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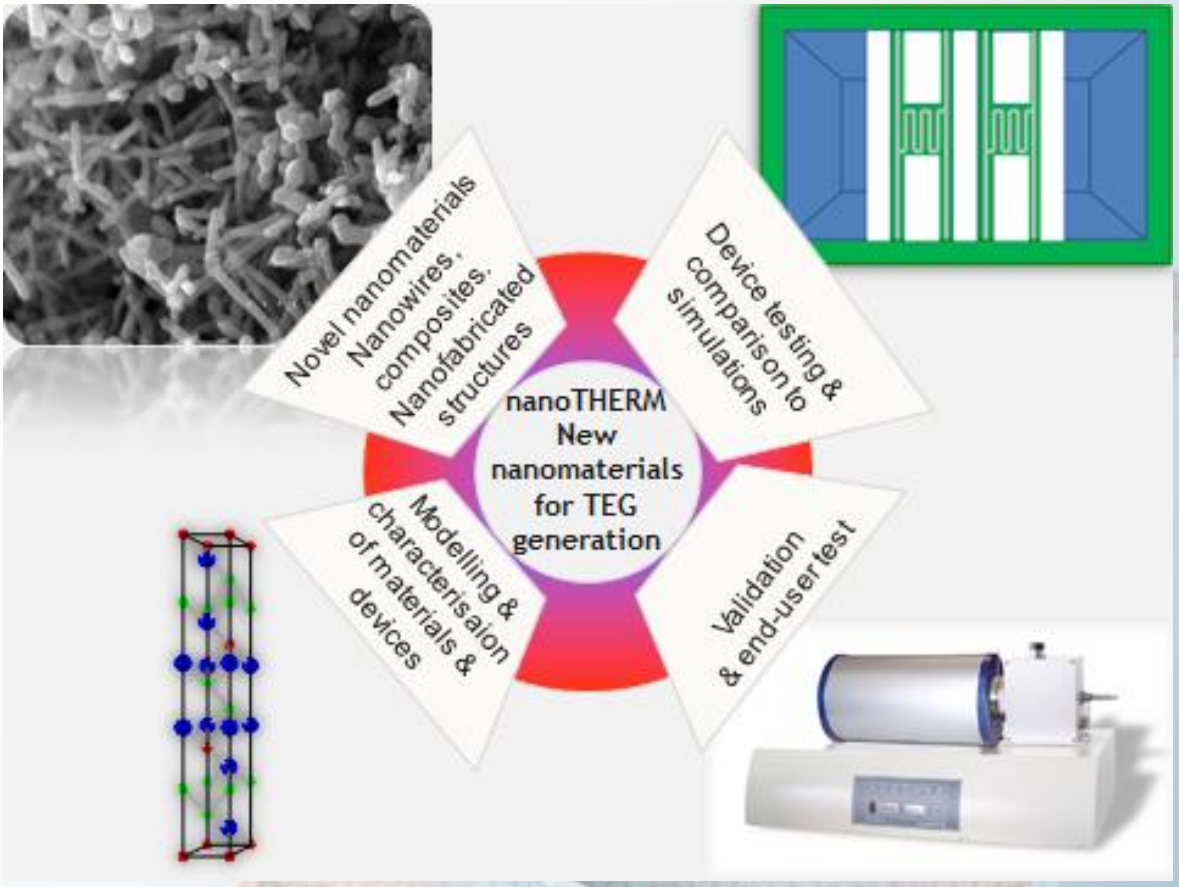
nanoTHERM – tailoring electronic and phononic properties of nanomaterials: towards ideal thermoelectricity is a **CONSOLIDER-Ingenio 2010** research program that runs from 2010 to 2015. It aims at producing a considerable breakthrough in the understanding of the fundamental physics underlying thermoelectricity to produce next-generation thermoelectric materials and devices



In this issue:

Perspectives of advanced thermoelectric materials in energy generators

Worldwide energy demand is expected to exponentially grow, in agreement with world population projections. Renewable energy technologies have attracted significant attention. Thermoelectric modules are solid-state devices that directly convert thermal energy into electrical energy

Renewable energy technologies have attracted significant attention (e.g. solar, wind or geothermal, to name a few). For instance, the installed photovoltaic capacity has reached values of 39.6 GW in 2010, being led by EU as a result of sustainable policies (e.g. 2020 targets) in conjunction with feed-in-tariffs. Grid parity is expected to be achieved during 2015-2017 for this relatively mature technology [1].

Thermoelectric modules are solid-state devices that directly convert thermal energy into electrical energy (Seebeck effect in TEGs). Or viceversa, they produce a temperature gradient upon the application of voltage (Peltier effect). Currently, thermoelectric devices are predominantly used in cooling, such as small and mobile refrigerators, cooled car seats, temperature regulators of semiconductors as well as medical and scientific instruments [2]. For power generation, the thermoelectric efficiency is defined by combining the Carnot efficiency and the figure-of-merit. Therefore, increasing energy efficiency requires both high ZT and a large gradient across the thermoelectric materials. Commercial thermoelectric devices possess a ZT of 0.8 and operate at an efficiency of only around 5-6%. However, TEGs with materials performing ZT=4 would exhibit energy efficiencies close to 30% [2]. In fact, with relatively small progress in materials the efficiency of present thermoelectric devices would reach efficiency levels comparable to thin film single junction photovoltaic i.e., around 10%. Taking into account that an average of 60% input of the energy on the society is wasted as heat. There are many “free” or “sustainable” energy sources. The key is to design systems with competitive electricity cost i.e., investment cost €/Wp [3].

For practical applications, several factors have to be in the choice or materials properties is necessary, taking into account temperature range, thermoelectric efficiency, materials abundance and toxicity, cost and device reliability [4]. These requirements should be evaluated for any specific application through engineering parametric analysis, which still missing in the thermoelectric field in most cases, especially for high temperature, T>200ºC applications.

While power applications, thermoelectric generators have demonstrated their use in space applications, a set of terrestrial applications are expected in the 10-20 years horizon for TEGs: especially for residual waste-heat recovery, as well as other emerging ones such as solar thermal energy conversion technologies. In fact, a key driving force for the technology is the renewed industrial interest from the automotive industry [2, 4]. Giants of the sector are interested in recovering waste-heat from exhaust engines and radiators, which accounts for about 70% of the fuel energy since the mechanical efficiency is approximately only 20-30%. In fact from 2012, European legislation will penalize manufacturers exceeding the CO2 emissions limit [4]. Commercial deployment is expected to lead to a huge economic impact with projections of 175-200 €M from 2015 to2020. If a figure-of-merit of ZT=2 can be obtained, the total market for TEGs could

increase by a factor of between 10 and 100.

The nanoTHERM project targets tailoring electronic and phononic properties of nanomaterials. The final goal is improving ZT of beyond present limitations of materials for bases low and medium temperature ranges. In particular, LEITAT is involved in the development of organic thermoelectric materials based on intrinsically conductive polymers.

The interest in relies on the fabrication of future thermoelectric devices by means of low-cost printing technologies, in analogy with other printed electronic devices or emerging polymer solar cells.

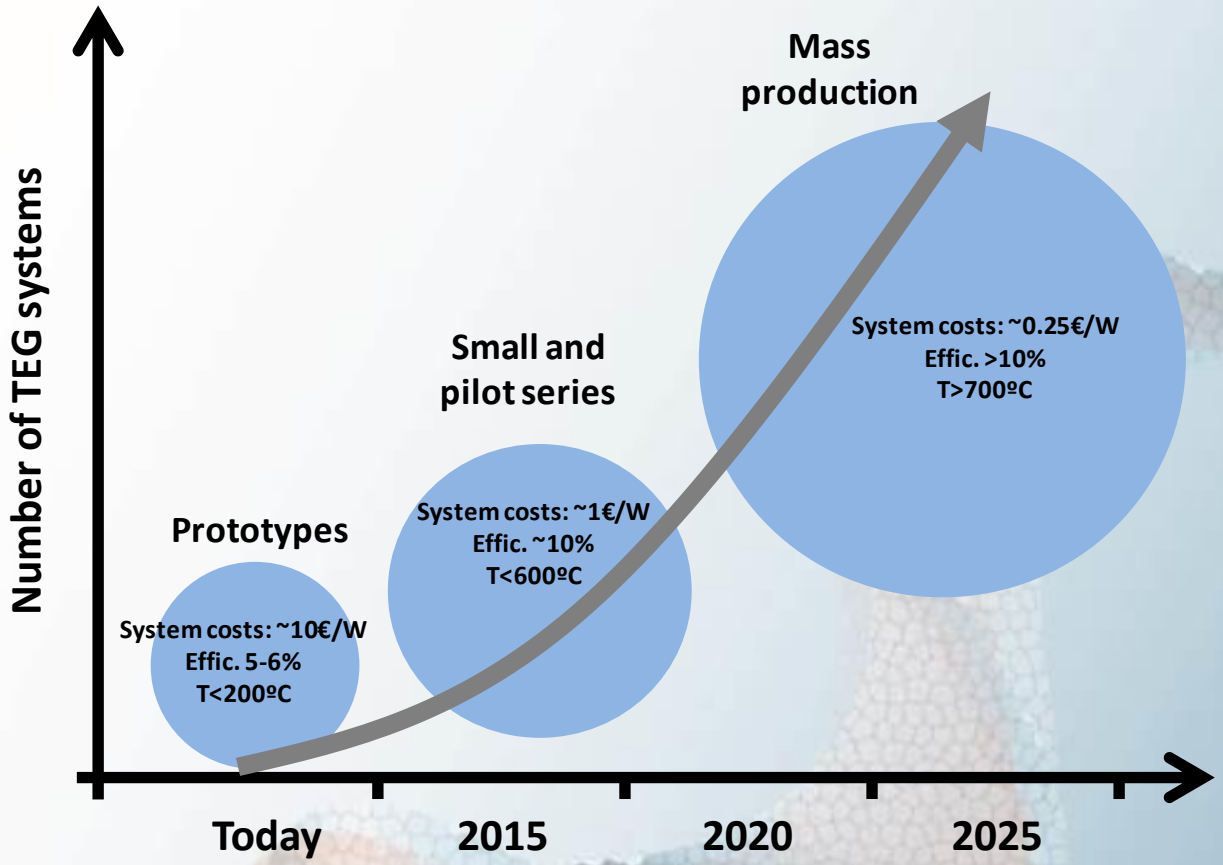


Figure 1. Market requirements roadmap for thermoelectric generator systems. Adapted from ref. [4]

References:

1. Annual ASIF report 2010(http://www.fotovoltaica.com/iasif10.pdf)
2. J R Sootsman, DY Chung, MGKanatzidis: New and old concepts in thermoelectric materials, *Angew. Chem. Int*. **48** 8616 (2009)
3. M Zebarjadi, K Esfarjani, MS Desselhaus, ZF Ren, G Chen: Perspectives of thermoelectric: from fundamentals to device applications, *E Env Sci* **5** 5147 (2012)
4. Observatory NANO briefing nº 17: Thermoelectricity for energy harvesting June 2011 (http://www.nanopinion.eu/sites/default/files/observatorynano_briefing_no.17_thermoelectricity_for_energy_harvesting.pdf)

Dr. David Gutierrez, LEITAT

Pushing the state-of-the-art of organic nanocomposite thermoelectric materials

Within the NanoTHERM consortium we were able to produce composite films of poly(3-hexylthiophene) and carbon nanotubes (P3HT/CNTs),an produced offering a very competitive room temperature thermoelectric performance.

Thermoelectric power generators of TEGS are solid-state devices that directly convert heat flow to electricity. Unique advantages are their scalability and ability to function with small heat sources and limited temperature differences. Thin and flexible designs that can cover large areas are particularly suited for waste recovery in industrial settings from chimneys to data centres.

On the other hand, a miniature power source would be of great benefit for myriad of autonomous electronic components such as wireless sensors and identification tags, envisaged to make up tomorrow's Internet of Things. Without doubt, large-area as well as small-scale applications will only become viable if cost-effective and robust materials with good thermoelectric properties can be identified. In this paper we concentrate on organic semiconductors and demonstrate that optimally doped conjugated polymer–carbon nanotube composites can offer a competitive performance.

We produced composite films of poly(3-hexylthiophene) and single- as well as multi-walled carbon nanotubes (P3HT/CNTs), with a very competitive thermoelectric performance at room temperature. The power factor significantly exceeds values obtained with either constituent alone, provided that the conjugated polymer is sufficiently p-doped. The use of single-walled carbon nanotubes consistently results in a much improved electrical conductivity with a maximum value above 1000 S/cm, giving rise to a top power factor of near 100 mW/(m.K2) for compositions in the 40 to 80 wt% range.

Moreover, since a carbon nanotube content of about 10 wt% does not appear to compromise the low bulk thermal conductivity of the polymer matrix, we can foresee that a thermoelectric figure of merit ZT (300 K) of ca. 0.2 is within reach with this type of composite material.

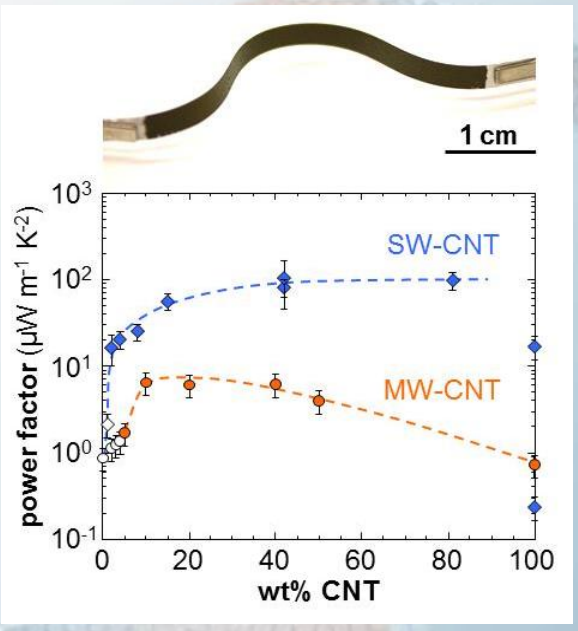


Fig. 4 Thermoelectric properties of $FeCl_3$-doped P3HT/CNT composites.S_2s of composites based onMW-CNTs (red circles) and SW-CNTs(blue diamonds) that were doped for one hour with 0.03 M $FeCl_3$ in nitromethane. Solid lines represent fits: s of P3HT/MW-CNT was fitted with a linear regression and s of P3HT/SW-CNT was fitted with eqn; the average hSi of all doped samples excluding reference CNT was calculated; S_2s fits were produced by combining the fits of s and S. Filled symbols: s measured with the van der Pauw technique; open symbols: s measured in 2-point configuration.

References: C Bounioux, P Díaz-Chao, M Campoy-Quiles, M S Martín-González, A R Goñi, R Yerushalmi-Rozen and C Müller, Thermoelectric Composites of Poly(3-hexylthiophene) and Carbon Nanotubes with a Large Power Factor, *Energy Environ Sci* **6** 918 (2013)

Prof Alejandro Goñi, ICMAB-CSIC

Thermal diffusivity of polyaniline and polyaniline/nanoclay composites

For low temperature, thermoelectric applications polymer-based materials contribute possible cadidates. However they present forming double challenges. Here, an initial work on polymer-based composite's presented.

Her poster presented the first measurements of thermal diffusivity on polyaniline and nanoclay-embedded polyaniline samples fabricated by Leitat Technological Center in the frame of the CONSOLIDER project nanoTHERM.

In the search of cleaner source of energy, thermo-electrical materials are good candidates for cost-effective energy harvesting. The mechanical flexibility of polymers makes them material of interest and among them polyaniline is promising for its intrinsic properties: high electrical conductivity, ease of processing, simple doping chemistry and environmental stability. The incorporation of nanoclays in the polymer is expected to act as phonon scatterimgcentres, reducing the thermal conductivity without affecting the electrical properties, thus increasing the figure-of-merit ZT.

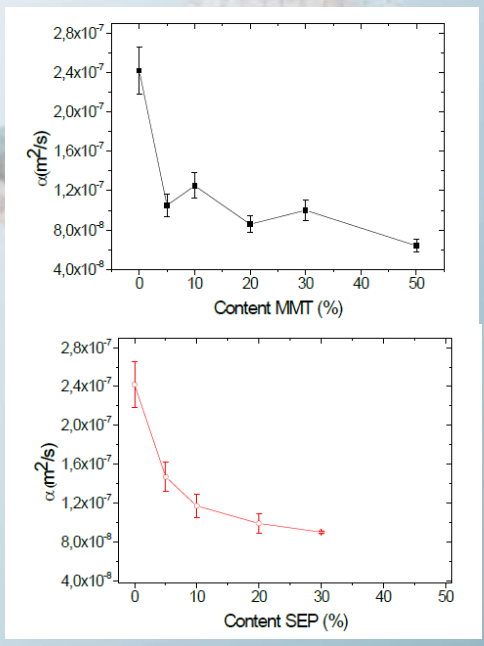
In this work, the thermal diffusivity of the polyaniline and polyaniline with nanoclays was studied, using a new experimental set-up at IMM developed under NANOTHERM project. The novel experimental set-up is based on the steady-state method and used to obtain the thermal diffusivity of the different bulk thermoelectrics materials, which is a property not easy to measure..

The thermal diffusivity is directly related with the thermal conductivity following $\alpha = \kappa/\rho C_e$. The new experimental set-up designed and build at IMM was able to measure the thermal diffusivity of PANI and nanoclay-embedded PANI samples.

These were prepared at LEITAT Technological centre where also the specific heat was measured by Differential Scanning Calorimetry and from which the thermal conductivity was determinate.

Motivated by these good results on the thermal properties, the research is now focusing on the Seebeck coefficient and the electrical conductivity. However, they need further improvement to be considered as thermoelectric commercial material. .

Figure 1: Thermal diffusivity decreases with nanoclay content. Figure 2.Nanoclaysact as dispersive centres of phonons



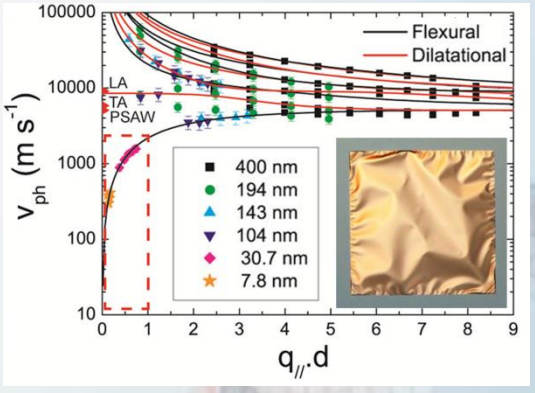
PhD Student IMM-CSIC Dra. Marisol Martin Gonzalez Best Poster award at SINANO2012, the 1st bilateral Spanish/Japanese school/ workshop on nanotechnology and new materials with environmental challenges

Thermal properties of silicon ultra-thin membranes: A theoretical and experimental approach

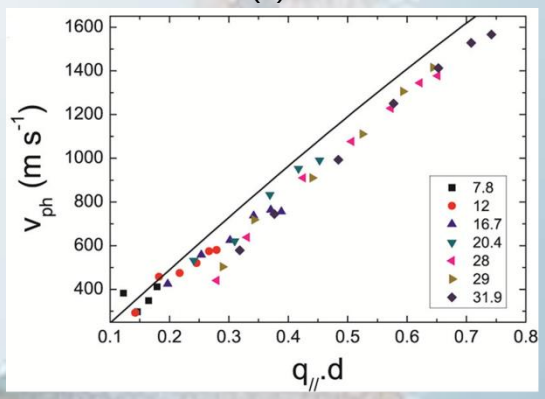
A deep understanding of heat transport in low-dimensional semiconductor structures is crucial to find solutions for low power electronics A model system is used to study phonon transport in Si.

Recent experimental and theoretical reports point to an enhancement of the figure of merit in thin films [2] [1], nanowires [3] and superlattices [4] [5], primarily as a result of the decrease of the thermal conductivity compared to the bulk counterpart, without a corresponding decrease in electrical conductivity. The reduced dimensions lead to the confinement of acoustics modes and the discretization of their spectrum, resulting in the modification of phonon density of states [6] and a dramatic decrease of group/phase velocity [7] and a phonon lifetime [8].

We study theoretically and experimentally the thickness-dependence of the thermal properties of silicon membranes with thicknesses ranging from 9 to 1500 nm. We investigate the dispersion relations and the corresponding modification of the phase velocities of the acoustic modes, which are mostly responsible for the heat transport, using inelastic Brillouin light scattering spectroscopy. A reduction of the phase/group velocities of the fundamental flexural mode by more than one order of magnitude compared to bulk values was observed and is theoretically explained [7]. In addition, the lifetime of coherent acoustic phonon modes with frequencies up to 500 GHz was also studied using state-of-the-art ultrafast pump-probe, i.e. asynchronous optical sampling (ASOPS). We observed that the lifetime of the first-order dilatational mode decreases significantly from ~ 4.7 ns to 5 ps with decreasing membrane thickness from ~ 194 to 8 nm [8]. Finally, the thermal conductivity of the membranes was investigated using a contactless technique known as Raman thermometry. We found that the thermal conductivity of the membranes gradually reduces with their thickness, reaching values as low as 9 W/mK for the thinnest membrane.



(a)

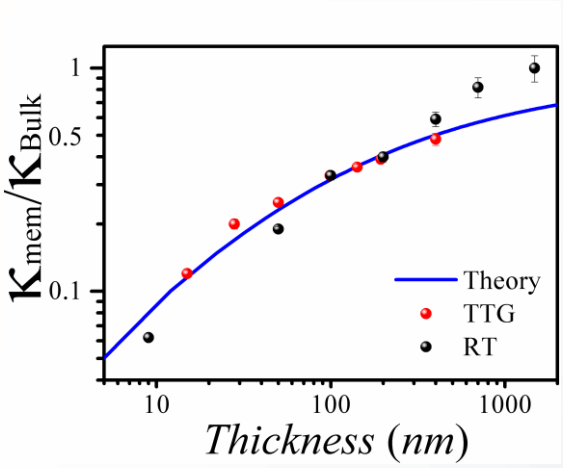


(b)

Figure 1 (a) Dispersion curves plotted in terms of the phase velocity as a function of dimensionless wave vector (q//·d) for membranes with thickness values ranging from 400 to 7.8 nm. Inset: Optical microscope image of the 30 nm Si membrane. (b) Magnified image of the highlighted region in showing data for membranes of thickness from 7.8 to 31.9 nm. The linear relationship observed is a direct result of the quadratic dispersion relation. A phase velocity down to approximately 300 ± 40 m/s is recorded for the 7.8 nm membrane [7].

To account for the observed thermal behaviour of the ultra-thin membranes we developed different theoretical approaches to explain the size dependence of the dispersion relations based on an elastic continuum approach, Debye model and fitting models. The size dependence of the lifetimes was modelled considering

intrinsic phonon-phonon processes and extrinsic phonon scatterings. The thermal conductivity was modelled using a modified 2D Debye approach and Srivastava-Callaway-Debye model.



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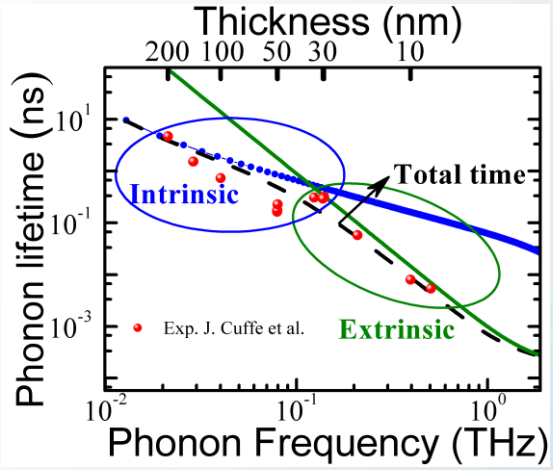

(b)

Fig. 2 (a) Experimental and theoretical phonon lifetime in free-standing silicon membrane, red dots: experimental data [8]. Green line: extrinsic boundary scattering processes. Blue-dotted line intrinsic three-phonon normal scattering processes. Black-dashed line: total contribution, calculated through Matthiessen's rule. (b) Experimental and theoretical thermal conductivity. Red dots: Experimental thermal conductivity measured by transient thermal gradient technique [9]. Black dots: Experimental thermal conductivity measured by Raman thermometry. Blue line Theoretical prediction

References:

1. R Venkatasubramanian, E Siivola, T Colpitts and B O'Quinn, Nature 413 597 (2001).
2. A I Boukai, Y Bunimovich, J Tahir-Kheli, J-K Yu, W A Goddard and J R Heath, *Nature* **451** 168 (2008).
3. G D Mahan and H B Lyon, *Journal of Applied Physics* **76** 1899 (1994).
4. D Broido and T Reinecke *Physical Review B* **51** 13797 (1995).
5. E Chávez, J Cuffe, F Alzina, and C M S Torres, *Journal of Physics: Conference Series* **395** 012105 (2012).
6. J Cuffe, E Chávez, A Shchepetov, P-O Chapuis, E H El Boudouti, F Alzina, T Kehoe, J Gomis-Bresco, D Dudek, Y Pennec, B Djafari-Rouhani, M Prunnila, J Ahopelto and CM Sotomayor Torres, *Nano Letters* **12** 3569 (2012).
7. J Cuffe, O Ristow, E Chávez, A Shchepetov, P-O Chapuis, F Alzina, M Hettich, M Prunnila, J. Ahopelto, T Dekorsy, and C M Sotomayor Torres *Physical Review Letters* **110** 095503 (2013).
8. PhD Tesis, J Cuffe, Phonon-Photon Interactions in Nanostructures, University College of Cork, 2011.

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Prof. Dr. Clivia Sotomayor Torres

Ge Nanowires on Si Substrates Patterned by Focused Beams of Au ions

A method to obtain Nanowire was developed by molecular beam Epitaxy using FIB-Written Au seed catalyst controlling this size and density by varying the Au Nanoclusters features.

Silicon-germanium alloys are used in thermoelectric applications due to their excellent reliability and performance at high operating temperatures. Probably, the most impressive application to date are thermoelements powered by radioisotopes which proved to be a reliable power source on several space missions as well as in remote weather stations. But large scale deployment of Si-Ge based thermoelectric elements would be enabled if suitable materials could be effectively integrated into microelectronic devices. In this context, nanostructured materials are the preferred choice to boost the thermoelectric figure-of-merit ZT. For example, Si nanowires (NWs) have been reported to greatly outperform bulk Si [1]. Compared with Si NWs, Ge NWs are of interest due to them higher carrier motilities and its complementarity to Si for further device miniaturization electrowires.

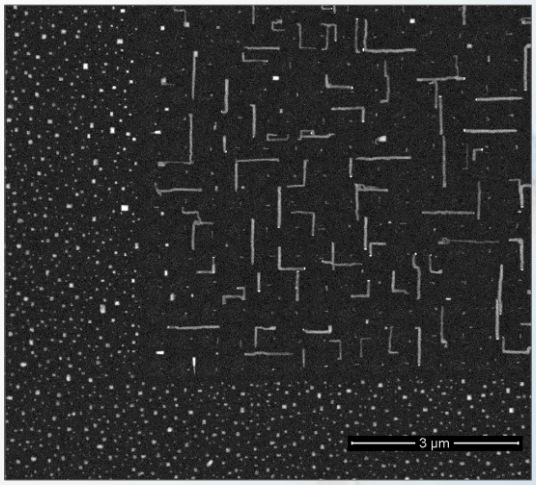

Figure 1: Detail of Ge growth inside and outside a patterned region on a Si (001) substrate. Image taken by scanning electron microscopy using both secondary and backscattered electron detectors, the light color of the nanowire tips indicates Au-rich composition.

Furthermore, SiGe serves as an ideal base for simulation studies of thermoelectric device optimization due to its well-known material parameters.

We studied the formation of Ge NWs by Molecular Beam Epitaxy (MBE) on Si Substrates Patterned by Focused Ion

Beam (FIB) using Au2+ ions [2]. The aim of our study was to develop a method to obtain NWs using Au seed catalysts and to control the size and the density of NWs by varying the Au nanocluster features. For this purpose we applied mass-filtered FIB direct writing to provide ordered patterns for nucleation of the NWs. Figure 1 shows a scanning electron microscope (SEM) image of the influence of the patterning on the growth mode of the Ge nanostructures on Si (001) substrates. The pattern consisted of Au implanted by FIB into a square array of 500 nm pitch, which were aligned with [110] crystallographic directions. Outside the patterned region the formation of Ge islands by a standard Stranski-Krastanow process was observed. In contrast, inside the patterned region an interesting epitaxial process where wires crawled along given directions of the substrate took place, giving rise to the reproducible achievement of self-assembled in-plane Ge NWs on Si (001). Despite the relative lack of order in the experiments on Si (001), the process is of technological importance: the NW dimensions are quite homogeneous and we believe this is a result of epitaxial and strain-driven mechanisms, which could be applied to other lattice-mismatched semiconductor systems other than Ge/Si. In the few cases where in-plane NWs were produced in the past, they were usually mixed with other geometries, whereas our method allows to produce homogeneous distribution.

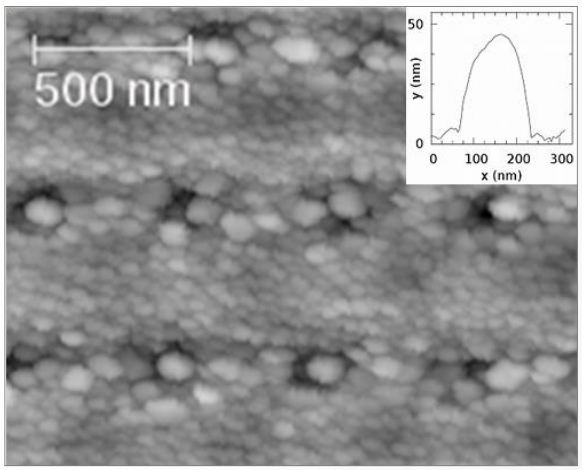

Figure 2 : Atomic force microscopy image of Ge growth on a patterned Si(111) substrate. The inset shows in detail the profile of one of the observed nanostructures.

For comparison, we made a limited number of experiments on Si(111). One result is shown in figure 2. In this orientation, the growth is along the [111] direction perpendicular to the substrate. Ordering effects given by the 500 nm pitch patterned holes are much stronger in this orientation but obviously the FIB induced surface damage is a drawback of this method.

We will continue research of NWs of this promising material system focusing on their thermal properties. New insight is expertly not from compositionally uniform structures but from NWs in which the properties, such as composition and doping, change along the length or diameter of the wire. Therefore, our research should focus on alloy and heterostructure nanowires

This work has been performed as part of the PhD Thesis of I. C. Marcus and in collaboration with the group of Dr. I. Berbezier of the IM2NP-CNRS in Marseilles, France.

References

1. A I Boukai, Y Bunimovich, J Tahir-Kheli, J-K Yu, W A Goddard III and J R Heath Nature 451 168 (2008).
2. I C Marcus, I Berbezier, A Ronda, M I Alonso, M Garriga, AR Goñi, E Gomes, L Favre, A Delobbe, and P. Sudraud, Crystal Growth and Design 11 3190 (2011).

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Latest Publications:

1. C de Tomás, A Cantarero, A F Lopeandia and F X Alvarez, Lattice thermal conductivity of silicon nanowires. *J. Therm. 2013* **4** 11-18 (2013)
2. M Culebras, C M Gómez and A Cantarero,Thermoelectric materials based on poly (3, 4-ethylendioxythiophene) *J. Therm. 2013* **4** 36-42 (2013).
3. M Criado-Sancho, FX Alvarez, D Jou, Thermal rectification in inhomogeneous nanoporous Si devices *Journal of applied physics* **114** 053512 (2013)
4. RC Bounioux, P Díaz-Chao, M Campoy-Quiles, M S Martín-González, A R Goñi, R Yerushalmi-Rozen and C Müller, Thermoelectric Composites of Poly(3-hexylthiophene) and Carbon Nanotubes with a LargePower Factor., *Energy Environ. Sci*. **6** 918 (2013).
5. C Bounioux, P Diaz-Chao, M Campoy-Quiles, MS Martin-Gonzalez, Ar Goni, R Yerushalmi-Rozene and C Muller "Thermoelectric composites of poly(3-hexylthiophene) and carbon nanotubes with a large power factor, *Energy & Environamental* **6** 918 (2013)
6. B Abad, I Alda, P Diaz-Chao, H Kawakami, A Almarza, D Amatia, D Guitierrez, L Aubouy and M Martín-González, Improved power factor of polyaniline nanocomposites with industrial graphene nanoplatelets, *J. Mater Chem* A **1** 10450 (2013)
7. R D'Agosta, Towards a dynamical approach to the calculation of the figure of merit of thermoelectric nanoscale devices *Physical Chemistry Chemical Physics* **15** 1758 (2013).
8. R D'Agosta and M Di Ventra, Foundations of stochastic time-dependent current-density functional theory for open quantum systems: Potential pitfalls and rigorous results, *Physical Review B* **87** 155129 (2013).
9. E Chávez, J Gomis-Bresco, F Alzina, JS Reparaz, VA Shah, M. Myronov, DR Leadley and CM Sotomayor Torres, Flexural mode dispersion in ultra-thin Ge membranes, *IEEE Proc. of ULIS conference 2013* **185** (2013).
10. A Shchepetov, M Prunnila, F Alzina, L Schneider, J Cuffe, H Jiang, E I Kauppinen, C M Sotomayor Torres, J Ahopelto, Ultra-Thin Free-Standing Single Crystalline Silicon Membranes With Strain Control, *Applied Physics Letters* **102** 192108 (2013)
11. J Cuffe, O Ristow, E Chávez, A Shchepetov, P-O Chapuis, F Alzina, M Hettich, M Prunnila, J Ahopelto, T Dekorsy and C M Sotomayor Torres, Lifetimes of confined acoustic phonons in ultra-thin silicon membranes, *Physical Review Letters* **110** 095503(2013)
12. C Mota, A Madroñero, J M Amo, J I Robla, M Culebras and A Cantarero, Variations in the Electrical Resistivity of Vapour Grown Carbon Fibres by Effect of Successive Operations of Intake and Outgassing of Hydrogen, *J. Mat. Sci. Res.* **2** 163 (2013)
13. M Culebras, C M Gomez and A Cantarero, Thermoelectric measurements of PEDOT:PSS/ expanded graphite composites *J. Mater. Sci.* **48** 2855 (2013)
14. JS Reparaz, N Peica, R Kirste, AR Goñi, MR Wagner, G Callsen, MI.Alonso, M Garriga, IC Marcus, I Berbezier, J Maultzsch, C Thomsen and A Hoffmann, Probing Local Strain and Composition in Ge Nanowires by means of Tip-Enhanced Raman Scattering *Nanotechnology* **24** 185704 (2013)
15. M Osiak, W Khunsin, E Armstrong, T Kennedy, C M Sotomayor Torres, K M Ryan, and C O'Dwyer, Epitaxial growth of visible to infra-red transparent conducting In2O3 nanodot dispersions and reversible charge storage as a Li-ion battery anode, *Nanotechnology* **24** 065401 (2013)
16. M Muñoz, O Caballero, A F Lopeandia, J Rodriguez-Viejo and M Martín-Gonzalez, Review on measurement techniques of transport properties of nanowires, *Nanoscale, 2013*, in press

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