European Network on New Sensing Technologies for Air Pollution Control and Environmental Sustainability - *EuNetAir*

COST Action TD1105

INTERNATIONAL WG1-WG4 MEETING on

New Sensing Technologies and Modelling for Air-Pollution Monitoring

Institute for Environment and Development - IDAD

Aveiro, Portugal, 14 - 15 October 2014

Action Start date: 01/07/2012 - Action End date: 30/06/2016 - Year 3: 2014-15 (*Ongoing Action*)

MULTI SENSOR PLATFORM FOR SMART BUILDING MANAGEMENT - PROGRESS AND ASPECTS OF NANOWIRE INTEGRATION

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Outline

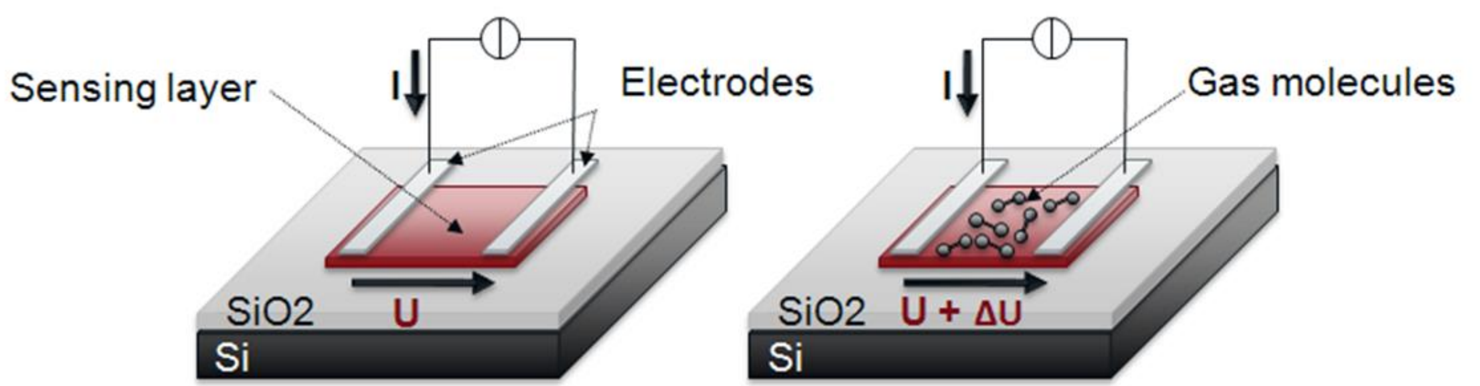
1. Overview MCL
2. Overview MSP-Project
3. Metal Oxide Nanowires
   3.1 SnO_2-NWs
   3.2 CuO-NWs
4. Summary & Outlook

1. Overview MCL

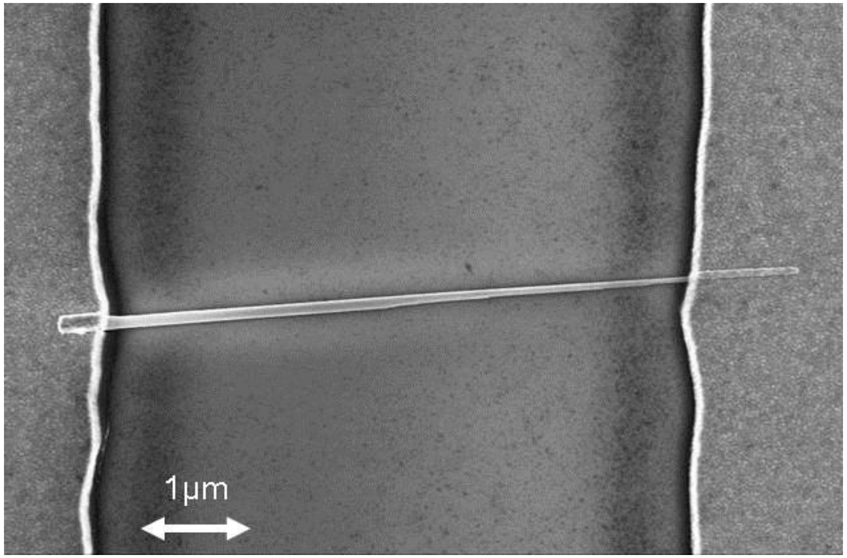
Thin film and nanowire sensors

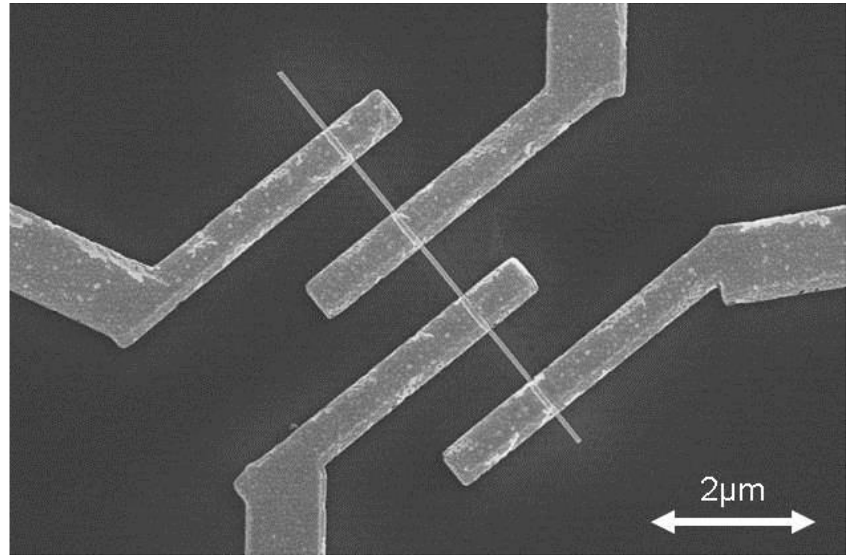
- SnO_2-thin films
- SnO_2-NWs (n-type)
- CuO-NWs (p-type)
- ZnO-NWs (n-type)

Target gases:
CO, H_2, H_2S, O_3
CO_2, VOCs, NO_2
In dry and humid air



Single NW-devices (SnO_2, CuO, ZnO)

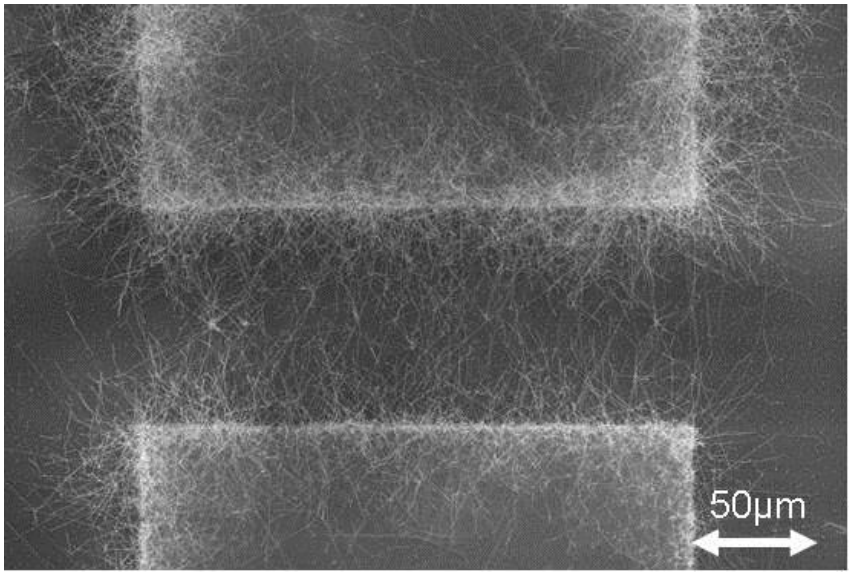


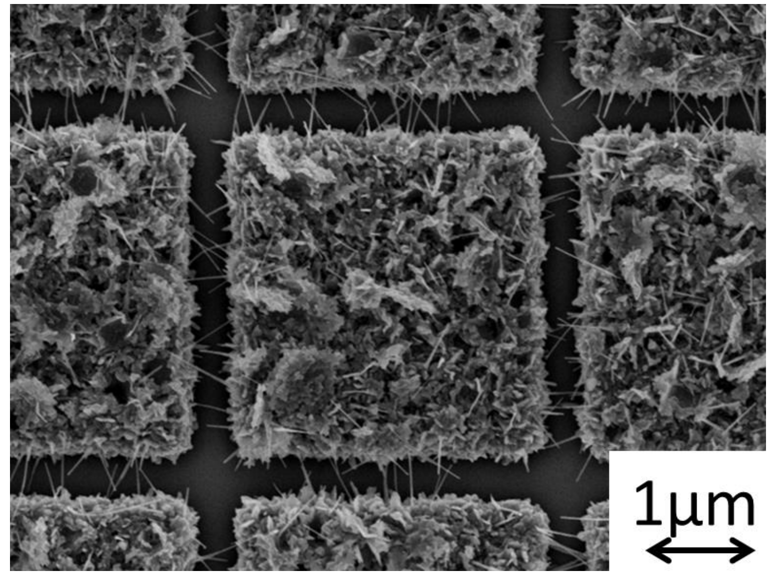


- CuO NW sensor fabricated by optical lithography
- 2-point measurement
- L ~ 6,5 µm, diameter ~120 nm

- CuO NW sensor fabricated by e-beam lithography
- 4-point measurement
- L ~ 900 nm, diameter ~ 50 nm

Multi NW-devices (SnO_2, CuO, ZnO)

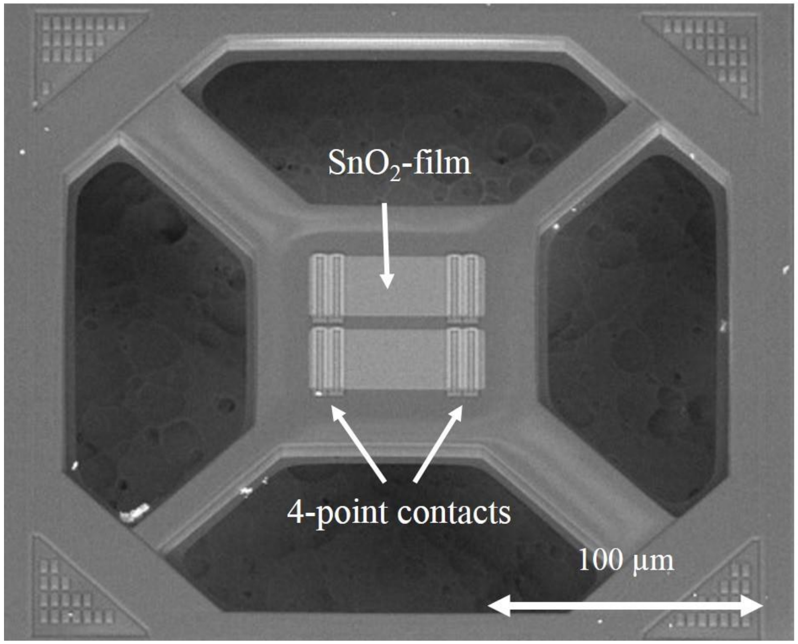


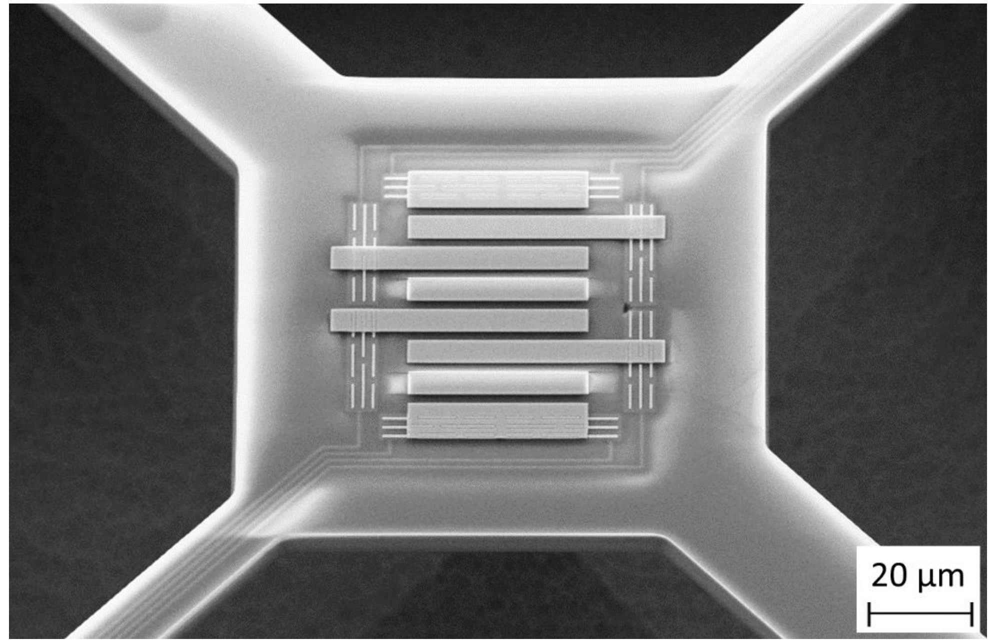


- SnO_2 nanowires locally synthesized on 200 µm wide metal stripes

- Thermal oxidation at 400ºC in ambient atmosphere for 1h
- ZnO NWs bridging the gaps

Integration on CMOS µhp (SnO_2 thin film, SnO_2, CuO, ZnO-NWs)



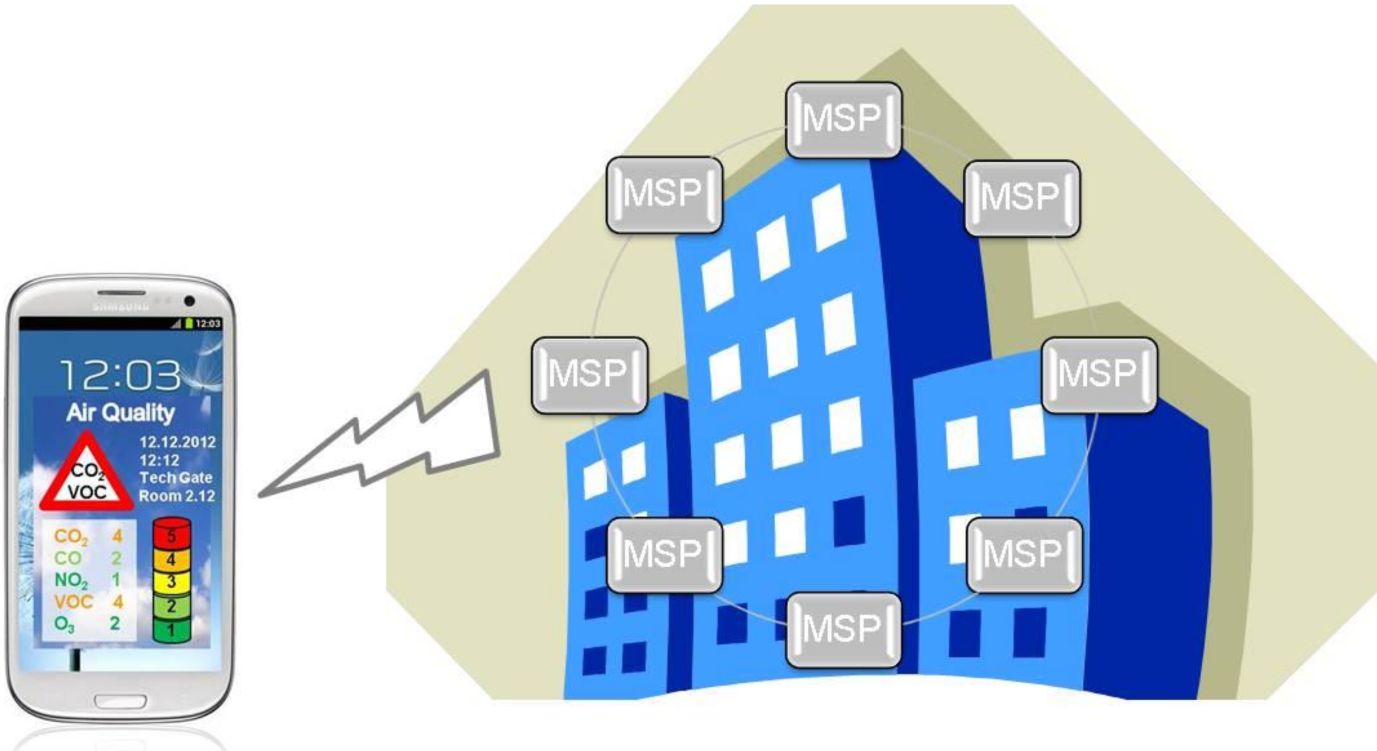


- Post processing
- Spray pyrolysis
- 50nm SnO_2 film (T_{max} = 400ºC)

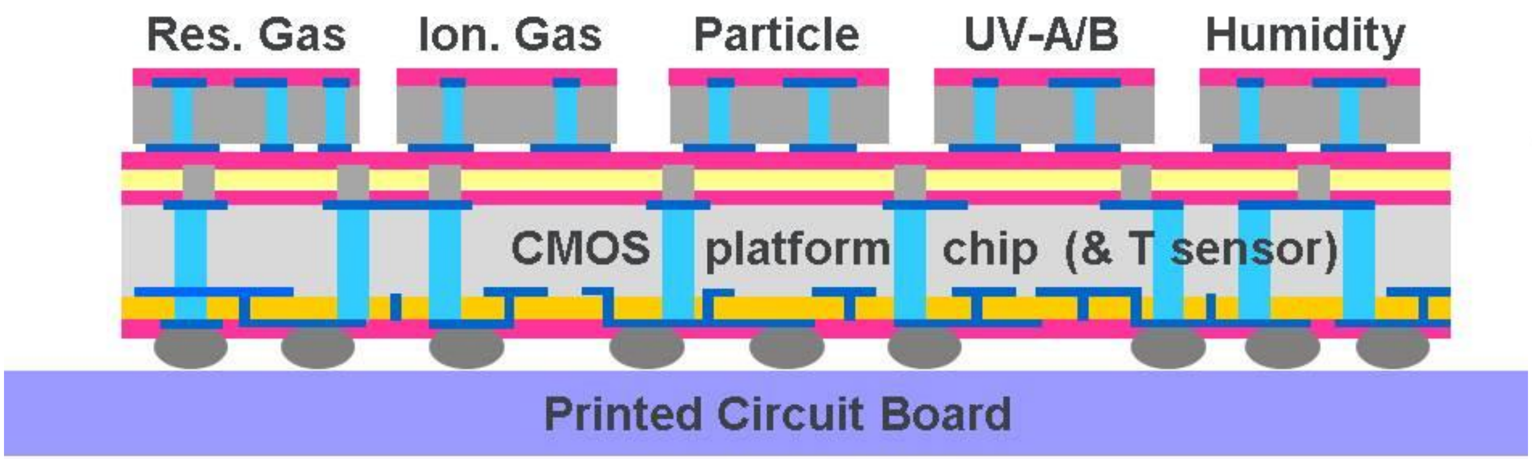
- 500 nm Cu on CMOS - Gap 2µm
- Thermal oxidation process on CMOS µhp
- 350ºC for 1h in air (< 400ºC!)

2. Overview MSP Project

MSP - Multi Sensor Platform
for Smart Building Management



- Platform chip as basic “LEGO™” building block for 3D-integration to MSP Multi Sensor Systems
- Development of processes and technologies for 3D-integration of sensors and devices
- “Other than CMOS compatible materials” (GaN, CNTs,…)



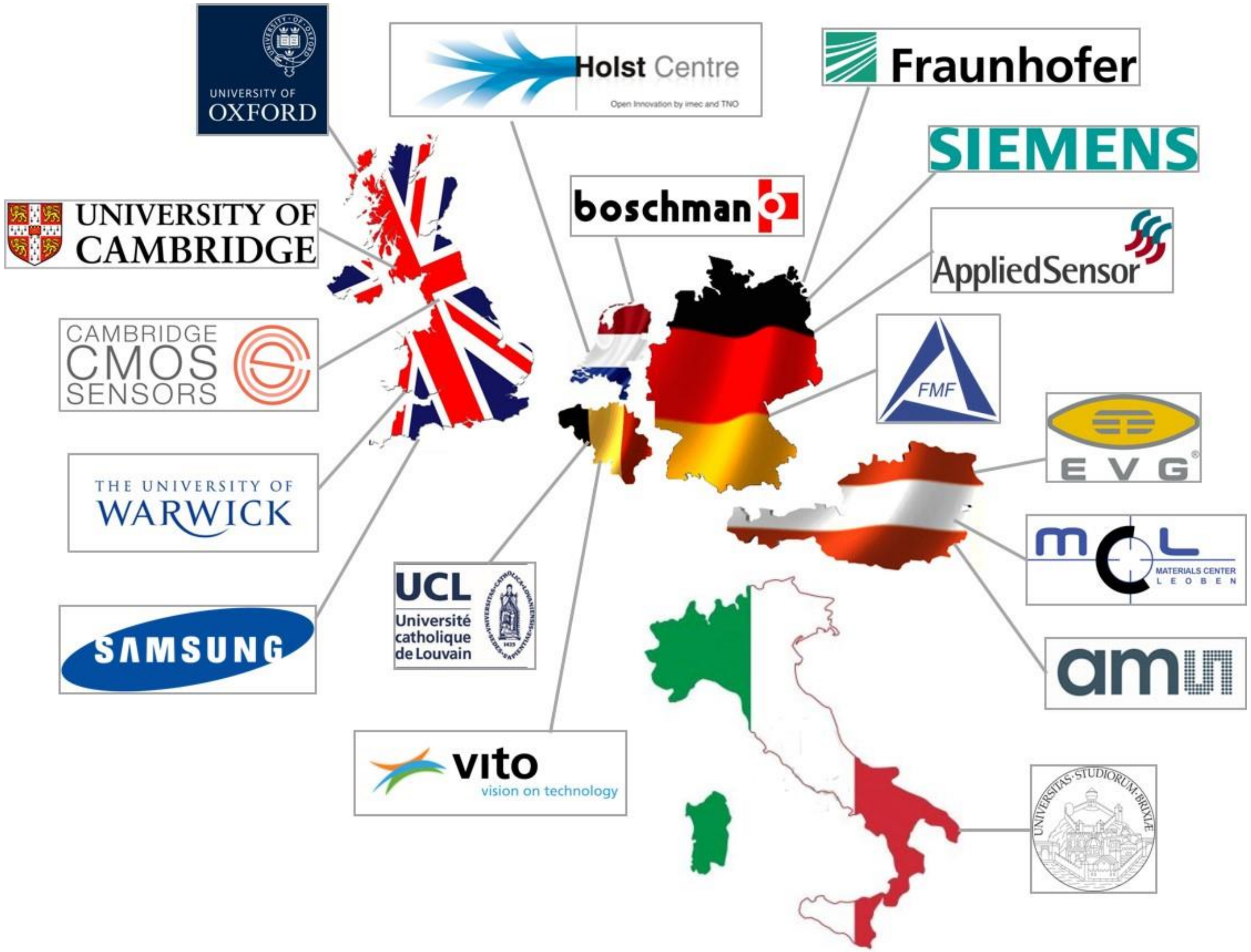
MULTI SENSOR PLATFORM

Target Parameters

Indoors
CO, CO_2, VOCs, PM

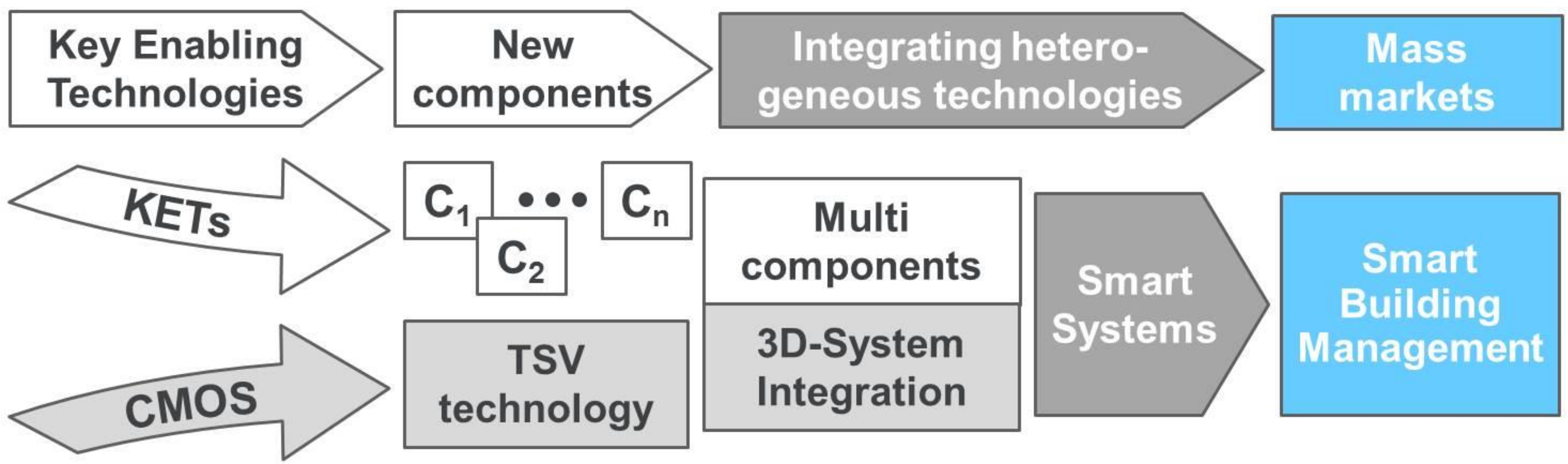
Outdoors
NO_2, O_3, CO, PM_{10}, $PM_{2.5}$, UFPs

- 17 partners from 6 countries



MSP Concept & Objectives

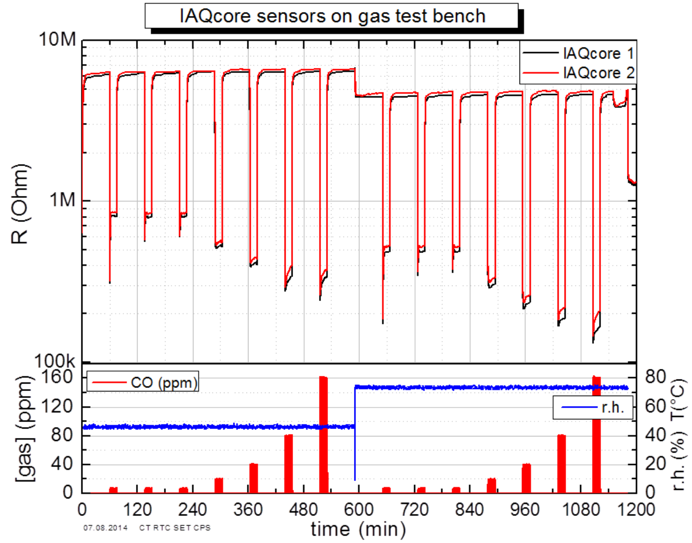
- CMOS technology as sound foundation to ensure cost efficient mass fabrication
- Take-up of Key Enabling Technologies for new components and devices
- Integrating heterogeneous technologies for realization of smart systems



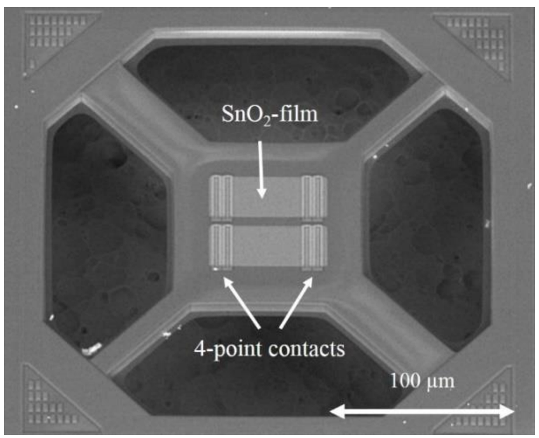
MSP-specific KETs: Nanotechnology

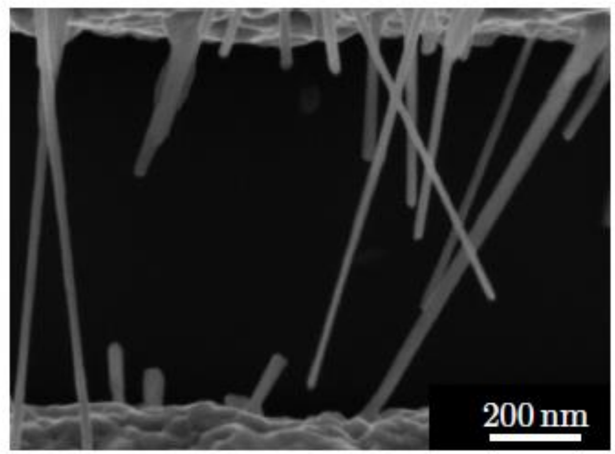
- APPS: SnO_2 film
- MCL: SnO_2 thin film + (SnO_2, CuO, ZnO)-NWs
- IMEC: GaN/AlGaN
- UCAM: Graphene & CNTs
- ALU-FR: (bi)metallic Nanoparticles
- UCL: Graphene
- UNIBS: SnO_2, CuO, ZnO, RuO-NWs

APPS: SnO_2 film

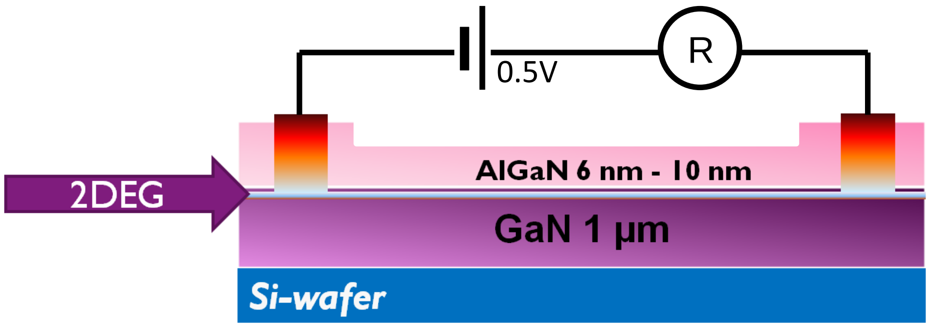


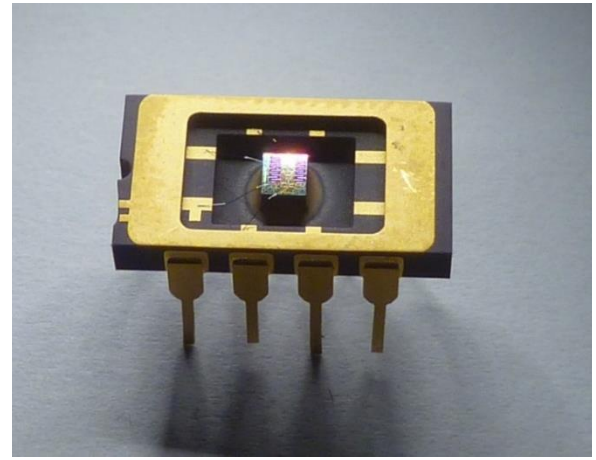
MCL: SnO_2 film & NWs



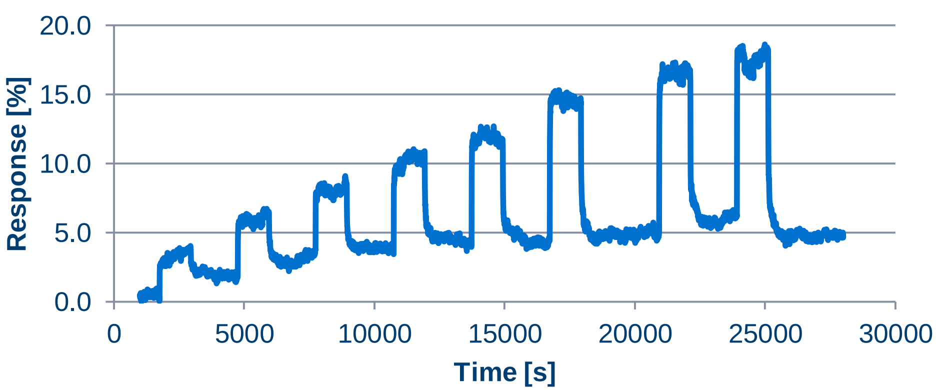


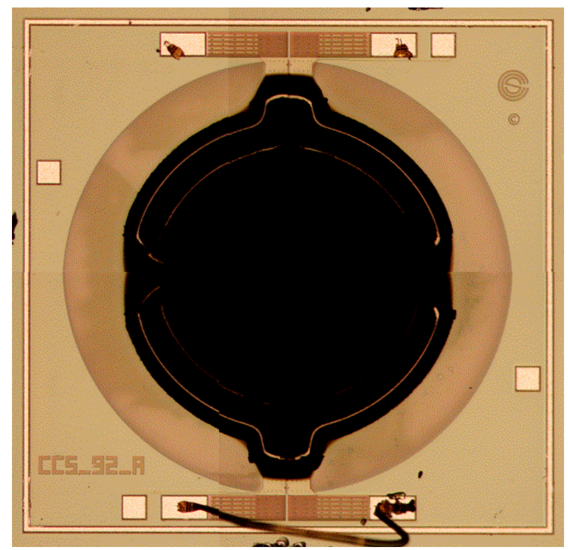
IMEC: GaN/AlGaN





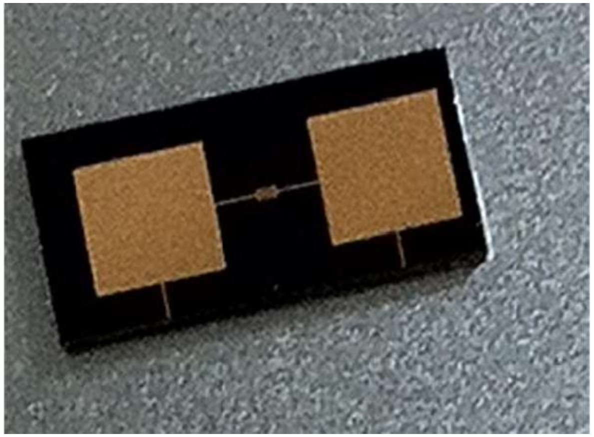
UCAM: Graphene & CNTs

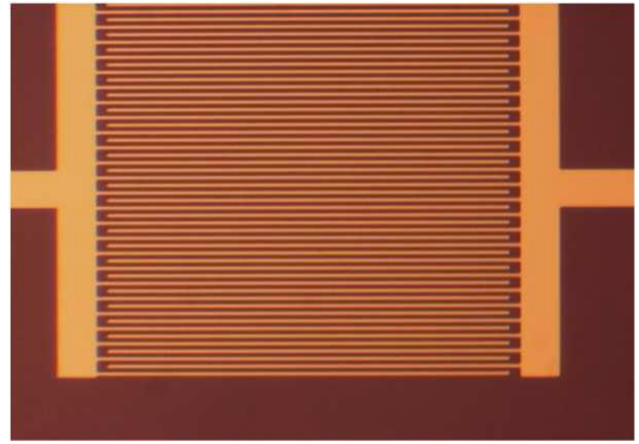




Multi Sensor Platform

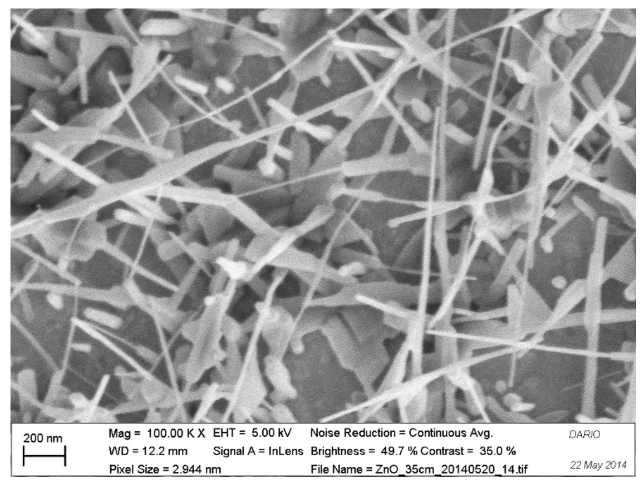
UCL: Graphene





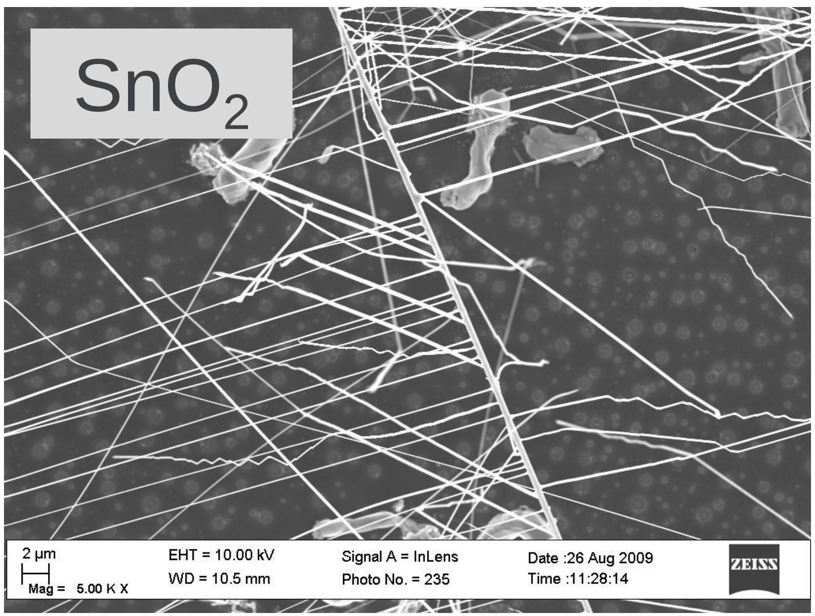
UNIBS: Nanowires

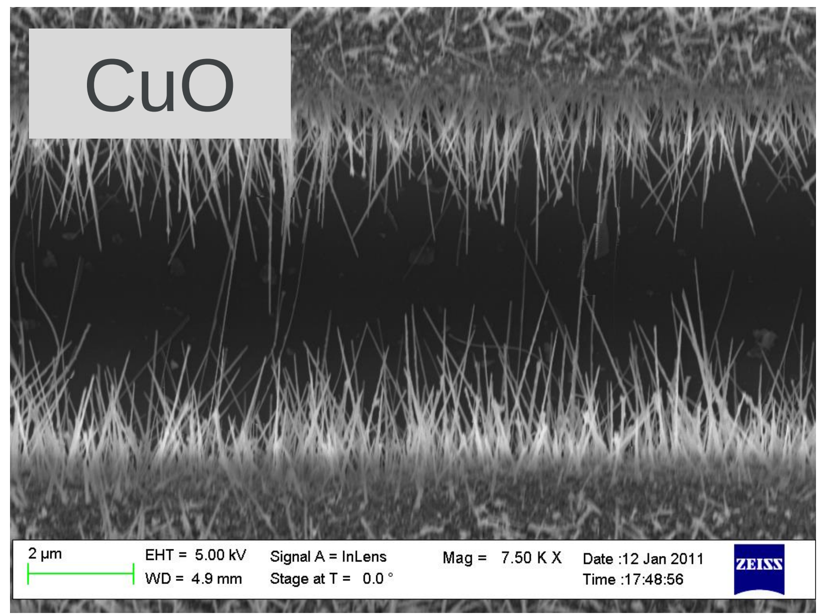
- Vapour Phase Growth (PVD)
- Thermal Evaporation
- Thermal Oxidation
- Anodization



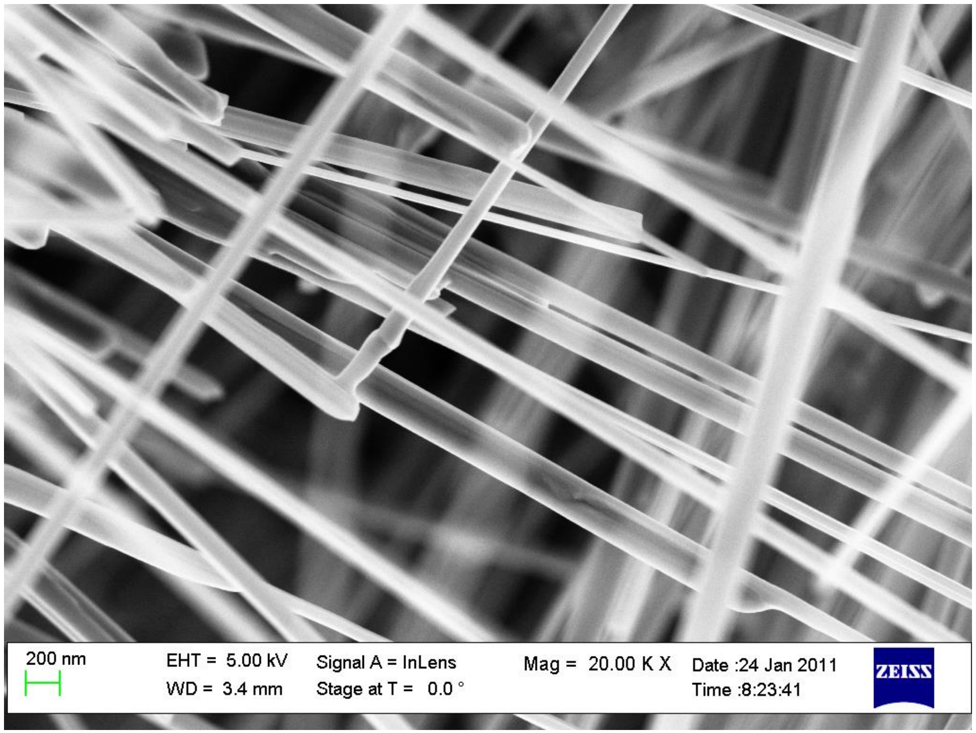
3. Metal Oxide Nanowires

- Versatile tools for many applications !
- Variety of materials (Si, III-V, polymers, CNTs, metal oxides,…)
- Different geometries (length, diameter, shape,…)

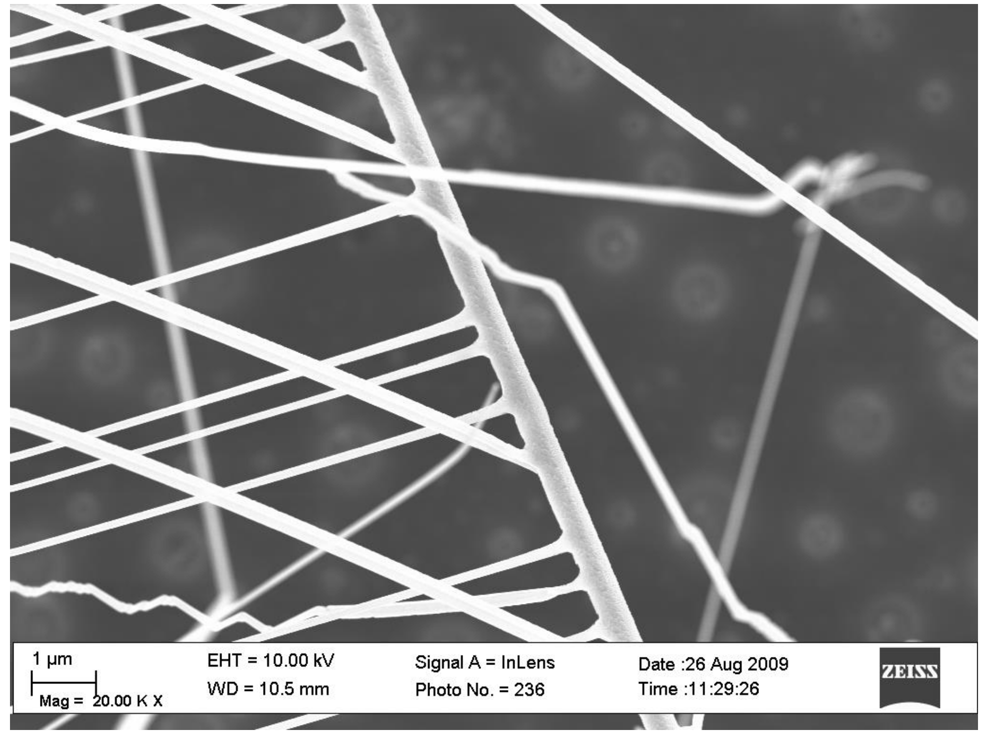




CuO


200 nm
EHT = 5.00 kV
WD = 3.4 mm
Signal A = InLens
Stage at T = 0.0 °
Mag = 20.00 K X
Date :24 Jan 2011
Time :8:23:41
ZEISS

SnO_2


1 µm
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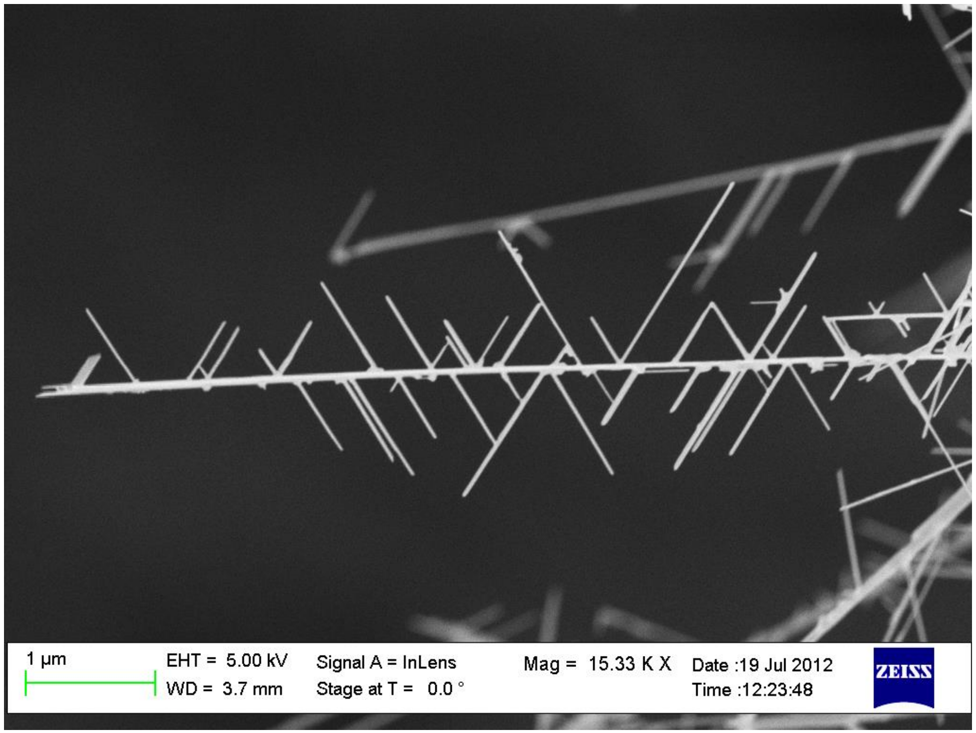
EHT = 10.00 kV
WD = 10.5 mm
Signal A = InLens
Photo No. = 236
Date :26 Aug 2009
Time :11:29:26
ZEISS

ZnO


1 µm
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WD = 3.7 mm
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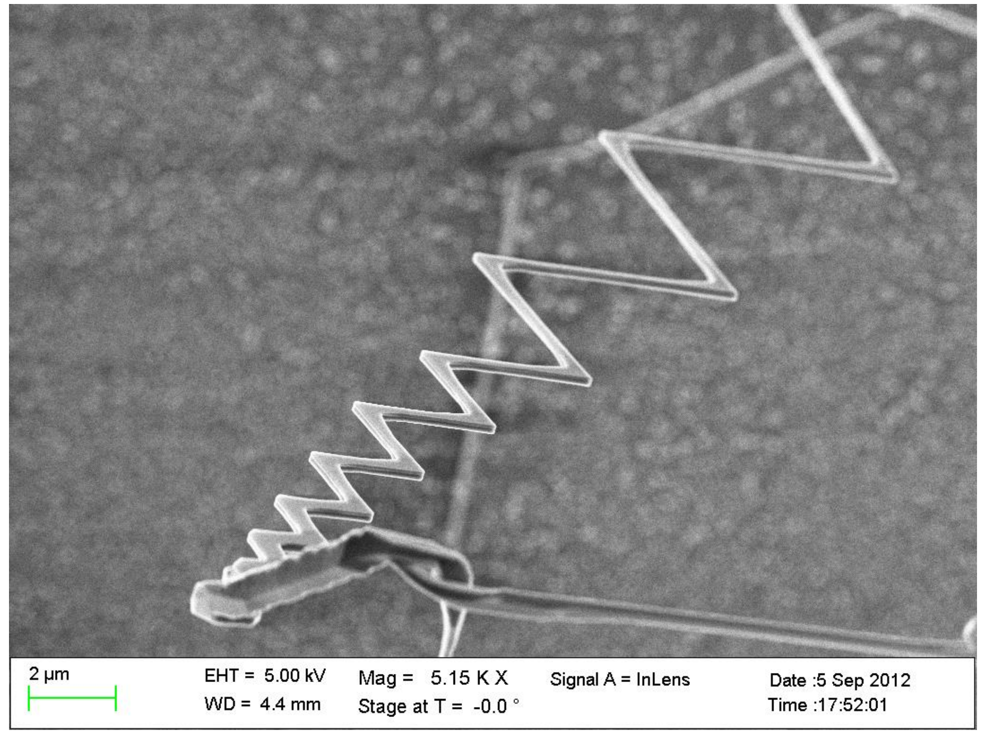
ZEISS

SnO_2


2 µm
EHT = 5.00 kV
WD = 4.4 mm
Mag = 5.15 K X
Stage at T = -0.0 °
Signal A = InLens
Date :5 Sep 2012
Time :17:52:01

Single crystalline,….

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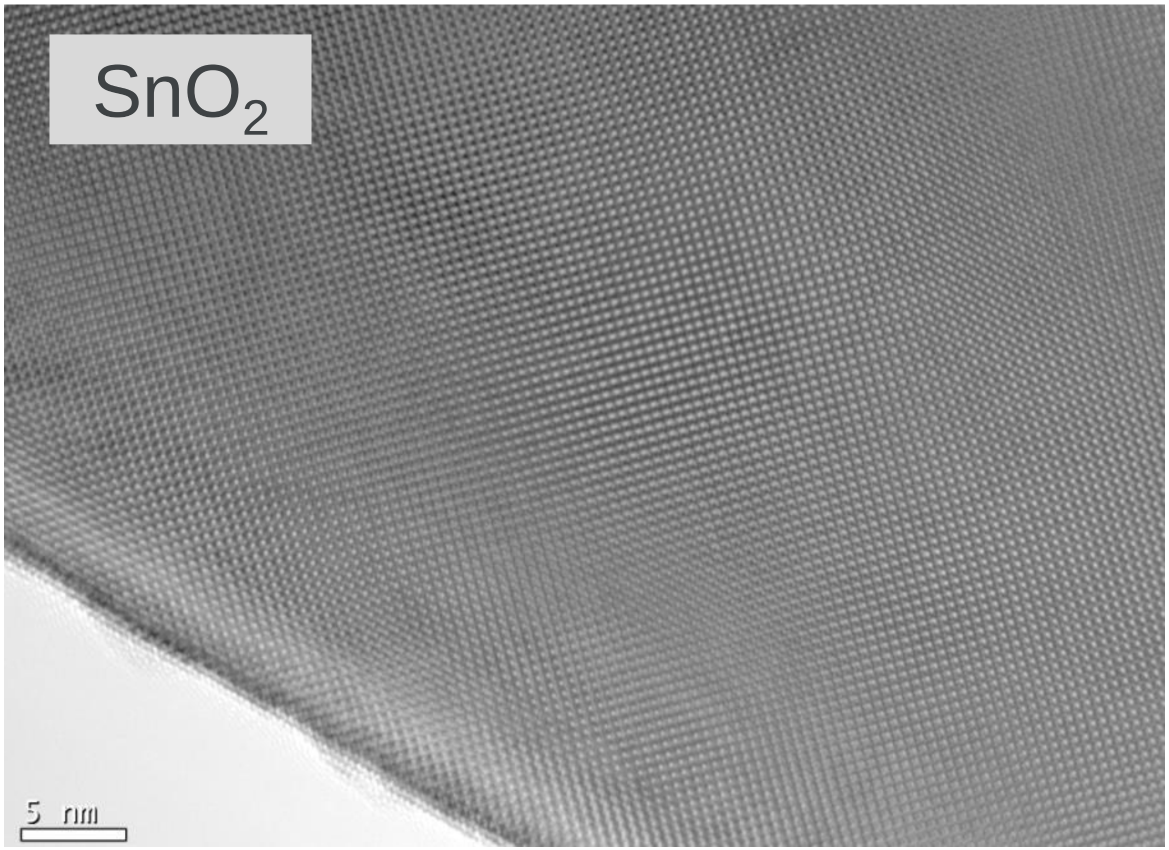
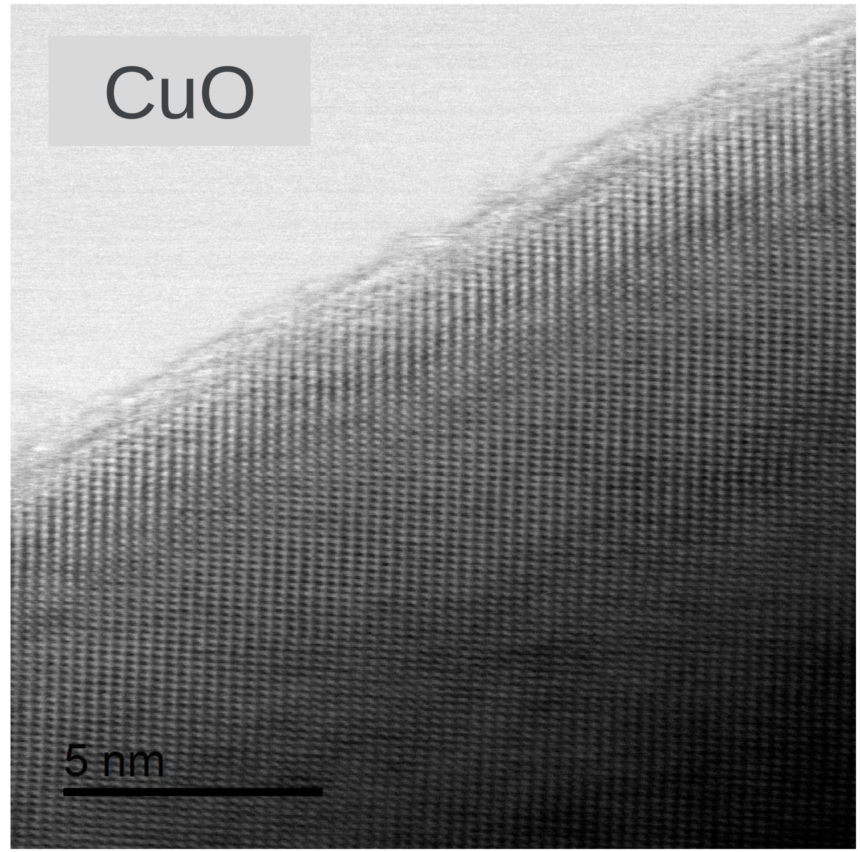
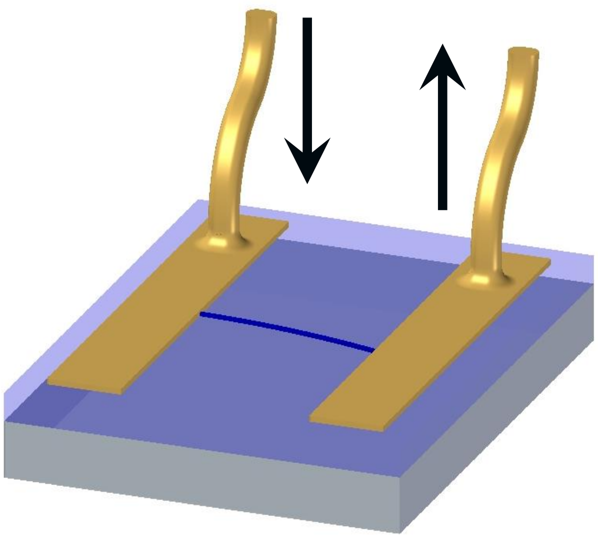
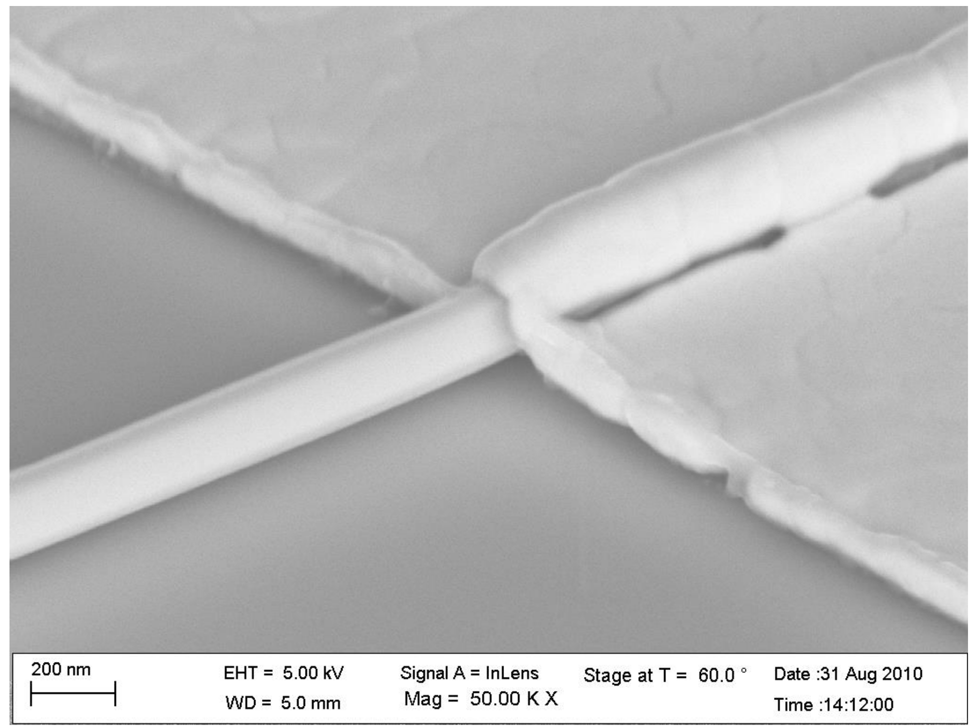




3.1 SnO_2-NW Gas Sensor

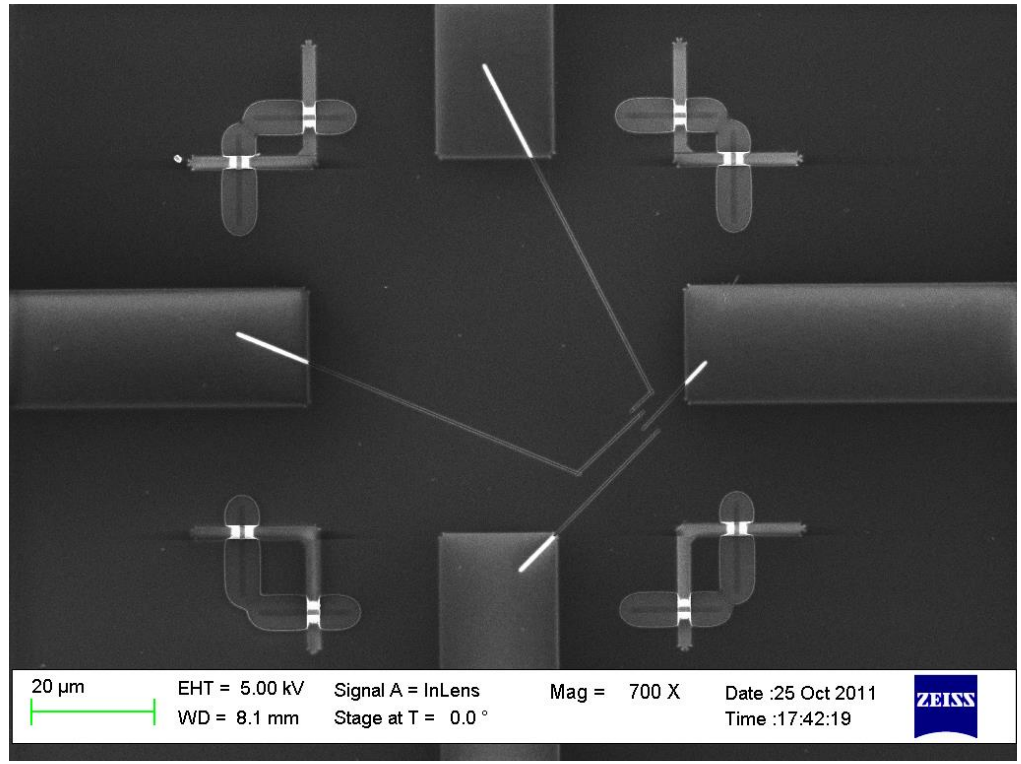
- Growth of NWs and harvesting in Isopropanol
- Transfer of SnO_2-NWs on SiO_2/Si-Substrate
- Spin coating of NW suspension
- Photolithography
- 200 nm Ti-Au + lift-off



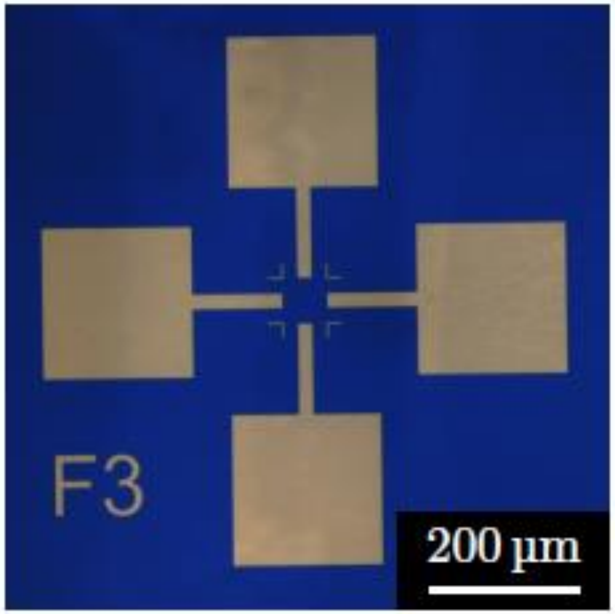


Device fabrication

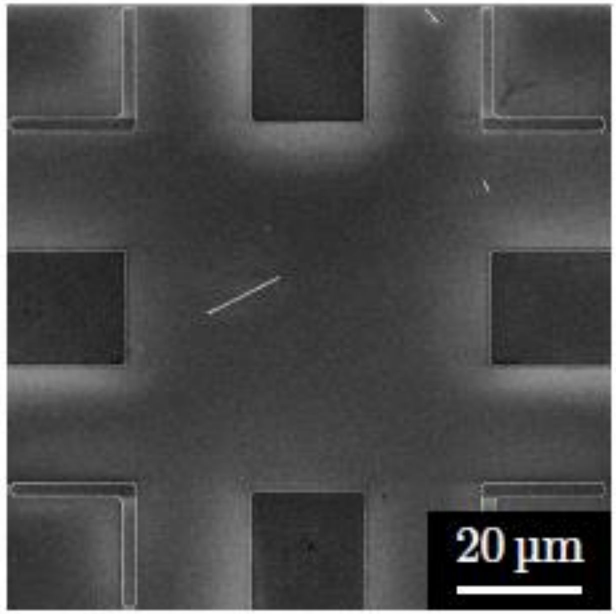
- Optical Lithography
- Spin coating of CuO NWs
- SEM imaging of NW
- Spin coating e-beam resist
- Writefield alignment
- E-beam exposure
- Metallization + lift-off



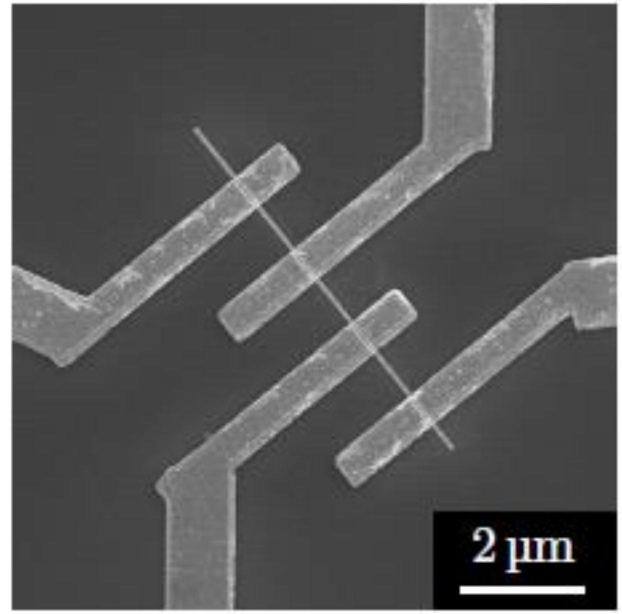
Single NW-devices



(a) Pre-patterned substrate



(b) Nanowire imaging



(c) Typical final device

Problems ?

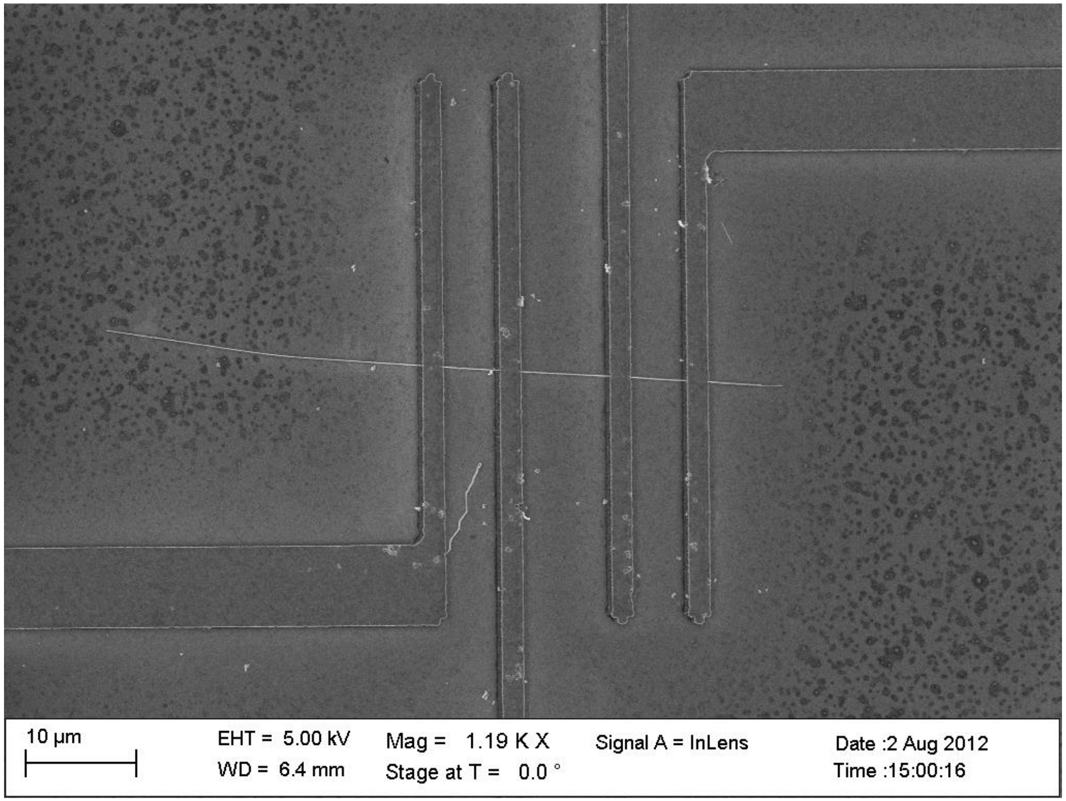
Yes !

Lot of problems with NWs concerning reproducibility and reliability!

Problems 1

- Reproducibility !
- Each device is a unique device !

Elise Brunet, PhD Thesis: "Fabrication of tin oxide nanowire gas sensors" (2014)



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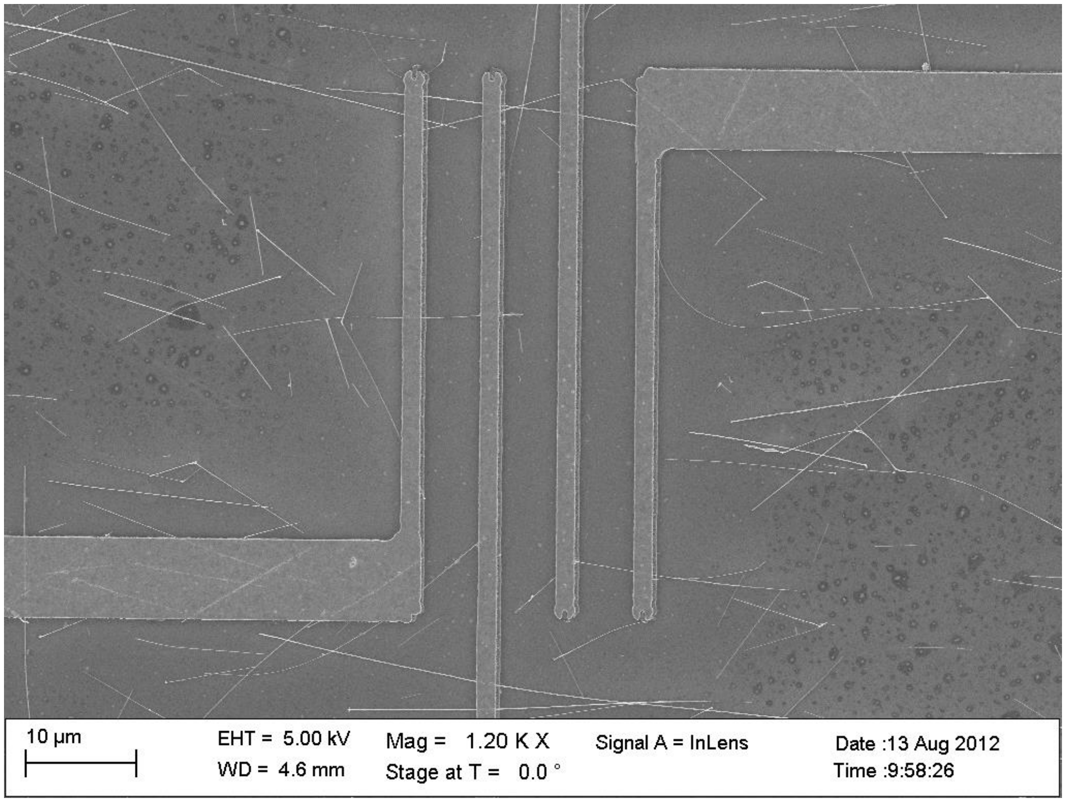

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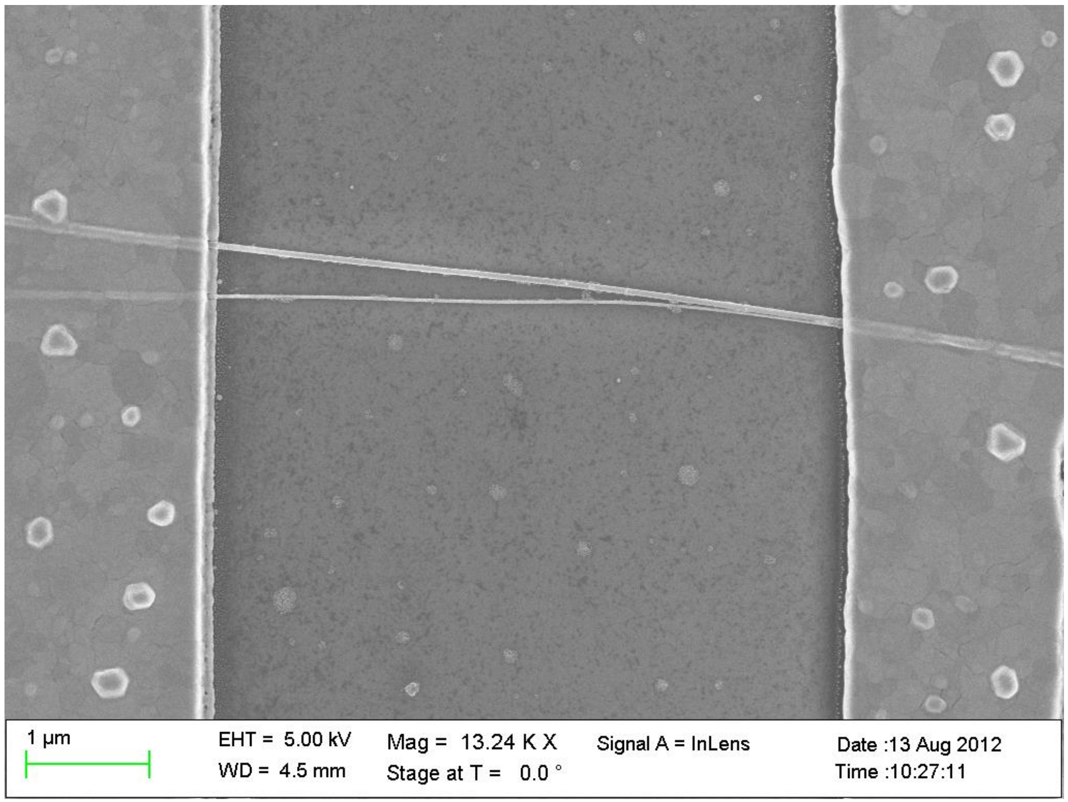

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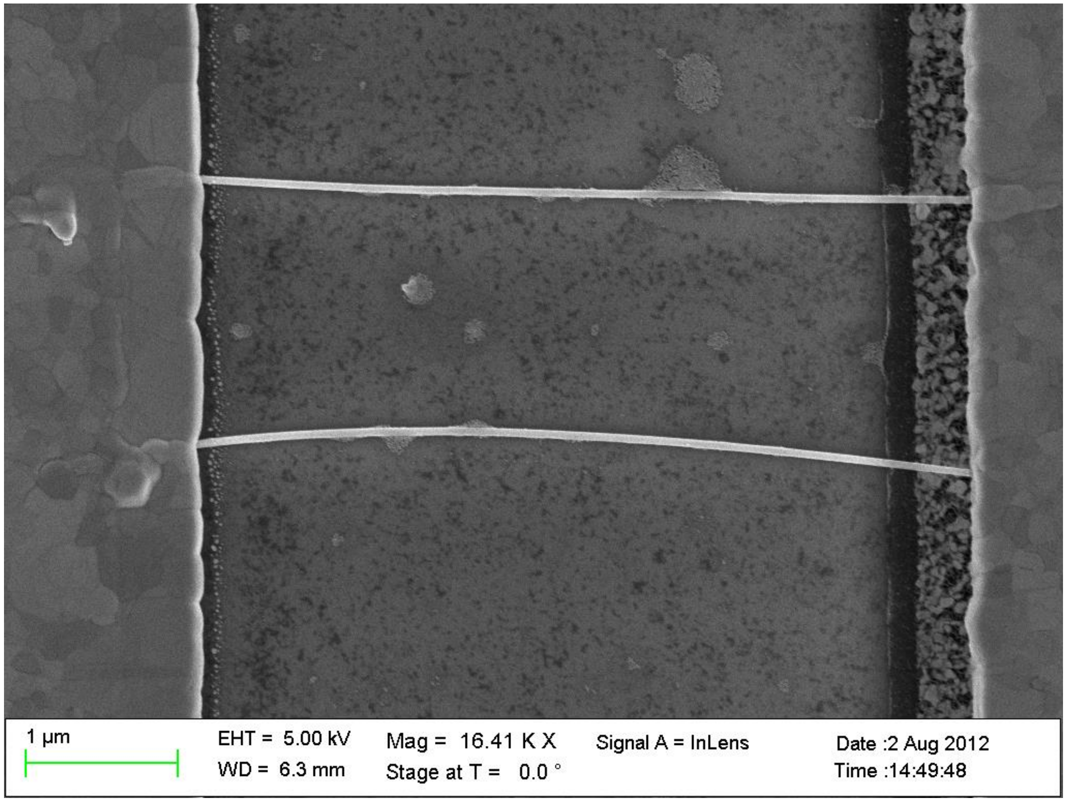
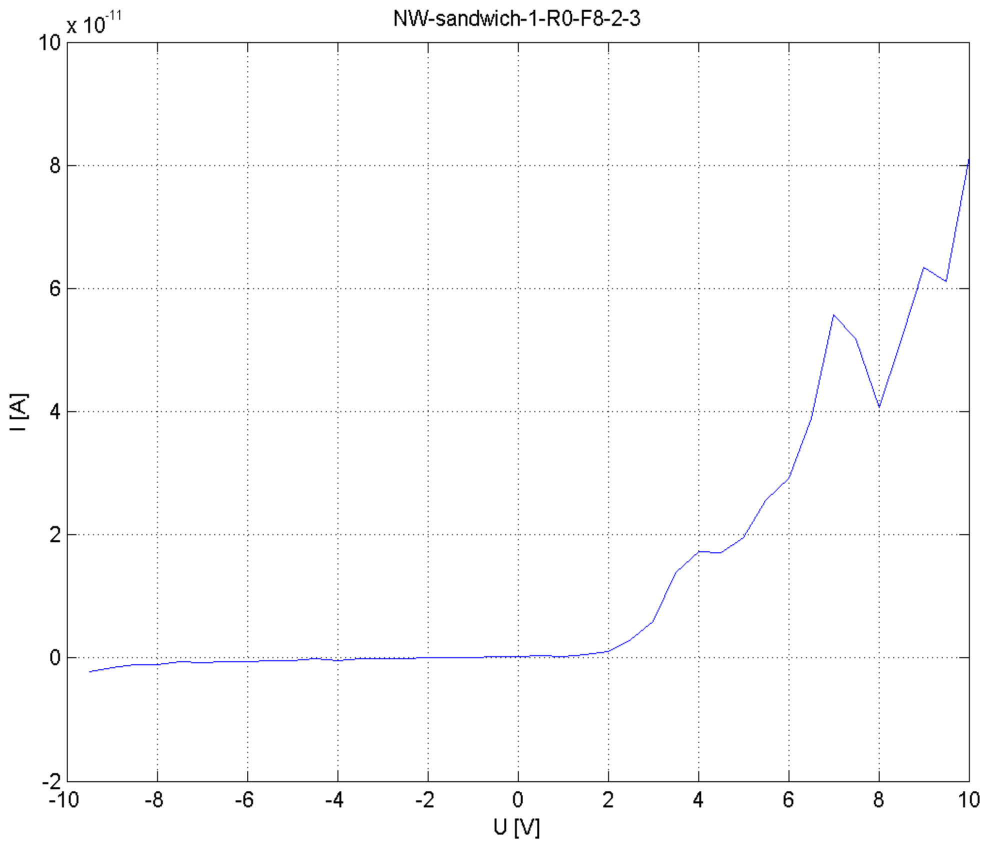
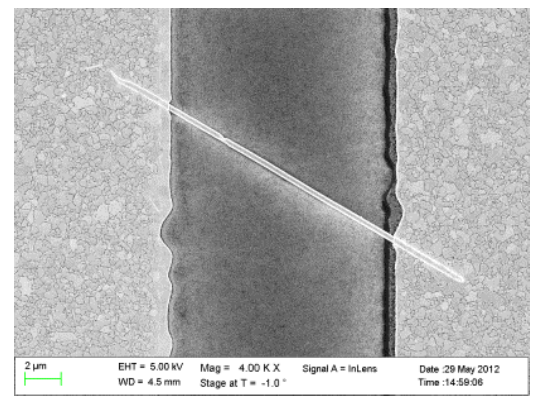


Problems 2

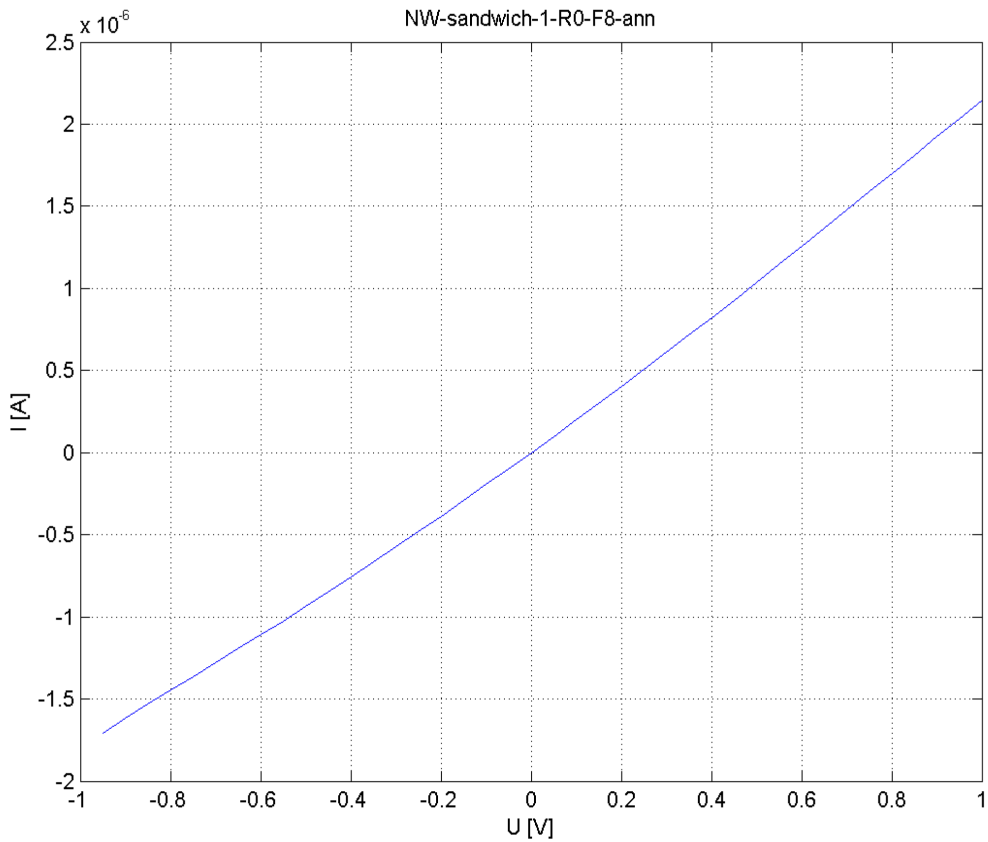
- Metal contacts !
- I-V characteristics (RT, no annealing)

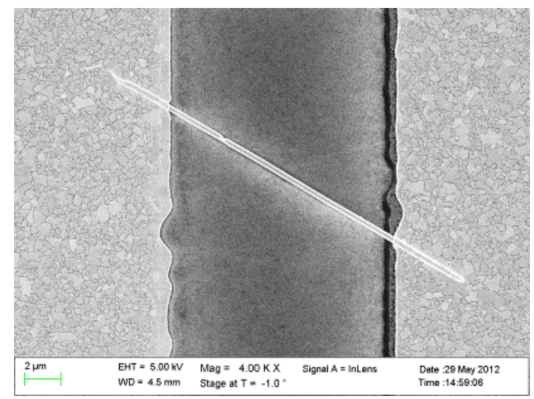




Problems 2

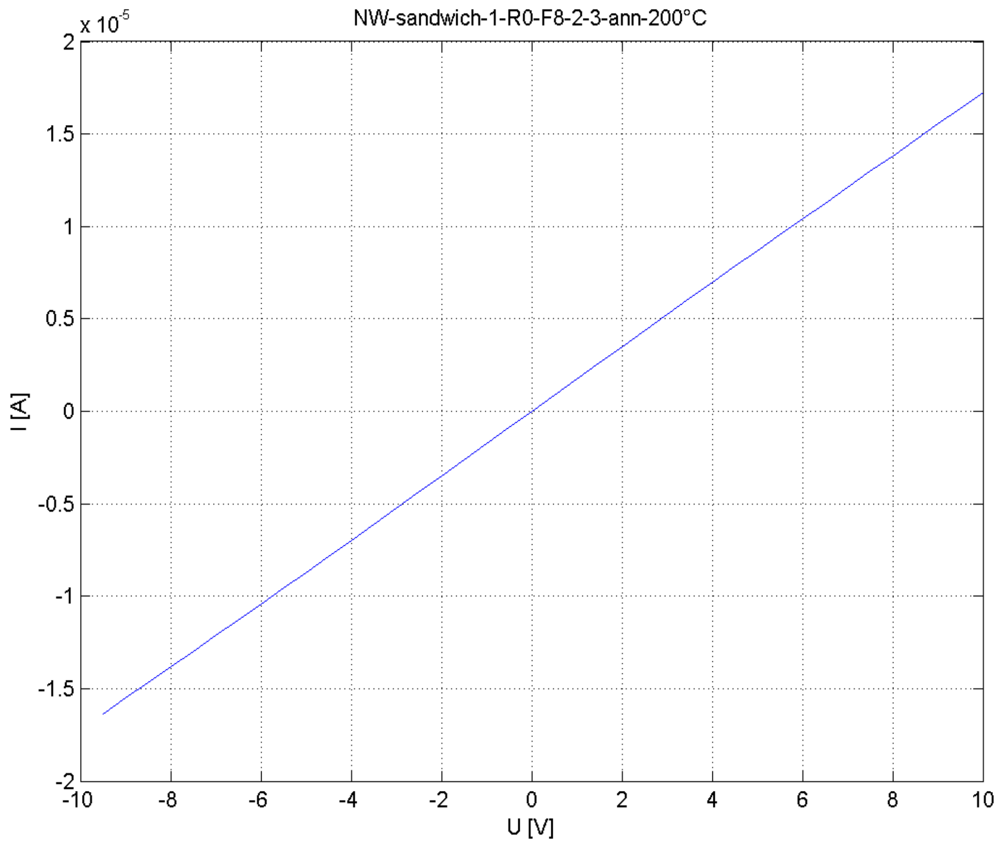
- Metal contacts !
- I-V characteristics (RT, annealing 5 min 400^{O}C)

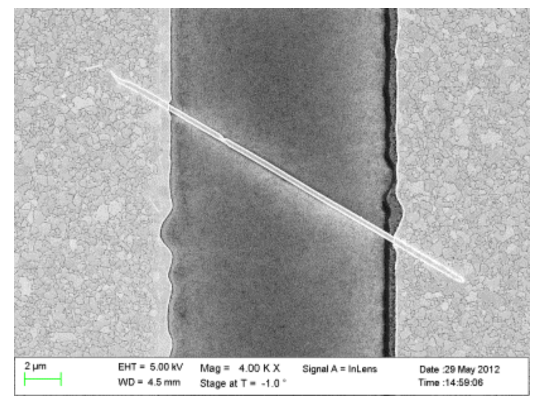




Problems 2

- Metal contacts !
- I-V characteristics (200^{O}C, annealing 5 min 400^{O}C)





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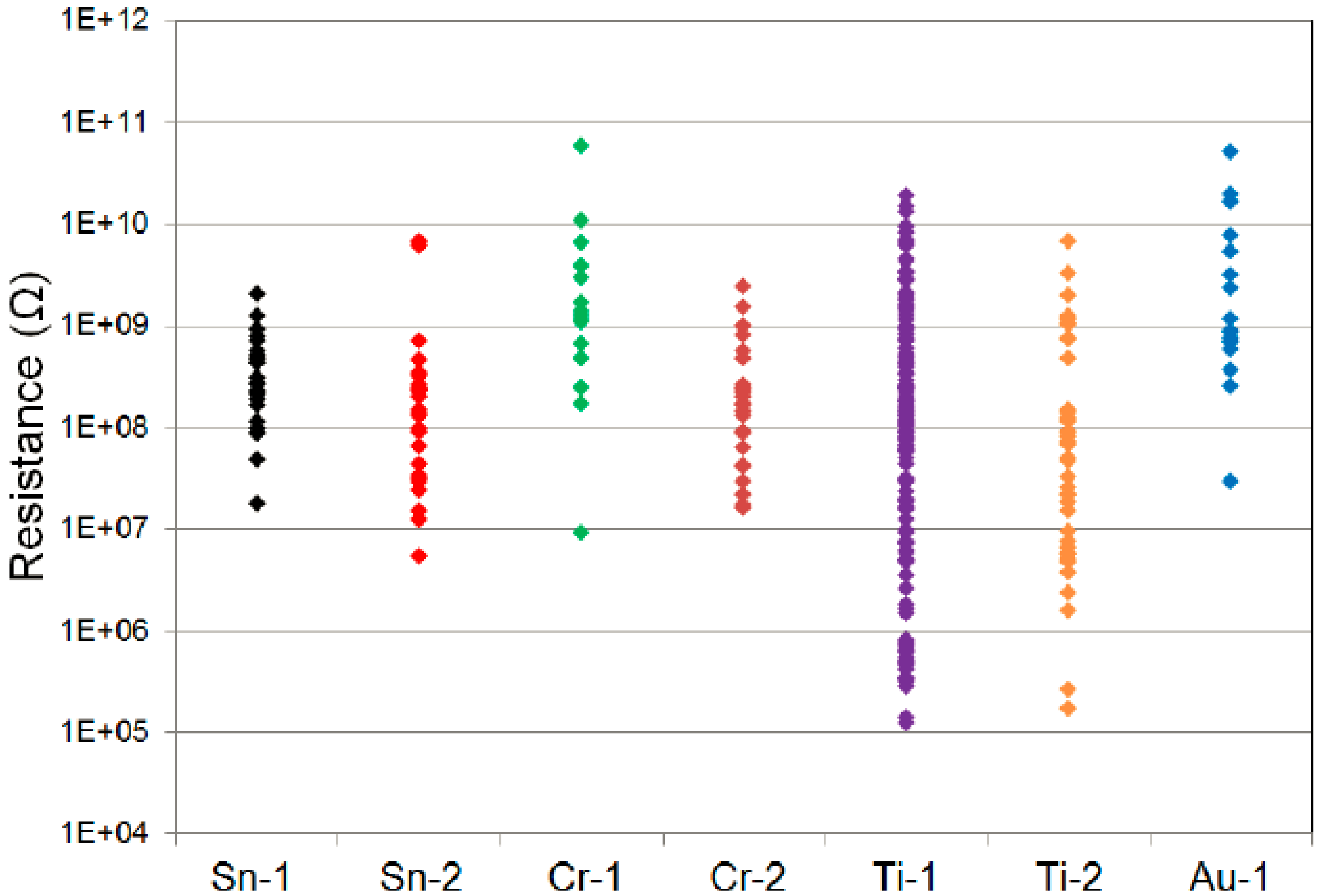


Figure 43: Distribution of resistance values of SnO_2 nanowires measured in a 2-point configuration at 200°C after annealing for different metal contacts. Each point represents the resistance of one nanowire with a linear I-V characteristic.

Problems 2

	no annealing room temperature	annealing 400°C room temperature	annealing 400°C 200°C
I-V Characteristics	16	12	28
bad contact	1	0	0
diode	13	2	2
almost symmetric	2	8	13
linear	0	2	13

Temperature	90 ppm CO Response [%] d ~ 70 nm	90 ppm CO Response [%] d ~ 90 nm
200°C	44	23
250°C	42	27
300°C	54	46

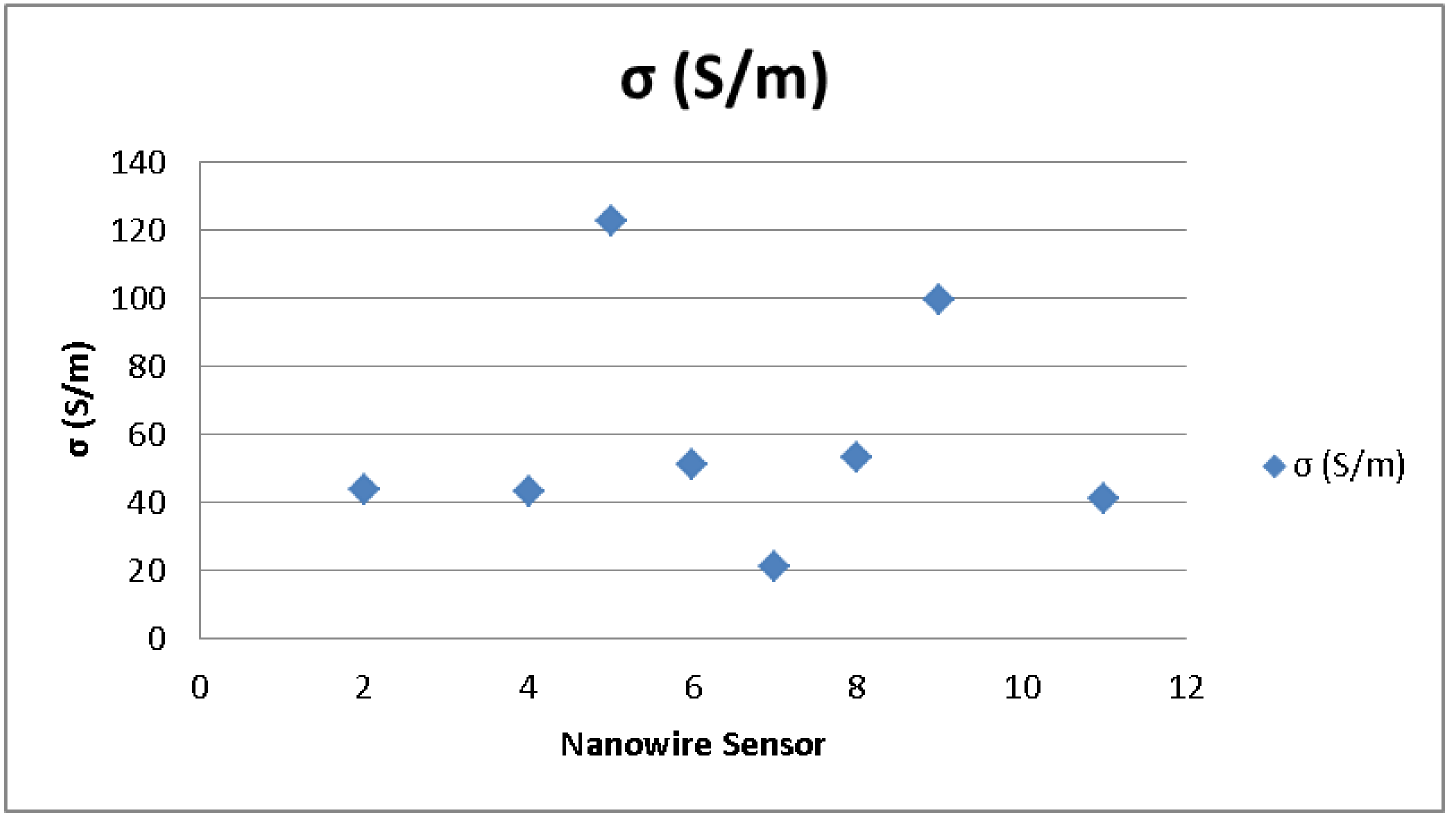
Problems 3

- Conductivity !
- No clear correlation with diameter of NW (200ºC)

Device name	R_{2pt} [MΩ]	R_{4pt} [MΩ]	R_C [MΩ]	R_C/R_{2pt} [%]	Diameter [nm]	Conductivity [S/m]
NW-ebeam-1	180	87	93	52	60	2.0
NW-ebeam-2	56	38	18	33	65	4.0
NW-ebeam-3	112	47	64	58	75	2.4
NW-ebeam-4	97	67	30	31	75	1.7
NW-ebeam-5	42	18	24	57	80	5.6
NW-ebeam-6	30	14	16	54	150	2.0

Problems 3

- Conductivity !
- No clear correlation with diameter and length of NW



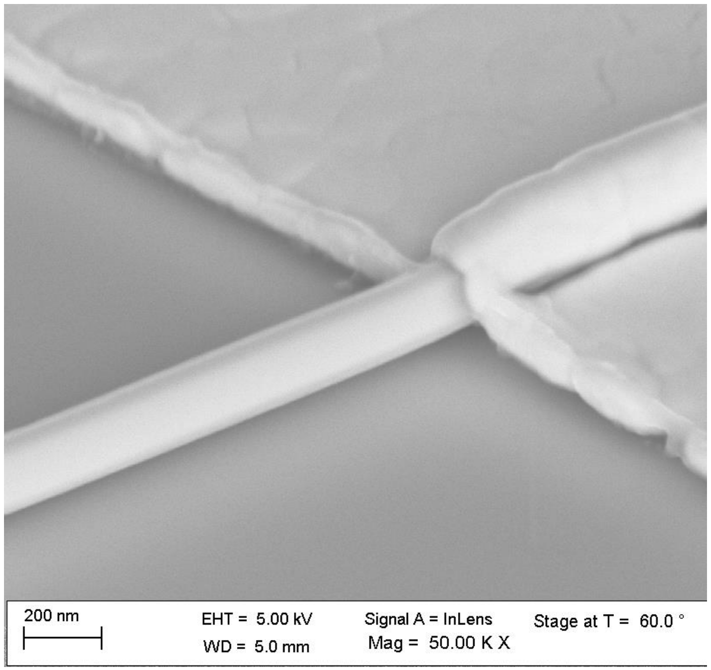
Problems 3

- 37 SnO_2 NW sensor investigated (2-point configuration)
- Length 1,4 – 5,2 µm
- Diameter 55 – 200 nm

- 8 nanowires present a conductivity at 200°C in the range 5-10 S/m,
- 15 in the range 20-100 S/m,
- 8 in the range 140-550 S/m,
- 6 in the range 850-2300 S/m.

Problems 4

- Additional barriers and crystallographic orientation



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Problems 4

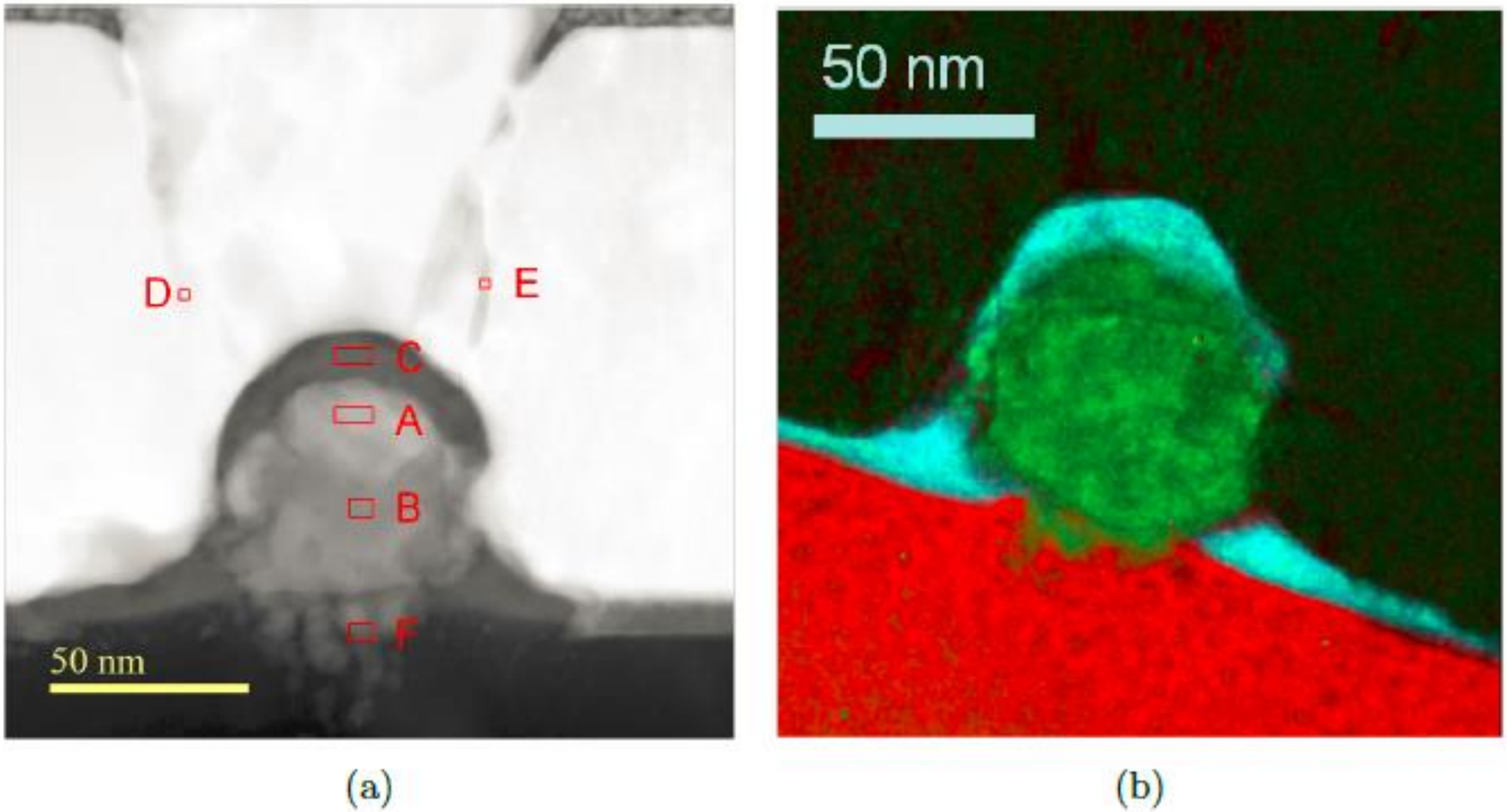
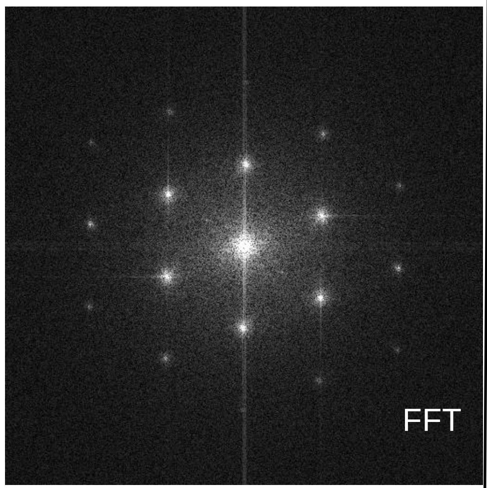


Figure 50: (a) HAADF image of NW-a. The positions A to F indicate the location where the EELS spectra have been measured. (b) Elemental mapping of NW-b: SnO_2 is represented in green, Ti in blue and SiO_x in red.

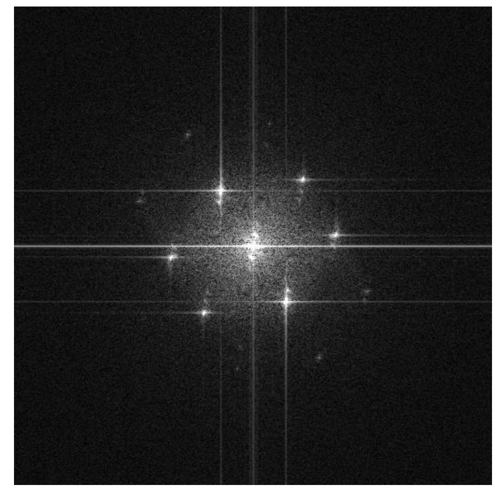
Different crystalline orientations of NWs

P2



[1 0 0]

Q7



[1 1 1]

Table 8: Properties of the two nanowires investigated by FIB-TEM.

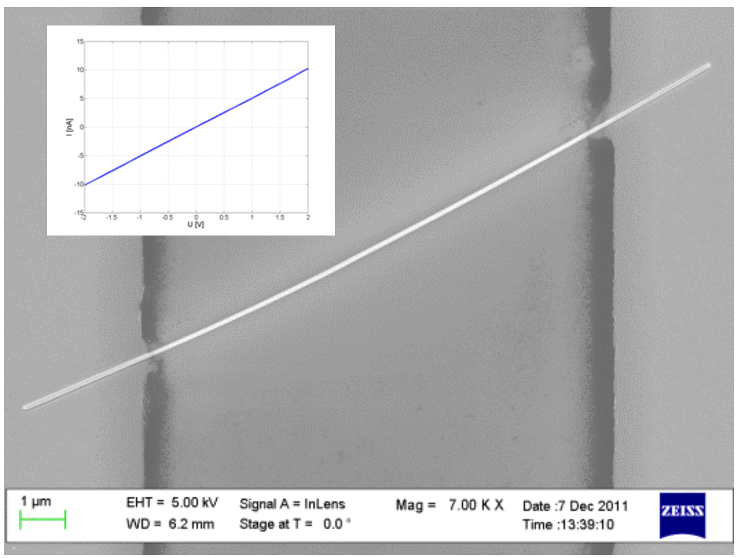
	NW-a	NW-b
Length [μm]	1.8	1.8
Diameter [nm]	70	70
Resistance at 200°C [kΩ]	270	75000
Conductivity at 200°C [S/m]	1730	6
Growth direction	[111]	[100]

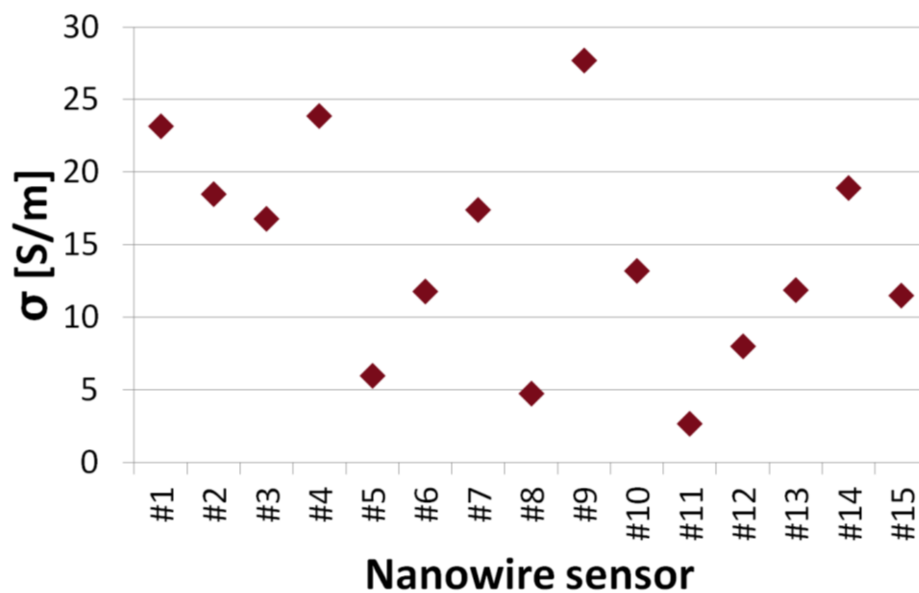
More experiments required, but extremely time (and cost) consuming !

3.2 CuO-NW Gas Sensor

- Evaporated Pt metallization layer
- Annealing at T=400^{O}C for 30 min
- 2-point measurement
- Strong variation of conductivity (factor 5) !

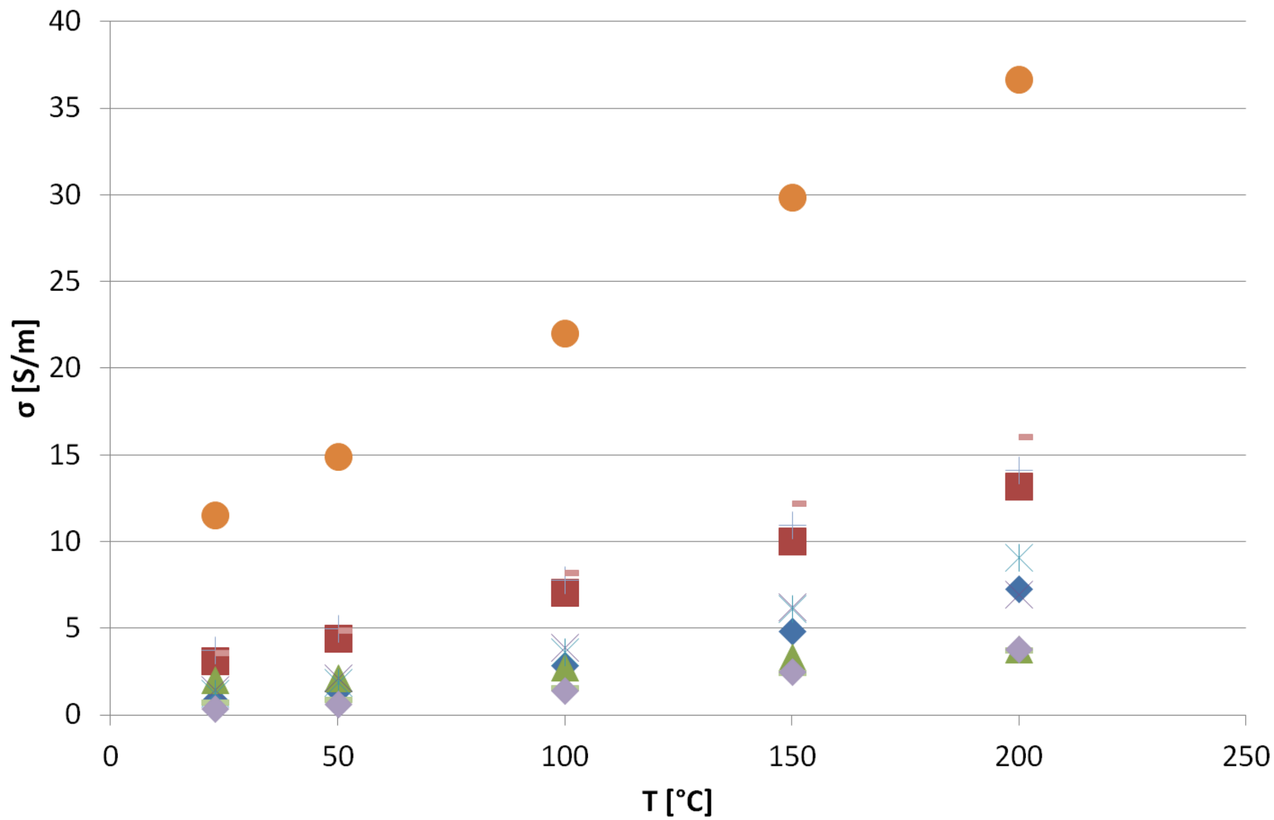
Stephan Steinhauer, PhD Thesis: "Gas Sensing Properties of Metal Oxide Nanowires and Their CMOS Integration" (2014)



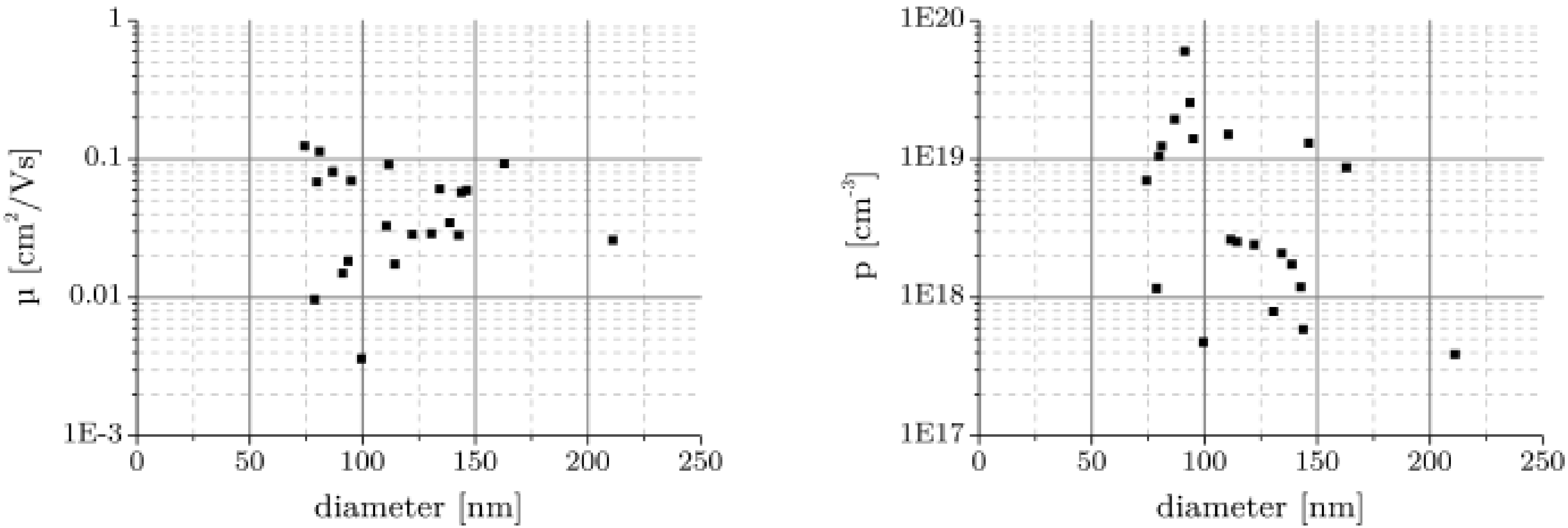


Electrical Characterization

- Conductivity of 10 NW devices tested
- No significant correlations with diameter or length of NW!



- D: 75 – 211 nm
- L: 5,2 – 25,4 µm
- σ: 0,2 – 20 S/m



(a) Field effect mobility

(b) Hole concentration

Figure 6.4: Transport parameters of single CuO nanowires (two-point configuration)

TEM reveals twinning defect

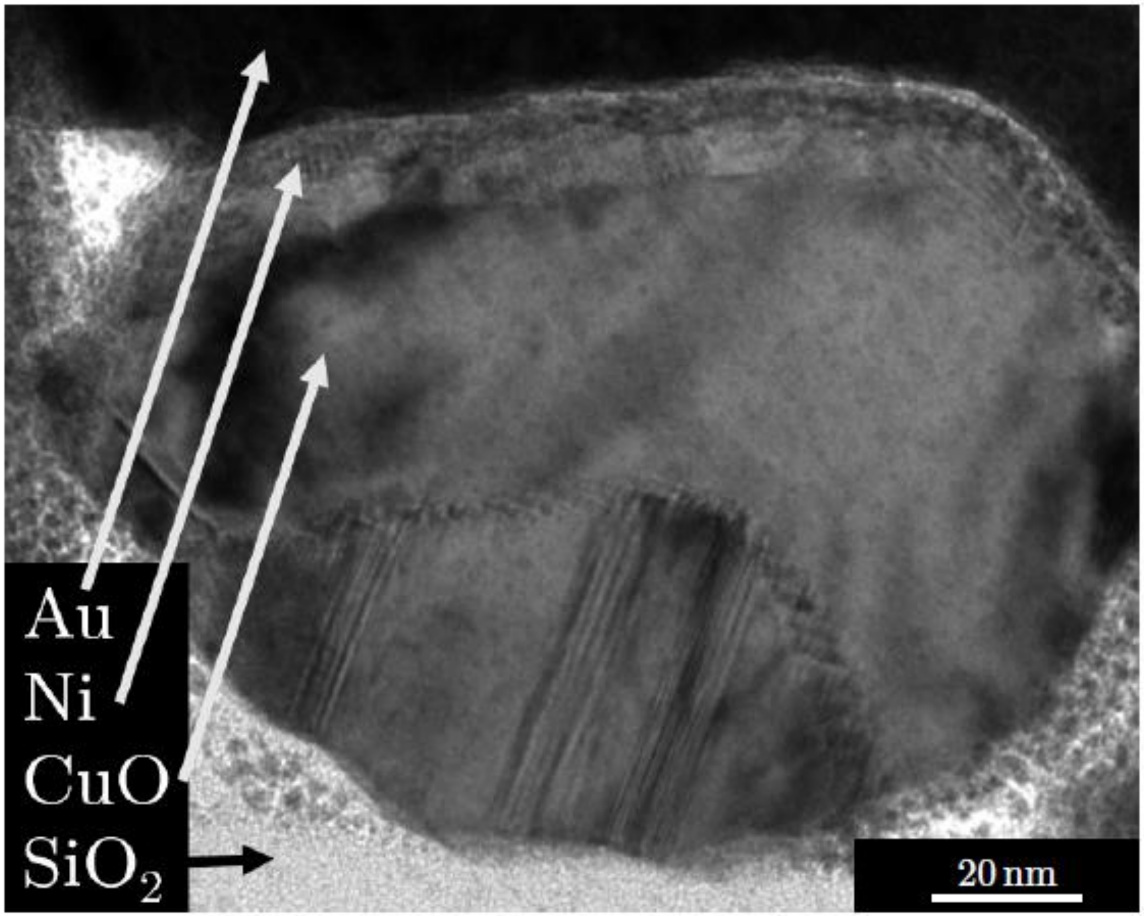
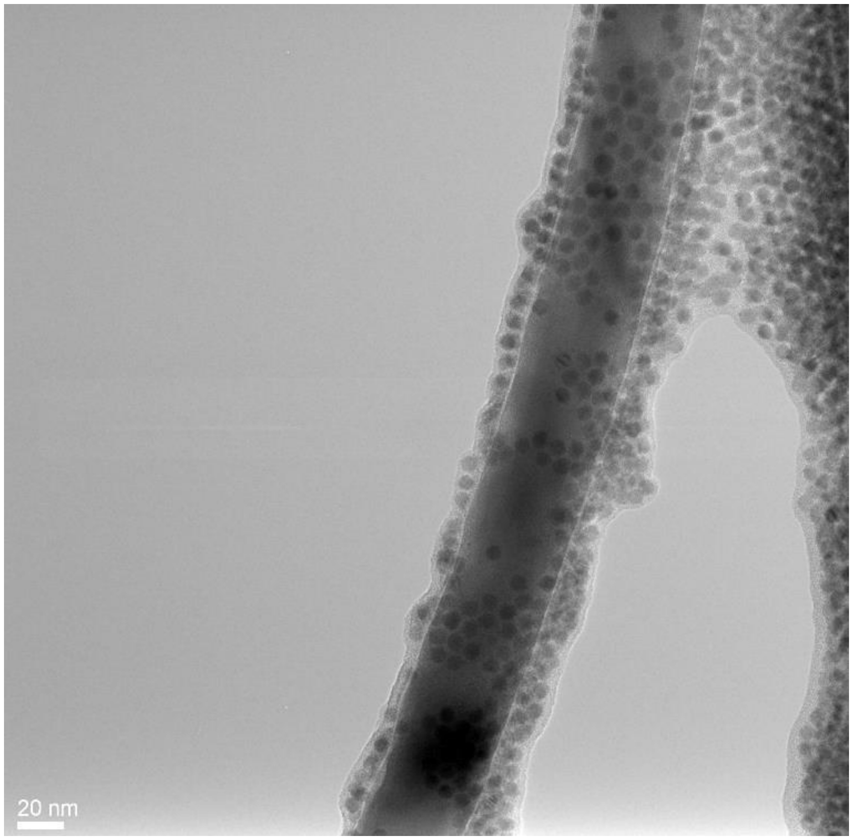
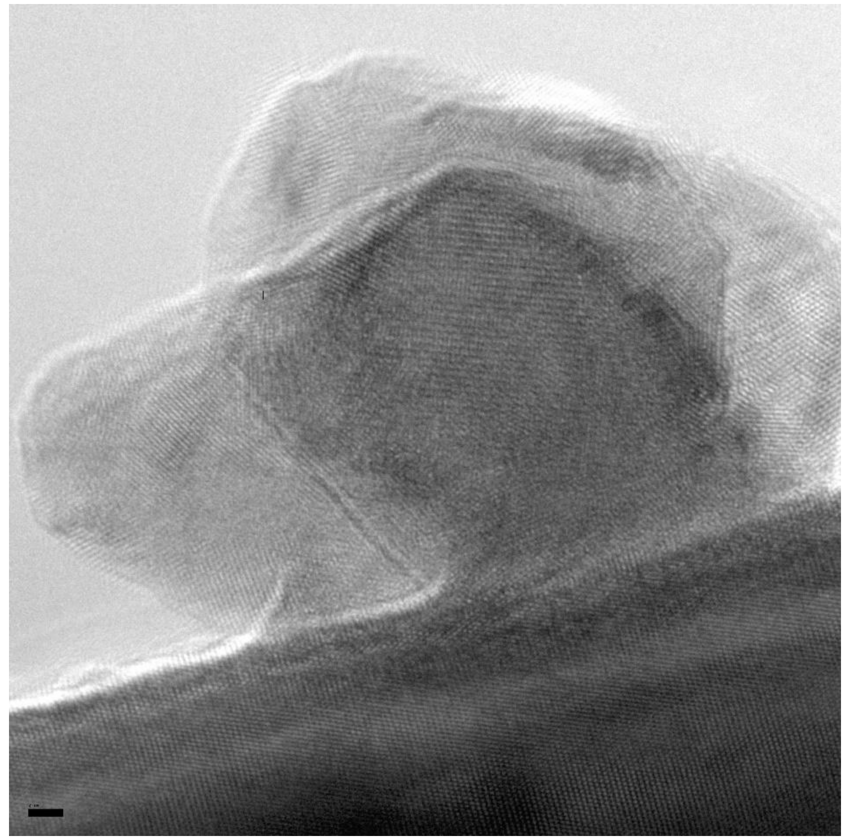


Figure 6.7: Cross-sectional transmission electron microscopy of Ni/Au contacts

NPs on SnO_2-NW for sensor optimization

- Au, AuPd, AuPt, PtPd
- Interface? Long term stability? etc.





4. Summary & Outlook

NWs are very useful components for gas sensor devices !

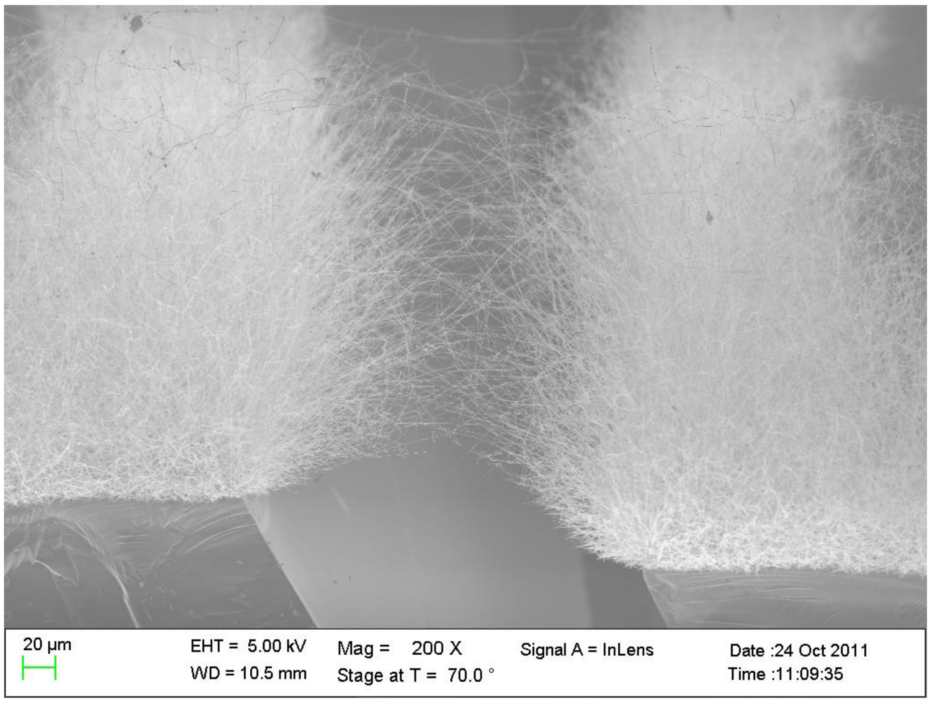
- Very good for basic characterization

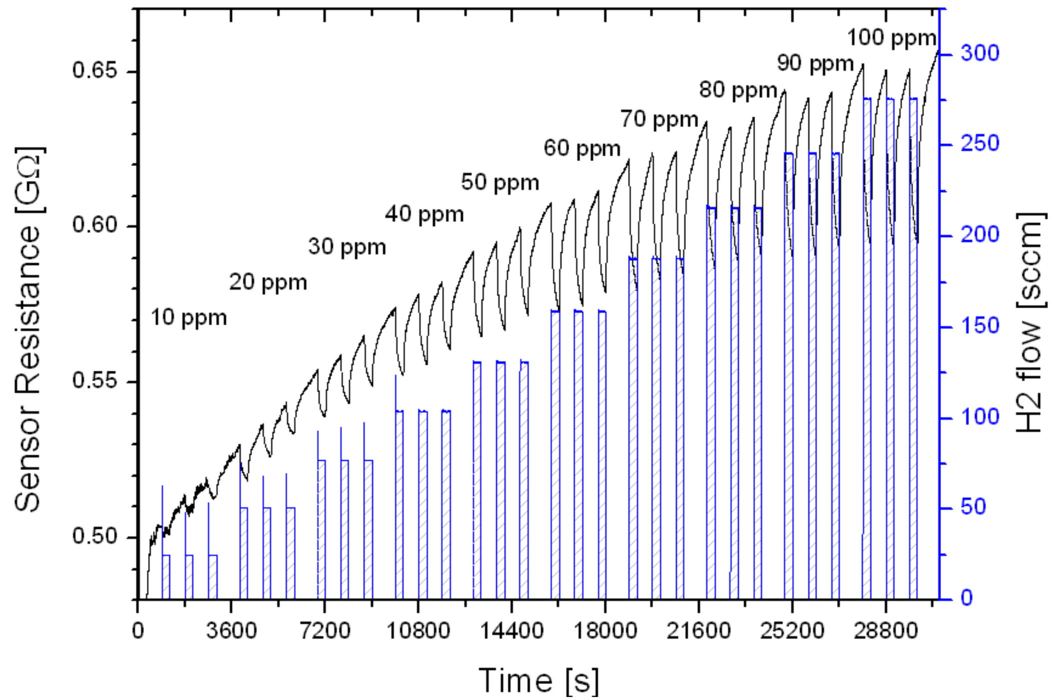
Single NW-Devices are problematic:

- Reproducibility
- Metal contacts
- Conductivity
- Different crystal growth directions
- Control is extremely difficult !

Multi-NW approach

- Numerous NWs with different diameter and length
- Statistic helps to „average“ properties





Multi-NW approach

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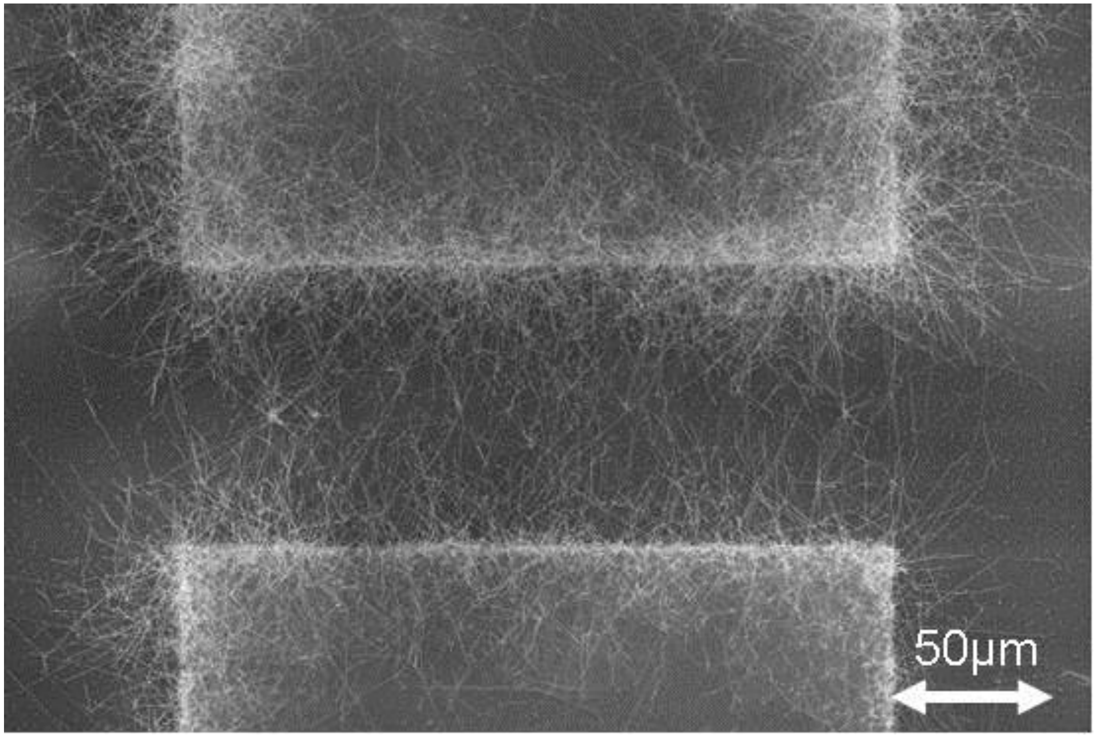
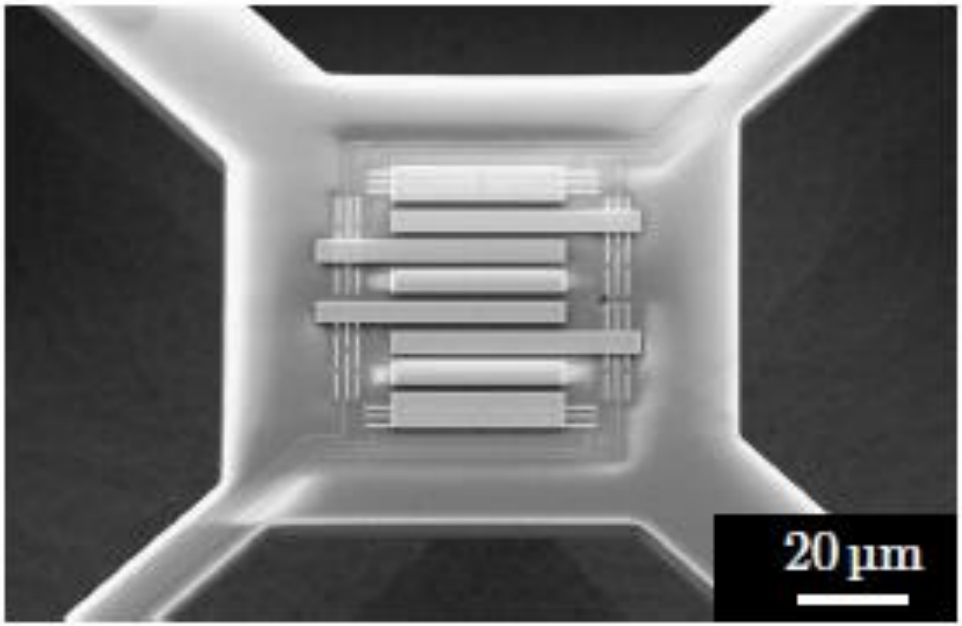
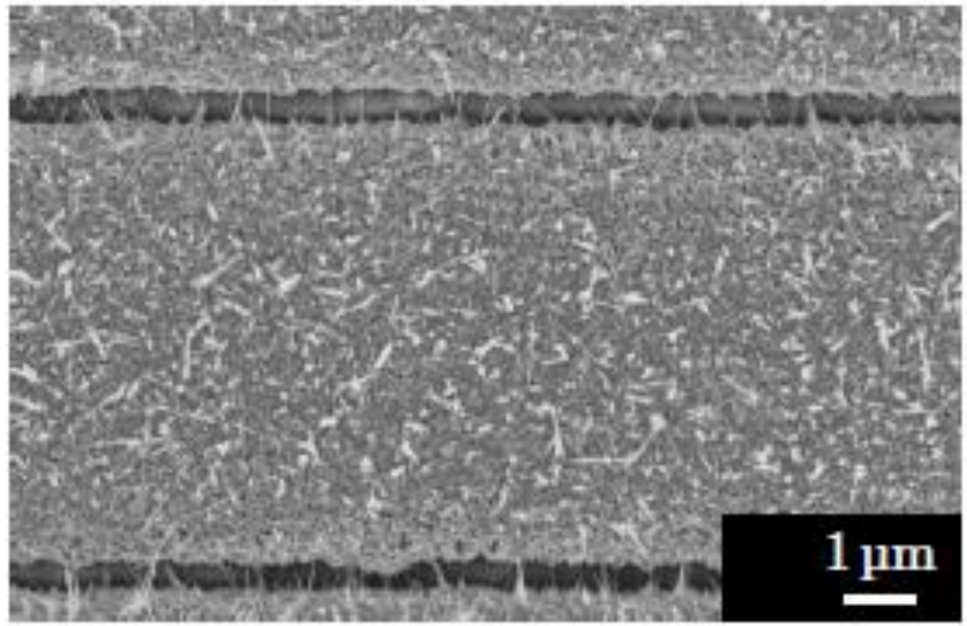


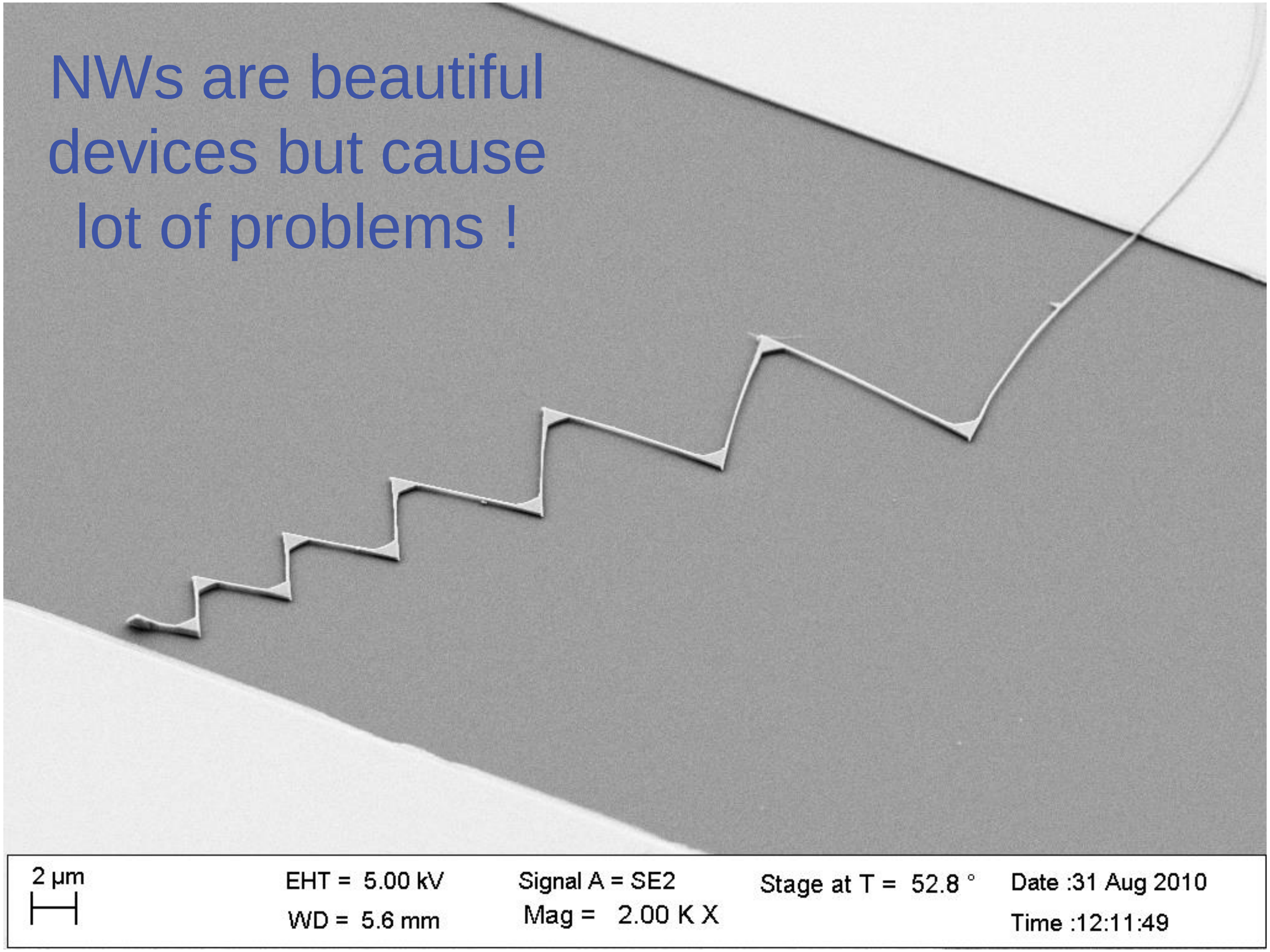
- Integration on CMOS feasible 400ºC (CuO, ZnO)
- Transfer processes have to be developed (SnO_2)





Need for R&D projects dedicated to reliability issues of NW-based (gas) sensor devices !

NWs are beautiful devices but cause lot of problems !



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Session C - **SYSTEM INTEGRATION & PACKAGING**
Session D - **RELIABILITY**
Session E - **INNOVATIVE MANUFACTURING PROCESSES**

PANEL DISCUSSION

"Airbus of Chips – Feasible European Reality or Science Fiction?"

Panel Leader

- ***Michael Wiesmüller,*** Austrian Federal Ministry for Transport, Innovation and Technology (Austria)

Panelists

- ***Willy van Puymbroeck,*** European Commission (Belgium)
- ***Jong Min Kim,*** University of Oxford (United Kingdom)
- ***Zhong Lin Wang,*** Georgia Institute of Technology (USA)
- ***Martin Schrems,*** ams AG (Austria)
- ***Livio Baldi,*** Micron Semiconductors Italia (Italy)

Key Note Speakers:

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Nanometer Structure Consortium, Lund (Sweden)

Zhong Lin Wang
Georgia Institute of Technology, Director of Center for Nanostructure Characterization, The Hightower Chair in Materials Science and Engineering, Atlanta (USA)

Pascale Maury
ASML (The Netherlands)