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Site-selective synthesis of SnO_2 nanowires for ammonia sensing in the presence of high levels of humidity

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SITE-SELECTIVE SYNTHESIS OF SnO_2 NANOWIRES FOR AMMONIA SENSING IN THE PRESENCE OF HIGH LEVELS OF HUMIDITY

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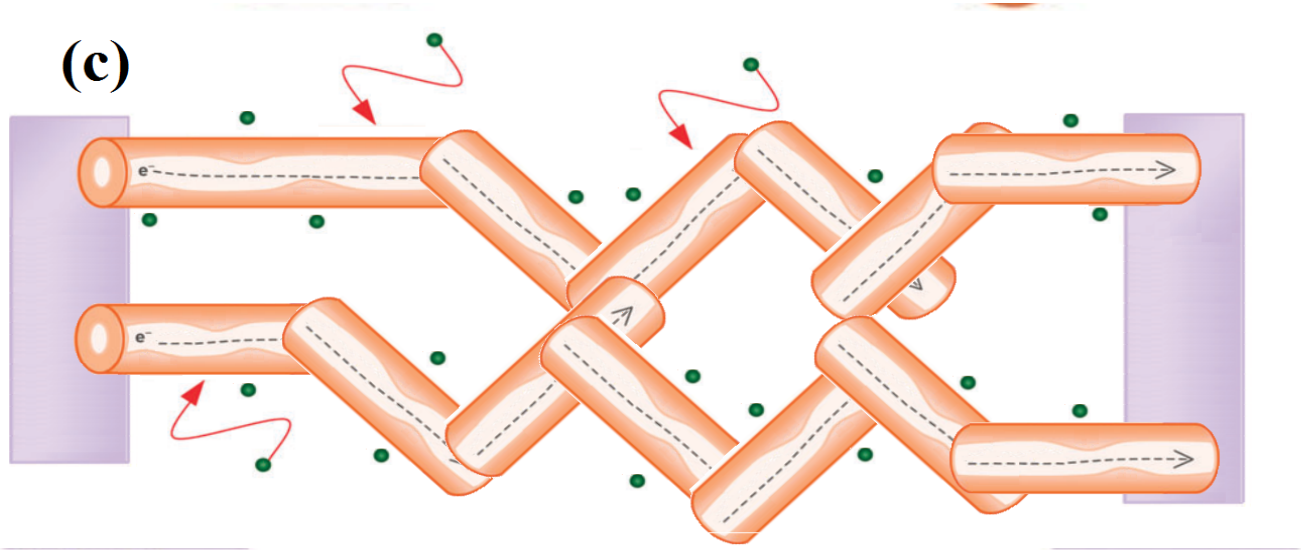
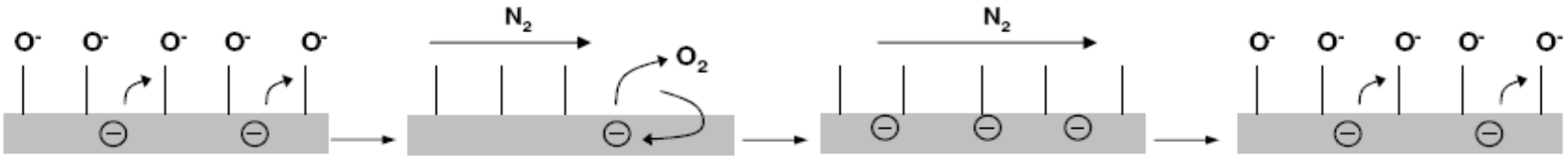
Outline

1. Motivation
2. Low power membranes and microhotplates with integrated heaters
3. Growth of nanowires on top of heated structures
4. NH_3 sensing properties of the devices
5. Conclusions and future work

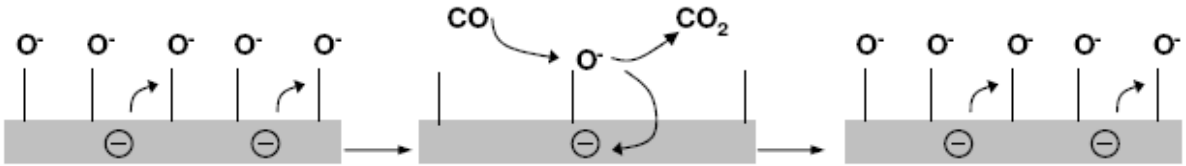
Motivation



Synthetic Air/Nitrogen (oxidising gas)



Carbon monoxide (reducing gas)



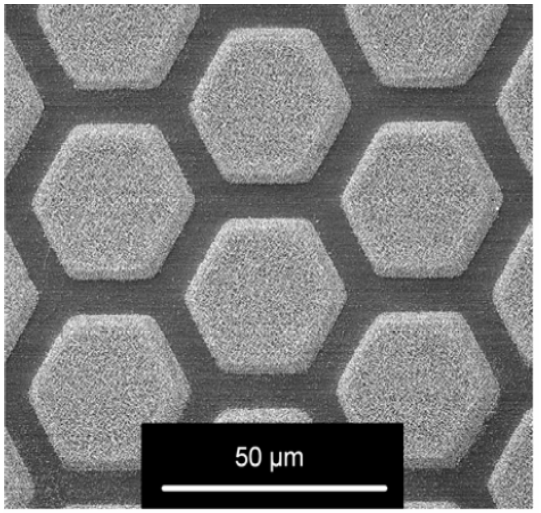
Requires heating at temperatures of at least 150ºC!!

Motivation

- Growth mechanisms of 1D nanostructures (nanowires, nanorods, ...) are quite well understood

- Heating is required to activate the process

- Localized growth of 1D nanostructures is possible by the use of masks in the process of catalyst deposition for VLS-growth



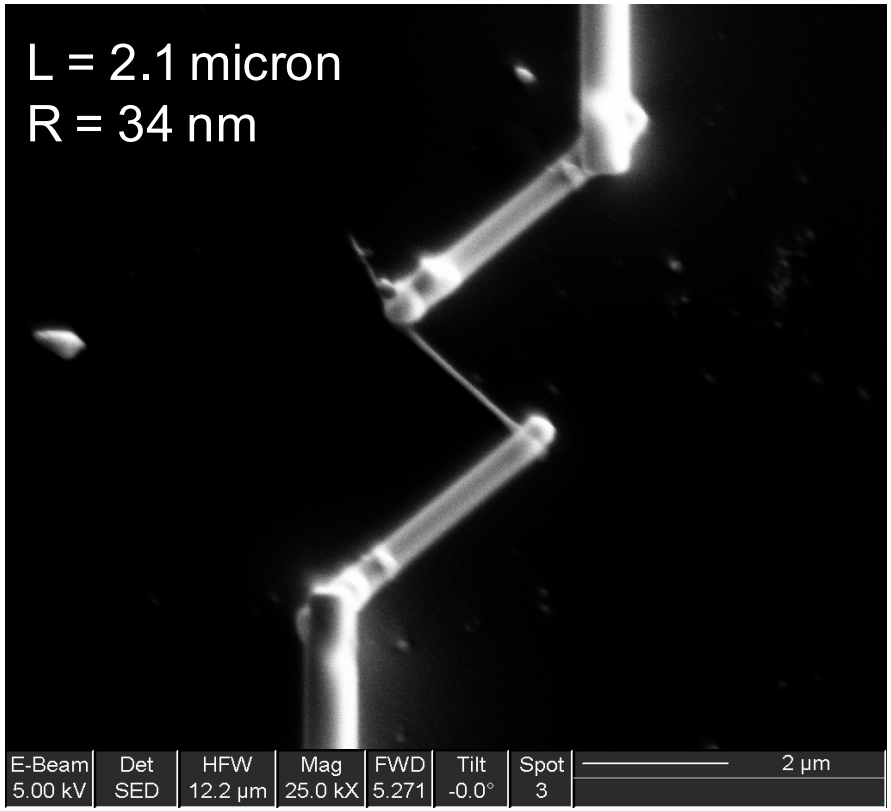
Small 3, 2070 (2007)

- Integration of the 1D nanostructures for device fabrication is challenging

Is there a way to grow locally 1D nanostructures in a more energetically efficient way, with a better thermal control and to easily integrate them for device fabrication?

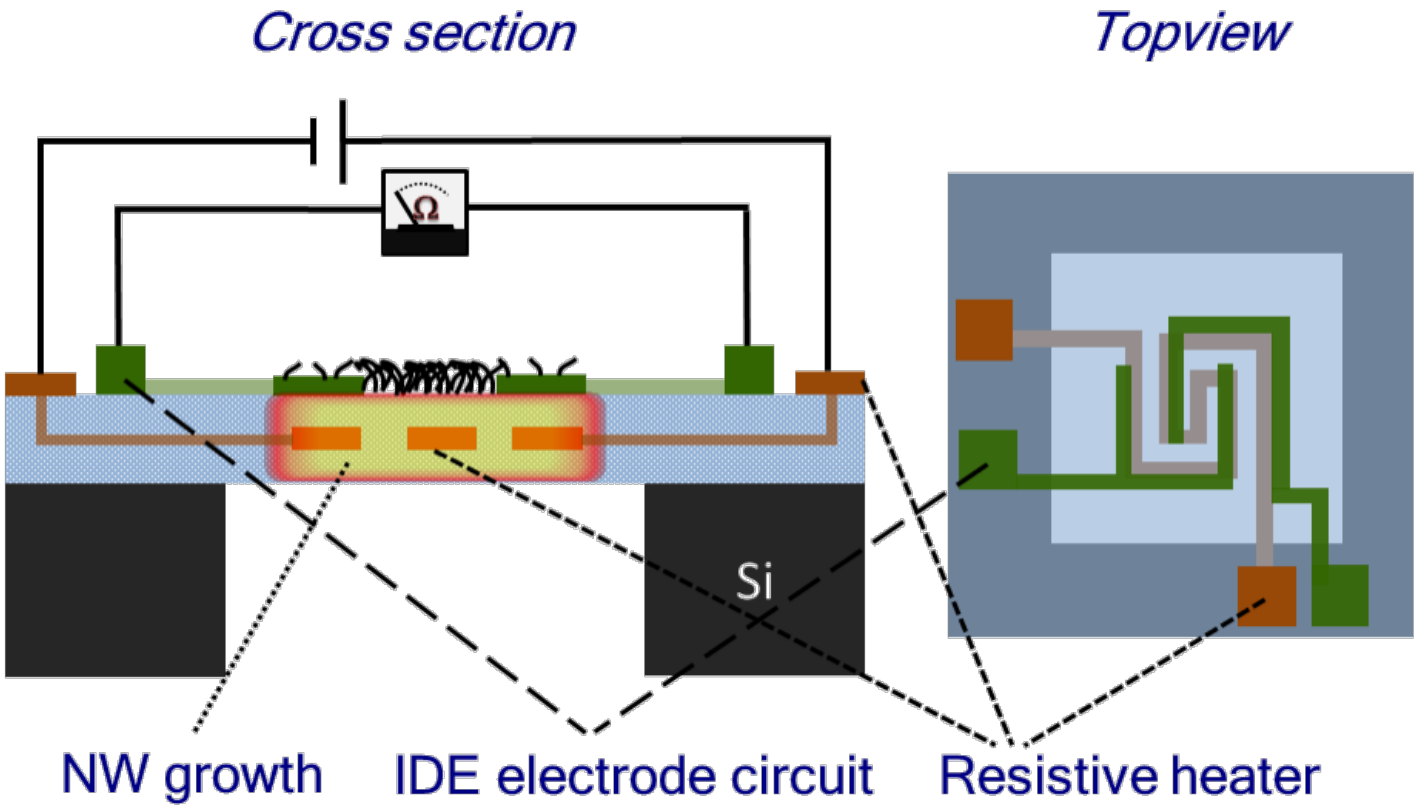
Low power membranes with integrated heater

- Successfully used for the development of low power gas sensors
- Allows controlled and localized heating



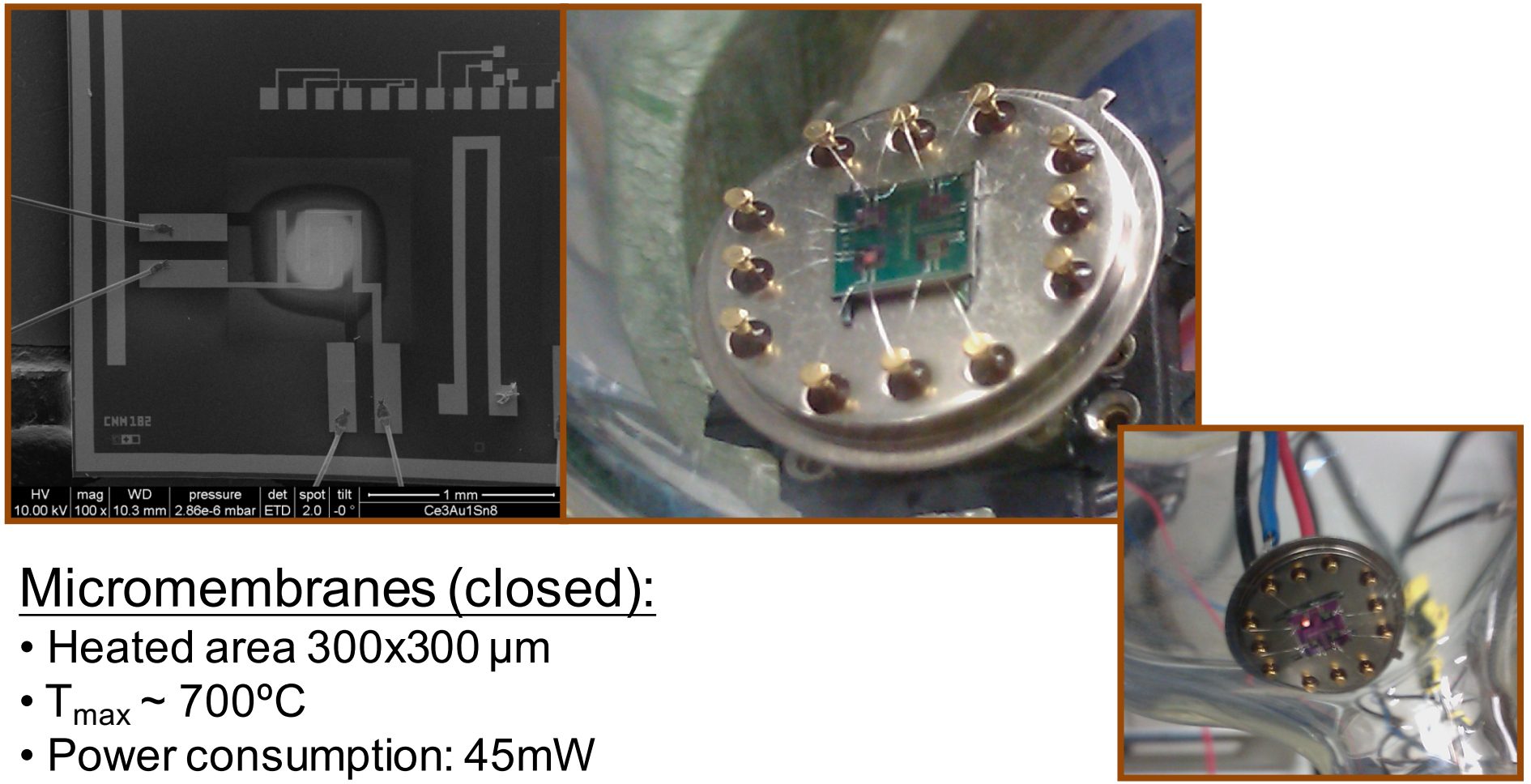
Low power membranes with integrated heater

Membranes with poly-Si heater and Pt IDE fabricated using bulk micromachining



Chemical Communications 48, 4734 (2012)

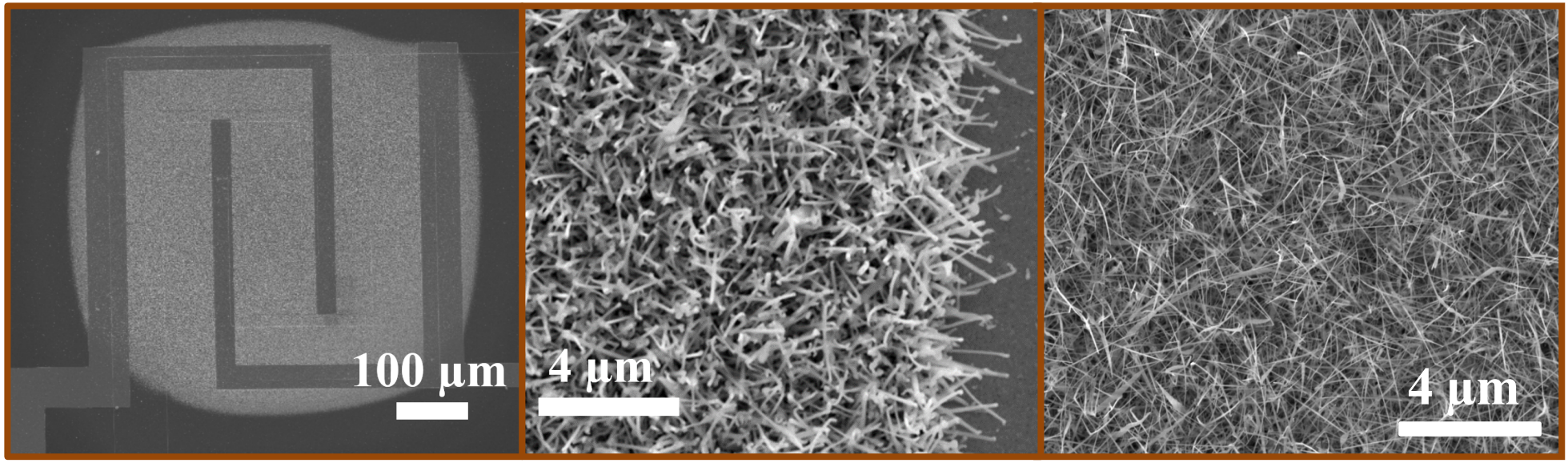
Growth of nanowires on top of heated structures



Micromembranes (closed):

- Heated area 300x300 μm
- T_{max} ~ 700ºC
- Power consumption: 45mW
- Non-continuous layer of Au sputtered on the whole sample
- Au islands formed during ramping up

Growth of nanowires on top of heated structures

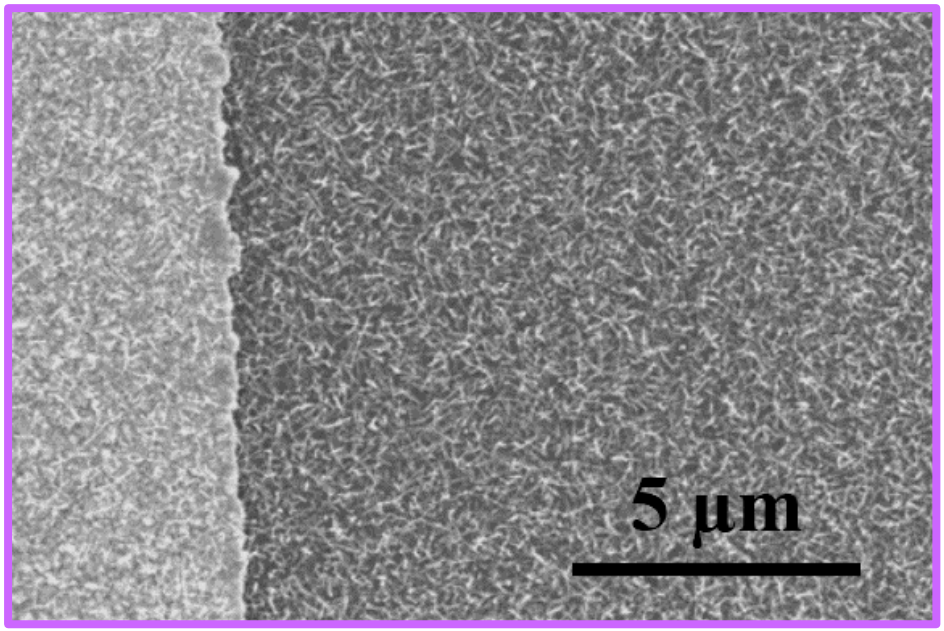


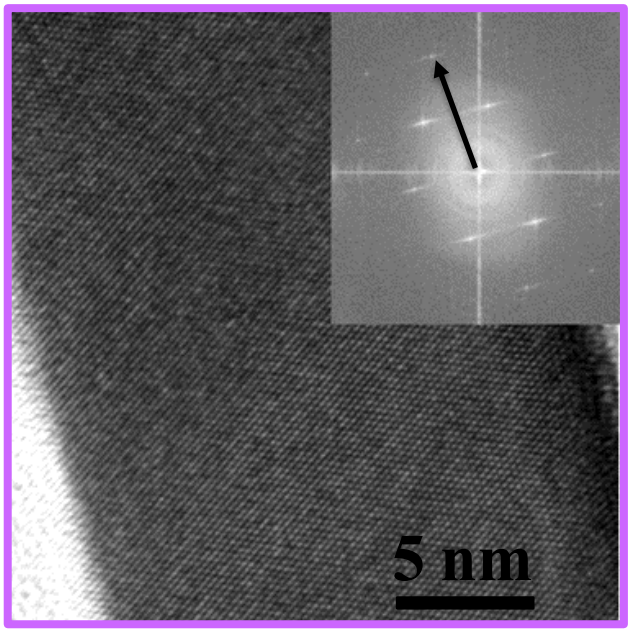
- 1D-SnO_2 growth from tin-tert-butoxide ($Sn(OtBu)_4$) according to temperature profile in the membrane
- Effect of synthesis temperature on 1D-objects
- Allows fast heating and cooling rates (quenching)
- High temperatures → stress in the membrane → Heater is affected

Growth of nanowires on top of heated structures

- Fabricated structures are similar to reference growth
- Influence of the underlying IDE electrode material (Au-Pt alloy)

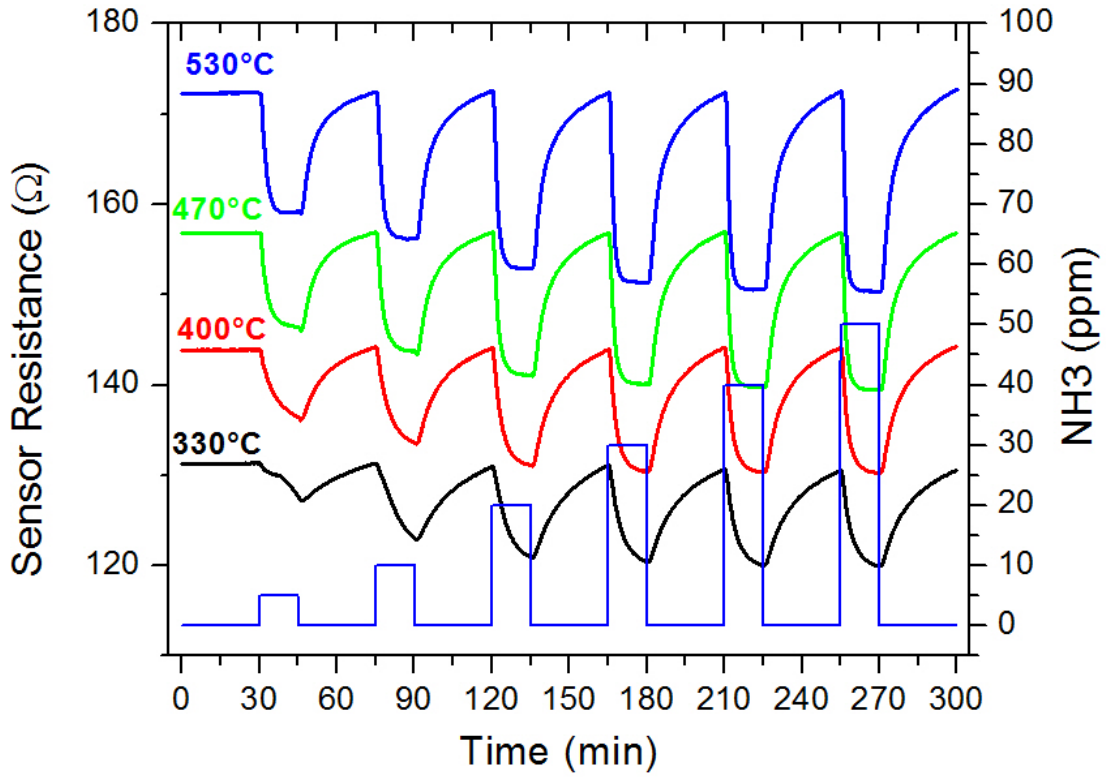
[101] Growth direction





Gas response

- Response to NH_3 pulses of 15 min. in dry synthetic air
- Operated at
  - 330ºC (28mW heating power)
  - 530ºC (46mW)



8h-TWA according to NIOSH: 25 ppm

Gas response of the device

$$2NH_{3\,(g)} + 3O^-_{(s)} \rightarrow N_{2(g)} + 3H_2O_{(g)} + 3e^- \quad (1)$$

$$2NH_{3\,(g)} + 4O^-_{(s)} \rightarrow N_2O_{(g)} + 3H_2O_{(g)} + 4e^- \quad (2)$$

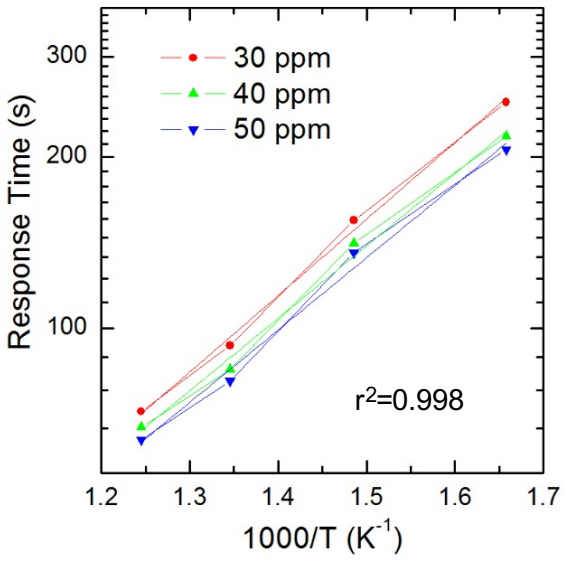
$T < 450°C\ (approx)$

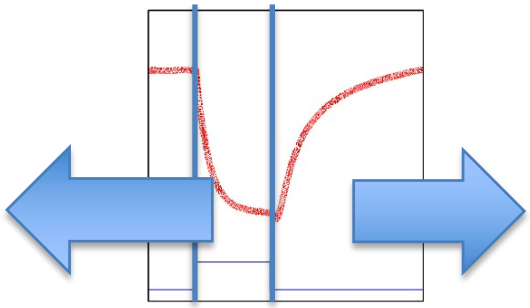
$$2NH_{3\,(g)} + 5O^-_{(s)} \rightarrow 2NO_{(g)} + 3H_2O_{(g)} + 5e^- \quad (3)$$

$T > 450°C\ (approx)$

M. De Boer; Catal. Today, 17, 189-200 (1993)

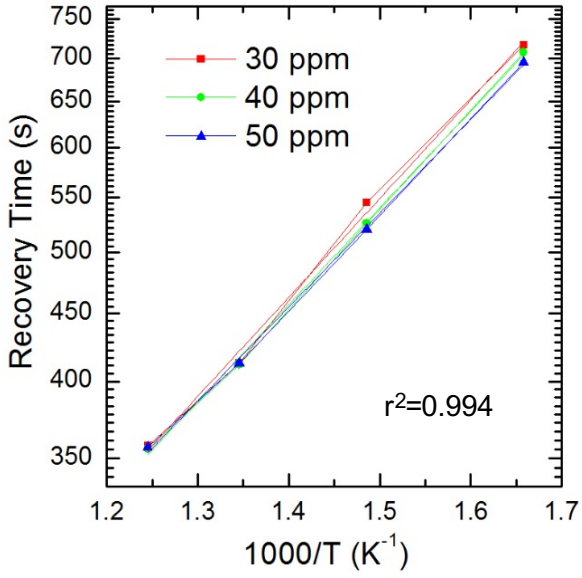
Adsorption





$$\tau_{response} \propto e^{\frac{E_{act}}{KT}}$$

Desorption



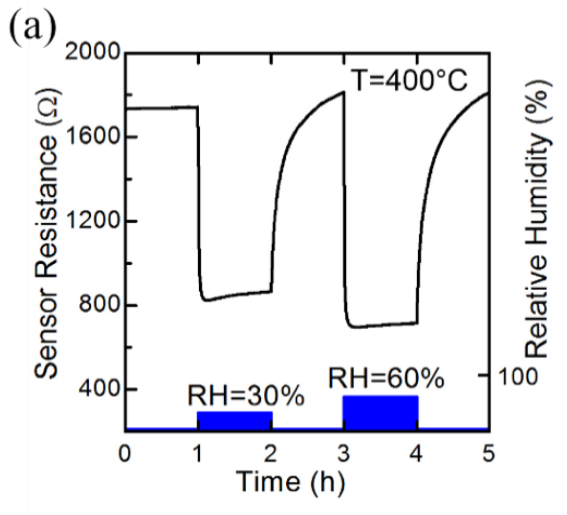
$\tau_{response} = 60s \quad 50ppm\ @530°C$

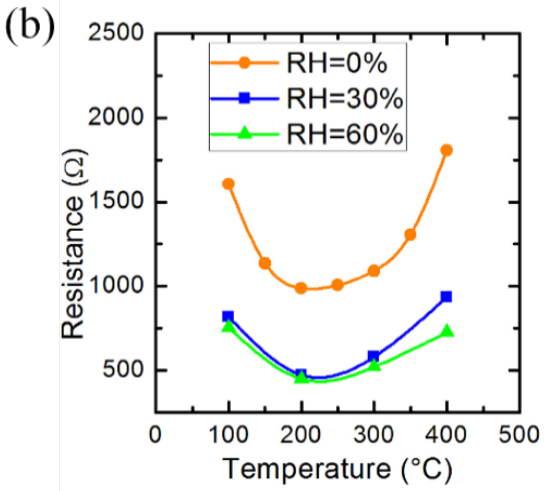
$E_{act\ response} = 0.26 \pm 0.02\ eV$

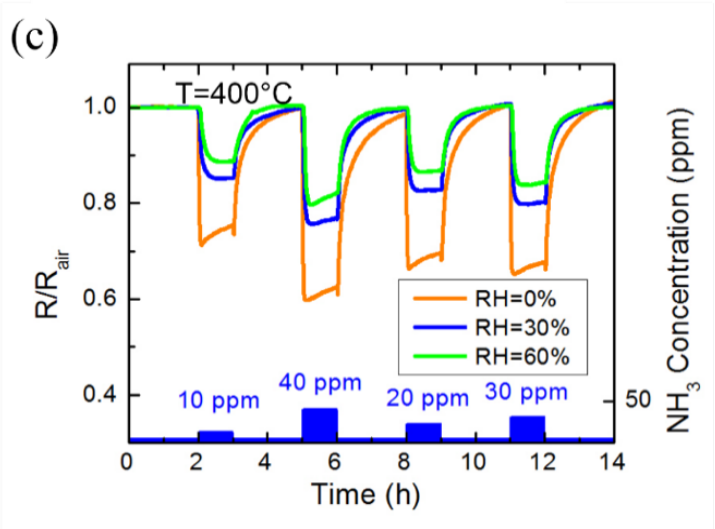
$E_{act\ recovery} = 0.14 \pm 0.01\ eV$

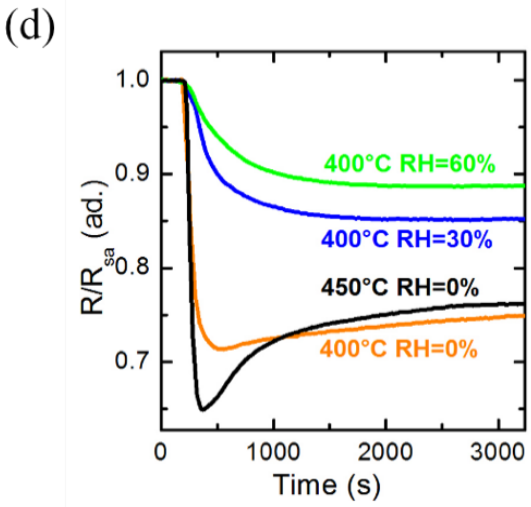
Operational life-time of more than 3 months

Gas response in the presence of water vapor



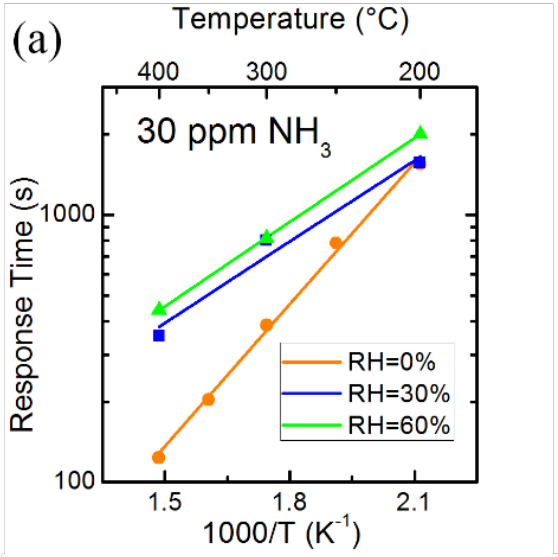


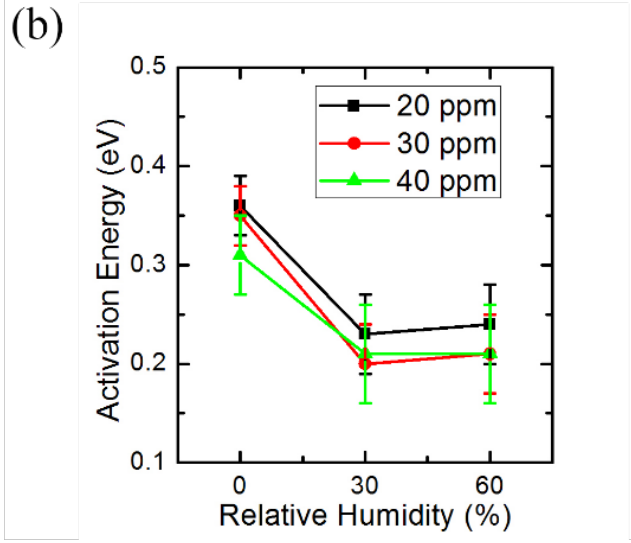


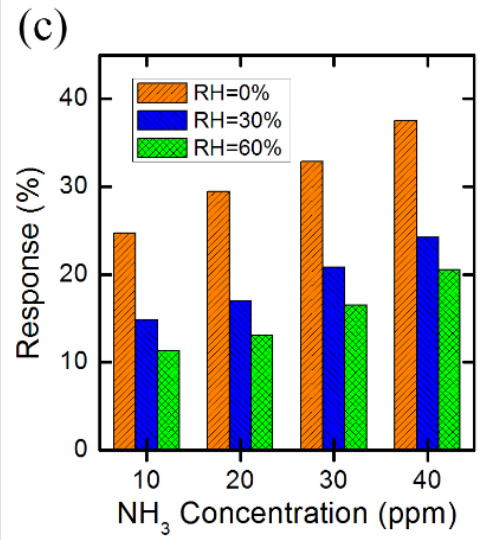


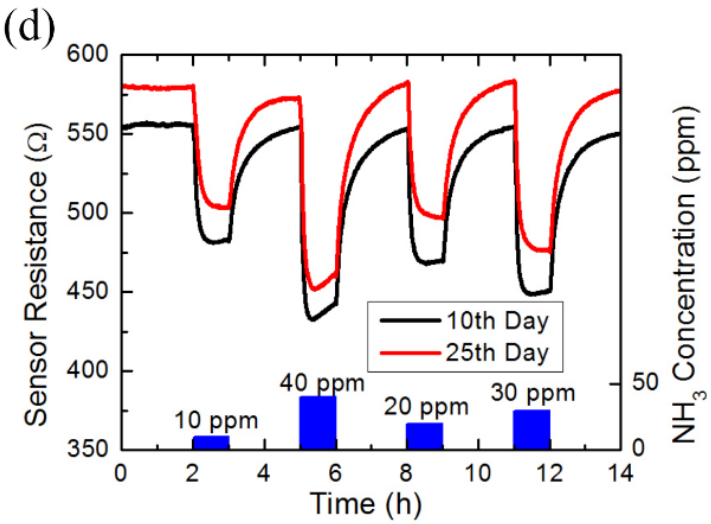
Overshoot due to Competition of different gas species

Gas response in the presence of water vapor









Quite good reproducible response with time

Evolution after 25 days is a modification of the base resistance (30%RH)

CONCLUSIONS

- SnO_2 nanowires have been locally grown on top of micromembranes using the VLS method.
- Low power (45mW for 700ºC) can be used for the growth.
- Functional NH_3 gas sensing devices have been fabricated.
- Ammonia response increases with temperature.
- Fastest response time of 60 s.
- Stable more than 3 months.

Future work

- Further characterisation to understand the stability of the devices
- Design of new optimized micromembranes.
- Standardization of growth parameters.