N A M e

GDR Nanomaterials for Energy Applications

ELABORATION
MEASUREMENTS & METROLOGY
SIMULATIONS & THEORY
APPLICATIONS

4-6 October 2021 Plenary Meeting
ESSIE, Paris

	Monday 4 October	Tuesday 5 October	Wednesday 6 October
8:15-8:30		Welcome	
8:30-9:45		S3 **Christophe COUTANCEAU**	
8:45-9:00		"Clean hydrogen production from electron-reforming of oxygenated organic compounds"	
9:00-9:15			
9:15-9:30		**Perspectives Atelier #3**	Welcome
9:30-9:45		Energy Conversion	**Perspectives Atelier #6**
9:45-10:00		#	Micro-Nano-Devices
10:00-10:15		Round Table #3	S7 #
10:15-10:30		#	Round Table #6
10:30-10:45		Coffee break/posters	#
10:45-11:00			Coffee break
11:00-11:15		S4 Prix These 2020	
11:15-11:30		**Claudia de Melo SANCHEZ**	S8 **Jérémie MAIRE**
11:30-11:45		Prix These 2021	Presentation on Thermal Management for 5G
11:45-12:00		**Zhelu HU**	Closing
12:00-12:15		Prix These 2021	
12:15-12:30		**Giulia LOMBARDI**	
12:30-12:45		Lunch	
12:45-13:00			
13:00-13:15	Welcome		
13:15-13:30			
13:30-13:45	Introduction	Posters	
13:45-14:00			
14:00-14:15	S1 **Jean-Paul KLEIDER**	S5 **Anne TANGUY**	
14:15-14:30	Photovoltaics today: an overview	"Thermal Transfer at the atomic scale in	
14:30-14:45		amorphous/nanostructured samples"	
14:45-:15:00	**Perspectives Atelier #1**	**Restitution Atelier #4**	
15:00- 15:15	Nanomaterials-Nanostructuration	Thermal Management	
15:15-15:30	#	**Perspectives Atelier #4**	
15:30-15:45	Round Table #1	Thermal Management	
15:45-16:00	#	#	
16:00-16:15	Coffee break	Round Table #4	
16:15-16:30		#	
16:30-16:45	S2 **Georges FAVRE**	Coffee break/posters	
16:45-17:00	"Paysage de la normalisation & opportunités pour		
17:00-17:15	valider des méthodes caracterisation nmateriaux"	S6 **Jean-Marie TARASCON**	
17:15-17:30	**Perspectives Atelier #2**	"Les materiaux de batteries: Quel intérêt pour	
17:30-17:45	Nanoscale Transport Properties	les physicens?"	
17:45-18:00	#	**Perspectives Atelier #5**	
18:00-18:15	Round Table #2	Energy Storage	
18:15-18:30	#	#	
18:30-18:45	**Laboratories Presentations**	Round Table #5	
18:45-19:00	(videos)	#	
19:00- 19:15	#	**Laboratories Presentations**	
19:15-19:30	#	(videos)	
19:30-19:45		**GALA**	
19:45-20:00			

In silico study of hexagonal diamond (HD) silicon nanowire surfaces

Romuald Béjaud* and Olivier Hardouin Duparc

LSI, Laboratoire Solides Irradiés, CEA-DRF-IRAMIS, CNRS, École Polytechnique, Institut Polytechnique de Paris, Palaiseau, France

*Now at CEA DAM ILE-DE-FRANCE, Bruyères le Châtel

Presenting person: Nathalie VAST

The hexagonal diamond phase (2H-HD polytype) of silicon is an excellent material for solar energy production. If in its crystal form, the electronic band structure gives an indirect gap of 0.95 eV, in the form of nanowires the gap becomes direct (for wires with diameter larger than 1nm). The opposite effect is observed for the common phase of silicon (cubic diamond or 3C polytype) whose gap is slightly larger (1.1 eV).

Silicon is a particularly common material, however its hexagonal phase is very rare, since only the 3C and the β-tin phases are predicted in the phase diagram (figure 1). Tang, Maurice *et al*. have recently demonstrated the presence of this rare phase in nanowires of very small diameters [2]. To understand why the HD phase is stabilized during the nanowire growth, we have undertaken a from-first-principles study of the structures and energies of the nanowires surfaces and edges.

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Figure 1: Phase diagram for bulk crystals, Ref. [1].

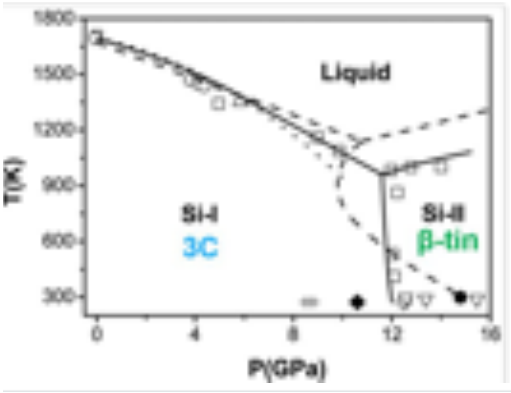
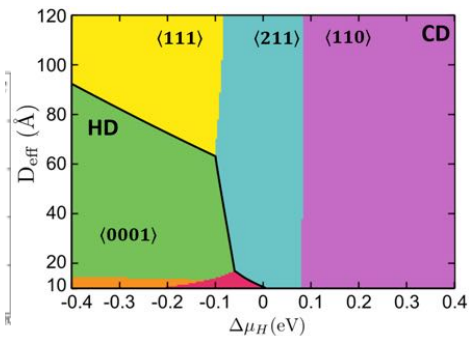


Figure 2 : Growth conditions of the HD phase in H-terminated nanowires. This work, from Ref. [3].



New insights on the charge storage mechanism of thin films electrode materials by Raman spectroscopy

Ankush Bhatia[1], Clement Leviel[2, 3, 4], Maxime Hallot[3, 4], Jean-Pierre Pereira-Ramos[1], Christophe Lethien[3, 4], Pascal Roussel[2] and Rita Baddour-Hadjean[1,*]

[1]Institut de Chimie et des Matériaux Paris Est (ICMPE), UMR 7182 CNRS et Université Paris Est Créteil, 2 rue Henri Dunant, 94320 Thiais, France
[2]Unité de Catalyse et de Chimie du Solide (UCCS), Université de Lille, CNRS, Centrale Lille, Université d'Artois, UMR 8181 – UCCS, F-59000 Lille, France
[3]Institut d'Electronique, de Microélectronique et de Nanotechnologie, Univ. Lille, CNRS, Centrale Lille, Univ. Polytechnique Hauts-de-France, UMR 8520 - IEMN, F-59000 Lille, France
[4]Réseau sur le Stockage Electrochimique de l'Energie (RS2E), CNRS FR 3459, 33 rue Saint Leu, 80039 Amiens Cedex, France

E-mail: bhatia@icmpe.cnrs.fr

Thin film solid-state Li-ion micro-batteries (TFMB) are promising candidates to power miniaturized sensors for Internet of Things (IoT) applications [1]. Such applications have created a high demand for the battery systems to provide larger power and energy densities. To fulfil the performance requirements, both positive and negative electrodes with high storage capacities should be developed. A promising candidate for the positive electrode is the spinel $LiMn_{1.5}Ni_{0.5}O_4$ (LMNO) which exhibits a mean operating potential of 4.75 V vs. Li/Li^+, a theoretical specific capacity of 147 $mAh \cdot g^{-1}$, and is inexpensive due to use of high amount of low cost and environmentally benign manganese [2]. On the other side, TiO_2 (anatase) is of great interest as negative electrode for TFMB because of its interesting capacity of 168 mAh g^{-1} and operating potential of 1.5 V vs. Li^+/Li . Other advantages of TiO_2 are its rapid discharge and charge properties as well as its low cost and non-toxicity [3].

In this work, Raman spectroscopy is carried out to explore the short range environment in sputtered disordered LMNO and ALD- deposited TiO_2 thin films during the electrochemical process. Significant and reversible evolution of the Raman spectra is displayed in both cases during the electrochemical cycle, signifying reversible change in the metal-oxygen bond strength on Li^+ extraction/insertion. In the case of Li_xMNO ($0 \leq x \leq 1$), pertinent descriptors of the $Ni^{2+}/Ni^{3+}/Ni^{4+}$ species are identified in the Raman spectra, and a proper analysis of the Raman features gives access to their relative ratio in the LNMO thin film. The obtained results demonstrate that Raman spectroscopy is able to probe the electrode state of charge (SOC), which makes it an efficient and simple diagnostic tool to measure the self-discharge phenomenon occurring in the LMNO cathode. On the other hand, a Raman spectroscopy

study performed on the anatase Li_xTiO_2 system ($0 \leq x \leq 0.5$) shows the homogeneous nature of the lithium insertion process in TiO_2 thin film electrodes. The structural transition from tetragonal TiO_2 to orthorhombic titanate Li_xTiO_2 is clearly evidenced by Raman spectroscopy. For the first time in the thin film configuration, the rich Raman fingerprint of the pure orthorhombic $Li_{0.5}TiO_2$ phase, made of 20 components, is fully observed for x = 0.5 (Figure 1). The high quality of the Raman spectra obtained on the thin film electrodes allows quantifying the amount of orthorhombic phase at different oxidation-reduction states, showing again the efficiency of Raman spectroscopy to evaluate the SOC of the TiO_2 thin film electrode material.

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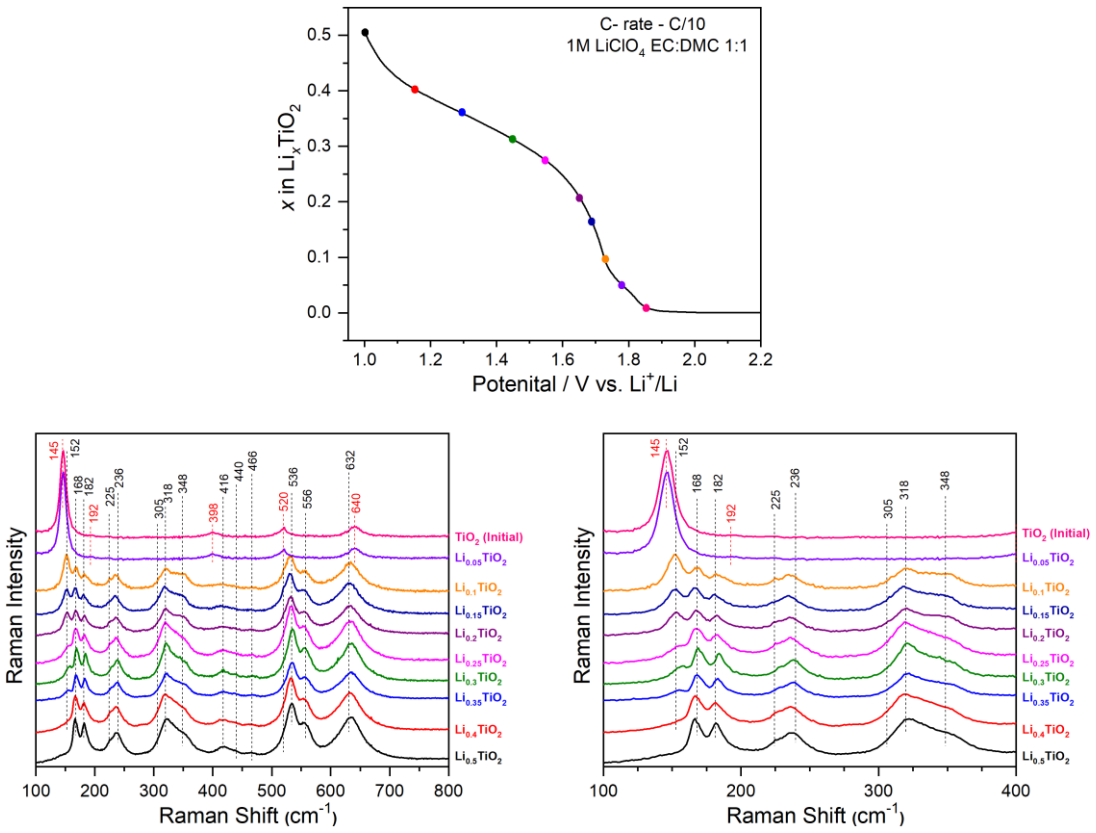

Figure 1. Ex-situ Raman study on anatase TiO2 thin film during 1st discharge: a) Evolution of the potential (vs. Li/Li+) from OCV to 1 V vs. x content in LixTiO2, b) Evolution of Raman spectra (100-800 cm-1 range) in electrochemically lithiated LixTiO2 for x=0 to 0.5, c) Enlarged view in the 100-400 cm-1 range.

3D Microsupercapacitor Configurations for Enhanced Energy Micro-Storage

Botayna Bounor[*1], David Bourrier[1], David Pech[*1]

[1]UPR-8001 LAAS, CNRS, Toulouse, France
e-mail addresses: bbounor@laas.fr, dpech@laas.fr

With the development of various technologies including electrical micro-systems and wireless technology, the question of miniaturization of energy storage devices arises. Microsupercapacitors[1] (MSCs) based on 3D pseudocapacitive electrodes seem to be the best candidates to provide a good autonomy for such small systems thanks to their long lifetime and high capacitance. Unfortunately, the low technological readiness level (TRL) of MSCs limits the large-scale deployment of smart miniaturized systems and the energy density value still too low to reach this goal. One attractive solution to improve the areal energy density of MSCs is to significantly enhance the specific surface of the electrode material thanks to high aspect ratio micro/nanostructured scaffold. So, in the frame of this study, we will present the microfabrication process of stacked and interdigitated MSCs based on highly porous electrodes prepared by using the dynamic hydrogen bubble templating (DHBT) of metallic current collectors[2]. To fully fill the porosity created by these 3D current collectors, ruthenium dioxide (RuO_2) film was electrodeposited as electrode material[3,4] by using cyclic voltammetry technique. In terms of miniaturization and integration of MSCs on chip, the interdigitated and the stack configurations were elaborated in this work and were tested in aqueous and solid-state electrolytes. For both configurations, MSCs have been provided a high areal energy density > 330 mJ cm^{-2} in [0.5 M] H_2SO_4 and > 250 mJ cm^{-2} in PVA- H_2SO_4-SiWA.

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Thermal probe microscopy: Toward a thermal analysis of nanomaterials

Nathaly CHAARAOUI, Patricia AL ALAM, Nathalie TRANNOY, Jaona RANDRIANALISOA

Nathaly.chaaraoui@univ-reims.fr

Nanotechnology requires characterization technics for nanosystems and nanomaterials. Since twenty years, Nanotechnology reveals new needs in understanding and management of heat distribution at micro/nanoscale and in nanoscale structures. Development in new materials requires advanced knowledge of nanoscale heat transfer and thermal properties of nanostructured materials. Scanning thermal microscopy (SThM) based on Atomic Force Microscopy (AFM) technique is a promising tool for investigating material's thermal measurements and heat transfer mechanisms at the micro/nanoscale [1, 2]. This project aims to investigate temperature and/or thermal properties of the studied material using a SThM probe with thermal sensor (thermoresistive) at the tip. This thermal tip allows us obtaining topographic and thermal images simultaneously with micrometer and sub-micrometer spatial resolution. In this matter, Wollaston is used as a resistive probe in order to: (i) study the influence of sample structure on the thermal signal of the probe, (ii) characterize and estimate the effect of probe volume on thermal conductivity measurements. For that, samples composed of buried silicon steps under polished CVD SiO_2 are considered.

We developped a numerical simulation to better understand the experimental data obtained by SThM. This was done by using COMSOL Multiphysics which is based on finite element method. This simulation allows comparison between experimental data and the model developed with all physical aspects considered. So that a well-defined heat transfer numerical model was developed for the probe-sample system with the surrounding medium. A 3D realistic geometry of the Wollaston probe is modelled in contact operation mode in order to obtain probe temperature behavior . The probe/sample numerical model reveals the evaluation of the dissipated flux by the thermal resistive wire (platinum-rhodium wire) and into the sample. By comparing the experimental measurements with the simulation, the developed models are in good agreement with experiment results. The models were capabale to rebuild experimental profiles obtained by SThM. More worthwhile , this study point out the sensitivity of the thermal signal to the internal nanostructure of the investigated samples. The thermal signal gives access to a thermal conductance that corresponds to a probed volume.

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Understanding thermal properties of GeTe and the effect of nanostructuration: towards energy harvesting on microelectronics

Roderic Cravero[1,2], Valentina M. Giordano[2], Olivier Bourgeois[1], and Pierre Noé[3]

[1]Institut Néel, CNRS-Université Grenoble Alpes, Equipe Thermodynamique des Petits Systèmes, Grenoble, France
[2]Institute Light and Matter (ILM), CNRS, team (Nano)Materials for Energy, Lyon, France
[3]Université Grenoble Alpes, CEA, LETI, Grenoble, France
contact: roderic.cravero@neel.cnrs.fr

Abstract

Heat management in microelectronics and the recycling of energy is a challenge in today's society. The study of the thermal properties of chalcogenide phase-change materials (PCMs) such as the prototypical GeTe compound will allow to improve and optimize future phase-change memories even if the latter are already mastered by industrials. To achieve this improvement reducing the thermal conductivity of the semiconducting PCM is a key tool. Obtaining a polycrystalline PCM with a thermal conductivity as low as possible can be achieved by the nanostructuration of the PCM in order to increase phonon scattering and block the phonon propagation. By this mean we can impact thermal transport properties without detrimental effect on the electronic transport properties.

In this experimental work, we first investigate thermal properties of crystalline GeTe, prior to any nanostructuration, providing an upper limit for the thermal conductivity of nanostructured GeTe, and of amorphous GeTe, whose thermal conductivity should represent the lowest possible reachable value.

In order to do so, we have developed a sensitive differential 3-omega method adapted for measurements on electrically conductive semiconducting thin films ; this method permits to perform thermal conductivity measurement. Here I will present my first results on thermal conductivity of crystalline GeTe as a function of temperature, allowing to identify the dominant phonon scattering mechanism in this material in the temperature range investigated.

New Electrochemically Protective Layer Based on Nanometric Dielectric Coating for Silicon Based Micro Supercapacitors.

Authors
Marc Dietrich[1,2], Loic Paillardet[2], Anthony Valero[1.2], Nicolas Pauc[1], Philippe Azaïs[3], Pascal Gentile[1], Saïd Sadki[2].

1 : Univ, Grenoble-Alpes, CEA, PHELIQS-SiNAPS, 38054 Grenoble
2 : Univ, Grenoble-Alpes, CEA, CNRS, IRIG-SyMMES, 38054 Grenoble
3 : Univ, Grenoble-Alpes CEA, LITEN
Corresponding Author ; Pasca.Gentile@cea.fr

Abstract

Dielectric materials have been used for decades for micro and nanoelectronics where their insulation and polarizability properties are critical. However, in the energy storage field, material scientists tends to consider high-k dielectric layers in contact with an active material only as an insulating passivation layer. In microelectronics, this conception has been modified with the study of dielectrics at nanoscale level [1-2] revealing interesting properties scarcely known by other fields [3]. We propose to reconsider the vision of high-k dielectric materials for energy at nanoscale specifically.

Based on microelectronic techniques [4], a nanometric-scale thick layer of dielectric is deposited by Atomic Layer Deposition (ALD). Allowing us to create an ultra-thin, pinhole-free alumina (Al_2O_3) nanometric layers on complex architectures as the entanglement of Silicon nanowires. [5]

Microelectronics measurements on a single silicon nanowire (SiNW) is shown to display thickness dependent tunneling electrical conduction. This result brings a new light on this material class in the energy field and allows original approaches : achieving scientific leaps by using thin layers of dielectric to protect the active materials and enhance their lifetime in new environments. As an illustrative application, a silicon based micro-supercapacitor (µSC) protected by a 3 nm alumina layer exhibits Electrical Double Layer Capacitance (EDLC) by means of tunneling current in aqueous electrolyte. This result is an unprecedented for this material, allowing an outstanding lifetime capacity and retaining 99% of its initial capacitance after 2 million cycles. Extended to multiple energy materials, such method could lead to notable progresses [6].

This new approach of energy storage materials for microsupercapacitors application, open the field of new possibilities and work in aqueous media. This allows silicon nanostructures compatibility with pseudocapacitive materials to enhance their capacitance while keeping a high stability thanks to the ALD protective barrier. It has been shown in this work that, the addition of a conductive polymer like PEDOT-PSS is forming a an homogeneous matrix that benefits from the properties of the protected SiNWs, enhancing it's performances during the cycling, allowing the new composite to reach 500.000 cycles in aqueous media, while maintaing remarquable electrochemical performances [7].

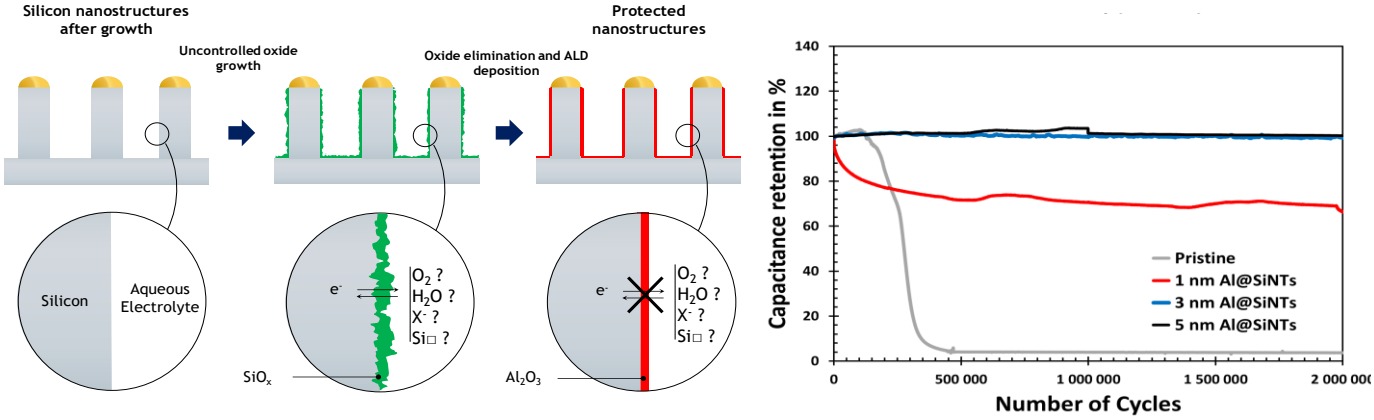

Figure 1 : Pristine SiNWs exposed to aqueuous electrolyte and creating a native SiO_2 layer reacting in aqueous electrolyte and leading to capacity loss throughout the cycles. And SiNWs protected by different thickness nanometric-layers, performances towards long life cycling at 0,5 $mA.cm^{-2}$.

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Influencing parameters for thermal conductivity measurements by SThM technique: first results

S. DOURI [a], N. FLEURENCE [a], J. HAMEURY [a], S. GOMES [b]

a. Laboratoire National de Métrologie et d'Essais (LNE), 29 avenue Roger Hennequin, 78197 Trappes Cedex - France

b. CETHIL UMR5008, CNRS, INSA-Lyon, Université Claude Bernard Lyon 1, F-69621 Villeurbanne, France

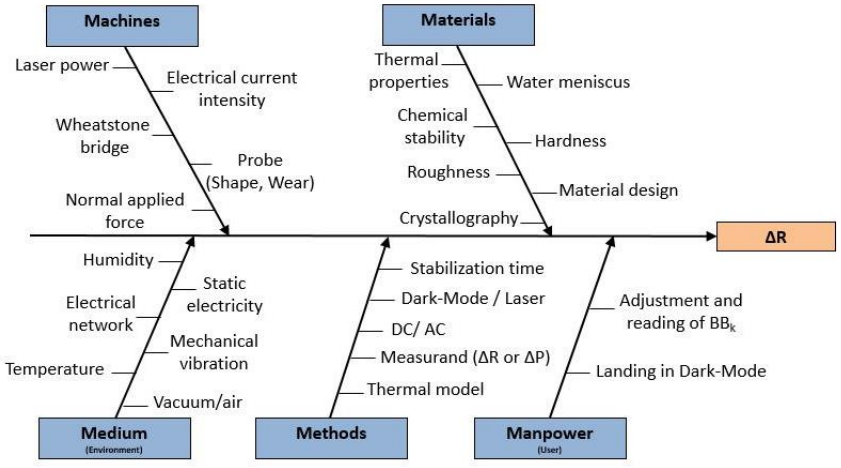
E-mail: sarah.douri@lne.fr

Abstract (300-500 words, 1-2 pages maximum)

Scanning thermal microscopy (SThM), based on the AFM concept, is used to carry out quantitative thermal conductivity measurements at the sub micrometric scales [1]. A thermoresistive prove, heated by Joule effect, acts as a heat source. Currently, a calibration of the technique, using bulk materials with well-known thermal conductivity at macroscale, is required to produce traceable quantitative measurements at nanoscale. The calibration curve established represents the probe electrical resistance variation as a function of the thermal conductivity of the sample.

In order to quantify uncertainties associated with the measurements and to improve the traceability to SI units of SThM thermal conductivity measurements, influencing parameters are studied (Figure X). The experimental dispersion of the measurements on the probe electrothermal response represents the majority of the uncertainty budget (76%) [2]. In our approach to optimize LNE's SThM, the following parameters have been first investigated in order to improve the measurement repeatability: the surrounding medium temperature, the electrical current through the probe and finally the temperature inside the microscope.

Figure X: **Ishikawa diagram [2]**



When the microscope is uncovered in the air, the surrounding medium temperature variations effect the measurement repeatability due to thermal disturbances that alter the stability of the probe electrothermal response. The use of a polystyrene covering box reduced these thermal disturbances, enhancing the probe electrothermal response's stability (10 times more stable) and reducing the noise (2.5 times less noise). Furthermore, an optimal electrical intensity through the probe (850 µA) has been determined. When measurements are taken without using the optical system to detect the cantilever deflection [3] (composed of a laser and a photo detector), the electrical intensity determined provides for good measurement repeatability (experimental dispersion < 4.10^{-3}) as well as a quick stabilization time. Finally, a thermal mapping was performed by introducing calibrated T-type thermocouples inside

the microscope (near the probe and the sample). This thermal mapping has highlighted the presence of hot sources other than the heated probe. One of them is the optical system laser that induces a heating of the probe and a thermal drift on the measurements. To address this problem, measurements will be performed in "Dark-Mode" [3]. The displacement system, which ensures the sample movement in the three directions in our microscope, is another heat source. Due to the system overheating, the sample is hotter than expected (+1.40°C). This lead to a loss of sensitivity as the probe electrical resistance variation is lower since the temperature variation between the probe and the sample is smaller. A solution to reduce this effect could be integrating a cooling system to the sample holder.

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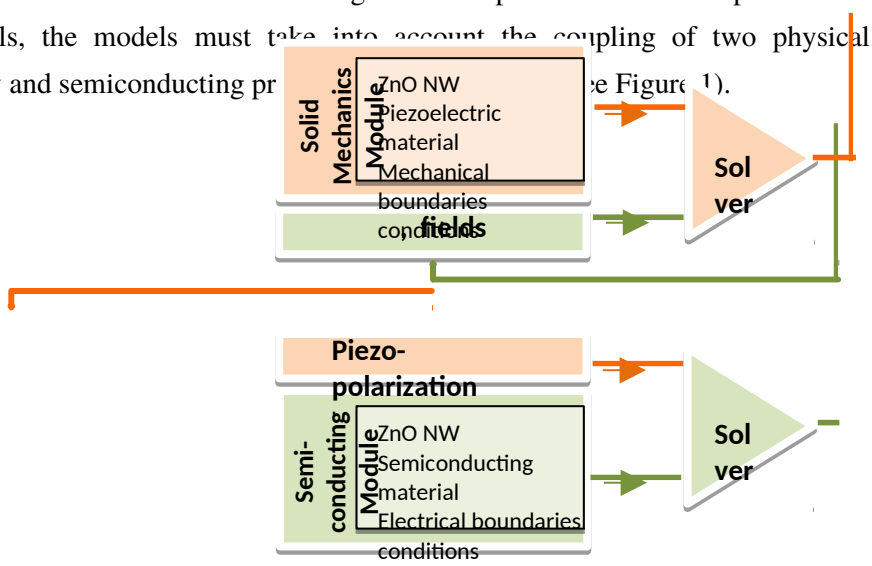
Electro-mechanical energy conversion in piezo-semiconducting ZnO nanowires, a theoretical study

Emmanuel DUMONS*, Guylaine POULIN-VITTRANT and Louis Pascal TRAN-HUU-HUE

GREMAN UMR 7347, INSA Centre Val de Loire, CNRS, Université de Tours, 3 rue de la Chocolaterie, CS 23410, 41034 BLOIS Cedex, FRANCE

*emmanuel.dumons@insa-cvl.fr

The harvesting of even small amounts of energy from free micro-sources is a strategic research area for consumer, industrial, military and medical electronics. Indeed, it meets a double objective: making autonomous sensors, which, for various reasons have a complicated energy "recharge" and responding to the issue of sustainable development by reducing the use of batteries and other accumulators. Developing micro- or nano-generators is therefore an important part of the research because they are essential building blocks in the development of autonomous systems (e.g. for transport [1] or space [2]) or communicating systems (e.g. the Internet of Things IoT [3]). In the context of mechanical energy harvesting from movements, different technologies exist. Among them, the direct piezoelectric effect allows a coupling of mechanical and electrical properties. One of the difficulties is to be able to compare the performances of the different systems using an adapted Figure of Merit (FoM) [4]. Since 2006 [5], piezoelectric semiconducting nanowires (e.g. zinc oxide ZnO, gallium nitride GaN…) have appeared as potential candidates for lead-free piezoelectric materials, with enhanced properties compared to their bulk counterparts [6]. Since then, many experimental or theoretical studies dedicated to ZnO based NG have shown significant improvement of their performances [7]. In the simulation tools, the models must take into account the coupling of two physical phenomena: piezoelectricity and semiconducting pr e Figure 1).



In the present work, we report the theoretical study of the electro-mechanical energy conversion using finite element method to model a unit cell of a nanogenerator (NG) with ZnO nanowires (NW). First, we verified the correct coupling of the piezoelectric and semiconducting properties of the ZnO by comparison between analytical and numerical solutions. Then, to know the efficiency of the energy conversion, we compared the electrical energy stored in the unit cell in different cases by modifying some relevant parameters.

Figure 1: Strong coupling created on COMSOL Multiphysics® to solve both physics

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CONFORMAL COATING BY LIQUID ROUTE ON THREE-DIMENSIONAL TOPOLOGY

Marie Gabard[1], Virginie Grimal[1], Mohamed Boufnichel[2], Morgane Dutour[2], Pierre-Ivan. Raynal[3], Rachel Omnee[4], Encarnacion Raymundo-Pinero[4], Nathalie Poirot[1]

[1]GREMAN-IUT de Blois, 15 rue de la Chocolaterie, 41000 Blois cedex France
[2]STMicroelectronics 10 rue Thalès de Milet 37071 TOURS cedex 2
[3]Laboratoire de Biologie Cellulaire - Microscopie Electronique, 10 bd Tonnellé, 37032 TOURS Cedex France
[4]*CNRS, CEMHTI UPR3079, 1D avenue de la Recherche Scientfique, 45071, Orléans*

Corresponding author : nathalie.poirot@univ-tours.fr

Résumé

In the past few years, the development of miniaturized energy systems and the diversification of micro devices have raised the interest on tri-dimensional structuration (3D). The advantages of 3D structuration of materials in such devices are the reduction of size and cost and the increase of the reliability and energy density stored. The experimental techniques for depositing thin films on 3D subtracts are divided into two categories: physical and chemical. The most reported physical techniques are physical vapor deposition (PVD), vacuum evaporation, molecular beam epitaxy and sputtering. These techniques require a combination of high voltage, vacuum and low deposition speeds. Chemical techniques consist of electrophoresis by electrophoresis, chemical vapor deposition, atomic layer deposition (ALD), etc.

In our case we propose a new approach for depositing homogeneous thin films over 3D subtracts using a liquid route. The main technological issue to overcome for implementing such a fast and cheap route is the viscosity of the solution. The success of the method relies on the modification of the precursor solution by adding a viscous liquid. The procedure is therefore based in three steps: the preparation of a viscous precursor solution, the deposition of the solution over the 3D subtracts by spin coating and a thermal treatment [1-2]. Here we present the results obtained on the deposition of metallic oxides over 3D micro structured silicon subtracts. Different architectures with high area enlargement factor have been used in order to obtain high surface electrodes for batteries and supercapacitors. The electrochemical results show a direct impact of the developed surface on the energy storage capacity.

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A nanostructured silicon foam for surface-enhanced steam generation using solar energy

Lan GAO*, Frédéric Marty, Elyes NEFZAOUI, Yamin LEPRINCE-WANG, Tarik BOUROUINA

lan.gao@esiee.fr.

Abstract

Enhanced solar steam generation (SSG) is a promising process for water purification[1]. With a black absorber sheet (BAS), evaporation efficiency can be increased by localizing the heating process at the water-air interface. To improve the evaporation efficiency, a bilayer BAS concept was proposed where two different materials are integrated to ensure two key roles : the top layer for incident radiation absorption and the bottom layer for both thermal insulation and capillary water pumping.. As of late, numerous bilayer BAS have been developed, with micro/nanostructured porous media such as wood[2], polyurethane foam[3], etc., exhibiting remarkable properties in terms of solar radiation-to-heat conversion to achieve efficient steam generation[4].

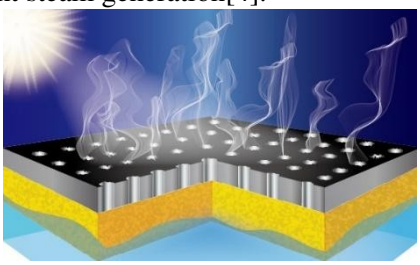

Figure 1. Schematic of the bilayer silicon-based metafoam for surface enhanced solar steam generation.

In this contribution, we report on a metafoam fabricated by precise control of a micro-pore array drilled on black silicon (BSi) (Figure 1) and combined with a low cost commercial foam used as the bottom layer. This BSi metafoam was designed by numerical simulations to guide the optimization of the bilayer BAS. By taking advantage of the optimized porous structure of the BAS, heat localization and thermal insulation functions are simultaneously achieved for the maximization of the evaporation rate. The validation experiment shows that the evaporation rate reaches 1.34 kg/(h·m^2) under 1 sun illumination, an unmatched value so far, while the theoretical limit is estimated at 1.5 kg/(h·m^2).

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A Molecular Dynamics Investigation of the Interfacial Thermal Resistance between nanoconfined water and silicon/silica with realistic surface chemistry

William Gonçalves[1*], Konstantinos Termentzidis[1]

* william.goncalves@insa-lyon.fr

[1] Univ Lyon, INSA-Lyon, CETHIL CNRS-UMR5008, F-69621, Villeurbanne, France

The fabrication of nano-architected materials has improved considerably over the last decade. It is now possible to synthesize series of nanoporous materials with functionalized internal surfaces. However, the impact of humidity on heat transfer at the nanoscale is not fully understood. The structural and vibrational properties of nanoconfined water differ from those of the bulk near the solid/liquid interface [1]. Thus, for materials with nanoscale features, macroscopic models such as Fourier's law or the Effective Media Approach (EMA) can not predict the effective thermal properties of solid/liquid composites [1]. In addition, experimental measurements are difficult due to humidity. During Scanning Thermal Microscopy (STM) experiments, the presence of a water meniscus at the mechanical contact between the tip and the sample creates capillary forces that impact the thermal conductance [2,3].

In this study, we simulate solid/liquid interfaces using molecular dynamics (MD) simulations. The interfacial thermal resistance (Kapitza resistance) is calculated between a film of water and various solids such as crystalline and amorphous silicon or amorphous silica with functionalized surfaces. The impact of the average temperature, the heat flux and the thickness of the water slab on the Kapitza resistance is investigated. Finally, we modified the hydrophobicity level of the silica by grafting hydrophobic molecules on the hydroxylated surface. The results of this study provide interesting insights about the nanoscale heat transfer through solid/liquid interfaces.

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Measurement and simulation of the three-dimensional temperature field in an RF SOI chip

Tuyen-Duc Nguyen[1], Isaac Haïk Dunn[1], Elyes Nefzaoui[1], Georges Hamaoui[1], Philippe Basset[1], Jérôme Loraine[2], Imene Lahbib[2], Brice Grandchamp[2], Gregory U'Ren[2]

[1] ESYCOM Lab., Univ Gustave Eiffel, CNRS F-77454 Marne-la-Vallée, France

[2] X-FAB France, 91105 Corbeil-Essonnes, France

Corresponding authors: isaac.haikdunn@esiee.fr, elyes.nefzaoui@esiee.fr

In the past twenty years, integrated circuits based on silicon on insulator substrates (SOI) have become ubiquitous. The buried silicon oxide layer (BOX) has a thermal conductivity about two orders of magnitude smaller than that of silicon. Therefore, the thermal management of the chips may heavily depend on the thickness of the BOX, which, if too big, may cause severe undesired self-heating in the devices. In order to improve the thermal management of 4G/5G chips under operating conditions, we present a novel way to determine the three-dimensional (3D) temperature field of a Radio Frequency Silicon On Insulator (RF SOI) electronic chip, using several resistance temperature detectors (RTDs) embedded at different locations around the chip. The placement of the RTDs at key locations enables the calibration of a multiphysical numerical model that provides the 3D temperature field in the whole chip under operating conditions. The obtained results provide useful insights on the role of different parameters (e.g. used materials properties, heat source power, substrate, boundary conditions, etc.) to engineers interested in the modelling and optimization of heat transport and thermal management of electronic chips for RF applications.

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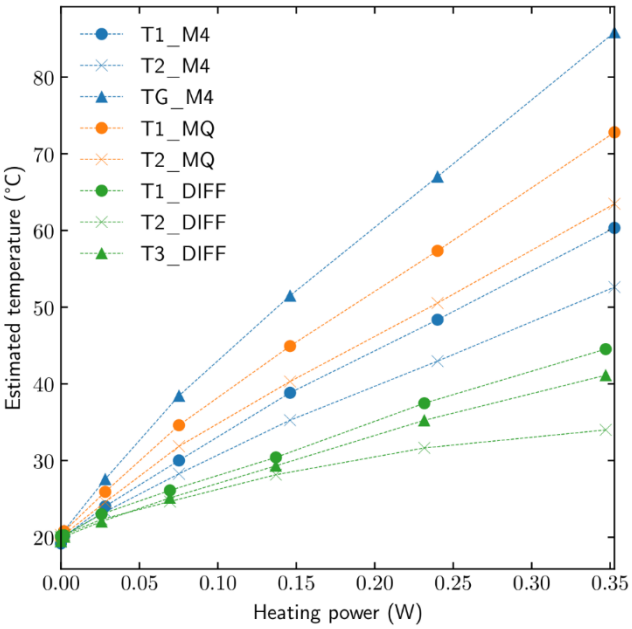


Figure 1: Temperature at 8 locations around the transistor, in function of transistor heating power

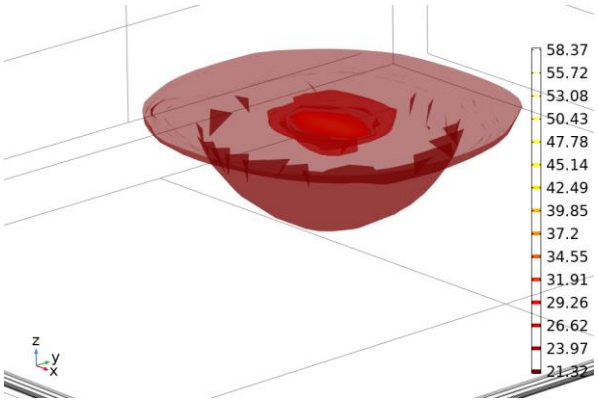


Figure 2: Simulated temperature field around the heating chip, for a dissipated power of 0.18W

Flame Spray Pyrolysis Platform for Nanomaterials Elaboration

Yann Leconte

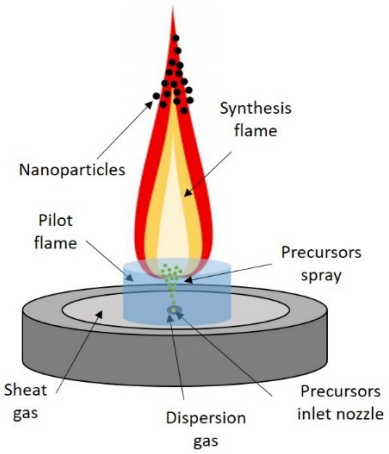
Université Paris-Saclay, CEA, CNRS, NIMBE, LEEL, 91191 Gif sur Yvette, France

Corresponding author yann.leconte@cea.fr

Abstract

As part of its research activities in the field of energy production and storage, the Laboratoire d'Etude des Elements Legers (LEEL) is setting up a Flame Spray Pyrolysis (FSP) device allowing the continuous, dry-route and one-step synthesis of nanopowders.

FSP is based on the thermal decomposition of a liquid precursor followed by the nucleation and growth of nanoparticles resulting in the formation of an agglomerates aerosol [1]. The liquid precursor is sprayed into a pilot combustion flame where high temperature but very short duration reactions take place, leading to pure, homogeneous, and small-sized primary particles.



Flame Spray Pyrolysis process scheme

Even if FSP was historically developed for oxide materials, the synthesis of non-oxide [2] or metallic [3] particles was reported, using reducing conditions in the pilot flame. More advanced structures or composites can also be obtained through doping, coating, or performing substitutions in the crystal via the precursors solution or an in-situ post-treatment. Thanks to this wide range of nanomaterials, FSP appears as a powerful tool to strengthen LEEL research efforts in the field of solid electrolytes and electrode materials development for batteries and fuel cells applicatons.

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2D semimetal/III-V hybrid photoelectrodes for solar fuel production

L. Chen[a], Y. Léger[a]*, G. Loget[b], M. Piriyev[a], I. Jadli[a], S. Tricot[c], T. Rohel[a], R. Bernard[a,c], A. Beck[a], J. Le-Pouliquen[a], P. Turban[c], P. Schieffer[c], C. Levallois[a], B. Fabre[b], L. Pedesseau[a], J. Even[a], N. Bertru[a] and C. Cornet[a]

a. Univ Rennes, INSA Rennes, CNRS, Institut FOTON–UMR 6082, F-35000 Rennes, France
b. Univ Rennes, CNRS, ISCR (Institut des Sciences Chimiques de Rennes)–UMR6226, F-35000 Rennes, France
c. Univ Rennes, CNRS, IPR (Institut de Physique de Rennes)–UMR 6251, F-35000 Rennes, France
* yoan.leger@insa-rennes.fr

Taking advantage of the complementary physical or chemical properties of their components, nanostructured materials have become highly attractive for numerous applications in today's science and technology, from hybrid inorganic-organic and composite materials to metamaterials. In the field of semiconductors, research on new type of heterostructures allowing to go beyond standard semiconducting properties is a promising route. This is the case of Anti-Phase Boundaries (APBs). These structural defects generated during the polar III-V epitaxial growth on the non-polar Si substrate, were for long considered as detrimental non-radiative defects [1]. Recent research suggests however to develop phase-engineering strategies in III-V/Si samples [2-4]. In addition, an unusual and strong electron-phonon interaction in stoichiometric APBs was also reported [5]. In this work, we combine structural analysis (AFM, SEM), multi-scale transport characterizations (C-AFM and Hall effect), photo-electrochemical characterizations with band-structure and Fermi level determination obtained from first-principle calculations, to demonstrate that non-stoichiometric APBs can be seen as semimetal singularities embedded within a III-V semiconductor matrix (see Figure 1) [6]. We especially demonstrate that bi-domain III-V/Si materials are able within the same layer to absorb light efficiently, separate laterally the photo-generated carriers, transfer them to semimetal singularities, and extract both electrons and holes vertically, leading to efficient carrier collection as shown in Fig.1 e). The original topological properties of the 2D semi-metal singularities are also discussed.

This comb-like III-V/Si heterostructure not only merges the superior optical properties of semiconductors with good transport properties of metallic materials, but also combines the high efficiency and tunability afforded by III-V inorganic bulk materials with the flexible management of nano-scale charge carriers usually offered by blends of organic materials. This work opens up new horizons for energy harvesting, photonics, electronics or computing device applications.

The authors acknowledge RENATECH (French Network of Major Technology Centers) within Nanorennes for technological support.

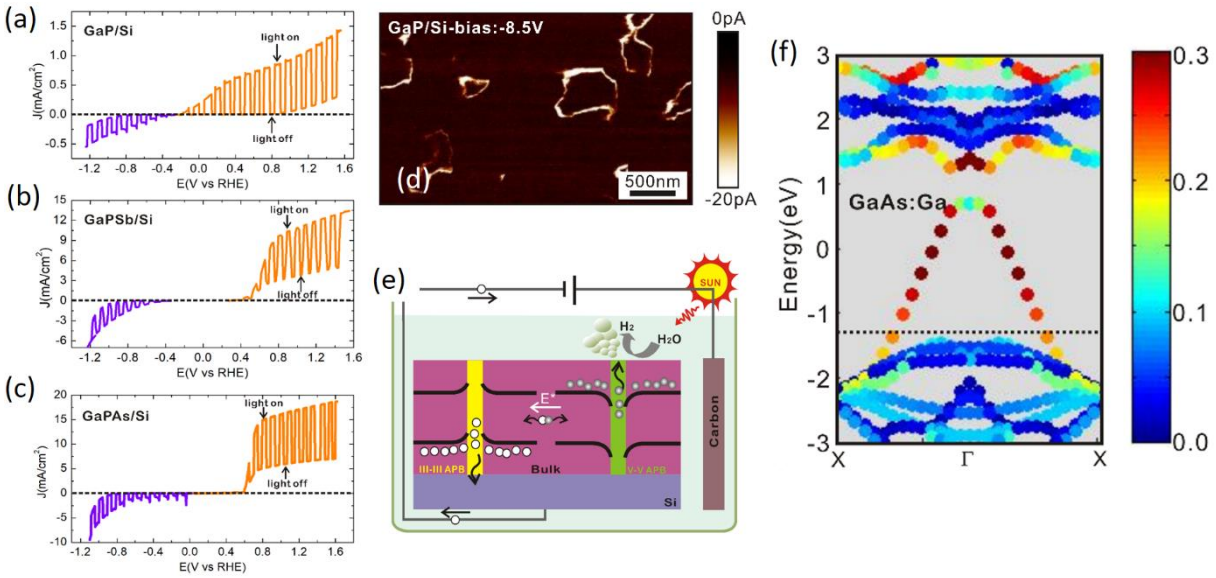

FIGURE 1: Chopped-light linear sweep voltammetry curves (scan rate = 50 mV/s) of bi-domain GaP/Si:n (a), GaPSb/Si:n (b) and GaPAs/Si:n (c) samples in 1.0M H2SO4 (pH=0.3) electrolyte under simulated sunlight illumination (100 mW.cm-2, AM 1.5G) (d) Conductive-AFM measurements highlighting the conduction by APBs, (e) Scheme of the carriers photo-generation and extraction in a III-V/Si sample for solar hydrogen production, (f) the semi-metallic bandstructure calculated for an APB in GaAs.

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Micro-diffraction study of sputtered $LiMn_{1.5}Ni_{0.5}O_4$ thin films for Li-ion micro-batteries

Clément Leviel[1,2,4], Ankush Bhatia[3], Maxime Hallot[2,4], Florent Blanchard[1], Jean-Pierre Peireira Ramos[3], Christophe Lethien[2,4], Rita Baddour-Hadjean[3], Pascal Roussel[1]

[1]Unité de Catalyse et de Chimie du Solide, Université de Lille, CNRS, UMR 8181 – UCCS, Lille, France
[2]Institut d'Électronique, de Microélectronique et de Nanotechnologies, Université de Lille, CNRS, UMR 8520 - IEMN, Lille, France
[3]Institut de Chimie et des Matériaux Paris-Est, Université Paris-Est Créteil, CNRS, UMR 7182 – ICMPE, Thiais, France
[4]Réseau sur le Stockage Electrochimique de l'Energie (RS2E), CNRS FR 3459, Amiens, France
clement.leviel.etu@univ-lille.fr

Abstract

The emergence of new miniaturized and autonomous electronic technology results in demand for effective micro devices for the energy storage. The development of Li-ion all solid state micro batteries is an attractive way to increase considerably the surface of active material and thus to obtain high level of storage capacity while keeping a low surface footprint.

We are currently working on a promising spinel type electrode material, $LiMn_{1.5}Ni_{0.5}O_4$ (LMNO), developed in thin film, by RF magnetron sputtering on $Si/Al_2O_3/Pt$ substrate [1].

LMNO is a high working voltage electrode (E_{Li/Li^+} = 4.8V vs Li/Li^+) with a good experimental discharge capacity (60µAh cm^{-2} $µm^{-1}$) really close to the theoretical value (65µAh cm^{-2} $µm^{-1}$) and is able to sustain high rate cycling. However, the electrochemical properties are closely related to various parameters such as the crystal orientation, Ni and Mn cation ordering (ordered or disordered spinel) [2] and thickness of the films. In order to improve the performance of micro-batteries, it is crucial to understand the different mechanisms involved, but also their evolution during the different cycles of charge/discharge. It is therefore important to adapt characterization techniques allowing the analysis of the structural evolution of micro-batteries active materials such as X-ray diffraction (XRD), X-ray absorption spectroscopy (XAS) or transmission electron microscopy (TEM). If it is relatively common to follow in situ / operando bulk material for large scale Li-ion batteries, adapting these techniques to their miniaturized counterparts (i.e. the micro-batteries) is challenging as highlighted in the article published by Qu, Z & al. in 2020 [3]. However, we have shown that the XAS synchrotron operando

study of vanadium nitride thin films used as electrode materials for micro supercapacitors could give valuable insights on the storage mechanism [4].
We thus decided to study this material by X-ray micro-diffraction on a Rigaku SmartLab with 9 kW rotating anode X-ray source. This technique allows performing XRD patterns on 400 microns area [5].
We use this technique for mapping our thin films to verify their homogeneity, perform ex-situ analyses at different state of electrode charge or after different number of charge/discharge cycles.
For example, Figure 1 shows the integrated intensity of the (111) diffraction peak of a 1-micron thick wafer of LMNO.

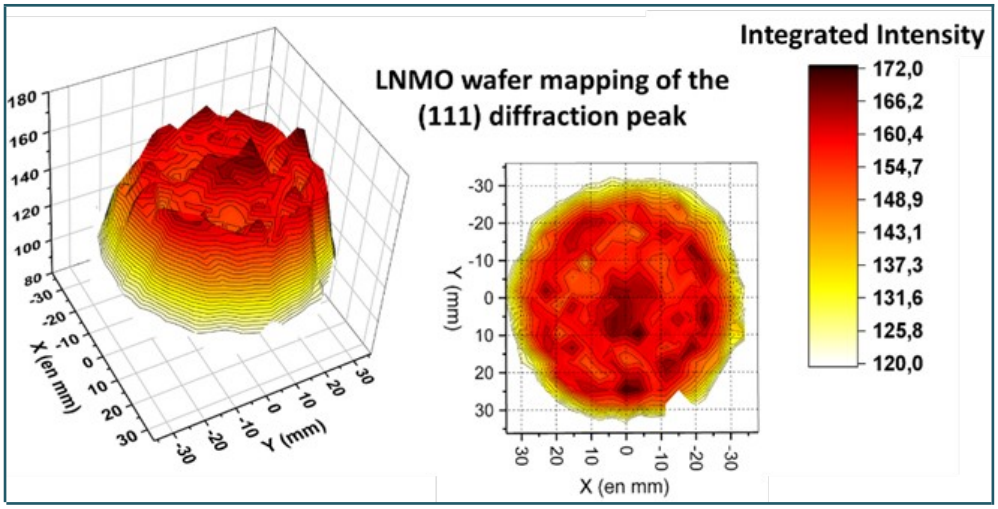

Figure 1: LMNO wafer mapping of the (111) diffraction peak

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Role of semiconductor properties in the performance of ZnO nanowires-based transducers

Andrés Jenaro Lopez Garcia, Manojit Pusty, Thomas Jalabert, Ran Tao, Alessandro Cresti, Mireille Mouis, Gustavo Ardila

andres-jenaro.lopez-garcia@grenoble-inp.fr

Piezoelectric transducers integrating nanowires (also known as nanogenerators-NGs) have been extensively studied over the last decade as an emerging technology for self-powered systems such as wearable devices. NGs-based on ZnO nanowires are good candidates for developing energy harvesting devices and mechanical sensors thanks to its low-cost, environment friendly, easy to process and low temperature fabrication process. Moreover, it has been demonstrated that ZnO NGs can produce a high output potential, in order of volts by applying a mechanical excitation [1], [2]. Most of the theoretical works considering the semiconducting properties such as the doping level in ZnO, could not account for this high piezoelectric response since the output potential decreases because of the screening effect of free electrons. A Surface Fermi Level Pining (SFLP) mechanism has then been proposed as an intrinsic property of ZnO NWs to solve this contradiction [3]. However, other important electrical parameters for the energy conversion efficiency, such as the piezoelectric coefficient d33, have not yet been investigated using models, led by coupling together semiconducting and piezoelectric properties.

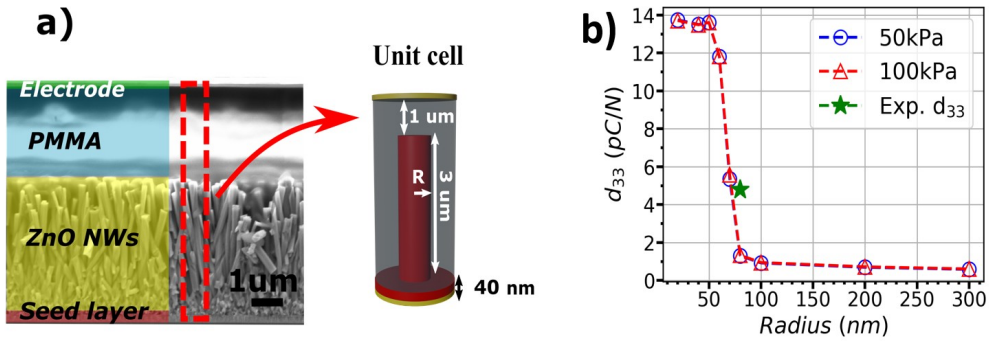

Figure 1. a) SEM cross section of a ZnO VING model and b) d33 values as a function of the NW radius for two values of applied pressure (adapted from [4]).

In this work, we present a new strategy both experimentally and numerically to determine the d33 coefficient [4]. The experimental procedure analyzes the generated voltage pulse after applying a

controlled compressive force over the ZnO NG. For a ZnO NW which is 3 μm in length and has diameter between 80 to 110 nm deduced from Figure 1a, we found an experimental d33 coefficient value of 4.8 pC/N (see green start in Figure 1b). This value is in good agreement with the numerical simulations we have performed by Finite Element Method (FEM), using the same geometry input parameters and the doping level and surface traps density from the literature for CBD grown NWs [5]. Finally, our numerical simulations also predict a significant dependence of d33 on the NW radius, from 14 pC/N for the smaller ones to 1 pC/N for the larger ones as depicted in Figure 1b. In our model, this dependency is governed by the material semiconducting properties such as doping level and surface trap density.

Acknowledgements

This work was supported by the Federation of Micro Nano Technologies (FMNT) in Grenoble, France and has received funding from project PULSE-COM of the European Union's Horizon 2020 research and innovation programme under grant agreement No 863227. The authors further acknowledge the support from the CNRS Renatech Network through the "Plateforme Technologique Amont" in a cleanroom environment.

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ZnO Nanowires Grown at Low Temperature on Gravure Printed ZnO Nanoparticle Seed Layers for Flexible Electronic Applications

Andres Jenaro Lopez Garcia, Giuliano Sico, Maria Montanino, Viktor Defoor, Manojit Pusty, Xavier Mescot, Fausta Loffredo, Fulvia Villani, Thomas Jalabert, Giuseppe Nenna[†] and Gustavo Ardila*

[†]giuseppe.nenna@enea.it
*ardilarg@minatec.grenoble-inp.fr

Zinc oxide (ZnO) thin films and nanostructures have received an increasing interest in the last decade due to its bio compatibility and the versatility of applications. ZnO nanowires (NWs) are excellent candidates for the fabrication of energy harvesters, mechanical sensors, piezotronic and piezo-phototronic devices thanks to the interplay between piezoelectric and semiconducting properties.[1] The growth of ZnO NWs on flexible substrates would further broaden its possible applications. However, such a growth requires low temperature synthesis to prevent any damage to the flexible polymer.[2] Another difficulty lies in the fact that the deposition of patterned ceramic thin films on flexible substrates is challenging, especially under vacuum free conditions. The gravure printing method is an interesting method to grow functional thin films due to its ability to produce excellent results at high speeds over a wide surface area.[3] Therefore, printing thin films using gravure printing offers several advantages like cost efficiency, use of low temperature, high throughput, and the possibility of patterning during the deposition process.

In this work, we report the chemical bath deposition (CBD) growth of high quality ZnO NWs on polyethylene terephthalate (PET) using gravure printing method to deposit a seed layer constituted of ZnO nanoparticles.

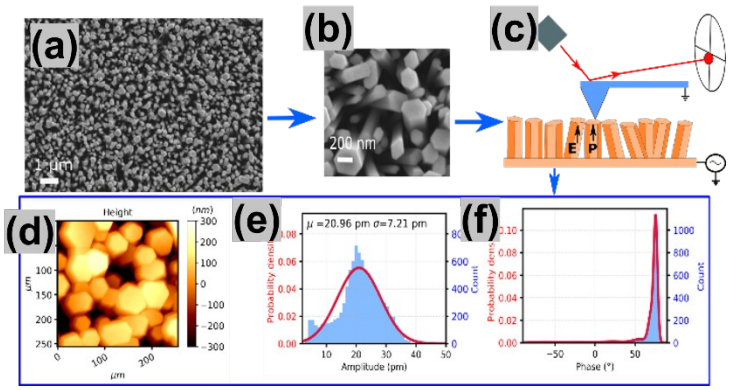

Figure 1: Shows the (*a*) SEM image of the ZnO NWs grown on PET, (*b*) magnified SEM image, (*c*) schematics of the PFM technique on the ZnO NWs, (*d*) PFM topography image of the ZnO NWs, (*e*) piezoelectric response amplitude histogram of ZnO NWs, (*f*) piezoelectric response phase histogram showing the homogeneity of the Zn poled domains.
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Using piezo-response force microscopy (PFM), we observed that the Zn-polar domains are homogeneously distributed within the grown ZnO NWs with a piezoelectric coefficient (d_{33}) close to 4 pm/V. This work demonstrates the decisive advantage of gravure printing over previous methods to deposit seed layers at low temperature on flexible substrates.[4] This opens the possibility of manufacturing completely vacuum-free solution-based flexible piezoelectric devices.

Acknowledgements

This work was supported by the Federation of Micro Nano Technologies (FMNT) in Grenoble, France and has received funding from project PULSE-COM of the European Union's Horizon 2020 research and innovation programme under grant agreement No 863227. The authors further acknowledge the support from the CNRS Renatech Network through the "Plateforme Technologique Amont" in a cleanroom environment.

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Simulation of the coupling between electrical current and energy current in a thermoelectric network

M-A. Mamouni[1,2,*] C. Goupil[2] Ph. Lecoeur[1]

[1] Center for Nanoscience and Nanotechnology (C2N), CNRS, Université Paris-Saclay, 91120 Palaiseau, France
[2] Laboratoire Interdisciplinaire des Energies de Demain(LIED), CNRS UMR 8236, Université Paris Diderot, 5 Rue Thomas Mann, F-75013 Paris, France

Contact : [*] Mahdi-Amine.mamouni@u-psud.fr

Known for nearly two centuries, thermoelectricity still raises many questions both at the fundamental level but also at the technological level to go beyond niche applications. For several decades, research in this field has therefore mainly focused on the search for materials with a better conversion efficiency, the latter being generally evaluated by the merit factor ZT historically proposed by the Russian physicist A. Ioffe [1]. This value depends on the intrinsic parameters of the material such as its Seebeck coefficient, electrical resistivity and thermal conductivity. This figure of merit reflects the capacity of the electron gas to transport entropy with regard to conduction losses, i.e. through the phonon network. The increase of the ZT is therefore generally sought in the reduction of the thermal conductivity of the material while maintaining a good electrical conductivity. This factor of merit is directly related to the ratio of the specific heat of the electron gas $\gamma=1+ZT$, which makes it possible to consider thermoelectricity as a study object combining electronics and thermodynamics. Although knowledge and manipulation of the various quantities, thermal conductivity, electrical resistivity and Seebeck coefficient is indispensable for the study and improvement of the materials, it is still insufficient for the development of thermoelectric systems. In particular, it is necessary to identify and characterize the coupling conditions of the developed devices with the thermal reservoirs, which complicates the measurements to be implemented and the understanding of the results.

PyDyCo is a solver able to compute the coupling between particle flux and energy flux in a thermoelectrical network. Using the nodal approach [2][3], the network is composed of small thermoelectrical dipoles with different properties each, on which a Dirichlet condition in terms of temperature and electrochemical potential at the network's boundaries is imposed. The calculation is made using the Spice library on Python, and with consideration of two distinct subnets, an electrical one and a thermal one. The two subnets are then coupled by the Onsager matrix. This approach aids in the consideration of different exotic inclusions in the network with varying properties and in the extracting of values of

temperature and electrical potential in every node of the network. PyDyCo solver can calculate the response of a network at the steady and at dynamical state and gives information on the latter. Two situations would be presented, one in steady state and one in dynamical state. Considering the results, the indented use of PyDyCo is to dimension complex thermoelectrical systems.

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Black Silicon as an Infrared Broadband Absorber

Sreyash Sarkar*, Frédéric Marty, Philippe Basset, Elyes Nefzaoui[§] and, Tarik Bourouina

ESYCOM, Univ Gustave Eiffel, CNRS, CNAM, ESIEE Paris, F-77454 Marne-la-Vallée, France.

corresponding author: *sreyash.sarkar@esiee.fr; [§]elyes.nefzaoui@esiee.fr

Radiative properties engineering is critical for a variety of applications involving the conversion and management of thermal radiation, including thermo-photovoltaics, thermal rectification, thermal memories, logical circuits, and radiative cooling, and has garnered increased attention in recent years [1]. We report on the infrared radiative properties of Black Silicon (BSi) in the thermal radiation spectrum region up to 20 µm, along with a morphological analysis of its surface features. BSi is a bottom-up nanostructured silicon surface that may be created using a variety of processes [2, 3], including wafer-level cryogenic plasma etching. Since [3, 4], it has been well known that such nanoscale structures result in a considerable increase in silicon absorptivity in the visible range [4]. We fabricated two BSi wafers with n-type doping of levels: $2 \times 10^{15} cm^{-3} (low\ doping), 5 \times 10^{19} cm^{-3}$ (high doping). The mean values of periodicity and height of the BSi structures were extracted from top and side-view SEM images using grey-level analysis in MATLAB: all hole centers were detected and each pixel corresponded to a height. The 3D reconstruction from side view SEM images of those two BSi samples are shown in Figure 1(a). One can plainly detect a considerable rise of the BSi peak's density with heavy doping. This is confirmed and quantified by statistical image processing using grey-level analysis : the number of etched holes has increased by a factor of more than three, the mean periodicity has decreased from 330 to 200 nm, and the number of higher structures (above 5 µm) has also increased significantly. Total reflectance and transmittance measurements of these samples were made experimentally using a Perkin Elmer Spectrum 3 FTIR Spectrometer in the spectral region of 2.5 to 20 µm at room temperature. Figure 1(b), shows the experimental spectral absorptance responses of these two samples along with their respective 20° tilt-view SEM images. As seen in Fig 1(b), one can note a clear difference between the absorptance of low doped sample and the highly doped one. For the highly doped sample, absorptance reaches 99.5% till 10 µm and then drops to 98%, whereas for the low doped sample the highest absorptance reached is 96% till 10 µm. At a given temperature, Kirchhoff's law of thermal radiation states that spectral emissivity equals spectral absorptivity. As a result, such high absorptance corresponds to a high emissivity in this particular wavelength range (1 – 15 µm). Due to these exceptional features, doped BSi can be an excellent choice for highly emissive infrared sources used in sensing applications or for thermal management applications such as passive radiative cooling.

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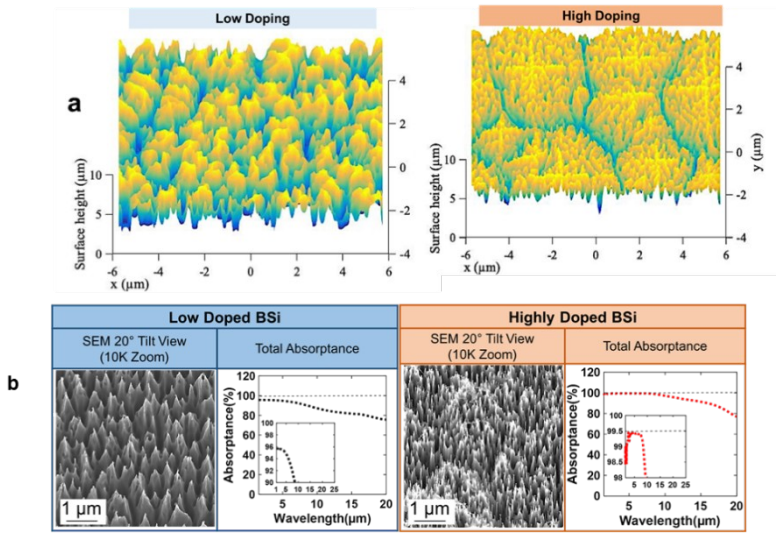

Figure 1: (a)*3D reconstruction using gray-level technique from SEM images and side-view SEM for low and highly doped silicon for a similar etching process: high-level doping results in the increase of the density of nano-structurations.*
(b) Measurements of absorptance on two BSi samples having low and high doping compared with their respective SEM 20° tilt micrographs, which shows the evidence of highest absorptance of 99.6% for highly doped sample till 10µm.

Abstract

Title: *Ab initio* calculations of electronic transport properties and of the thermoelectric phonon drag effect in semiconductors

Authors: Raja Sen[#], Jelena Sjakste, and Nathalie Vast

Affiliation: Laboratoire des Solides Irradiés, CEA-DRF-IRAMIS, École Polytechnique, CNRS UMR 7642, Institut Polytechnique de Paris, 91120 Palaiseau, France

[#]Presenting author

In the present work, we first consider the state-of-the-art computational techniques to accurately calculate the electronic transport properties of *n*-doped silicon. The calculations, performed with the EPW code [1], are based on the iterative solution of the linearized Boltzmann transport equation (BTE) coupled to the data obtained using density functional theory and density functional perturbation theory. Concurrently, a special focus is made in understanding the enhancement of the Seebeck coefficient by electron-phonon coupling, known as the "phonon-drag" effect [2]. To take this effect into account, we modified the standard EPW code so that it allows us to solve the BTE for electronic transport in presence of non-equilibrium phonon populations introduced by a temperature gradient. We will present our recent results related to electron-phonon scattering times, phonon and/or impurity limited carrier mobility, as well as the Seebeck coefficient of silicon. Our results for *n*-doped silicon not only show a good agreement with the experimental data [3] but also pave the way to further understand the contribution of phonon-drag in semiconductor nanostructures, which still remains largely unexplored.

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High throughput multiscale modelling of the thermal conductivity

B. H. Silva, D. Lacroix, M. Isaiev, L. Chaput

brunohartmann.silva@gmail.com

Abstract

In an ever more digital and electronic world, energy efficiency is a topic of increasing importance. In this context, new technologies often rely on new materials and compounds which can be tailored at micro and nanoscales. The relevance of electrical and thermal conductivity in such nano devices demands more accurate techniques to evaluate them; fine knowledge of the later is a key point to reduce energy consumption and manufacturing costs. Bulk properties of materials can be obtained experimentally or theoretically, and the quantum behaviour of crystal vibrational modes is somewhat well known [1, 2]. Nonetheless, the translation of phonon bulk properties to the thermal characteristics of nano and microscale devices, which can comprise different shapes and materials, is a problem yet to be solved. Our work proposes to use a Monte Carlo approach [3, 4] to statistically estimate the Boltzmann Transport Equation for phonons in nano and microscale geometries.

The method comprises in the sampling of vibrational modes from ab-initio calculations. These modes are represented by particles carrying information about the number of phonons of that mode, drifting through the domain according to their correspondent group velocity. In the Monte Carlo approach, these particles are randomly generated according to the imposed boundary conditions and simulation parameters. Scattering is calculated using the relaxation time approximation, which is obtained from ab initio calculations. The effective thermal conductivity of the simulated device can then be calculated from the results. Preliminary studies in thin films in the out of plane direction show good predictions of thermal conductivity with different temperatures and film thickness, agreeing with previous studies [1, 2]. As temperature decreases, the higher relaxation times reflect in an increase of ballistic transport. The same evolution can be seen as the thickness of the thin film decreases, deviating from the linear temperature profile predicted by Fourier's law.

In our work, the whole code is written in Python, relying on modules such as NumPy [5] for vectorization and Trimesh [6] for geometry handling. Next improvements include geometry generalisation, convergence detection, imposed heat flux and surface roughness as boundary condition. The final framework will include coupling of the Monte Carlo simulation to artificial intelligence algorithms to optimise nanodevices.

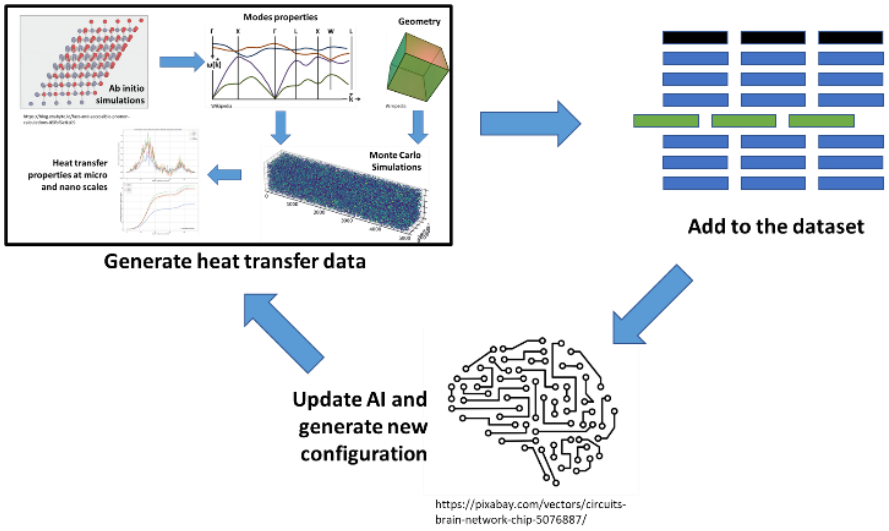

Figure 1: Schematics of the coupling of artificial intelligence to the Monte Carlo simulation to optimise nano devices' thermal properties from ab-initio data.

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Flexible and wearable plasmonic-enabled organic/inorganic hybrid photothermoelectric generators

Chenghao Xin, Lionel Aigouy and Zhuoying Chen*

LPEM, ESPCI Paris, PSL Research University, Sorbonne Université, CNRS, 10 Rue Vauquelin, F-75005 Paris, France

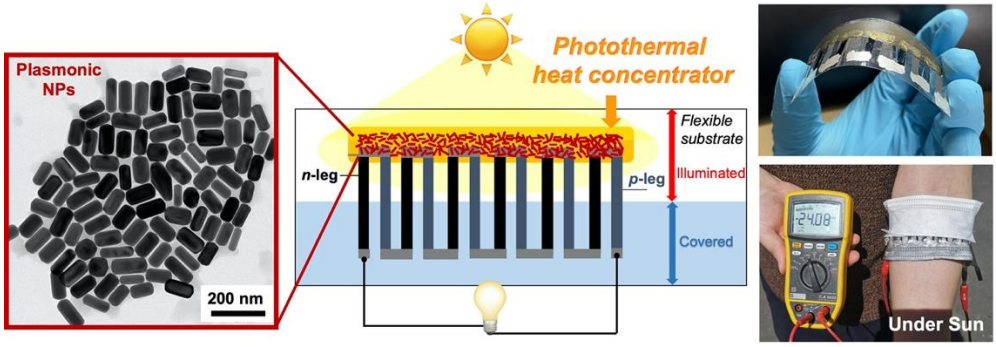
*** Corresponding author. Email address: zhuoying.chen@espci.fr (Z. Chen)**

Thermoelectric (TE) devices based on solution-processed conjugated organic and organic-inorganic hybrid materials represent currently an emerging system for near-ambient energy harvesting applications (< 200 °C). While many previous examples demonstrated only TE conversion, recently, new application needs have emerged requiring photothermoelectric conversions, aiming to perform light harvesting and in some case positioning for device integration into multifunctional smart textile. By comparison photovoltaic technologies, photothermoelectric generators can offer their unique functionality in both situations with light (e.g. by light-induced temperature difference) or without light (e.g. by environment-induced temperature difference). So far, flexible organic and hybrid photothermoelectric generators exhibited only modest performance (e.g. a voltage output of 1.48 mV under sun light; [1]0.677 mV and 0.0636 nW under sun light when worn on arm; [2]9.8 nW under 1-sun illumination.[3] How to achieve flexible photothermoelectric generators with more significant voltage and power output remain currently a hot topic of research.

Solution-processed organic and organic-inorganic hybrid thermoelectric (TE) devices are currently emerging systems for multifunctional energy harvesting and smart textile integration. In this work, [4] a series of solution-processed and flexible organic-inorganic hybrid photothermoelectric generators are fabricated, applying the strong photothermal effect of colloidal plasmonic gold nanoparticles (Au NPs) on optimized *p/n*-type TE modules based on the coupling PEDOT:PSS and with different *n*-type materials. Under simulated 1-sun illumination, optimized hybrid photothermoelectric generators on polyethylene terephthalate (PET) substrates were achieved by Au-NP-coated PEDOT:PSS/Ag_2Se couples, capable to generate a voltage output of 34 mV and a maximum power output of 146 nW, which is drastically larger (by 13 folds) than that achieved on the control devices without NPs. Wearable photothermoelectric generators were further fabricated on polypropylene nonwoven fabrics, exhibiting a voltage output of 24 mV under natural sun light in air when worn on arm. This work highlights the strong potentials of the plasmonic photothermal NPs and their integrations into organic and hybrid TE devices for light harvesting without the need of complex light concentration techniques.

* Corresponding author. Email address: zhuoying.chen@espci.fr (Z. Chen).

The optimized hybrid photothermoelectric generators achieved offer also bright perspectives for the development of energy harvesting smart textiles.



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