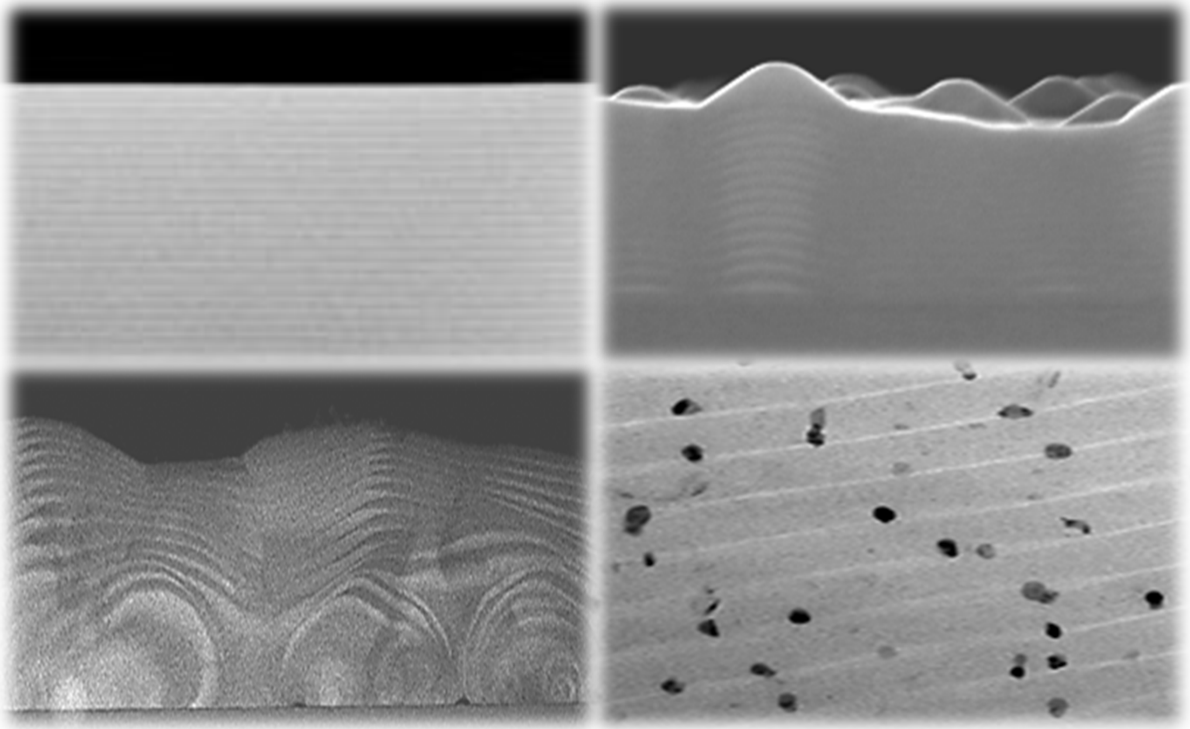


NANOSTRUCTURED THIN FILMS FOR THERMOELECTRICS APPLICATIONS

EMN Summer 2016 Conference | 05-09/06/2016 | SAVELLI Guillaume

EMN ENERGY MATERIALS NANOTECHNOLOGY

SUMMER MEETING

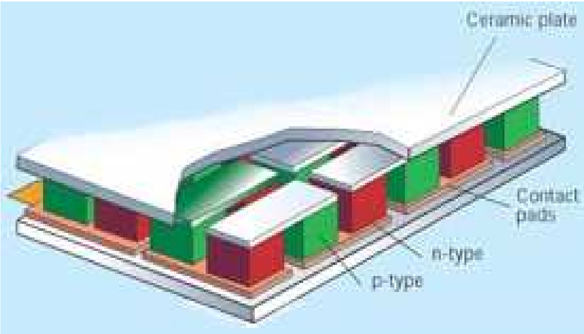
Cancun, Mexico 5 - 9 June, 2016

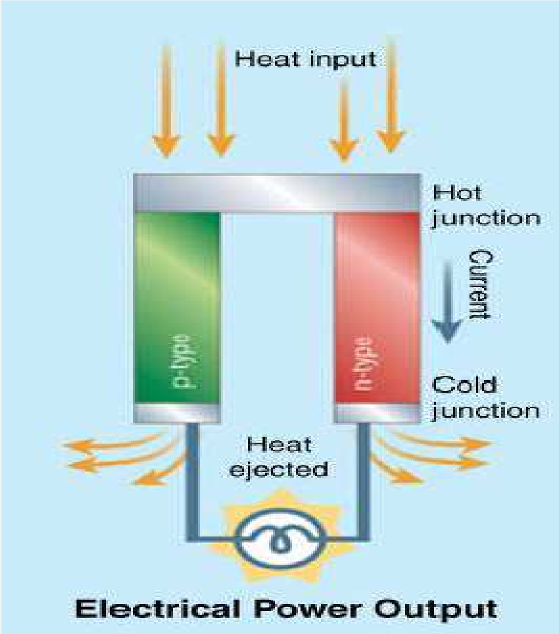
CONTENTS

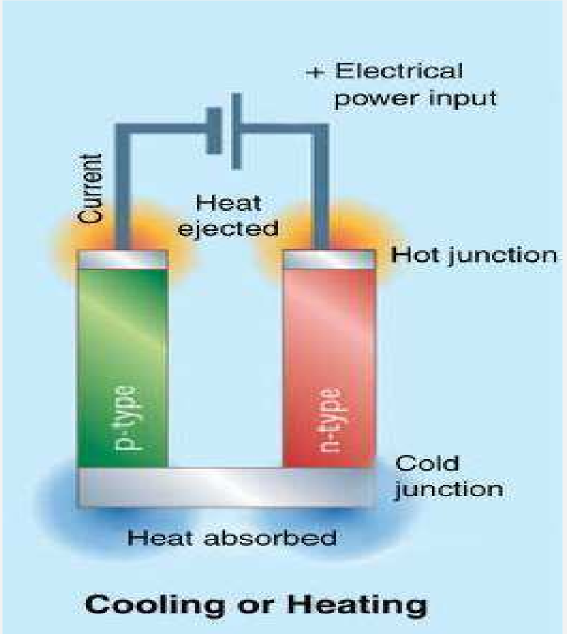
CONTENTS

THERMOELECTRIC EFFECTS AND PRINCIPLES

Standard structure of a thermoelectric device







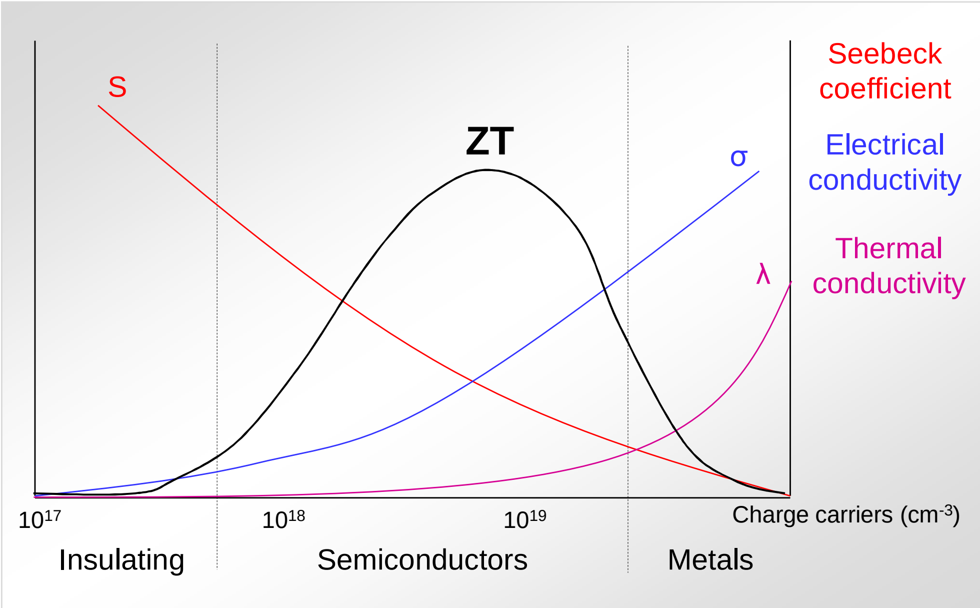
Effect	Seebeck effect	Peltier effect
Principle	Temperature gradient induces Seebeck voltage	Electrical current induces cooling/heating effect
Applications	→ Power generation → Thermal flow sensor	→ Cooling → Thermal management

DEFINITION OF FIGURE OF MERIT

- Three important properties for TE materials :

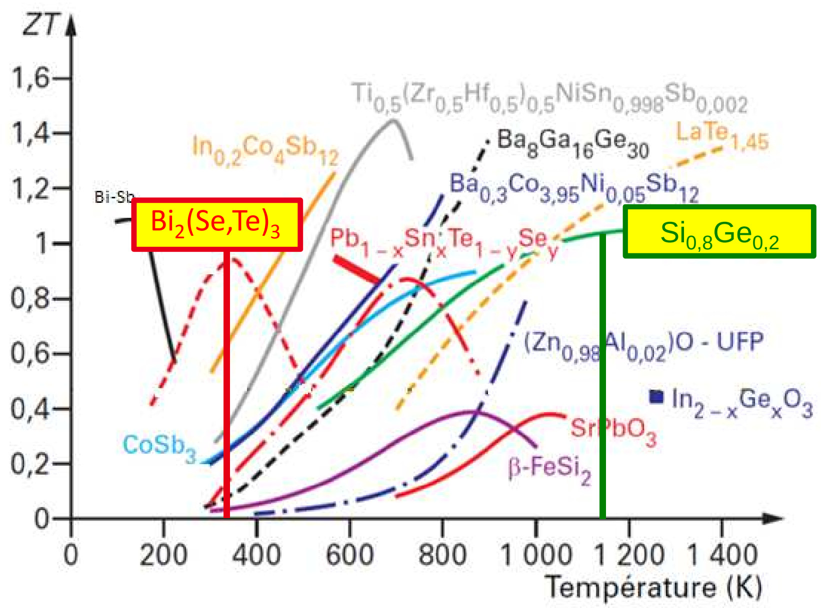
  → S = Seebeck coefficient ($\mu V.K^{-1}$)
  → σ = electrical conductivity ($S.m^{-1}$)
  → λ = thermal conductivity ($W.m^{-1}.K^{-1}$)

- Definition of the dimensionless figure of merit $ZT = \frac{\sigma \times S^2}{\lambda} T$

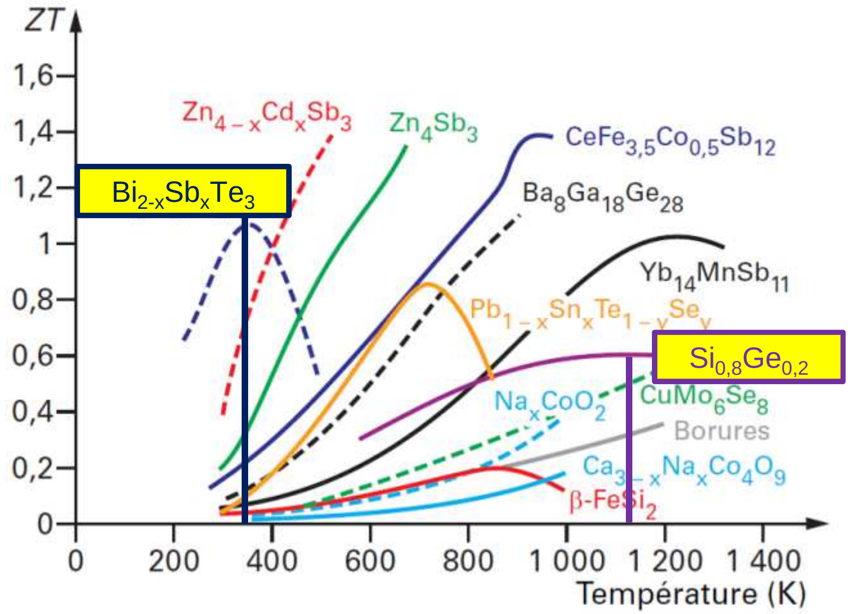


→ Best TE materials correspond to highly doped semiconductors

THERMOELECTRIC MATERIALS



N-type



P-type

N-type:
- H-H: TiNiSn & dérivés (430°C max)
- skutterudites: $CoSb_3$ & dérivés (530 °C max)
- clathrates: $Ba_8Ga_{16}Ge_{30}$ (630 °C max)
- $Pb_{1-x}Sn_xTe_{1-y}Se_y$ (530 °C max)
- $Si_{0.8}Ge_{0.2}$ (1000 °C max)
- Mg_2Si & dérivés (530 °C max)

P-type:
- Zn_4Sb_3 & dérivés(400 °C max)
- skutterudites: $CeFe_{3.5}Co_{0.5}Sb_{12}$ (710 °C max)
- clathrates: $Ba_8Ga_{16}Ge_{30}$ (630 °C max)
- $Pb_{1-x}Sn_xTe_{1-y}Se_y$ (530 °C max)
- $Si_{0.8}Ge_{0.2}$ (1000 °C max)
- $MnSi_{1.75-x}$ (T_{max} mal connue)

→ A lot of TE materials, function of temperatures and applications

THERMOELECTRIC MATERIALS: OUR GOAL

- Development of TE materials dictated by our applications at thin films scale:
  - environment: microelectronic
  - applications: thermal sensors and power generation
  - temperature: room temperatures (20 - 150 °C)
- Use of green materials (non toxic, abundant, non expensive…)
- Use of nanostructuration to increase TE performances
- Materials deposition compatible with microelectronic technology

→ **Silicon and Silicon-Germanium alloys based materials:**

- well-known in microelectronic environment
- green materials
- possibility to use nanostructuration
- deposition technique compatible with microelectronic technology
- but low ZT at room temperature…

CONTENTS

THERMOELECTRIC MATERIALS: HOW TO INCREASE ZT ?

- To increase $ZT = \frac{\sigma \times S^2}{\lambda} T$, two possibilities :

  - increase of power factor σS^2
  - decrease of thermal conductivity λ

- About twenty years ago, Hicks and Dresselhaus have introduced the concept of electron and holes quantum confinement in low dimensional materials which could increase the ZT significantly *

→ Introduction of nanostructuration for TE

** L. D. Hicks and M. S. Dresselhaus, Phys. Rev. B 47, 12727, (1993)*

THERMOELECTRIC MATERIALS: HOW TO INCREASE ZT ?

- Increase of power factor σS^2

→ Mott's equation: $$S = -\frac{\pi^2}{3}\frac{k_B}{e}k_B T\left(\frac{\partial \ln\sigma(E)}{\partial E}\right)_{E_F}$$

→ Expression of σ: $$\sigma(E) = \mu(E)n(E)e$$

→ So: $$S = \frac{\pi^2}{3}\frac{k_B}{e}k_B T\left[\frac{1}{\mu(E_F)}\left(\frac{\partial \mu(E)}{\partial E}\right)_{E_F} + \frac{1}{n(E_F)}\left(\frac{\partial n(E)}{\partial E}\right)_{E_F}\right]$$

derivative in energy of state density

derivative in energy of mobility

→ Increase of power factor can be obtained by increasing the electron state density near Fermi level (increase of electron quantum confinement)

→ Increase of power factor by imposing judicious defaults at the electronic structure (increase of carriers number for example)

THERMOELECTRIC MATERIALS: HOW TO INCREASE ZT ?

- Decrease of the thermal conductivity λ

→ Thermal conductivity: sum of two terms:

$$\lambda = \lambda_e + \lambda_p$$

with λ_e electronic thermal conductivity
λ_p lattice thermal conductivity (phonons)

→ According to the Wiedemann-Franz law:

$$\lambda_e = L_0 \times \sigma \times T$$

with L_0 Lorenz constant ($2{,}44.10^{-8}$ W.Ω.K^{-2})
σ electrical conductivity
T temperature

→ Decrease of the lattice thermal conductivity λ_p

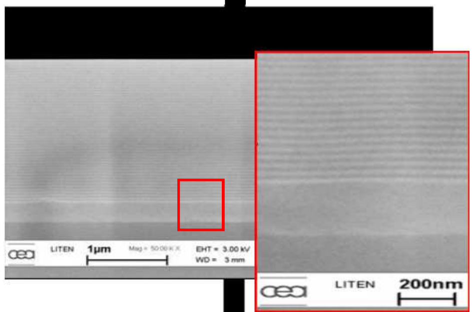
→ Decrease of thermal conductivity by increasing phonons scattering

NANOSTRUCTURATION OF THERMOELECTRIC MATERIALS

- Several kinds of nanostructuration for thin films thermoelectric materials

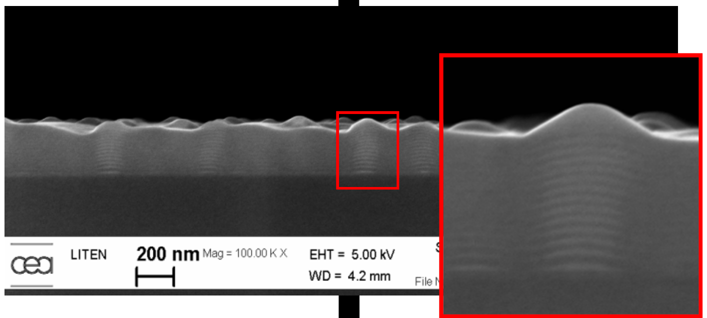
Nanostructuration of thin films

Superlattices (SL)



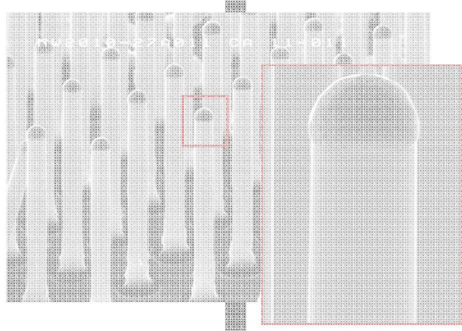
→ periodic structures alternating layers of two or more materials

Quantum Dot Superlattices (QDSL)



→ superlattices where one of the continuous layers is replaced by an array of dots

Nanowires (NW)



→ structures with diameter constrained to tens of nanometers

NANOSTRUCTURATION OF THERMOELECTRIC MATERIALS

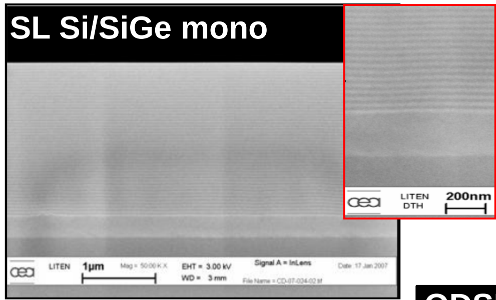
- Growth by Reduced Pressure (RP)CVD of thin films nanostructured materials, compatible with microelectronic environment

- Progress on thin films nanostructured materials

2007
2008
2009
2010
2011
2012
2013
2014
2015

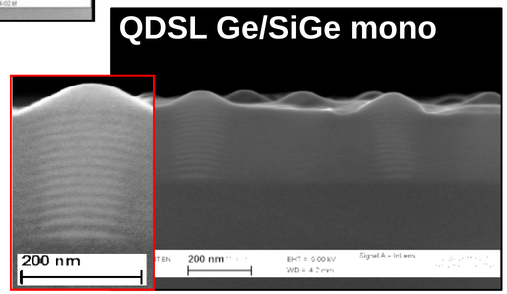
- GEN1 - Si/SiGe SuperLattices

G. Savelli et al., J. Micromech. Microeng. 18 (2008)



- GEN2 - Ge/SiGe Quantum Dot Superlattices

D. Hauser et al., ECT10, Italy (2010)
D. Hauser et al., Thin Solid Films 520 (2012)
G. Savelli et al., AIP Conf. Proc. 1449 (2012)

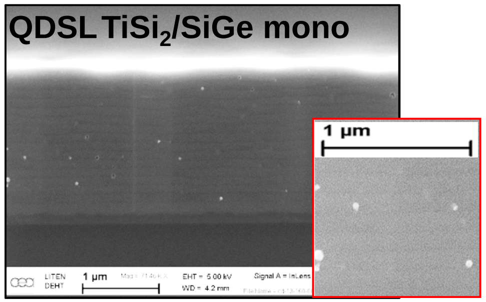


- GEN3 - Silicide Quantum Dot Superlattices

- QDSL $TiSi_x$ / SiGe

- QDSL $MoSi_x$ / SiGe

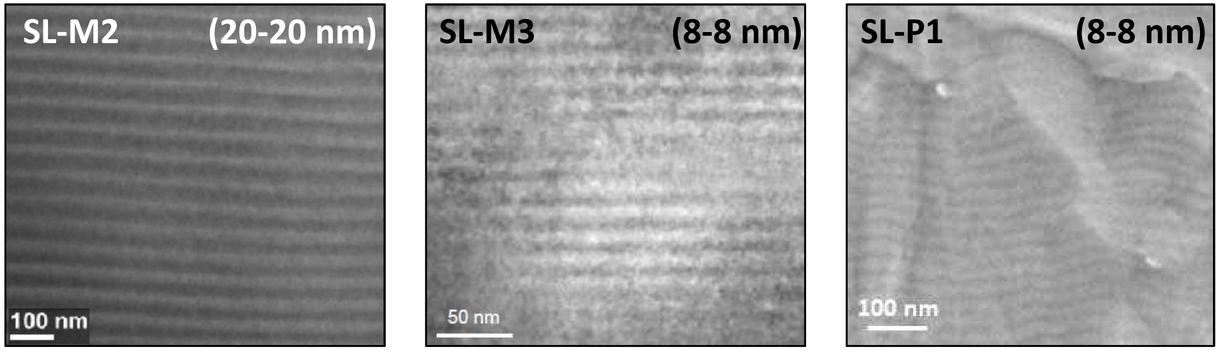
S. Silveira Stein et al., IEEE Nano, Canada (2014)
G. Savelli et al., Nanotechnology 26 (2015)
G. Savelli et al., Superlattice Microst. 92 (2016)



CONTENTS

SI/SIGE SUPERLATTICES (SL)

- TEM views of Si/SiGe SL with different periods and structures



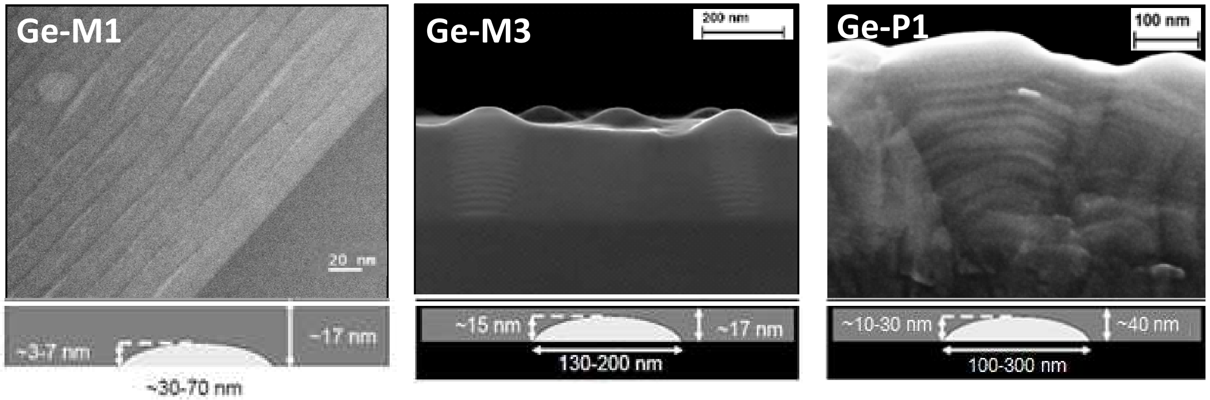
- Influence of undoped SL on thermal conductivity

Sample	Structure	Type	Si/SiGe SL period (nm)	Ge content (%)	$\lambda_{\perp}$ ($W.m^{-1}.K^{-1}$)
SL-M1	mono	SL	40-40 (x4)	~ 15	**14**
SL-M2	mono	SL	20-20 (x8)	~ 15	**7**
SL-M3	mono	SL	8-8 (x20)	~ 15	**5.4**
SL-M4	mono	SL	4-8 (x25)	~ 15	**5**
SL-P1	poly	SL	8-8 (x20)	~ 15	**2.8**

→ Decrease of thermal conductivity by decreasing SL period

GE-BASED QUANTUM DOT SUPERLATTICES (QDSL)

- TEM and SEM views of Ge-based QDSL with different periods and structures



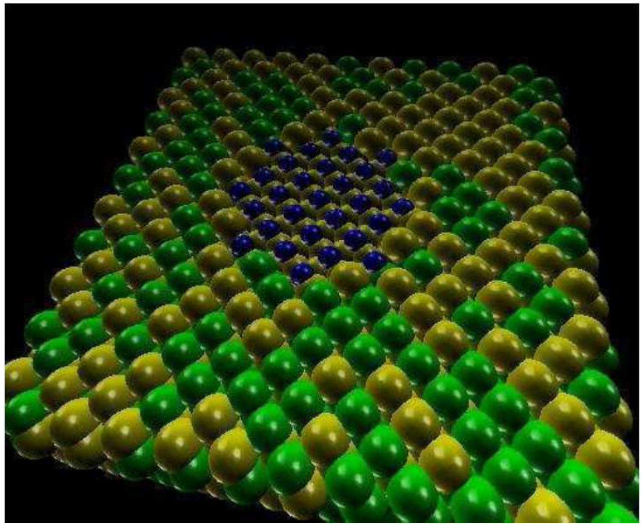
- Influence of p-doped QDSL on electrical and thermal conductivities

Sample	Structure	Type	Thickness / width of dots (nm)	Ge content (%)	$\rho_{//}$ (mΩ.cm)	$\lambda_{\perp}$ (W.m^{-1}.K^{-1})
Ge-MR	mono	REF	-	7.7	2.2	**10.5**
Ge-M1	mono	QDSL	3-7 / 30-70 (x15)	7.6	3.8	**6.1**
Ge-M2	mono	QDSL	12 / 100-170 (x15)	9.4	2.7	**6**
Ge-M3	mono	QDSL	15 / 130-200 (x15)	11.8	1.9	**5.3**
Ge-PR	poly	REF	-	13.3	3.6	**4.5**
Ge-P1	poly	QDSL	10-30 / 100-300 (x15)	14.2	3	**4**

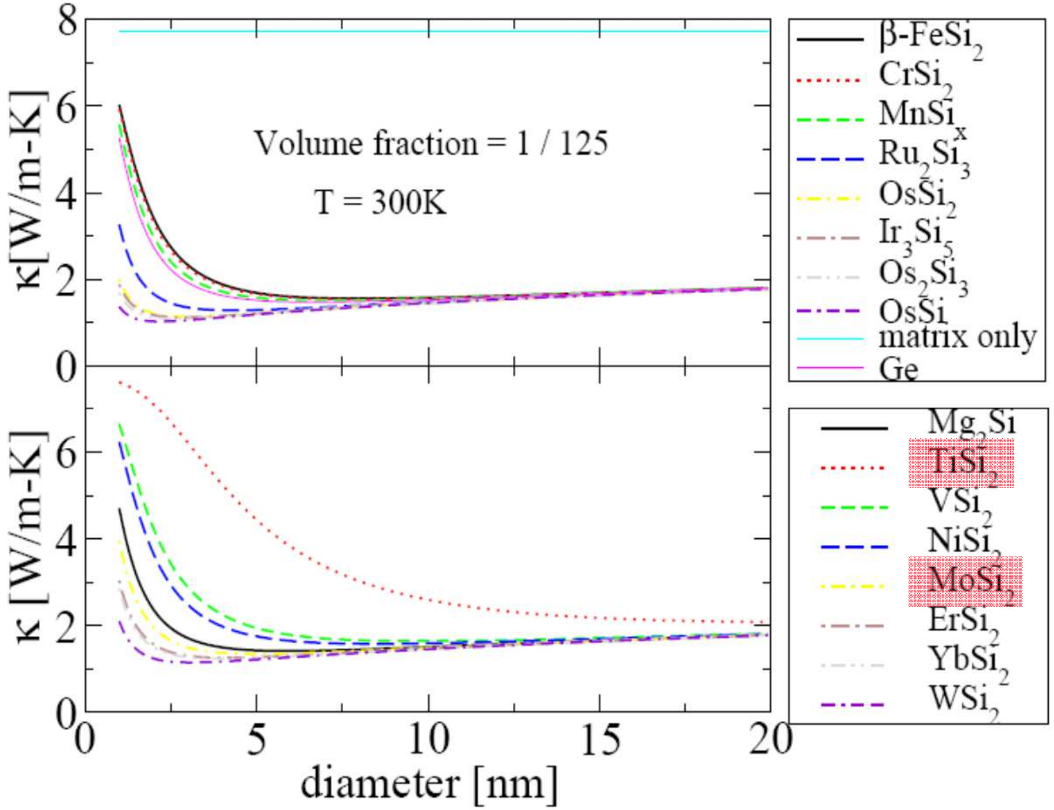
→ Decrease of thermal conductivity thanks to the nanodots inclusion

SILICIDE-BASED QUANTUM DOT SUPERLATTICES (QDSL)

- New nanomaterial concept: *nano-inclusions of metallic silicide in SiGe matrix **
- Use of ab-initio phonon transport calculations to choose the good silicide



Example of a nano-inclusion embedded in a SiGe matrix.



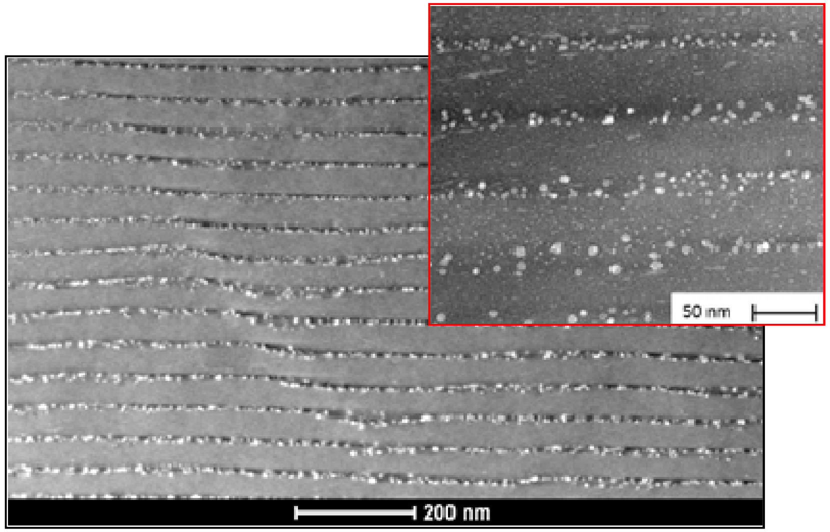
Evolution of the thermal conductivity as a function of nature and size of nanoparticles.

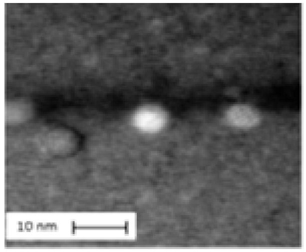
→ High performances predicted by theory for these new materials

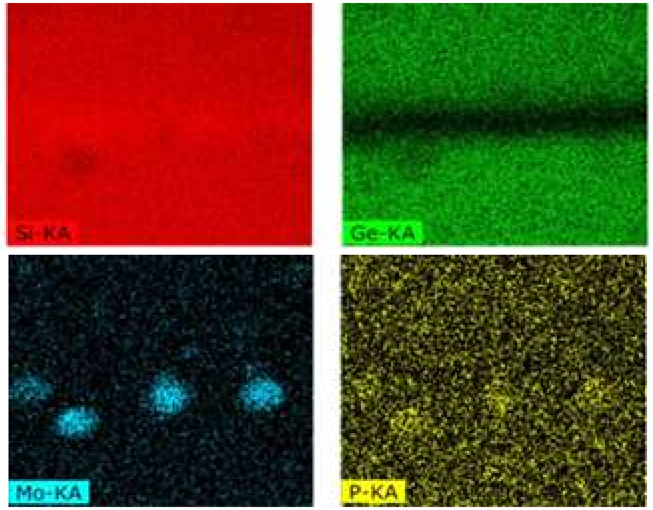
** N. Mingo et al., Nanoletters 9 (2009)*

MO-BASED QUANTUM DOT SUPERLATTICES (QDSL)

- STEM views and TE properties of monocrystalline Mo-based QDSL







Energy Dispersive X-ray Spectroscopy (EDS) analyses (Mo-M1 sample).

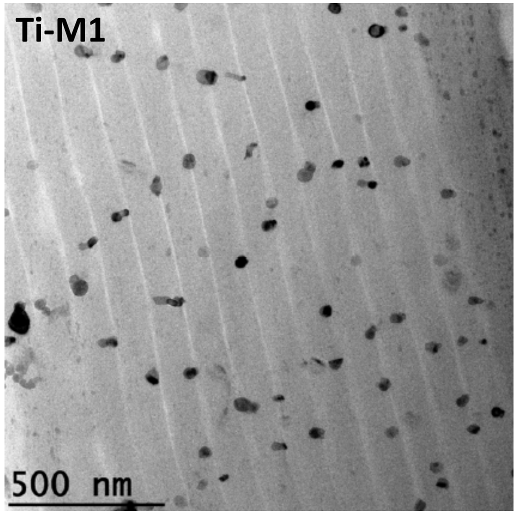
- Influence of n-doped QDSL on electrical and thermal conductivities

Sample	Structure	Type	Dots size - spacing (nm)	Ge content (%)	$\rho_{//}$ (mΩ.cm)	$\lambda_{\perp}$ (W.m^{-1}.K^{-1})
Mo-MR	mono	REF	-	10	1.35	**13**
Mo-M1	mono	QDSL	5 - 50	10	1.4	**9,5**

TI-BASED QUANTUM DOT SUPERLATTICES (QDSL)

- TEM views and TE properties of n-doped Ti-based QDSL

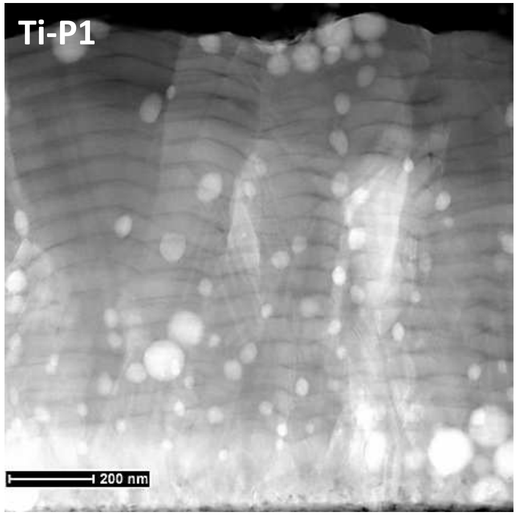
Monocrystalline $TiSi_2$/SiGe QDSL



Cross-plane TEM picture

Sample	$\rho_{//}$ (mΩ.cm)	$S_{//}$ (µV/K)	$PF_{//}$ (µW/cm/K²)	$\lambda_{\perp}$ (W/m/K)
Ti-MR (ref)	2,7	-104	4	8,5
Ti-M1	2,6	-190	**14**	**6,8**

Polycrystalline Ti_3Si/SiGe QDSL



Cross-plane STEM picture

Sample	$\rho_{//}$ (mΩ.cm)	$S_{//}$ (µV/K)	$PF_{//}$ (µW/cm/K²)	$\lambda_{\perp}$ (W/m/K)
Ti-PR (ref)	11	-130	1,5	4,6
Ti-P1	12,5	-215	**3,7**	**4,2**

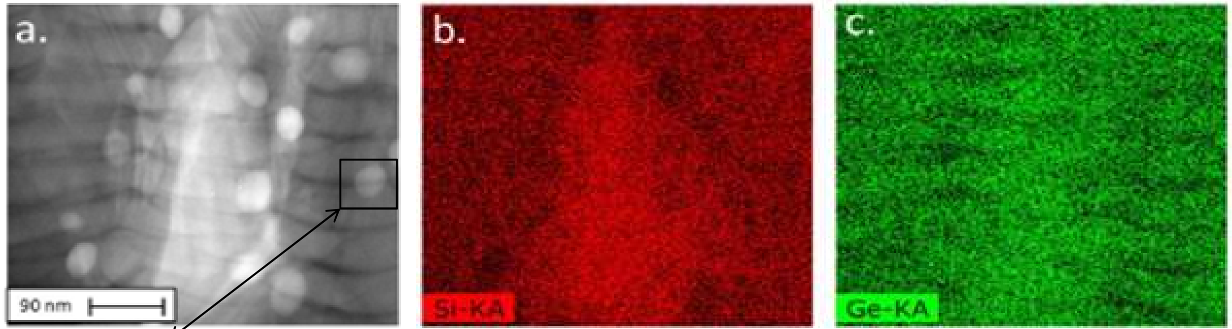
→ increase of TE properties thanks to the nanostructuration
→ in good agreement with the theoretical predictions

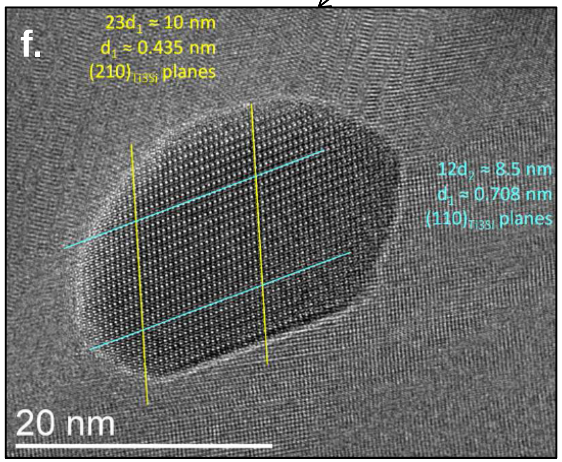
$TiSi_2$-BASED QUANTUM DOT SUPERLATTICES (QDSL)

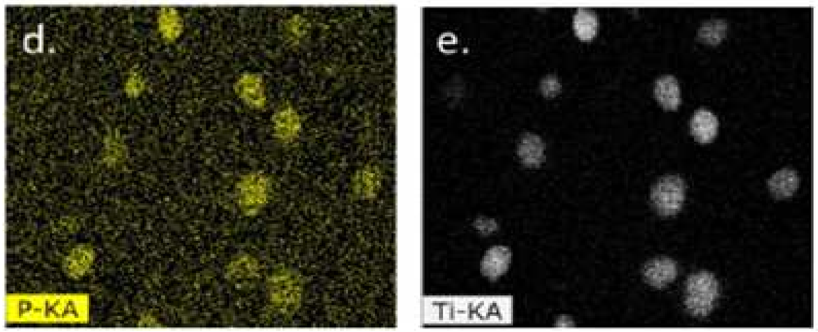
- Chemical analyses of $TiSi_2$-based QDSL

→ dots accumulation at the grains boundaries

→ dopant accumulation near the QD coming from a high affinity between the metal silicide and the dopant atoms







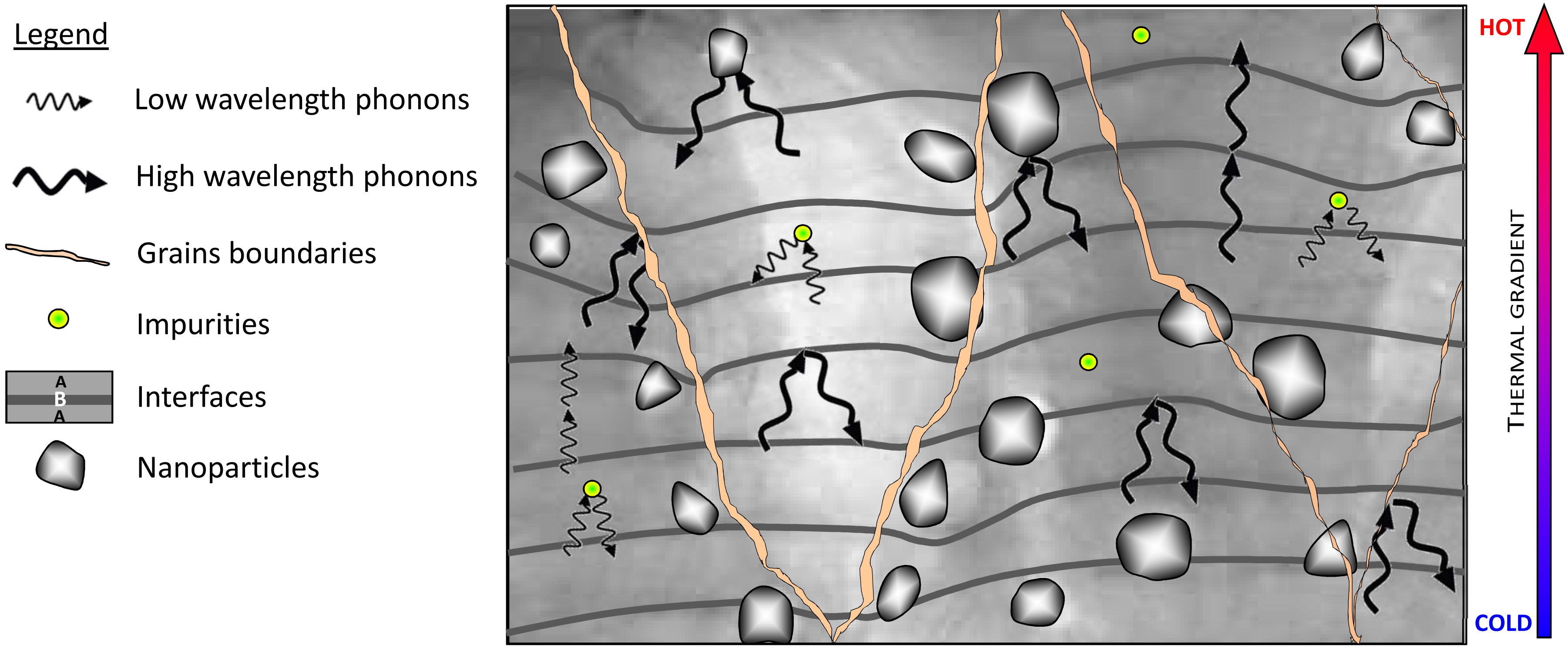
Energy Dispersive X-ray Spectroscopy (EDS) analyses (Ti-P1).

DIFFERENT MECHANISMS OF PHONON SCATTERING

- « classical » scattering mechanisms:
  - grains boundaries diffusion (for polycrystalline materials)
  - impurities diffusion

- « addition » of phonon scattering mechanisms thanks to nanostructuration:
  - scattering with interfaces
  - scattering with nanoparticles

Example with Ti-P1 sample.



CONTENTS

CONCLUSIONS & PERSPECTIVES

- Growth of several thin films nanostructures, superlattices and quantum dot superlattices, monocrystalline and polycrystalline
- Influence of thin films nanostructuration on thermoelectric properties has been highlighted
- In every instance, a decrease of thermal conductivity has been measured
- Specific growth mechanisms have been obtained for silicide-based QDSL (dots accumulation at the grains boundaries, dopant accumulation near the QD) highlighting the different phonon scattering mechanisms
- Next step: integration of QDSL into thermoelectric devices

ACKNOWLEDGEMENTS

- **EUROPEAN UNION**

The research leading to some of these results has been performed within the STREAMS project (www.project-streams.eu) and received funding from the European Union's Horizon 2020 program under Grant Agreement n° 688564

THANK YOU FOR YOUR ATTENTION

Commissariat à l'énergie atomique et aux énergies alternatives
17 rue des Martyrs | 38054 Grenoble Cedex
www-liten.cea.fr

Établissement public à caractère industriel et commercial | RCS Paris B 775 685 019