PROJECT III.1B
ENERGY HARVESTING MATERIALS AND DEVICES

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OBJECTIVES

- Design and optimization of Energy Scavengers for autonomous Microsystems
- Novel materials for high efficiency energy conversion (mechanical, thermal, etc)
- Development of MEMS-based vibrational harvesters with improved power characteristics
- Development of Flexible Energy Harvesters with Nanotextured Films
- Multifunctional ZnO Nanostructures for Smart Textiles & Biomedical Applications

FUNDING

- "*Development of Innovative sensor systems offering distributed intelligence – MEMSENSE*", National Funds and European Regional Development Funds, NSRF 2007–2013, contract no. 45 (5/2009 - 2/2013)
- "*Nanostructured ThermoElectric Systems for Green Transport & Energy Efficient Applications*", NanoTEG, EU ENIAC (7/2011-6/2014)
- *"Self-assembled ZnO Nanostructures for Engineered Neuronal Networks",* European Regional Development Fund (ERDF) under the Hellenic National Strategic Reference Framework (NSRF) 2007-2013, Hungarian-Greek Intergovernmental S&T Cooperation Programme, Contract No HUN53 (9/2012-8/2015)

MAIN RESULTS in 2012

Energy Scavenging from the ambient has been actively explored using several methods such as solar power, electromagnetic fields, thermal gradients, fluid flow, energy produced by the human body, and the action of gravitational fields. Mechanical vibration is a potential power source, which is easily accessible through Microelectromechanical Systems (MEMS) technology for conversion to electrical energy. The reported examples use a mass–spring system that resonates when the frame of the device is vibrated. The motion of the mass relative to the frame is damped by one of several energy conversion mechanisms, namely electromagnetic force, electrostatic force, or piezoelectric force.

From these scavenger types, the ones based on piezoelectric principle appear to be very promising and has been the main target of our activities. MEMS-based as well as microgenerators based on flexible substrate has been fabricated and characterized. Arrays of ZnO nanowires as well as nanostructured ZnO films have been exploited as the energy converting material. This is due to the unique properties of ZnO as well as the potentiality to growth ZnO at low temperatures using low cost, large area hydrothermal techniques.

In addition, new applications for ZnO technologies have been identified and pursued ranging from pyroelectric energy harvesters, smart textiles to control of surface wettability and biomedical applications.

SOI-based Vibrational Energy Harvesting Microgenerators

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The miniaturization of MEMS devices and the corresponding decrease of their consumption solves only partially the requirement for autonomous wireless sensor devices. Rendering a device completely autonomous and battery-free has as a prerequisite the development of equally miniaturized power micro/nanogenerators that can become an integral part of the sensor chips. ZnO-nanowire nanogenerators have successfully converted nanoscale mechanical energy into electricity, but the production of a viable, cost-efficient micro-nanogenerator that can be readily integrated on-chip along with the devices to be powered-up is still elusive. Towards this goal, we have successfully fabricated a cantilevered microgenerator based on SOI technology employing as its functional core a novel nanotextured ZnO film as the piezoelectric material.

As starting material, SOI wafers were used with a silicon overlayer thickness –and hence a cantilever thickness- of 5μm. The piezoelectric nanotextured layers, sandwiched between aluminum electrodes, were developed via the hydrothermal technique on seeding layers that were either deposited by sputtering or by spin-coating of solutions (sol-gels and zero-gels). During the growth the wafers were placed face down on the surface of aqueous equimolar solutions of zinc nitrate hexahydrate [$Zn(NO_3)_2.6H_2O$] and hexamine (HMTA). Depending on the growth conditions (solution concentration, temperature, duration) the properties of the piezoelectric material could be tuned according to the required specifications. Fig. 1 is a photograph of a single die containing 4 microgenerators. We can distinguish the proof mass as well as the electrodes of the device. Fig. 2 shows that the hydrothermal technique can produce in a controlled and repeatable way highly textured columnar ZnO films with a thickness of up to several μm.

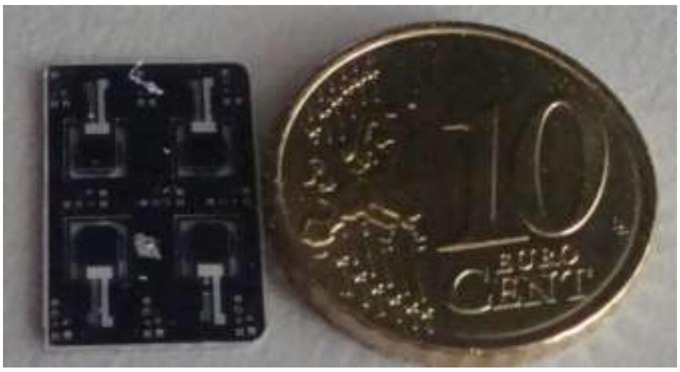

Fig. 1. *Photograph showing the actual size of single die containing 4 microgenerators.*

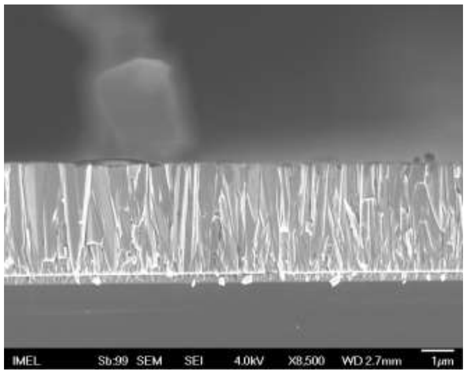

Fig 2. *ZnO nanotextured film on Al electrodes.*

The microgenerators containing the ZnO nantoextured films even when imposed to random impulses were able to provide output voltages up to hundreds of mV for open circuit (Fig.3, 4). Detailed measurements and a systematic analysis are performed for various mechanical excitations and external loads showing the feasibility of the proposed methodology for on-chip power generation. It is important to note that the measurements are performed in air. The presence or air has a significant impact of device performance due to damping phenomena and results in significant reduction (more than 2 orders of magnitude) of voltage and thus power output.

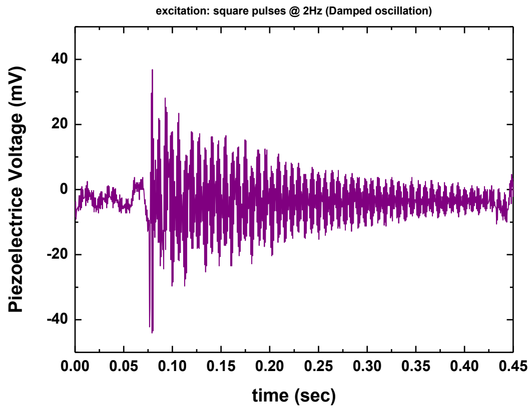

Fig. 3. Microgenerator voltage as a function of time upon excitation by square pulses. The measurements are performed in air.

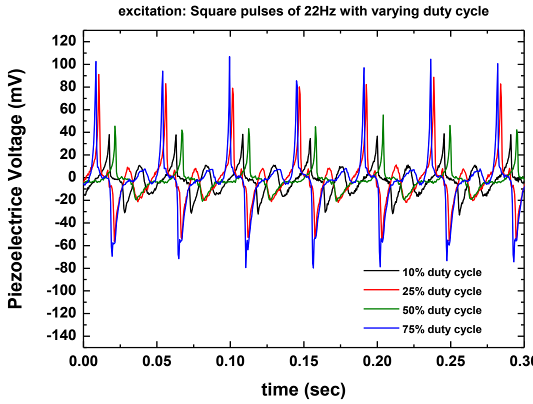

Fig. 4. Microgenerator response upon excitation of square pulses of various duty cycles :10%(black), 25% (red), 50% (green) και 75% (blue).

Flexible piezoelectric microgenerators based on nanotextured ZnO films

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Piezoelectric microgenerators were developed onto flexible substrates employing novel nanotextured ZnO grown on Kapton/PET substrates. It is known that the growth of ZnO nanowire arrays as well as nanostructured ZnO films requires the presence of a ZnO seeding layer onto the substrate. This layer provides the necessary nucleation sites upon which the ZnO nanostructures can grow and develop. Traditionally, fine (50-200nm) ZnO films deposited by sputtering have been used to facilitate the hydrothermal growth. However, in order to further reduce cost alternative methodologies are required. In our approach we have used two alternative chemical techniques based on zero-gels with the scope to further reduce the fabrication cost and complexity and to optimize the fabrication time.

All devices are employing either high-density vertical-ZnO nanorod arrays or nanotextured ZnO films grown via a facile, low-cost hydrothermal method on Kapton and Polyethylene terephthalate (PET) substrates (Fig. 1). The first method exploits ZnO seeding layers formed by sputtering, and the other two purely chemically developed seeding layers by spin-coating of HMTA-based sol-gel and zinc-acetate ethanol solution. Typical output voltages achieved under instantaneous and sinusoidal external excitation reached up to 4V (Fig. 2,3). The alternative fabrication techniques are compared in order to assess their performance in terms of output power versus cost and ease-of-fabrication and to optimize a rapid and cost-efficient method for driving small and low-power devices (Fig. 4).

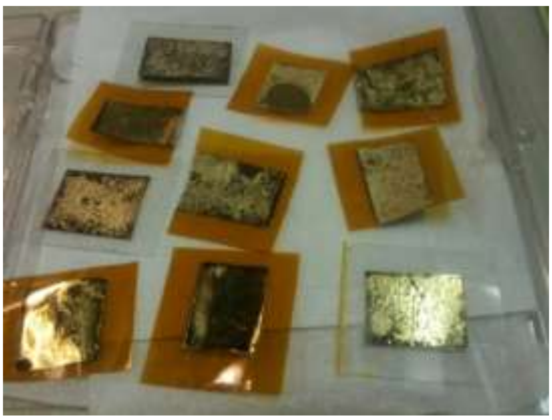


Fig 1: Photograph of microgenerators on kapton and PET.

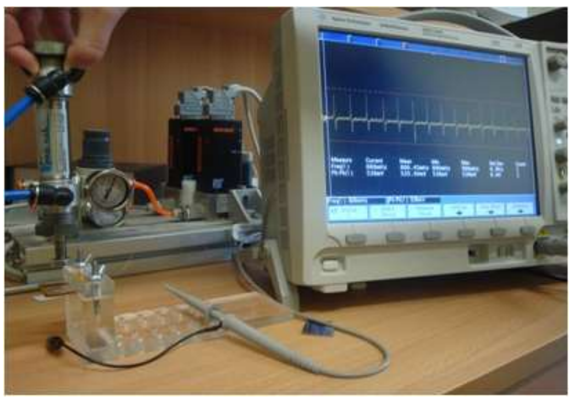


Fig. 2: Photograph of the measurement setup.

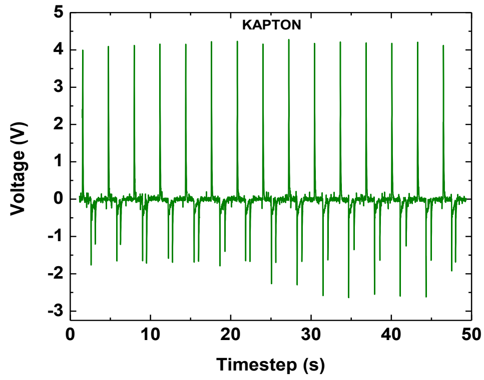


Fig. 3. Output voltage as a function of time for a flexible microgenerator on a Kapton substrate.

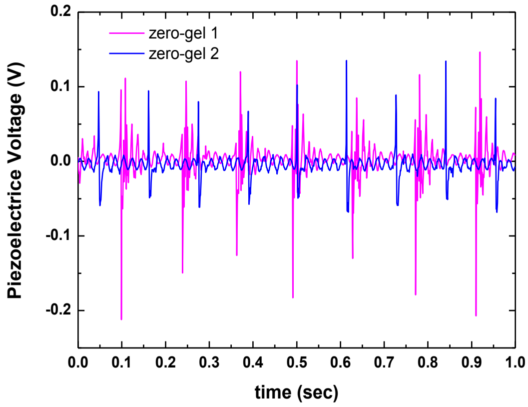


Fig. 4. Comparison of microgenerators on Kapton using the two alternative seeding layer techniques.

Multifunctional ZnO Nanostructures for Biomedical Applications & Smart Textiles

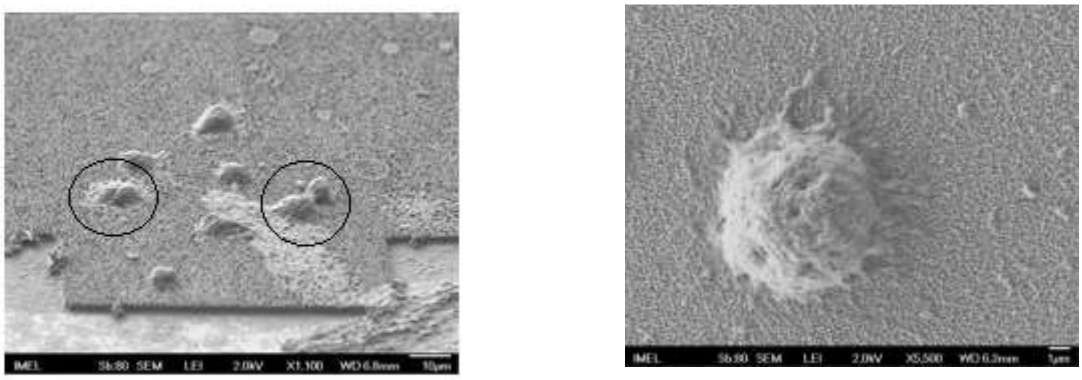
E. Makarona, Th. Kyrasta, Z. Georgoussi, A. Kritharidou and C. Tsamis

The human brain contains more than 100 billion neurons and at least nine more times glial cells. These cells connect among themselves through synapses building a network of immense complexity. In order to comprehend how the brain function, it is important to elucidate how synapse form and how the biochemical signals relate information to one another. So far neuroscientists and neurophysiologists employ tow different approaches: (i) either the use of thin brain slices –which even though they maintain the inner structuring of the brain intact, contain a very large number of cells rendering single-cell observation impossible, and (ii) neuronal cultures –which allow single-cell or cell-to-cell observation and the recording of biochemical events in cells, but in general are not easy to organize on predefined patterns or control the connectivity of the cells. One of the open issues is to fabricate templates where the cells will selectively adhere on predefined patterns while they will be guided to form connections on preselected pathways**.** Of course, such templates should maintain the viability and functionality of the cells over the course of several days, necessary for the full development of the networks.

Towards this goal a new methodology for the production of patterned templates suitable for the development of neuronal networks is currently being developed. The templates are designed to control through nanotopographical features the selective adhesion of neuronal cells on predefined locations of the pattern while preserving the viability of the cells and guiding the formation of synapses along preselected pathways. The methodology explored has at its core the hydrothermal growth of ZnO nanostructures which is a very versatile method allowing the control of the morphological characteristics of the nanostructures through tuning of simple key parameters. The methodology is mainly focusing on the development of ZnO nanostructures on Si wafers with standard microfabrication techniques in order to establish its potential for mass production and integration with other types of microelectronic devices.

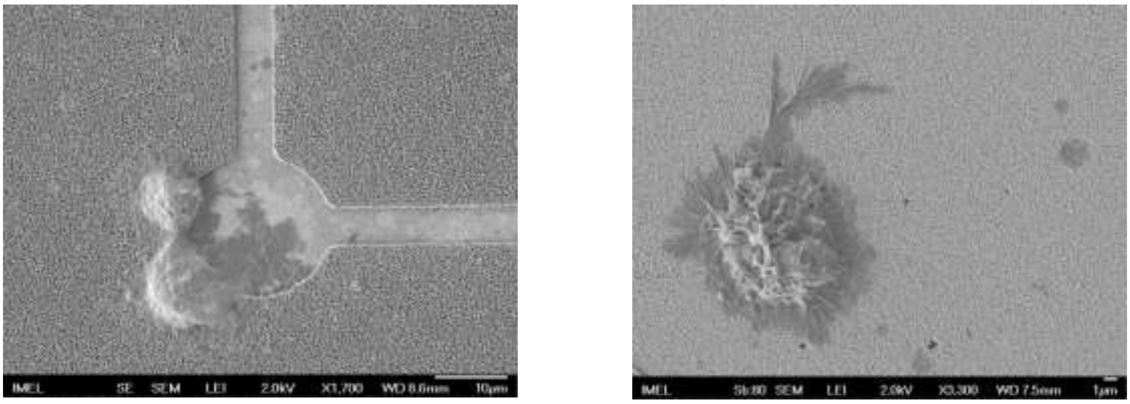
The biocompatibility and cell viability studies were performed in parallel with the template fabrication optimization studies. HEK (Human Embryonic Kidney) and Neuro2A (mouse neuroblastoma cells) were cultured onto the patterned templates and it was confirmed that the ZnO nanostructures are indeed biocompatible and can maintain cell viability and proliferation (Figure 5).

A very important finding was that the cells tended to adhere onto the nanorods, and a minimum amount, less than 15%, was attached to the flat surfaces, even though these surfaces are topographically more relevant to the conventional glass slides used for culturing. In addition, the cells tended to adapt to the shape of the lithographic patterns rather than migrate to the flat areas (Fig. 6a). The cells proliferated and neurite outgrowth was also observed (Figure 6b) suggesting that networking should be feasible upon activation of the neurons. In other words, selective adhesion of cells guided through nanotopographical features was achieved.



(a) (b)

Fig. 5. SEM images of Neuro2A cells after 72hrs of culturing on patterned Si wafers with ZnO nanorods where it is evident that the cells maintain their viability, their shape and functionality, and they can proliferate (encircled regions) and extend philopodia (magnification to the right)

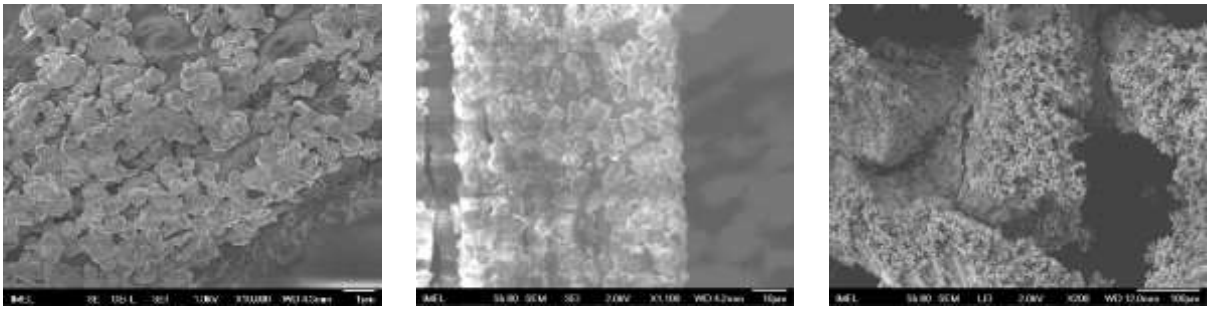


(a) (b)

Fig. 6. Characteristic SEM images of Neuro2A cells after 48hrs in culture over the templates with ZnO nanorods where (a) a clear preference of the cells to adhere onto the nanorods and conform to the borderlines of the patterns, and (b) neurite outgrowth were observed.

In parallel, a new activity has begun focusing onto the integration of ZnO on fabrics for the creation of smart textiles that can be employed in a plethora of applications such as antimicrobial coatings, energy harvesting fabrics and athletic garments. E-textiles, also known as electronic textiles or smart textiles, are fabrics that enable digital components and electronics to be embedded in them. Many intelligent clothing, smart clothing, wearable technology, and wearable computing projects involve the use of e-textiles. Electronic textiles are distinct from wearable computing because emphasis is placed on the seamless integration of textiles with electronic elements like microcontrollers, sensors, and actuators. Furthermore, e-textiles need not be wearable; for instance, e-textiles are also found in interior design.

Initial results where the hydrothermal growth of ZnO nanorods has been applied to several types of natural (cotton, silk and linen) and synthetic fabrics (polyester and acrylic) are very promising and already show a great potential for the production of smart textiles with an emphasis in energy harvesting applications (Fig.7).



(a) (b) (c)

Fig.7. Successful implementation of ZnO nanorods on (a) silk, (b) cotton and (c) polyester fabrics for the development of smart textiles for energy harvesting applications

PROJECT OUTPUT in 2012

Conference Presentations

1. *Comparison of ZnO-based Piezoelectric Nanogenerators on flexible substrates,*
   G. Niarchos, E. Makarona, Th. Kyrasta, G. Voulazeris, Th. Speliotis, C. Tsamis, L. Lin, Y. Hu, Z. L. Wang
   CIMTEC 2012, Symposium E: Next Generation Micro/Nano Systems, June 10-14, 2012, Montecatini Terme, Italy
2. *SOI-based Vibrational Energy Harvesting Microgenerators,*
   G. Niarchos, E. Makarona, G. Voulazeris, Th. Speliotis, A. Arapoyanni, C. Tsamis
   EUROSENSORS XXVI, 9-12 September 2012, Kraków, Poland
3. *ALD deposited ZrO_2 ultrathin films on Si substrates: morphology and electrical evaluation,*
   M. Botzakaki, G. Skoulatakis, N. Xanthopoulos, C.Tsamis, E. Makarona, S. Kennou, S. Ladas, S.N. Georga and C.A. Krontiras
   XXVIII Panhellenic Conference on Solid State Physics and Material Science
4. *ALD deposited ZrO_2 ultrathin layers on Si and Ge substrates: A multiple technique characterization¸*
   M. Botzakaki, G. Skoulatakis, N. Xanthopoulos, C.Tsamis, E. Makarona, S. Kennou, S. Ladas, S.N. Georga and C.A. Krontiras
   5th International Conference on Micro&Nanoelectronics, Nanotechnology and MEMs
5. *Flexible piezoelectric microgenerators based on nanotextured ZnO films,*
   E. Makarona, G. Niarchos, G. Voulazeris, C. Tsamis,
   To appear in SPIE Microtechnologies, 24 - 26 April 2013, Grenoble, France

Published Conference Proceedings

1. Special Issue: 25th Anniversary Eurosensors XXV, Sensors & Actuators: Physical, Eds.: C. Tsamis & G. Kaltsas (2012)
2. Special Issue: 25th Anniversary Eurosensors XXV, Sensors & Actuators: Chemical, Eds.: C. Tsamis & G. Kaltsas (2012)

Masters Dissertations completed in 2012

1. *Vibrational energy harvester for Wireless Sensor Networks,*
   S. Katsaridis,
   Dept. of Informatics and Telecommunications, Univ. of Athens, April 2012
2. *Modeling and Fabrication of a Piezoelectric Energy Harvester Collecting the Ambient Mechanical Energy From Environmental Vibrations,*
   G. Voulazeris
   Dept. of Informatics and Telecommunications, Univ. of Athens, October 2012