester chains were quantitatively determined by calibration of the characteristic IR band intensities,
• Immobilization of Acetylcholinesterase (with different concentrations) on the functionalized surfaces of silicon Si (111). The modified surface has been characterized by infrared spectroscopy (FTIR) in the ATR geometry. This analysis technique has been made in order to verify the presence of amide I and amide 2 groups,
• In order to quantify the number of immobilized enzymes it is necessary to do a calibration measuring with in-situ infrared study,
• Initials experiments of electrochemical detection of malathion with modified electrode.
• Functionalization of silicon surface with enzymes using multi-step strategy (acid grafting, surface activation, amidation reaction)
• FTIR-ATR Characterisation of functionalized silicon surfaces with enzymes
• AFM imaging
• SEM characterization
• Electrochemical and optical (UV-Vis) detection of pollutants
• calibration of amide bond absorption in acetylcholinesterase in order to measure the surface concentration of immobilized enzymes
• determination of the enzymatic activity of acetylcholinesterase immobilized at a silicon surface
• quantitative assessment of an enzyme sensor configuration
The twinning experiments have been performed by immobilizing a specific enzyme on well-controlled, atomically flat silicon surfaces. Nevertheless, the acquired skills will be of direct interest for the PhD project of Ms Khadidja KHALDI which deals with the use of the same enzyme for functionalizing porous silicon in view of performing the indirect electrochemical detection of phosphorous derivatives. In the framework of twinning activities, numerous discussions and working meeting have been organized for helping Ms Khadidja KHALDI to better define the requirements and conditions for setting the first assays in the framework of her project.
There are several reasons to quantify immobilized enzymes: Measuring Km,Vm and all characteristics of this enzymes, help in immobilization and electrochemical detection studies (to quantify the substrates, inhibitor). The twinning helped to study the kinetic of the amidation reaction using in situ infrared measurements and quantify the immobilization of Acetylcholin esterase on functionalized/porous silicon. Application to the realization of amperometric biosensors for the detection of toxic substances.
3/ The various activities performed with CNRS are listed below:
- Joint experiments on Plasma Enhanced Chemical Vapor Deposition
- Thin layer of amorphous silicon-carbon
- alloy on glass: optical bahavior
- Improving the a-SiC:H/glass structure
- Separating optics and chemistry
- Amorphous silicon carbon alloys for SPR Sensing
- Measurement of surface-plasmon-enhanced fluorescence
- Localized plasmon resonance of metal nanoparticles
- Influence of a thin a-Si1-xCxC:H layer
- Influence of a thin a-Si1-xCxC:H layer
- DNA hybridization
- Fluorescence on hybrid structures
- Kinetics: height dependency and sequence matching

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Research and Innovation
The twinning between CNRS and CRTSE concluded on the following initial statements:
- Porous silicon luminescence results from a mechanism taking place in the bulk part of the skeleton, arising from quantum-confinement effects
- Porous silicon luminescence is indirectly sensitive to the porous structure environment, especially through dielectric effects, which can be used for sensing but with a limited sensitivity
- As expected from a material with a high surface-to-volume ratio, luminescence can easily be affected by surface effects, but this can be used for sensing in special dedicated conditions only
- In any case, the question of selectivity remains difficult when using porous silicon luminescence for sensing
- Selectivity must be addressed through specific surface chemistry, which could as well incorporate specific fluorescent tags

Further twinning and joint research activities led to the following statements:
- In planar configurations, crystalline Si does not offer a good optical platform for the attachment of fluorescent probes
- In planar configurations, Si-based amorphous thin layers offer interesting alternatives; depending on the targeted architecture, tuning the refractive index is quite useful
- Well-suited thin-layer design offer photoluminescence amplification and allows for high sensitivity, allowing e.g. for kinetic studies
- Additional physical effects offer photoluminescence enhancement and allows for ultimate sensitivity
- If 3D architecture is needed, think of porous silicon enhancement, but beware of pore size vs. probe/target crowding
- In any case, most of the added value (selectivity) is in the control of surface chemistry

CRTSE and CNRS prepared the following joint papers:
• "Methylated silicon: A longer cycle-life material for Li-ion batteries"; Larbi Touahir, Abdelhak Cheriet, Daniel Alves Dalla Corte, Jean-Noël Chazalviel, Catherine Henry de Villeneuve, François Ozanam, Ionel Solomon, Aissa Keffous, Noureddine Gabouze, Michel Rosso; Journal of Power Sources; Vol. 240; 551-557
• "GlyHisGlyHis immobilization on silicon surface for copper detection"; Sabrina Sam, Anne Chantal Gouget-Laemmel, Jean-Noël Chazalviel, François Ozanam, Noureddine Gabouze; Applied Surface Science; Vol. 269; 166-170
• "Horseradish peroxidase-modified porous silicon for phenol monitoring"; A. Kermad, S. Sam, N. Ghellai, K. Khaldi, N. Gabouze; Materials Science and Engineering B: Solid-State Materials for Advanced Technology; Vol. 178/Issue 18; 1159-1164
• "Voltammetric Behavior of Peptide-Modified Porous Silicon after Metal Complexation"; Sabrina Sam, Anne Chantal Gouget-Laemmel, Jean-Noël Chazalviel, François Ozanam, Arnaud Etcheberry, S. Belhousse, N. Gabouze; Key Engineering Materials; Vol. 605; 119-122
• "Electrochemical Sensor for Detection of Para-Nitrophenol Based on Modified Porous Silicon"; S. Belhousse, K. Lasmi, I. Mezaache, T. Sedrati, N. Belhanache, S. Sam, N. Gabouze; Key Engineering Materials; Vol. 605; 115-118
• "Book: Macroporous Silicon"; Noureddine Gabouze, François Ozanam; Handbook of porous Silicon; Article 010-1

Twinning between CRTSE and INRIM
The various activities performed with INRIM are listed below:
• Short courses, presented by Dr. Emanuel Enrico, about the SEM (Scanning Electron Microscopy) principle and practice. Characterization of the silicon nanostructures obtained by stain etching and the Si/PANI structures prepared at UDTS with SEM Inspect F equipped with EDS (Energy Dispersive Spectroscopy)
• Learning the usage of LabView for the electric characterization of Si/PANI structures at different time of exposure. The first steps of this practice, were guided by Alessandro Cultrera in order to facilitate the understand all the principal of use of the new version of LabView.
• Visiting NIS "Nanostructured Interfaces and Surfaces", at the Universita degli Studi di Torino, and use the FTIR In-situ for the detection of gases and vapors. The FTIR analysis was done on the Si/PANI surfaces at different concentrations and times of exposure to the ammonia and the ethanol vapors.

The aim of this twinning was to use the new advances in the field of gas sensors and characterization of the silicon
nanostructures. After this period at INRIM, the visiting scientist could easily use the SEM to characterize the morphologies of silicon nanostructures and others. The assembly of the FTIR in-situ and make the analysis of gas concentrations was also part of the twinning. To improve electric characterization of gas sensing, the scientist was enabled to take the new version of the software “LabView”.

It would be advantageous if the development of silicon nanopillars could be experimented by stain etching using Vanadium Oxyde and fluorhydric acid in order to carry out SEM analysis. Related to the characterization of gas sensors, samples of Si/PANI prepared at CRTSE were used. Although, the detection could was not carried out for all, because the porous surface of silicon was disconnected. More time would be required in order to remake the structures at INRIM and to continue the characterization.

Among the developed activities, SEM characterization of Porous Silicon (PS) samples, PS impregnated with Ployaniline (PANI) and silicon nanostructures obtained by Metal Assisted Etching in presence of vanadium oxide (V2O5).

The nanostructured samples, after SEM detailed analysis, were electrically characterized under exposure to ethanol vapours, NO2 and NH3, with interesting preliminary results. Due to a failure on the NH3 bottle valve, this last part of characterization could not be terminated. It is important to dedicate a final part of activity to this task in the next period, in order to complete the investigation on this promising topic.

CRTSE and INRIM prepared the following joint papers:

- "Electrochemical gas sensors based on polypyrrole- porous silicon"; Fatma-Zohra Tebizi-Tighilt, Fawzi Zane, Naima Belhaneche-Bensemra, Samia Belhousse, Sabrina Sam, Nour-Eddine Gabouze; Applied Surface Science; Vol. 269; 180-183
- "Electrical characterization of ethanol sensing device based on Vanadium oxide/Porous Si/Si structure"; K. Chebout, A. Iratni, A. Bouremana, S. Sam, A. Keffous, N. Gabouze, Solid State Ionics; Vol. 253; 164-168
- "Electrochemical gas sensors based on polypyrrole- porous silicon"; Fatma-Zohra Tebizi-Tighilt, Fawzi Zane, Naima Belhaneche-Bensemra, Samia Belhousse, Sabrina Sam, Nour-Eddine Gabouze; Applied Surface Science; Vol. 269; 180-183

Twinning between CRTSE and Fraunhofer

1/ The various activities performed with Fraunhofer are listed below:

- Training on the available equipment and the different techniques used as well as the emerging scientific challenges,
- Contribution to project coordination and revision of project plan, Discussion on the research topics to develop in common and the experiments to implement (such as electrochemical cell for detection in solution)
- Discussion on the modalities for host of a student from CRTSE to Fraunhofer-Institut für Werkstoffmechanik IWM in 2013.
- Presentation of the main activities of the division of Thin Films and Applications (CMA).
- Nanostructured Silicon and its Applications
- Introducing CRTSE and its Research fields
- Nanostructures, Nanocomposites, Growth of SiC and a-Si:H layers, Surface Functionalization, Porous Silicon Functionalisation, Biosensors, Electrochemical study of the GlyHisGlyHis-modified PSI electrode, Electrochemical Detection of Phenolic Compounds, Gas sensors, Conducting polymer/PSi/Si structure, Al/V2O5/PSi/Si structure, Humidity sensors, Energy storage, Information storage, Optical devices, Valorisation

The visit of Algerian researchers from CRTSE to Fraunhofer-IWM was advantageous and successful. They had the opportunity to study and visit the research facilities and laboratories of the institute, to get trained on the available equipment and techniques, to discuss further steps in the project, to draft further cooperation, also to get introduced to thin film applications at Fraunhofer and gain further knowledge in the field of nano-structured material research, specifically related to the detection in liquid phase.
The various activities performed with Fraunhofer are listed below:
The researchers organised twinning activities related to the topics of Nanoporous Aluminum Oxide Membrane and Materials and techniques for biosensor developments. Below is presented the outline of both twinnings.

Outline of the twinning on Nanoporous Aluminum Oxide Membrane:
- Requirement of membranes
- Fabrication and Properties
- Fabrication of self-supporting and mechanically stabilized membranes
- Structure properties
- Optical Properties
- Filtration Properties
- Functionalization
- Application
- Filtration and Separation
- Cell Cultivation
- Crowing of Nanotubes
- Reactive Wet Coating
- Nano Structuring of Polymers

Outline of the twinning on Materials and techniques for biosensor developments:
- SEM and FIB on cell cultures and on silicon cell hybride systems
- Micromechanical measurements on mechanochemical proteins
- Mechanical Properties of Films Made from recombinant Spider Silk Proteins

The visit of German researchers from Fraunhofer-IWM to CRTSE was successful. They could get more familiar with CRTSE, its researchers and facilities and provided twinnings on the topics of Nanoporous Aluminum Oxide Membrane and Materials and techniques for biosensor developments, which are very important in the advancement of the project. For CRTSE it was beneficial, because they had the opportunity to introduce the institute and receive training on relevant topics on the spot.

CRTSE and Fraunhofer prepared the following joint papers:
- “Texture etching of monocrystalline silicon surface with sodium hypochlorite”; A. Lounas, A. Nait Bouda, H. Menari, Y. Belkacem, N. Gabouze; Surface Engineering; Vol. 30/Issue 2; 148-151
- “Influence of CHx thickness layer on the sensing properties of CHx/PS/Si structure against CO2 gas”; N. Zouadi, S. Belhousse, D. Bradaï, H. Cheraga, M. Ouchabane, A. Keffous, S. Sam, N. Gabouze; Superlattices and Microstructures; Vol. 63; 131-140

Potential Impact:
CRTSE is the leading Algerian nano-material research institute and its activities are supported by the Ministry of Higher Education and Scientific Research. They have strong connections with other Algerian research centres and universities (e.g. CDTA, CDER, USTHB, CERIST, etc.) and the industry (SONELGAZ, Sonatrach, etc.).

The NaS-ERA project was originally developed to raise the research excellence of CRTSE to compete with European research organisations. But since the very beginning of the project, CRTSE decided to support the Algerian research and industrial communities by involving them into some project activities. Thus many Algerian scientists interested in the project research topics attended the events organised within the project:
- The 1st NaS-ERA workshop has been organised the 21-23/05/2012 in the Hotel El Marsa (Algiers, Algeria). The event gathered 50+ people over the three days, amongst them representatives of the University of Tlemcen, the Algerian Development Centre for Advanced Technologies (CDTA), and University of Sciences and Technology Houari Boumediene.
- The 2nd NaS-ERA workshop has been organised the 30/09 and 01/10/2013 in the Hotel El Marsa, Algiers (Algeria). The workshop attracted 40+ attendees from Algeria including representatives from the University of Tlemcen and the University of Sciences and Technology Houari Boumediene.
The 3rd NaS-ERA workshop has been organised the 16/03/2014 in the Hotel Hilton, Algiers (Algeria) one day before the starting of the International Conference on Nanostructures for Sensing & Energy Conversion (NaSEC ‘14). The workshop attracted 40+ attendees from Algeria including representatives from universities: University Abou Baker Belkaid of Tlemcen, University of Sciences and Technology Houari Boumediène (USTHB), University Saad Dahleb of Blida; and research centers such as CDTA and CRNA.

The international conference NaSEC’14 was hosted in the Hotel Hilton (Algiers, Algeria) the 17-19 March 2014, gathering more than 150 participants. The NaSEC’14 event proposed different activities to its audience in order to learn, exchange and disseminate the latest S&T results. The scientific program consisted of the presentation of three (03) plenary lectures, thirty three (33) invited lectures, twenty (20) oral and one hundred and six (106) contributions as posters.

- Three (03) plenary sessions;
- Fourteen (14) invited talks given by world class scientists;
- Three (03) days conference: 35 oral presentations;
- Two (02) poster sessions: 106 poster presentations;

During the NaS-ERA project the consortium partners contributed to the preparation of promotional materials to target the nanostructured materials research communities in Algeria and Europe, as well as a wider audience. The following materials have been prepared in order to raise the impact of the project:

- Project leaflet and poster
- PowerPoint presentation of the project
- Project website frequently updated with news and downloadable documents
- NaSEC’14 conference website
- Promotion Brochure about CRTSE
- Four project newsletters have been prepared and disseminated through different communication channels (e.g. project website, LinkedIn interest groups, mailshot campaign, distribution of hard copiers during events, etc.)

The project impact on the Algerian research and business communities was extremely high and CRTSE confirmed its national leadership in the field of nanostructured materials while improving its image among other Algerian organisations. On the other hand the NaS-ERA project aimed to enhance CRTSE's international cooperation, and in this sense, the motivation and willingness of CRTSE's staff combined to a good quality of research increased the centre's visibility in Europe and promote its excellence. As a result the international conference held in Algeria in March 2014 attracted many international experts well-known in the scientific sphere. Also the participation of CRTSE to another FP7 proposal showed that the European research community is more enthusiast to work with them on high level research.

Dr. Noureddine GABOUZE - NaS-ERA Coordinator
gabouzenoureddine@crtse.dz
(+213)21 43 26 30

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