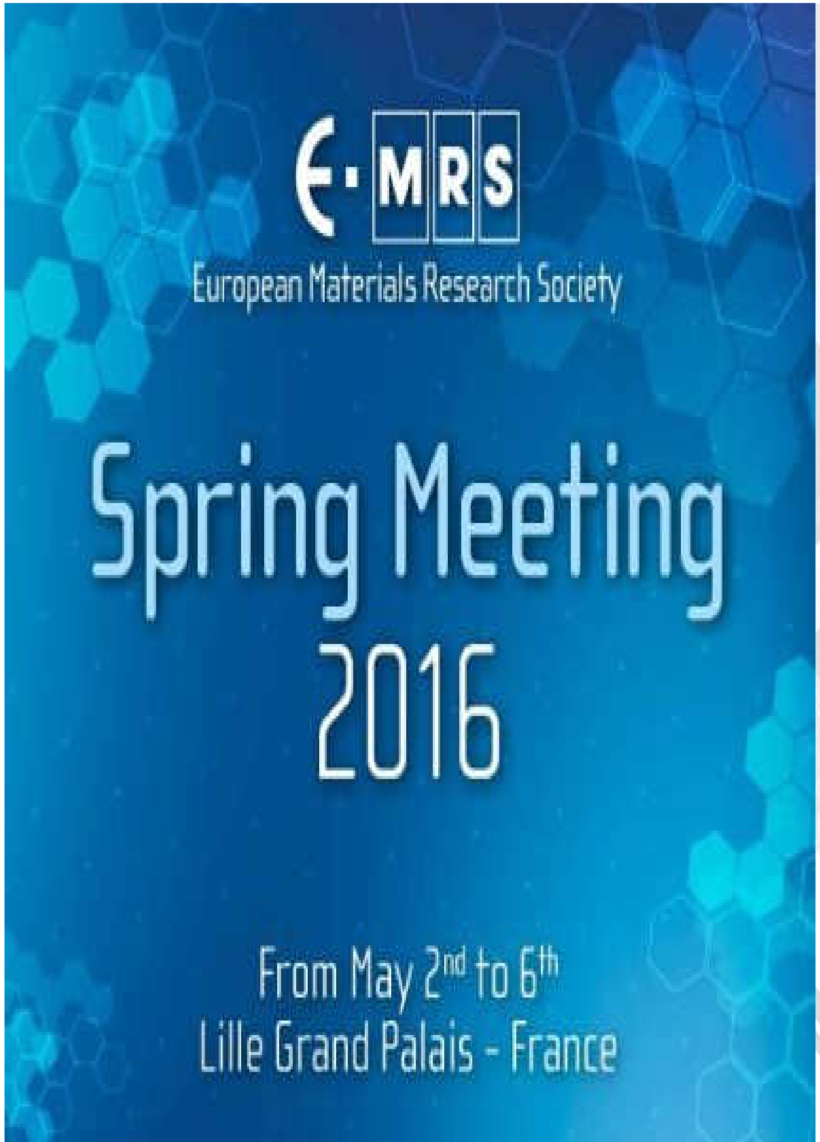


Annealing of heavily boron-doped silicon: effect on electric and thermoelectric properties

UNIVERSITA' DEGLI STUDI DI MILANO BICOCCA
AUDENTES FORTUNA IUVAT

Laura Zulian

Department of Material Science, University of Milano Bicocca

OUTLINE

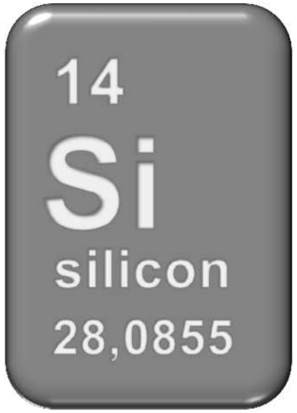
Introduction
- Silicon as thermoelectric material
- State of the art

Experimental work
- Seebeck measurements
- Hall measurements

Results
- Thermal treatments effect
- Transport properties: the two mechanism model

Conclusions and perspectives

SILICON AS THERMOELECTRIC MATERIAL



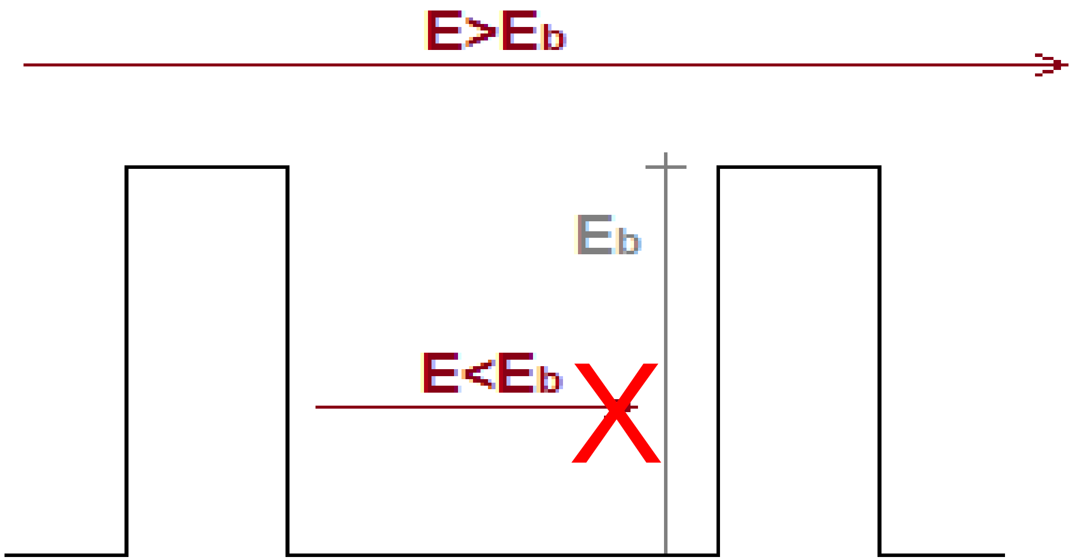
- Great abundance
- Low cost
- Huge know how of producion and manipulation

Poor thermoelectric performances
Si figure of merit ZT≈0.01

$$ZT = \frac{S^2 \sigma}{k_e + k_{ph}} T$$

Increasing power factor $S^2\sigma$ through energy filtering

ENERGY FILTERING

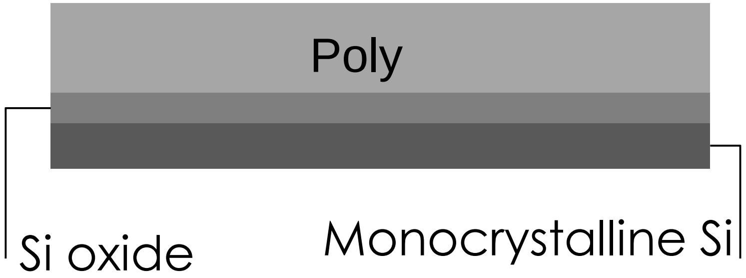


Seebeck coefficient can be increased eliminating low-energy carriers

N. Neophytou, et al;Journal of Electronic Materials **43**, 1896-1094 (2014)

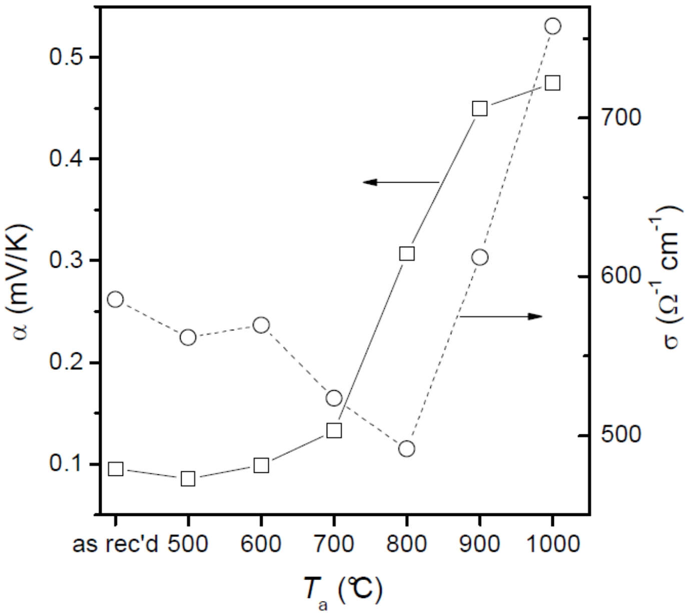
STATE OF THE ART

PolySi thin film (450-200 nm)

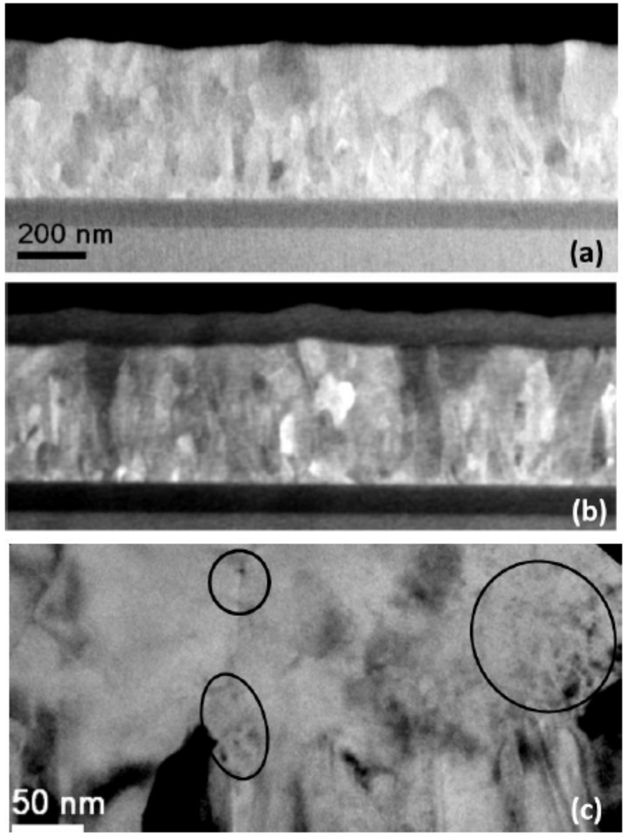


B. Lorenzi et al. Journal of ELECTRONIC MATERIALS, Vol. 43, No. 10, 2014

D. Narducci et al. Journal of Solid State Chemistry **193,** 19–25, (2012)



Annealing sequence from 500 to 1000 °C for 2 h



Formation of precipitates is evidenced by TEM images

EXPERIMENTAL

Polycrystalline silicon d=228 nm

Doping B 4.4 x 10^{20} cm^{-3}

Annealing in Ar following different protocols

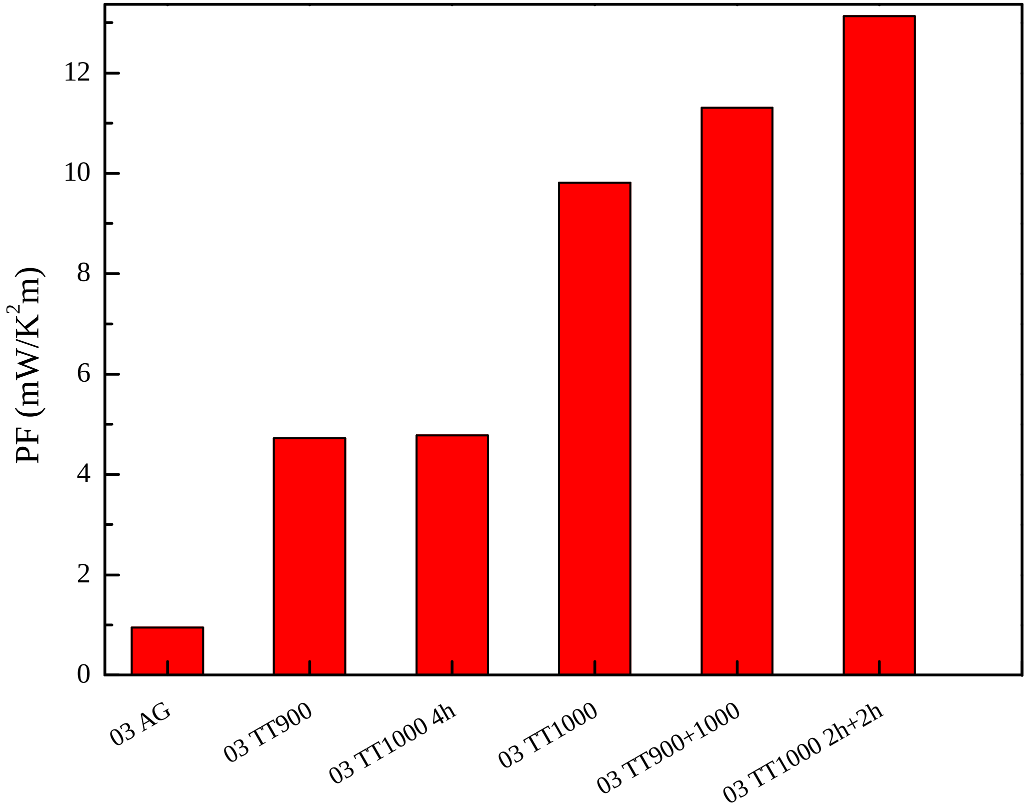
Samples have been submitted to different thermal treatment protocols in order to evaluate the effect of annealing on different TE properties.

Sample	T=900 °C	T=1000 °C	T=1000 °C
AG	-	-	-
TT900(2)	2h	-	-
TT1000(2)	-	2h	-
TT900(2)1000(2)	2h	2h	-
TT1000(2+2)	-	2h	2h
TT1000(4)	-	4h	-

Seebeck sample: 5x50 mm
Hall sample: 12x12 mm

POWER FACTORS

SAMPLE	Power Factor (mW/K^2m)
AG	0.95
TT900(2)	4.72
TT1000(2)	9.82
TT900(2)1000(2)	11.31
TT1000(2+2)	13.13
TT1000(4)	4.78

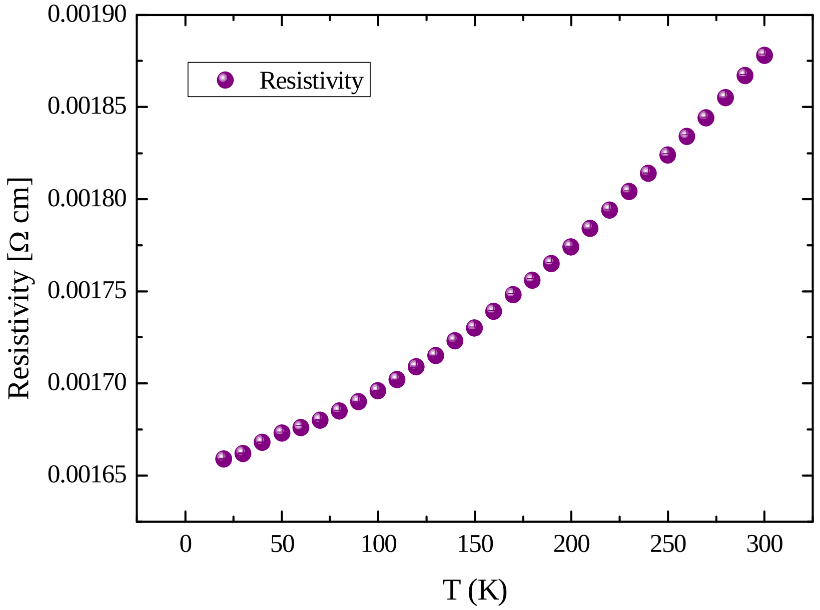


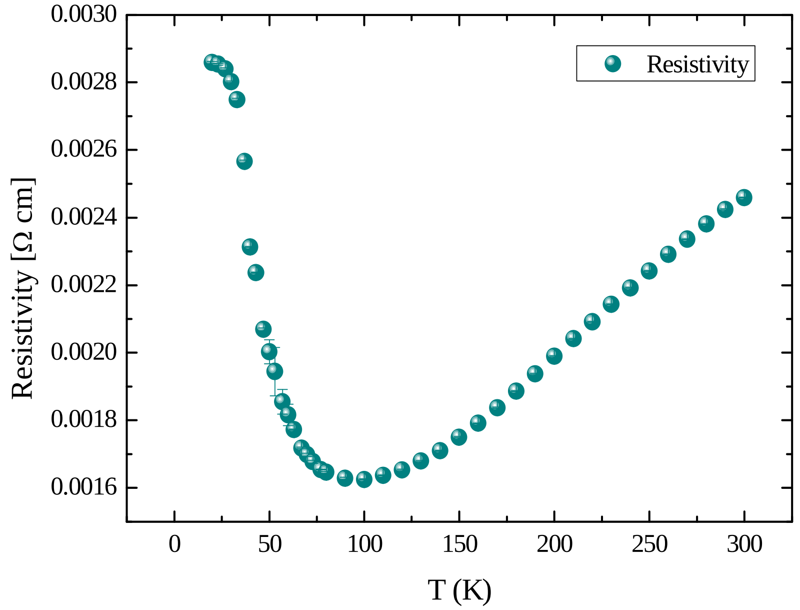
Best result obtained for TT1000(2+2)

Duration of TT is not the only crucial parameter to be taken into account!!

EFFECT OF THERMAL TREATMENTS

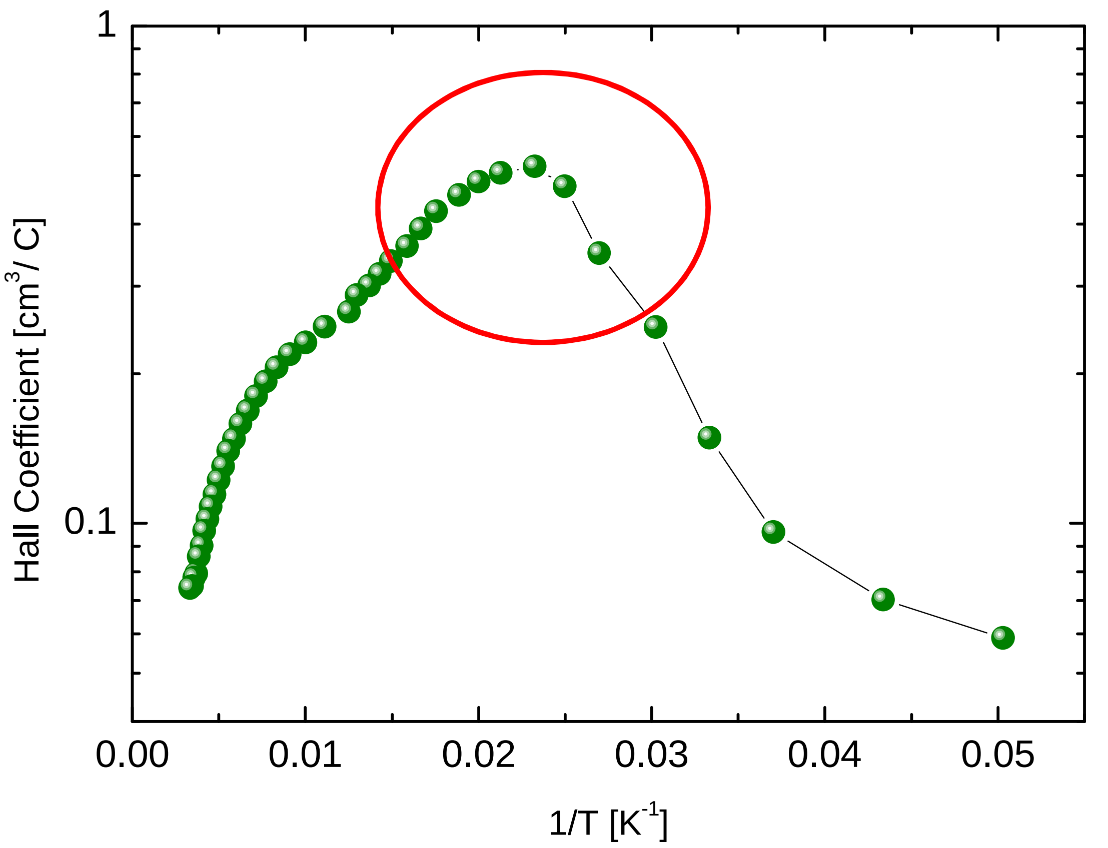
As grown Sample → After thermal treatment



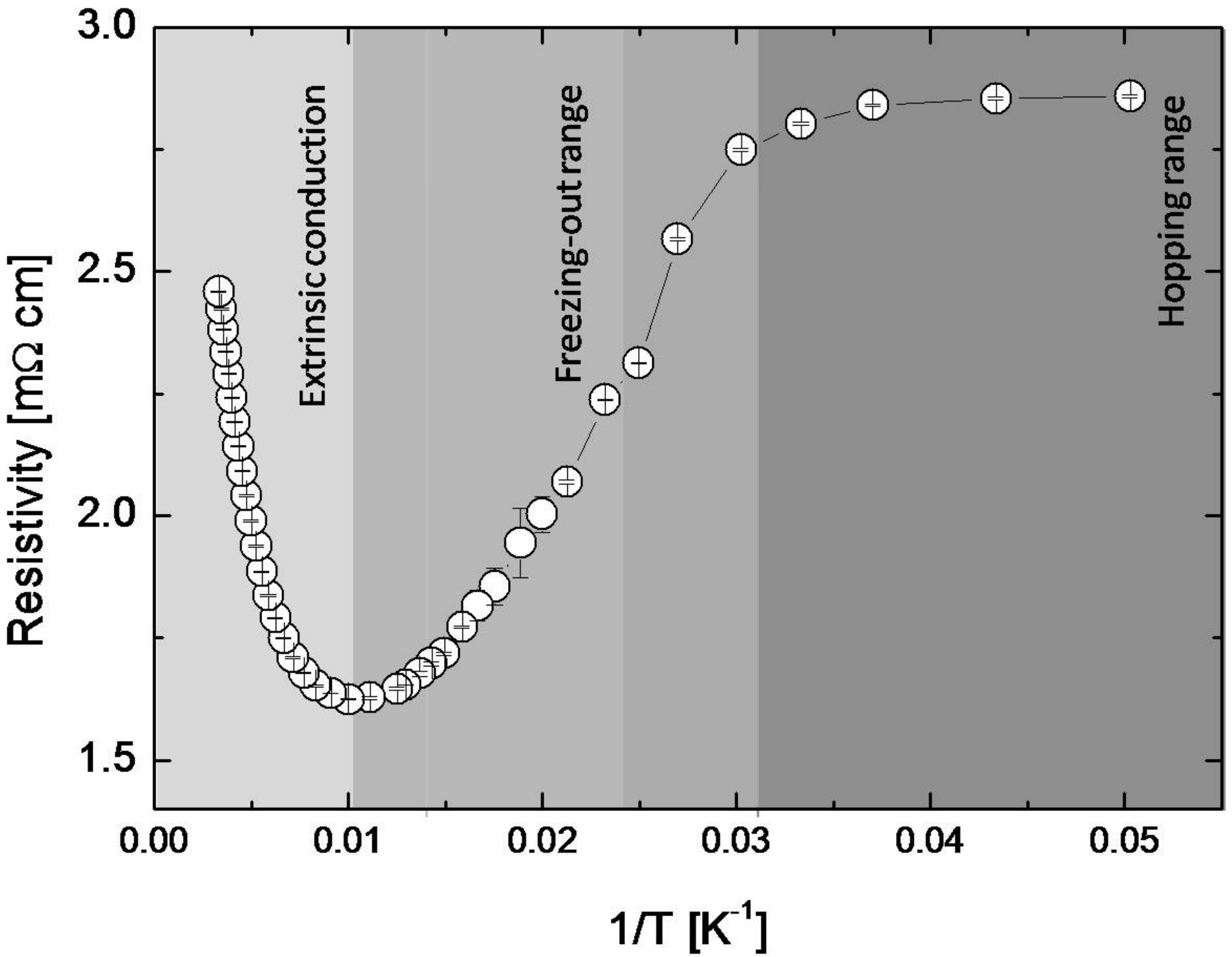


EFFECT OF THERMAL TREATMENTS

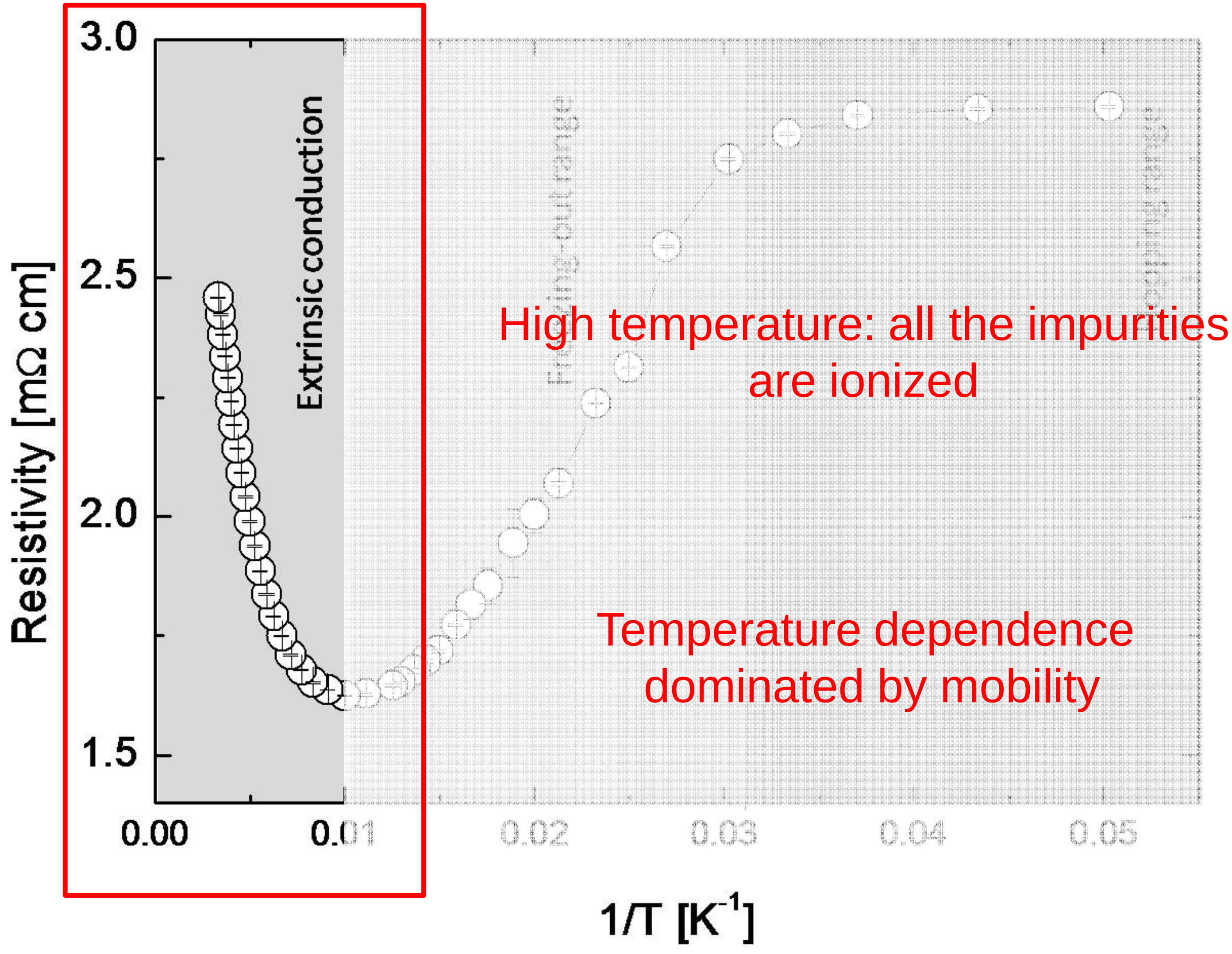
After thermal treatments: Hall coefficient $R = \frac{F}{n_c e}$



CONDUCTION REGIMES



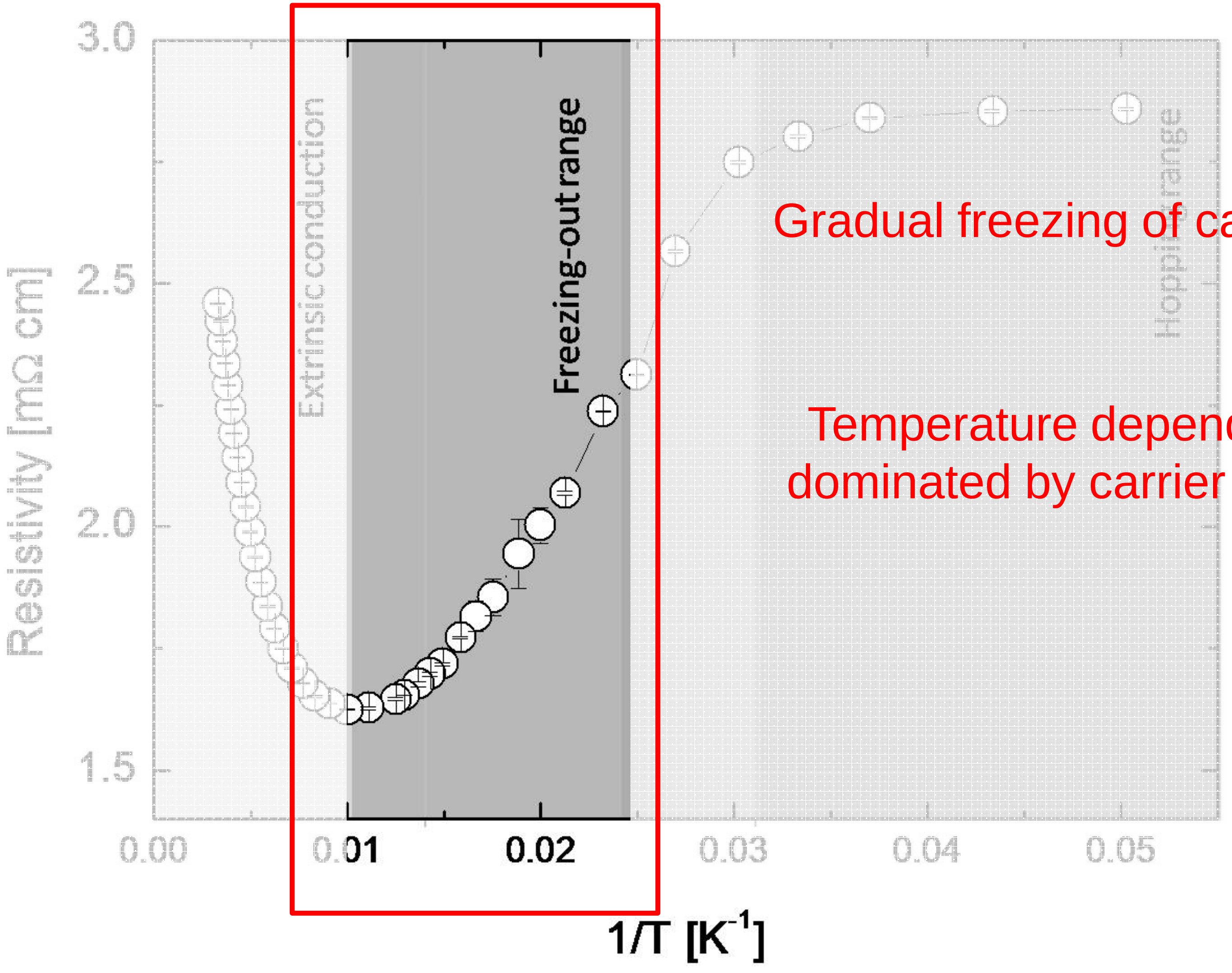
CONDUCTION REGIMES



High temperature: all the impurities are ionized

Temperature dependence dominated by mobility

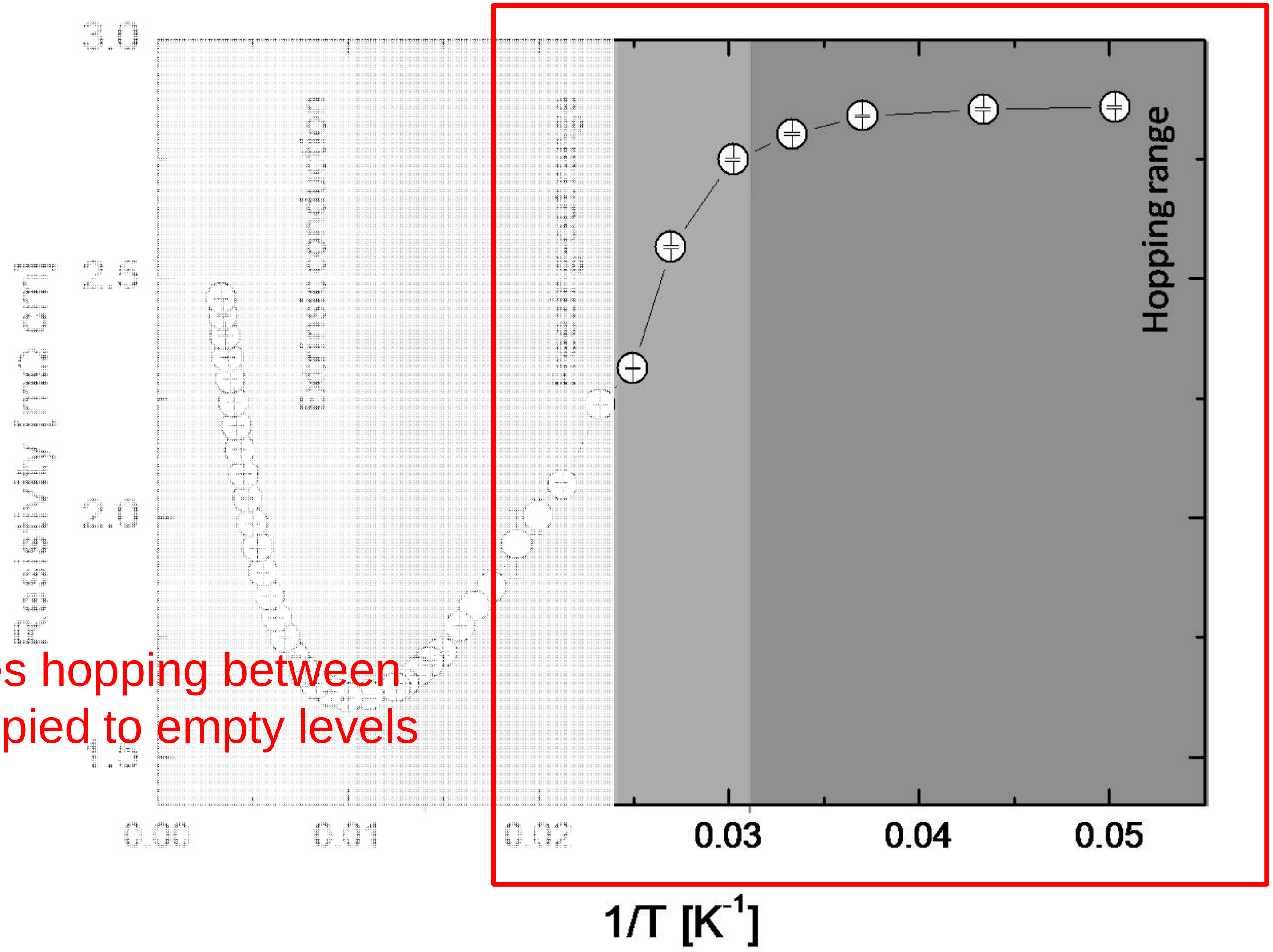
CONDUCTION REGIMES



Gradual freezing of carriers

Temperature dependence dominated by carrier density

CONDUCTION REGIMES



Holes hopping between occupied to empty levels

TWO COMPETING MECHANISM

Impurity semiconductor model (localized energy states)

$$\rho = \frac{1}{n_c e \mu_c}$$

$$R = \frac{F}{n_c e}$$

The model are not longer valid at low temperature!

Different kind of carriers plays a role with different mobility

- conduction band carriers:

σC, $\mu_c = cR_c\sigma_c$

- Hopping conduction carrier:

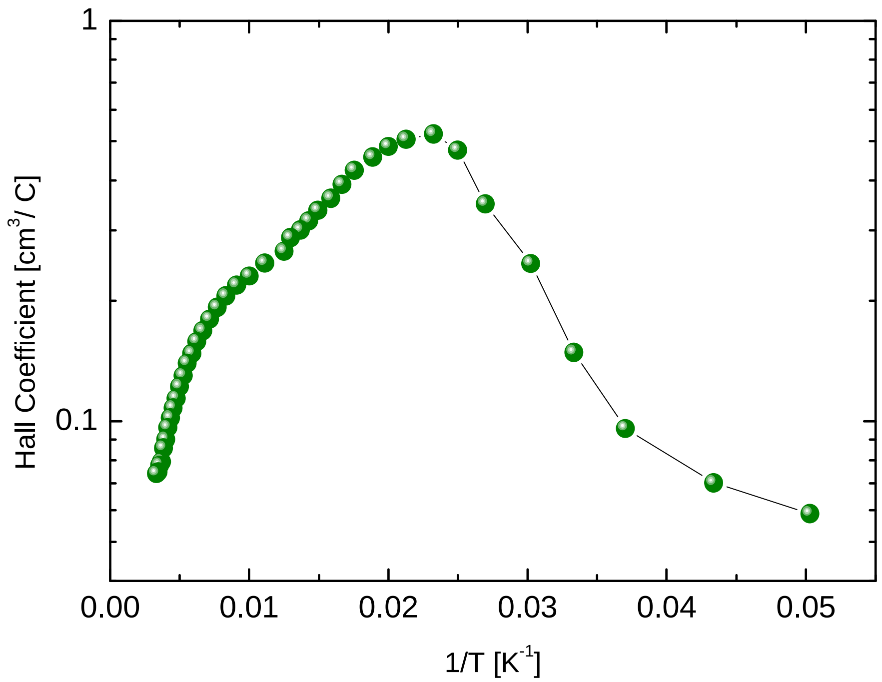
σh, $\mu_h = cR_h\sigma_h$

$$\rho = \frac{1}{n_c e \mu_c + n_h e \mu_h}$$

$$R = F\frac{n_c e \mu_c^2 + n_h e \mu_h^2}{(n_c e \mu_c + n_h e \mu_h)^2}$$

HALL COEFFICIENT

$$R_{c.h} = \frac{1}{en_{c,h}} \qquad \sigma_{c.h} = n_{c,h} e \mu_{c,h}$$



$$R = \frac{R_c \sigma_c^{\ 2} + R_h \sigma_h^{\ 2}}{(\sigma_c + \sigma_h)^2}$$

If $\quad \mu_h << \mu_c$

$$R \approx \frac{R_c \sigma_c^{\ 2}}{(\sigma_c + \sigma_h)^2}$$

We have a maximum for $\sigma_h \approx \sigma_c$

HALL COEFFICIENT

In the low temperature limit $n_c = 0$
(all the carrier are in the impurity band)

$$R = F\frac{1}{n_h e} \approx \frac{1}{ne}$$

In the high temperature limit $n_h = 0$
(all the carrier are in the conduction band)

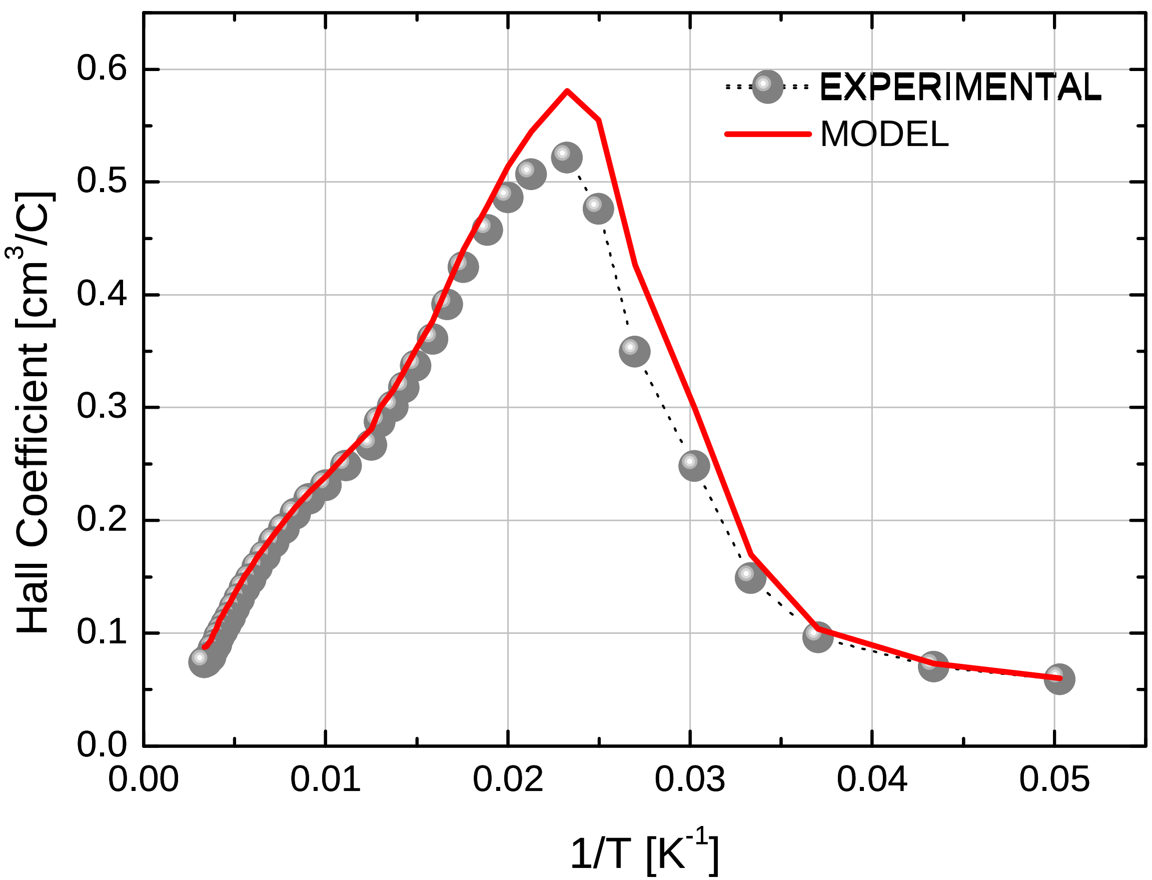
$$R = F\frac{1}{n_c e} \approx \frac{1}{ne}$$

We expect the value of R to be the same at low and high temperature

$$R_{LT}^{EXP} = 0.070 \pm 0.002$$

$$R_{HT}^{EXP} = 0.074 \pm 0.002$$

MODEL VS EXPERIMENTAL DATA



CONCLUSIONS

✓ Study on the annealing effect on TE performances heavily doped nanocrystalline silicon thin film

✓ Best performances for double thermal treatments at 1000 ℃ (power factor 13.13 mW/ K^2 m)

✓ The model used for homogeneous system is not longer valid at low temperature

✓ From resistivity measurements we can distinguish between three different conduction regime in temperature

✓A simply model (two conduction mechanism) reproduces experimental data

✓Relation between TE performances and transport mechanism is still unknow

✓Further investigation and ad hoc model are needed!

UNIVERSITA' DEGLI STUDI DI MILANO BICOCCA

AUDENTES FORTUNA IUVAT

Thermoelectrics Research Group

Prof. Dario Narducci
Laura Zulian
Bruno Lorenzi
Daniela Galliani

This work was supported by FP7-NMP-2013-SMALL-7, SiNERGY (Silicon Friendly Materials and Device Solutions for Microenergy Applications) Project, Contract n. 604169.