Nanostructured thermoelectric generators

Marisol Martin-Gonzalez and Fernando Briones
IMM-Instituto de Microelectrónica de Madrid (CNM-CSIC), Isaac Newton 8, PTM, E-28760 Tres Cantos, Madrid, Spain.
Email: marisol@imm.cnm.csic.es

Providing a sustainable supply of energy to the world's population will become a major societal problem for the 21st century. Thermoelectric materials, whose combination of thermal, electrical, and semiconducting properties, allows them to convert waste heat into electricity, are expected to play an increasingly important role in meeting the energy challenge of the future. Recent work on the theory of thermoelectric devices has led to the expectation that their performance could be enhanced if the diameter of the wires could be reduced to a point where quantum confinement effects increase charge-carrier mobility (thereby increasing the Seebeck coefficient) and reduce thermal conductivity. The predicted net effect of reducing diameters to the order of tens of nanometers would be to increase efficiency or ZT index by a factor of 3.

Our work in the thermoelectricity has been recently funded by the European ERC program "IDEAS" under ERC contract 240497, granted to Dr. Marisol Martin at IMM-CSIC, and also by a bilateral collaboration (NANO-THERMA) within the Spanish team and a NIMS group in Japan.

Its main objective is to investigate and optimize nanostructures influencing ZT in order to achieve a power conversion efficiency >20%. For that, nanowire arrays of state of art n and p-type semiconductor materials will be prepared by cost-effective mass-production electrochemical methods and fabricate devices with a ZT >2 for applications in energy scavenging and as cooler/heating devices. Three lines of research are followed:

a) determination of the best materials for each temperature range (n and p type) optimizing composition, microstructure, shapes (core/shell nanowires, surface texture, heterostructures), interfaces and orientations,

b) advanced characterization, device development and modeling will be used iteratively during nanostructures and materials optimization, and

c) nano-engineering less conventional thermoelectric like "cage compounds" by electrodeposition methods.

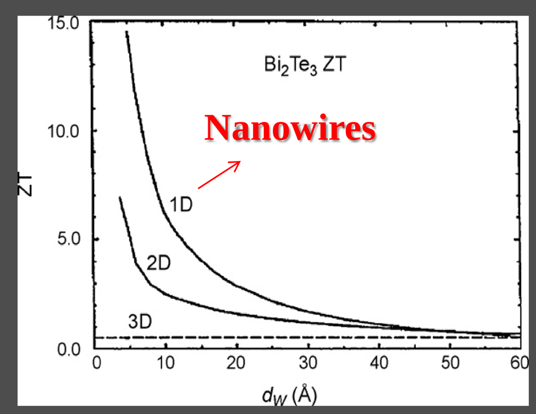
Theory of Low-dimensional Thermoelectrics

$$ZT = \frac{S^2\sigma}{k}T$$

Effects of reduced dimensionality

- Increase in S
  - quantum confinement effect
- Decrease in κ
  - introduction of interphases

Theoretical investigation



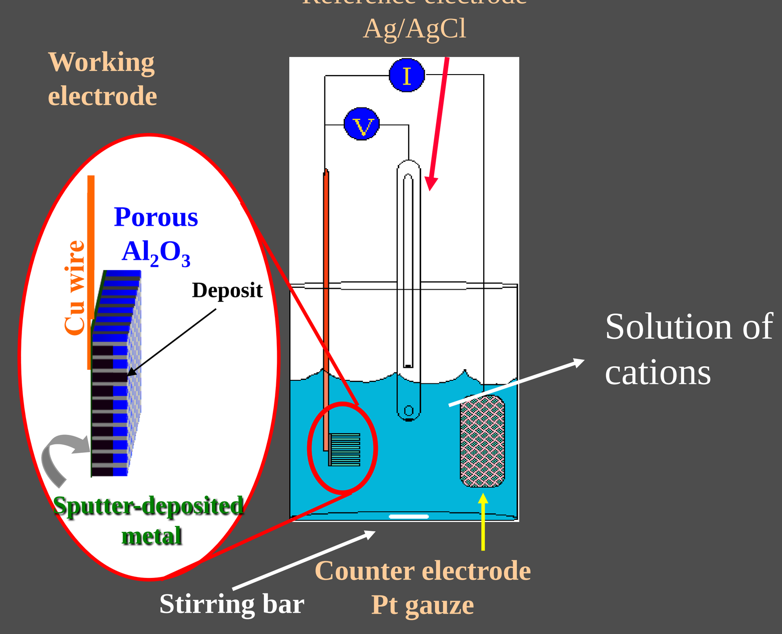
Dependence of $Z_{3D}T$ and $Z_{1D}T$ on quantum-well and quantum-wire widths d_W for bismuth

From L.D. Hicks & M.S. Dresselhaus, MIT

Low dimensionality should improve the properties of thermoelectric materials

Fabrication of Nanowires by electrodeposition

Electrochemical Cell



Nanowire Arrays

Bi$_2$Te$_3$

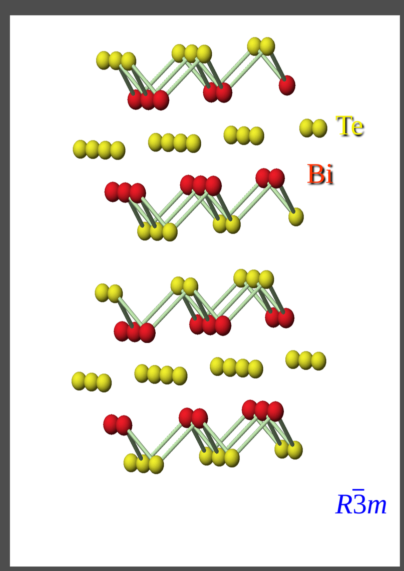
Why?

- Commercially used ZT~1 at 300K

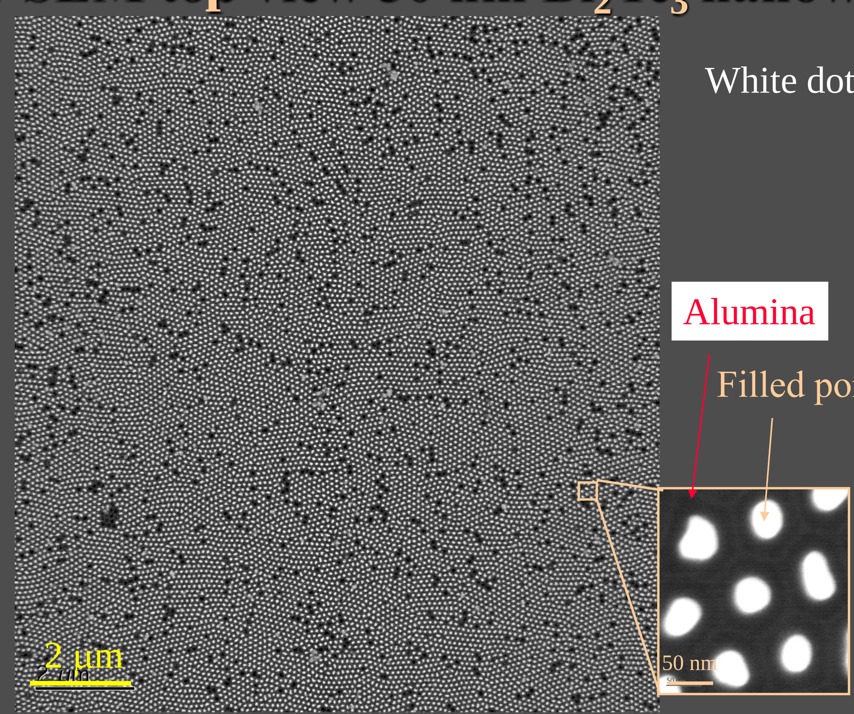
S ≈ -240 μV/K
σ ≈ 10 μΩ•m
κ ≈ 2.02 W/m•K

- It can be electrodeposit (Takahashi *et al.*, 1993)
- Anisotropy

Structure



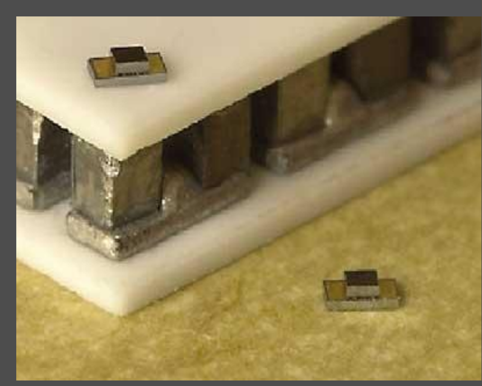
FE-SEM top view 50 nm Bi$_2$Te$_3$ nanowire

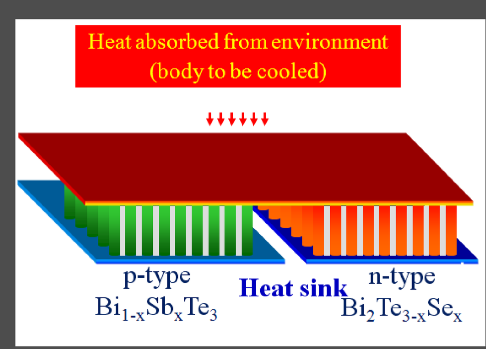


Well ordered, >90% Nucleation

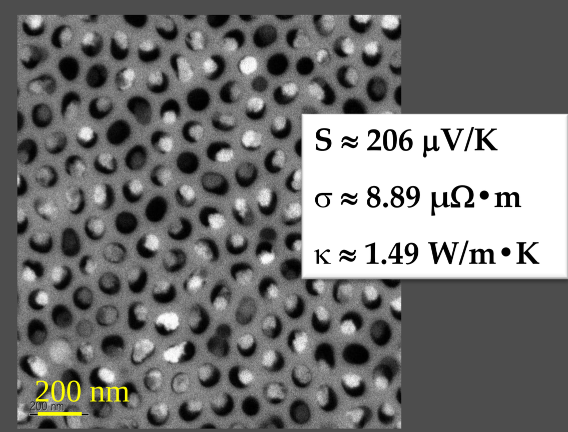
Bi$_2$Te$_3$ wires fill the pores completely → wetting effect

Thin film Peltier element.

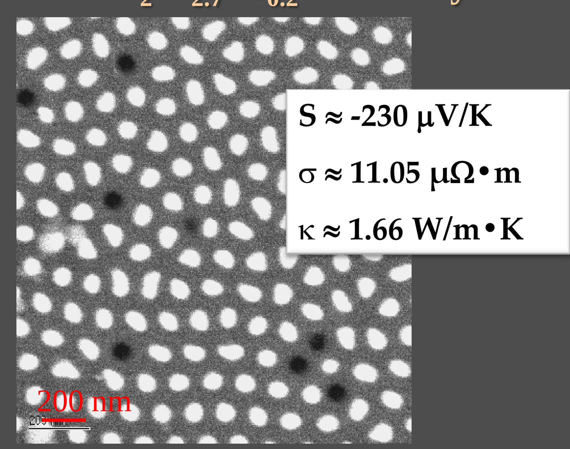




50 nm Bi$_{0.7}$Sb$_{1.4}$Te$_{2.9}$ wire array



50 nm Bi$_2$Te$_{2.7}$ Se$_{0.2}$wire array



Bi$_{1-x}$Sb$_x$

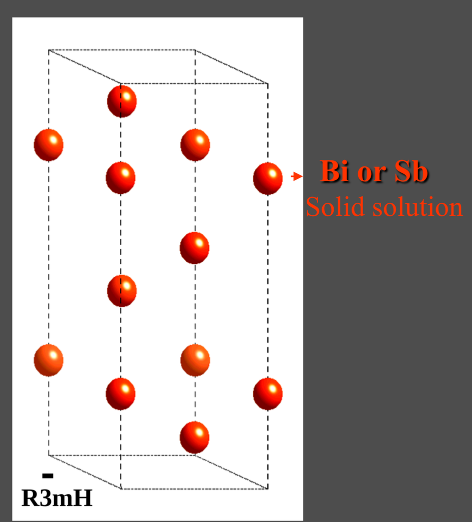
Why?

- Solid solution
- Best low temperature thermoelectric *ZT ~ 0.88 at 12% Sb and 80K*

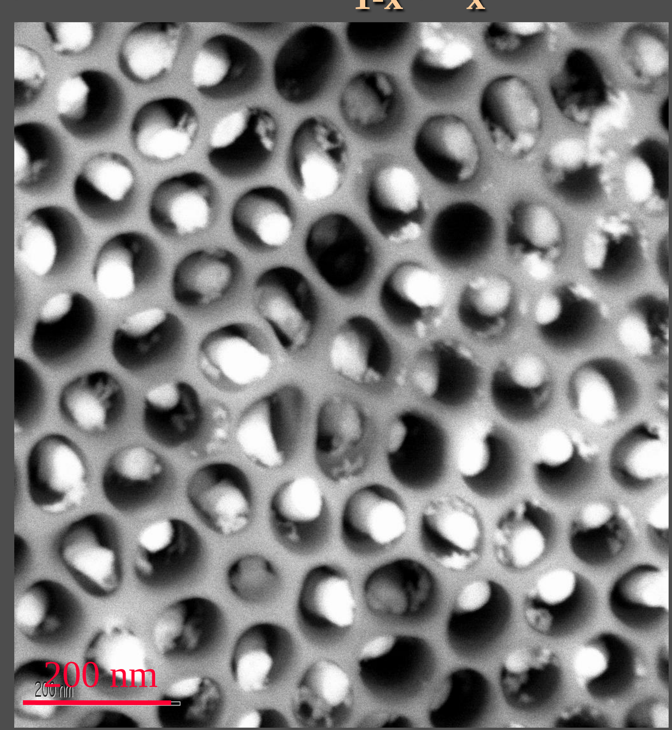
S ≈ -160 μV/K
σ ≈ 1.5 μΩ•m
κ ≈ 2.4 W/m•K

- Calculations by Dresselhaus *et al.* suggest a ZT ~ 1.25-1.5, diameters of ~40 nm, x ~0.13

Structure

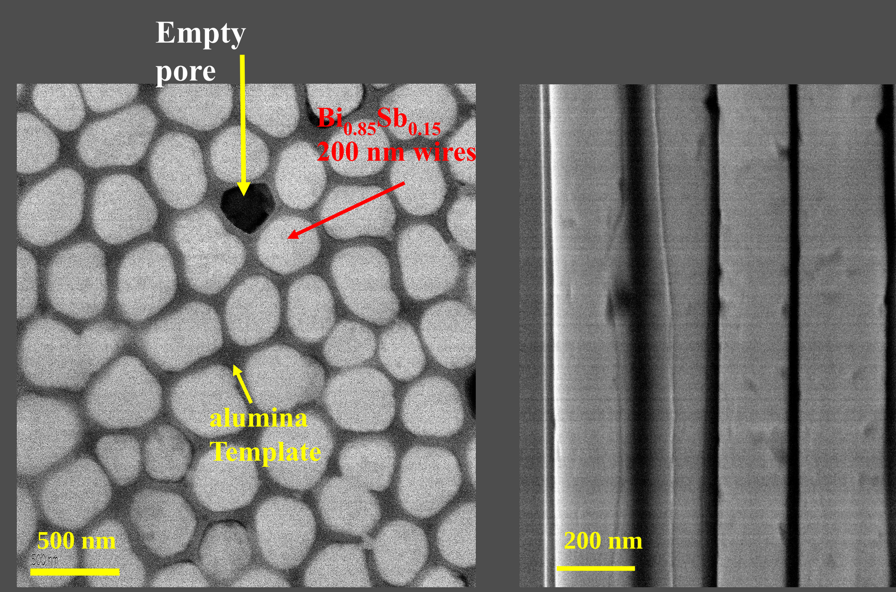


FE-SEM 40 nm Bi$_{1-x}$Sb$_x$ nanowire array



- The wire diameter is smaller than the pore diameter
- The wire grows concentrically in the pore but does not wet the alumina walls

FE- SEM of 200 nm Bi$_{0.85}$Sb$_{0.15}$ nanowires



- The pores can be filled by doing the process more slowly but non wetting effects are still observed

CoSb$_3$

Cage Compound

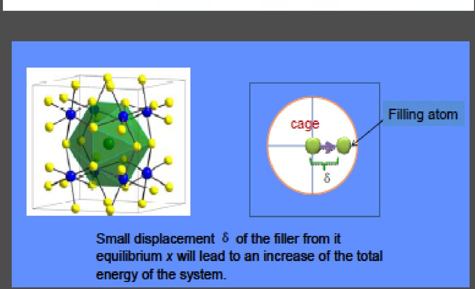
Why?

- Part of the Skutterudite (CoAs$_3$) family
- **ZT ≈ 1.47 at 573K**

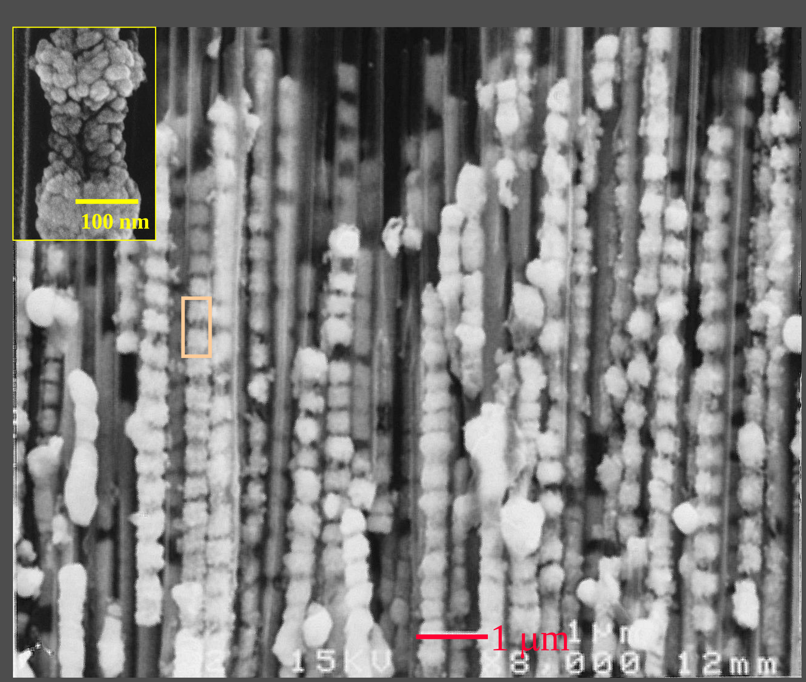
S ≈ 220 μV/K
σ ≈ 10 μΩ•m
κ≈ 3.2 W/m•K

- Separation:
  - electronic structure
  - thermal conductivity
- Isotropic

Rattler type Structure



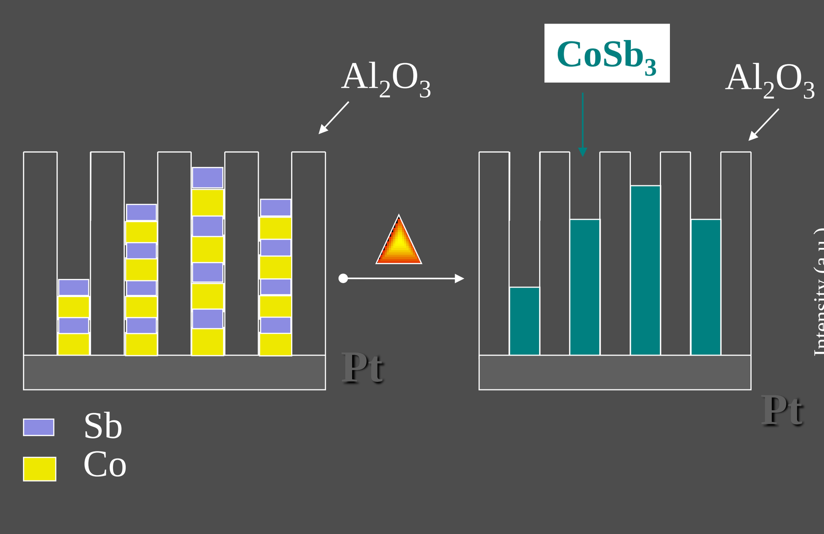
CoSb$_3$: Post-annealed *Morphology*



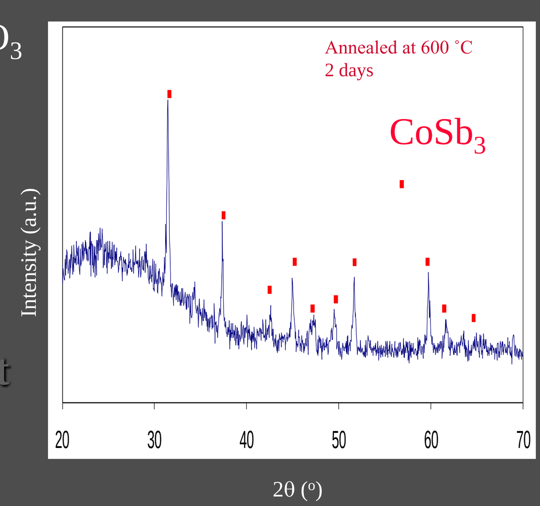
- **Co layer wet alumina walls while Sb layer do not.**
- **There is also a reduction in volume after heating.**
- **All that gives a very interesting periodic constriction along the length of the wire**

CoSb$_3$: Electrodeposition sequence

Multilayer deposition into 200 nm Al$_2$O$_3$ templates



XRD



Deposition: 8 to 30 multilayers, 50°C

Conclusions:

➢ **Nanowire arrays of thermoelectric materials like Bi$_2$Te$_3$, Bi$_{2-x}$Sb$_x$Te$_3$ Bi$_2$Te$_{3-x}$Se$_x$, Bi$_{1-x}$Sb$_x$ and CoSb$_3$ have been successfully prepared.**

➢ ***Because of the "wetting/non-wetting" effects between the porous alumina and the material inside the pore different and technologically interesting nanostructures can be found!!!!***

References::
(a) M.S. Dresselhaus, et al. Microscale Thermophysical Engineering 3 (1999) 89
(b) Martin, C. R., *Adv. Mater.* **1999**, *3*, 457.
(c) Martin, C. R., *Science* **1994**, *266*, 1961.
(d) Amy L. Prieto, Melissa S. Sander, Marisol S. Martín-González, et al. *J. Am. Chem. Soc.*, **123**, 7160 -7161, 2001.
(e) Marisol S. Martín-González, *et al. J. Electrochem. Soc.*, 2002, 149, C546-C554
(f) Marisol S. Martín-González, *et al. Chem. Mater.*, 2003; 15, 1676-1681.
(g) **M.S. Martín-González**, *et al. Adv. Mater.*, 2003, 15, 1003-1006
(h) **M.S. Martín-González**, *et al. Nano Letters*., 2003, 3, 973-977.
(i) A.L. Prieto, **M.S. Martín-González**, *et al. J. Am. Chem. Soc*, 2003, 125, 2388.
(j) D.-A. Borca-Tasciuc, G. Chen, A. Prieto, **M. S. Martín-González**, *et al. Appl. Phys. Lett.* 2004, 85: 6001-6003