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IAQSense
Air Quality in Closed Environments

IAQSense

Work package 7 – Final report

Date	**27/10/1016**
Project	**IAQSense – FP7 - 604325**
Starting date and duration	**01/09/2013 – 36 months**
Author, company	**Mathias Holz, nano analytik GmbH**

WP 7: Process alternative [M34 –M36]

Objectives

To prepare the porting of the sensing head technology developed during the project for mass market production.

Apart from NANO directly producing (but probably in limited quantities) the sensing head, two mass market production facilities will be investigated and process porting package reported and released:

- a standard package using all features and porting to MEMS type foundries,
- a custom package for porting to 3D printing process for low cost but limited performances

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SEVENTH FRAMEWORK PROGRAMME

WP 7.1: Porting validated process to traditional foundries for mass production

Objectives:

- Standard package for MEMS type foundries
- Porting to "on the shelf" MEMS type process
- Porting a custom process
- Extending capacity of the NANO technology line
- Documented process

Achieved results:

- Different established package solutions
- Foundries are identified porting of technology is ready
- Bonding/package capacity was increased

NANO has access to over 2000sqm clean room facilities equipped with newest micro- and nano-fabrication tools. NANO has great expertise in producing micro-sensor technology.

Consideration regarding NANO clean room for mass production

The ready sensors reached the dimensions of 1x1 mm^2 per chip. The first product cycles have been realized on 4" substrates (Silicon wafers). Considering a 6" production line, one wafer will carry up to 16k sensor units. For the outlook of the project a mass production where millions of units are produced yearly needs to be ensured. Realistically assuming a weekly production of five 6" substrates, over 4M units can be realized per year.

The key points for porting the process to external foundry are:

- The clean room used by NANO has a limited capability. Shifting to outside foundry was considered. To be prepared for this "fabless" operation, the process used during the project was fully documented, with materials, equipment, process steps with all their parameters, process capability evaluation see WP2
- Yield, root causes of rejects (hard defects, Gaussian distribution border rejects) have been documented and criteria for process release in the context of NANO clean room,
- Cost calculation have been provided, with distribution of costs, impact of instability and defects.

Extending capacity of the NANO technology line

The production of the sensors has been established in nano analytik GmbH on 4" and can be scaled to 6". Mass production must cover the CMOS part, MEMS part up to packaging and should consider this already in early stages of sensor production. The full 4" and 6" production can be covered in all aspects in Ilmenau. Especially with thanks to the European Union and the consortium the packaging capabilities and production capabilities have been increased due to the procurement of a wire bonder. An semi-automated procedure was established for the different sensor- and package types. The production capability was increased with ~60% and is covering 6" production with up to 4M Sensors per year.

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SEVENTH FRAMEWORK PROGRAMME

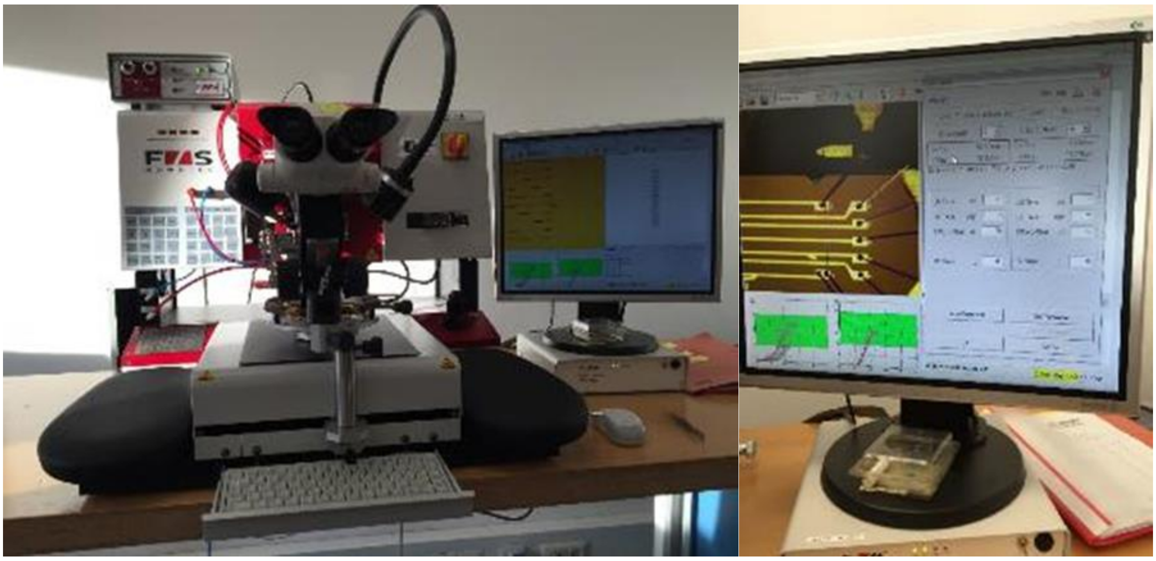
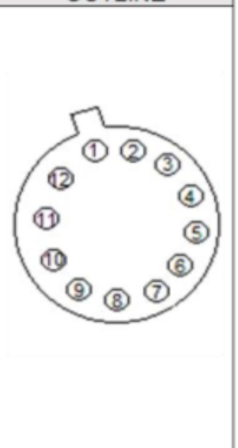
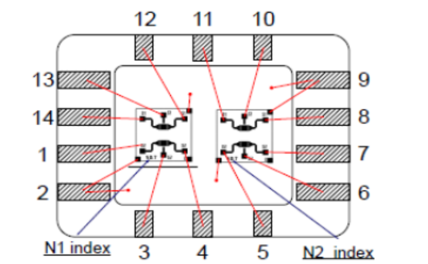


Figure 1 Installed bonding system with screenshot of bonded IAQSense sensor.

PIN	DESCRIPTION	SIMPLIFIED OUTLINE
1	G2 – T2 gate	
2	S2 – T2 source	
3	SUB- substrate connection	
4	H1 - heater contacts	
5	H2- heater contacts	
6	S1 – T1 source	
7	G1 – T1 gate	
8	D1 – T1 drain	
9	SUB- substrate connection	
10	DI1- temperature measurement diode- anode	
11	DI2- temperature measurement diode- cathode	
12	D2 – T2 drain	



N channel spectrometer in DIL14 packed



On the illustration above, are given additional bonds from pins 2 and 9 to the substrate of the package.

DIL14 Pin	Die / Pad
1	N1 / D2
2	N1 / B (Sub)
3	N1 / G2
4	N1 / S2
5	N2 / D2
6	N2 / G2
7	N2 / S2
8	N2 / S1
9	N2 / B (Sub)
10	N2 / G1
11	N2 / D1
12	N1 / S1
13	N1 / G1
14	N1 / D1

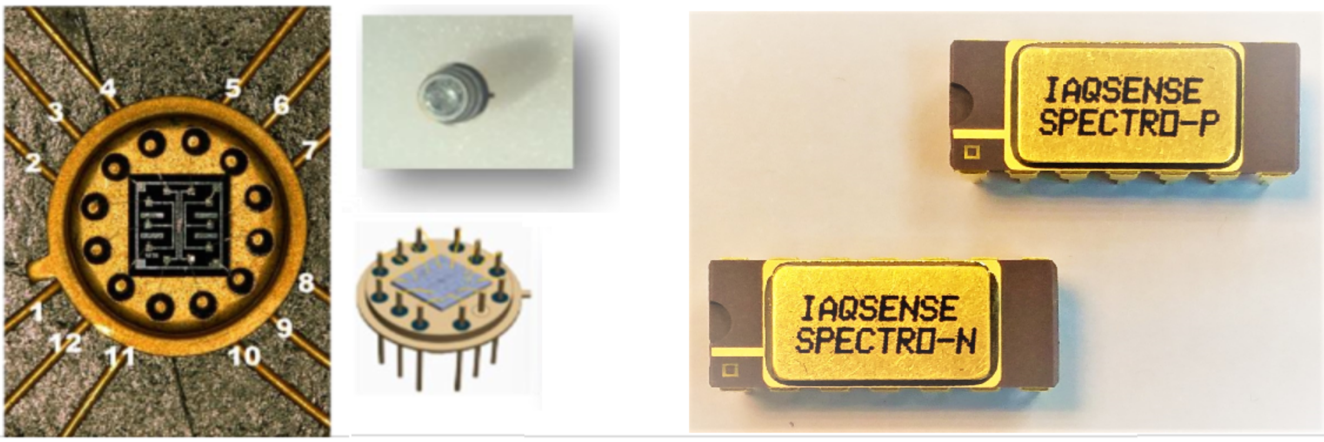


Figure 2 Used for the purpose of the project TO packages and DIL alternatives for spectrometer sensors.

Manufactured silicon chips spectrometer sensors are glued with insulating glue to the package and certain contact pads are wire – bonded to the corresponding leads of the TO 12-pin metal can package. Because of the developmental and measuring purposes the housing cover is not permanently attached to the package, and can be easily removed by removing thin strips of paper-adhesive tape. Because of the wire-bonding needs and to ease shipping, leads were bent to become flat (parallel) relative to the package.

Establisher standard packages for cantilever on chip:

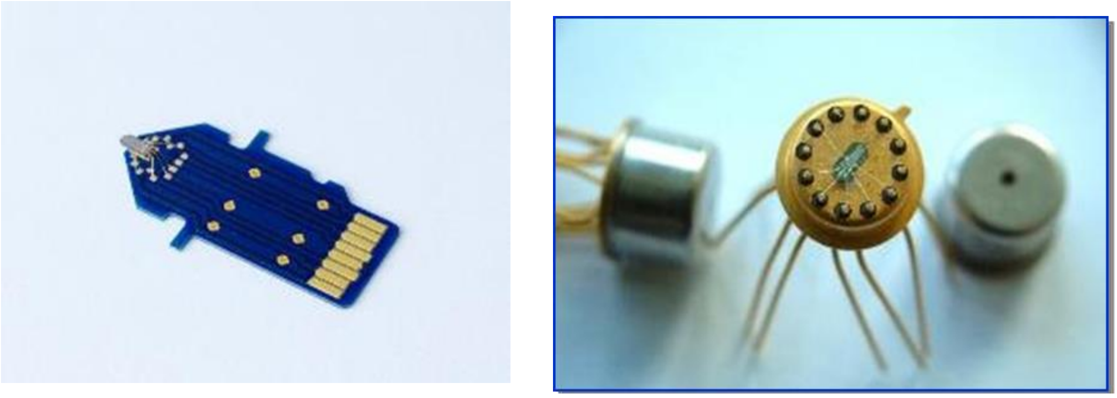


Figure 3 Cantilever bonded on a custom PCB holder (on the left) and cantilever bonded in standard TO12 package (on the right).

In figure 3 are shown both variants for packaging of the active piezo-resistive nanostructured cantilever. NANO has developed a custom PCB holder. This is universal solution that covers all requirements for mass production. Usage of a TO12 package is also available.

Cantilever bonds can be covered and protected with top glue when this demanded.

Discussed aspects during the technology transfer:

Critical aspects:

- If a trade secret was to become known, its exclusive value would disappear

If trade secret:

- Porting validated process to traditional foundries for mass production is critical
  → process negotiations is requiring a certain level of input, different fabs means loss of know how
  → if negotiations fail, added value is already transported
  → even if the porting succeed, the developed and transferred know-how can be used for other technologies

Critical aspects:

patenting process involves making the invention open to public inspection. If a patent application is rejected (in the worst-case scenario), the subject matter of the invention is then freely available to all

If protected:

- Processes are known
  → Process cannot be patented, maximum process chain
  → a way could be identified to achieve the same results with other process combination
- Processes are unknown
  → generating an interest for other applications
  → for research can be used anyways, becomes commonly used, the follow up is impossible

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Demo Board for Spectrometer on Chip is shown in figure xx.
- 2 P-type sensors in DIL 14 package
- 2 N-type sensors
- Processing ASIC IM452A with embedded 16bits processor – 4 + 2 channels
- UVC LED driver and control on board

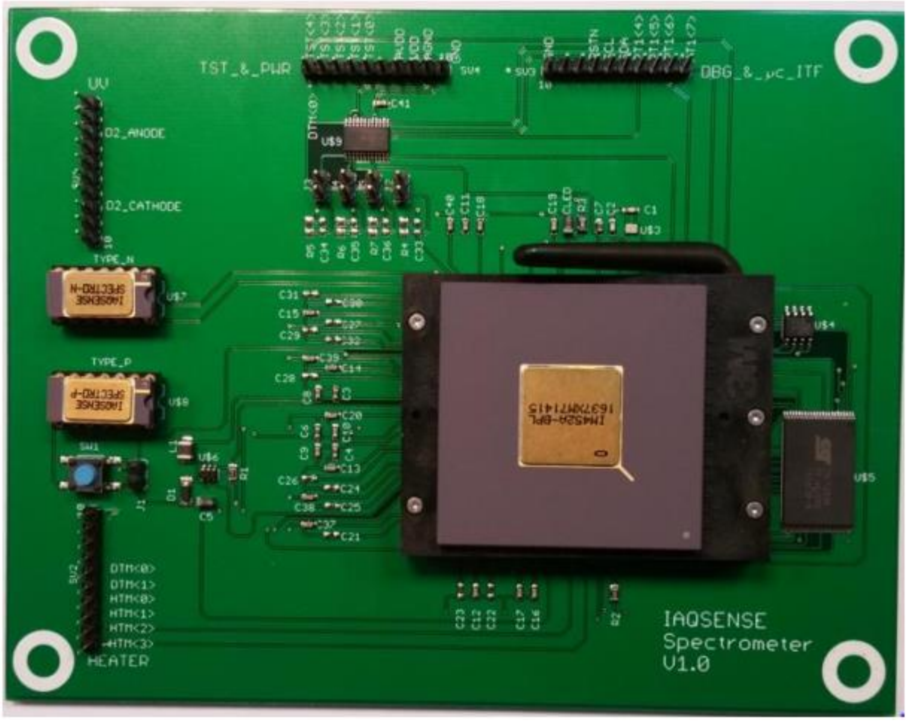


Figure 5 MOSFET spectrometer on chip demo board design by EELEO

Figure 4 ASIC based (IM309D) 8-Cantilever board plus 2 optional piezo pumps for inject/purge pattern

The same board is suitable for 8 functionalized cantilever molecule detection and for 2 channels particle detection.

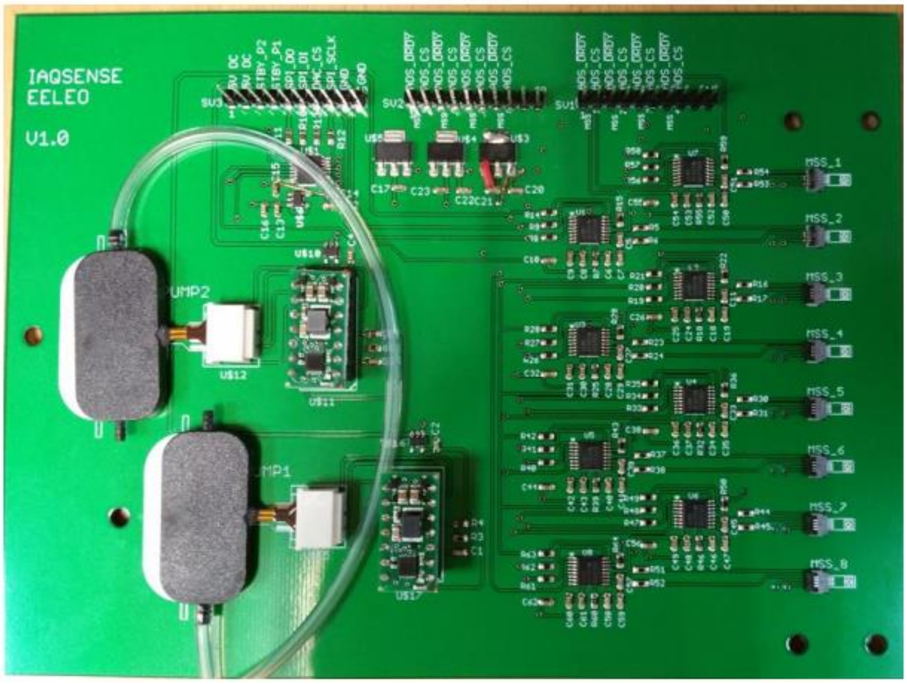


Figure 6 Board for 8-MSS (surface stress membranes) detection of VOC after individual functionalization with polymers. Used as reference for benchmarking. 2 piezo-umps for inject/purge dynamic pattern.

Conclusion:

Negotiations with traditionally foundries have been done carefully without harming intellectual properties of any partner in the consortium. Critical aspects like the functionalization are not std. CMOS compatible. For that reason, a process hand over must be found to cover certain steps in other external fabs or in the own facilities. To guarantee technologies compatibility the wafer size has to be 6”. For a complete or partial external 6” production, the requested sensor quantity should be bigger than 2M pieces per year.

1 st.	**Raw 4” substrate (Si wafer)**	14 st.	**Lithography and oxide etching (BOE)**
2 st.	**RC1 & RC2 (wafer cleaning)**	15 st.	**Boron implantation and annealing**
3 st.	**Wafer oxidation**	16 st.	**Wafer dry oxidation**
4 st.	**Lithography & Si etching**	17 st.	**Contacts**
5 st.	**Wet oxidation**	18 st.	**Al deposition**
6 st.	**Lithography & oxide etching (BOE)**	19 st.	**Lithography**
7 st.	**Phosphor implantation**	20 st.	**Al Etching, resist remove**
8 st.	**Phosphor drive in**	21 st.	**Annealing**
9 st.	**Wet oxide etching**	21 st.	**Lithography for SnO2 Lift-off**
10 st.	**Wafer wet oxidation**	22 st.	**SnO2 deposition**
11 st.	**Lithography & oxide etching (BOE)**	23 st.	**SnO2 Lift-off**
12 st.	**Boron implantation**	24 st.	**Passivation**
13 st.	**Boron drive in**	26 st.	**Transistor release**

Figure 7 Flowchart - main steps in the spectrometer production and functionalization

1 st.	Raw 4" substrate (Si wafer)
2 st.	RC1 & RC2 (wafer cleaning)
3 st.	Wafer oxidation
4 st.	Lithography & Si etching
5 st.	Wet oxidation
6 st.	Lithography & oxide etching (BOE)
7 st.	Phosphor implantation
8 st.	Phosphor drive in
9 st.	Wet oxide etching
10 st.	Wafer wet oxidation
11 st.	Lithography & oxide etching (BOE)
12 st.	Boron implantation
13 st.	Phosphor drive in
14 st.	Lithography and oxide etching (BOE)
15 st.	Boron implantation and annealing
16 st.	Wafer oxidation
17 st.	Contacts
18 st.	Al deposition
19 st.	Lithography
20 st.	Al etching & resist remove
21 st.	Annealing
22 st.	Passivation
23 st.	Lithography and etching (top side)
24 st.	CuO nano tubes formation (top side)
25 st.	Cantilever release

Figure 8 Flowchart - main steps in the cantilever production and functionalization

The manufacturing of sensitive and selective sensor devices requires the establishment of combining the fundamental technological CMOS steps on one side and CuO_2 and SnO_2 layer for spectrometer on the other side because the deposition on these two materials is not a standard CMOS process.

There are several providers of MEMS processes around the world. Generally, they are dedicated to MEMS only without considering the CMOS integration.

CMOS integration for gas sensor, looking to high volumes to be considered, is a must.

Consequently, the question should be reversed:

- Which CMOS Foundry is providing a standard process on which MEMS can be added

Several foundries providing mix analog/digital process are suitable but most of them are doing proprietary devices and are not open, except if deal for very large quantities are considered. Foundries like ST, Analog Devices, are in this case.

Some may offer access to a custom process, like TSMC but investment to build a custom process is large and should be justified in terms of ROI (Return on Investment). European Foundries to be considered for Xfab and AMS. Xfab has for example a contract with Micronas (former Bundeswehr design) but for a proprietary process also.

The case of AMS is more interesting as they have a real policy for Gas Sensors (with several take-overs) and process opened to post-processing. An entry point to test the feasibility of such approach is with the CMP/Grenoble organisation which provides MPW (Multi-Project Wafers). Two process based on CMOS 0.35μm are available for our devices:

- Spectrometer on Chip integrated in CMOS thanks to the so-called BARC option which provides a well on the needed place and isolation with Silicon Nitride. This is a standard process with official option which can easily translated to mass production with AMS.

- The Cantilevers thanks to the standard process with additional post-processing (well documented and with history) managed by CMP outside AMS for the post-processing (micro-machining) beyond the Standard CMOS process.

In all cases the functional layer must be considered separately directly by the owners of the gas sensors. Micronas for example has a custom/proprietary suspended gate made separately and added via a hybrid process.

In terms of economics:

- The Spectrometer on Chip integrated on CMOS has the only cost of the BARC option and can provide a very low cost solution, fully integrated. This is the case up to the functional layer
- The functional layer deposition is the central point for quality and costs.

Options for the functional layer:

- PLD (Pulse Laser Deposition) – This type of equipment is available for mass production and wafer level deposition in Picodeon (one of the member of SensIndoor project) and the equipment is available as service in other companies. The advantage of such equipment is the dimension (and consequently the binding energy of molecules) thanks to the small size of metal oxide grains deposited (below 5nm for SnO_2). To give an example, a grain size of 5nm will have 100 folds more adsorption energy than the grain size in the range 50-70nm we currently deposit on the Spectrometer on Chip, giving a 100 folds increased sensitivity of the device.
- Such PLD equipment is available in the Bulgarian Academy of Sciences (ISSP-BAS) Sofia for deposition at chip level and can be a good option to study functional layers with Prof. Stefan Andreev team.
- Depositing Hollow Spheres of metal oxide (tiny spheres of tin oxide currently envisioned for very energetic batteries) is also possible with new type of equipment like inkjet printers, spin coating, droplet coating, dip coating (at chip/sensor level)
- And with the same deposition method a large range of polymers can be considered.

The best range of functional materials, deposition techniques and economics should be further investigated beyond the IAQSense Project. In the Frame of WP7 several process alternatives for the functionalization has been identified and described in Task 7.2.

Currency exchange rate EUR/$	1,097	exchange rate 02/04/15	
ASIC			
Die size	9	mm2	w/o scribe line
Technology	0,35	µm	Mixed Analogue/Digital
Wafer size	200	mm	8” wafer
GDW	2570	dice	For 90% yield
Wafer price	1200	€	Mixed technology - Market price for 8” wafer
Cost per die	0,4669	€	

Probing of ASIC			
Duration	10	s	Delivered to packaging with wafer mapping
Unit price	0,01	$/s	1cent per s – market price
Total	0,1000	$	
Probe card and other amortization	0,0150	€	Set of equipment: 15K€ every 1Mpcs
Total per die	0,1062	€	
Spectrometer die			
Die size	1	mm2	
Wafer size	150	mm	6" wafer
GDW	11500	dice	With 90% yield
Wafer price	120	€	Market price for basic technology – customised
Cost per die	0,0104	€	Option Nano Analytik: 600€ per 100mm wafer- cost per die: 0,1304€ per die
Probing of spectrometer die			
Duration	1	s	Delivered to packaging with wafer mapping
Unit price	0,01	$/s	1cent per s – market price
Total	0,0100	$	
Probe card and other amortization	0,0050	€	Set of equipment: 5K€ every 1Mpcs
Total per 4 dice (dice and probe)	0,0982	€	Option Nano Analytik: 0,5782€
Packaging (stacked die)			
Base packaging cost	0,5	$	QFN 100pins = 0.50 $
			Inc. dicing & Inc. 100 wire bondings
Nbr of add wire	50		supply and power pins and stacked dice
Cost per wire	0,002	$	0.001$ per wire - 0.002$ per power wire
Add cost per die	0,1	$	
Total per die	0,5469	€	
Final test			
Duration	20	s	
Unit price	0,01	$/s	
Total	0,1823	$	
Total costs			
Dice + Tests + Packaging	1,4005	€	
After final test yield	1,5562	€	Yield 90%
With transportation costs	1,59	€	Transport 2%
With risk margin	**1,75**	€	Risk 10%
Selling price with 30% margin	**2,49**	€	

UV LED			
Wavelenght	240	nm	
Price trend	**0,50**	$	
Total w 4 spectrometers and LED	**2,2018**	€	Option Nano Analytik: 2,8002€
Components around ASIC (Asian source)			
Coil	0,05	$	
Diode	0,05	$	
5 decoupling capacitors	0,025	$	
Xtal – 12Mhz	0,1	$	
Electrolytic capacitor	0,1	$	
PCB 0.5dm2	0,5	$	
With 2% transportation costs	**0,77**	€	
General and RF processor			
Based on ATMEL			
ATSAMR21E16A	**3,00**	€	
Total set of components	**5,97**	€	
with Assembly cost 1/0,8	**7,46**	€	
Final test and programming			
Duration	20	s	
Unit price	0,01	€	
Total	**0,20**	€	
Total assembled and tested module	**7,66**	€	
With Provision for patent and royalties	**8,58**	€ w 12%	Value Tbc and basis for application
Selling price with 30% margin	**12,26**	€	
Distri price (2 to 1)	**24,52**	€	Option Nano Analytik: 26,91€

<u>Calculation is for 1Mpcs per year</u>			
Wafer lots for ASIC			
400 wafers / 200mm			
Purchasing costs	480 000,00	€	
Wafer lots for Spectrometer			
100 wafers / 150mm	12 000,00	€	Option Nano Analytik: 200w/100mm

			- 120 000€
Assembly costs (silicon)	546 946,22	€	
Test costs (silicon)	348 473,11	€	
Assembly costs (modules)	1 492 224,15	€	
Test costs (modules)	200 000,00	€	
Purchasing costs (ext. components)	3 767 092,07	€	
Total turn-over (sales to distri)	12 257 793,20	€	
Added value	5 958 003,87	€	
Inc. royalties	919 334,49	€	

Results:

the electrostatic focusing of the volcano-type gated tip we neglect the possible emission of electrons from the gate. To optimize the geometry of the emitter we included the gate emission.

The trajectories of the electrons are computed using a Velocity-Verlet algorithm. We note that we not include any scattering mechanism for this simulation since it will naturally result in damage of the volcano gate and so in a hardly predictable long-term behaviour.

Outcomes:

Process porting for mass production of the cantilever and the spectrometer was established. Critical aspects with respect to technology and to intellectual property have been identified and solutions have been presented. The specific challenge for the two technologies was the functionalization of the sensors. The functional material for cantilever and spectrometer is not a standard CMOS process and partially not compatible. Compromise between mass production and high quality, standardized functionalization process: 6" production in FAB and custom process in Ilmenau or other laboratory; 4" production was during the project fully established and understood, 6" scaling is standard process in Ilmenau. A solution for scaling the packaging and bonding capabilities was identified and established. Different package solutions up to custom solutions are established and routinely available.

Deviations

No deviations with respect to achieved results.

WP 7.2: Alternative process – printing

Objectives:

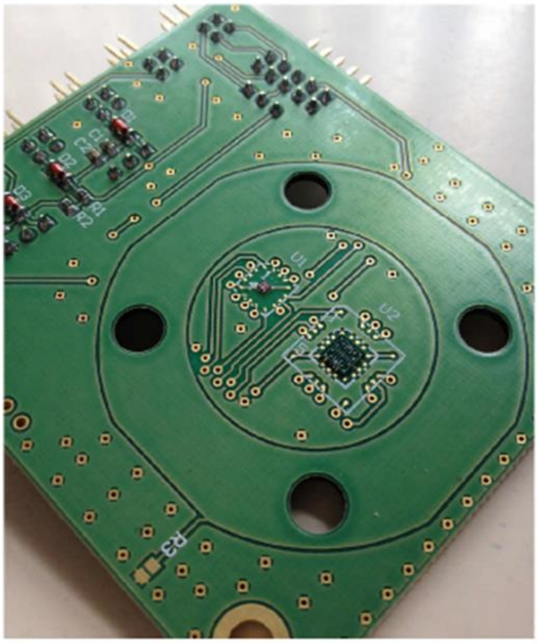
- Custom package for process alternatives
- Custom functionalization
- Basic realization of 3D printing

Achieved results:

- 3D printing and process alternatives are identified
- Process alternatives have been realized
- Cost saving, custom packages are established due to increase of own bonding capabilities

The established packaging technologies (presented in WP 7.2) for the cantilever are without limitations suitable for custom process alternatives. For the spectrometer, the most suitable investigated solution is a PCB based packaging like it was realized for 2 chips or in a stacked PCB solution like it was developed on the down right picture.

Housed multi layer PCB package with top opening for the spectrometer. For smaller custom quantities (<100pcs) cost saving compared to DIL is factor 10-20.



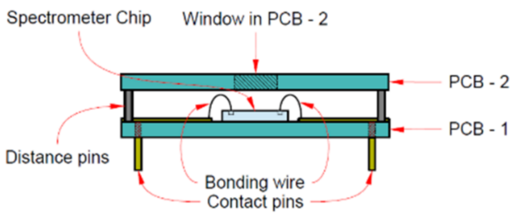


Figure 9 Custom Spectrometer interface board for N-channel and P-channel MOSFET spectrometers (on the left) and proposed custom PCB package for spectrometer mass production (on the right).

Commercial available solutions on the market have been investigated, the following have been identified as most promising:

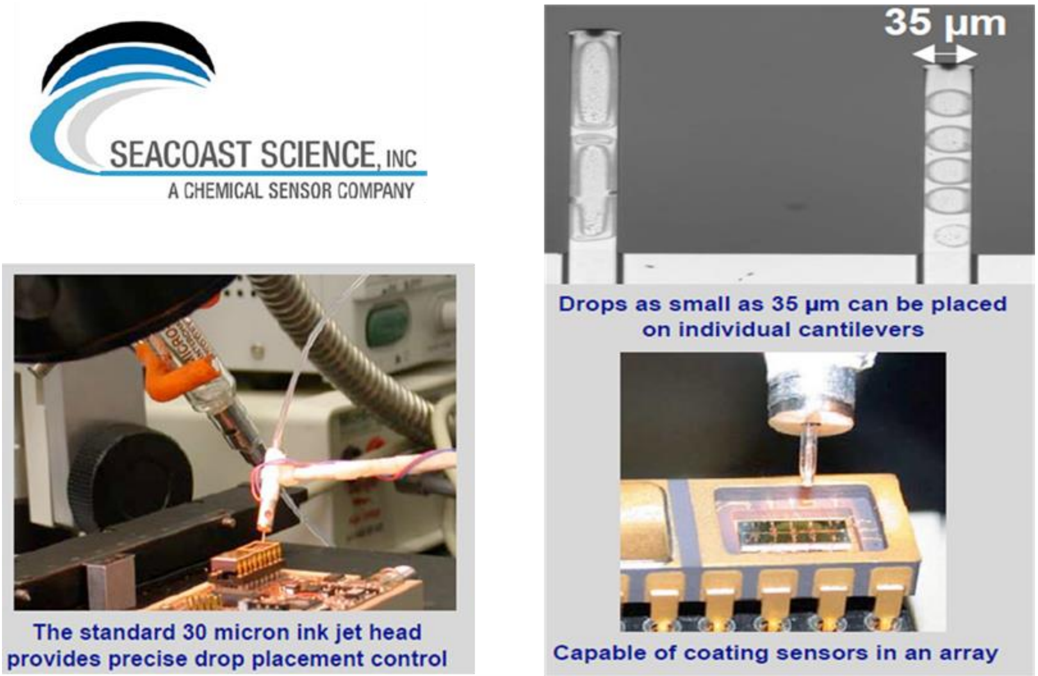


Figure 10SC-IJS Ink Jet System for Sensor Coating from Seacoast Science Inc.

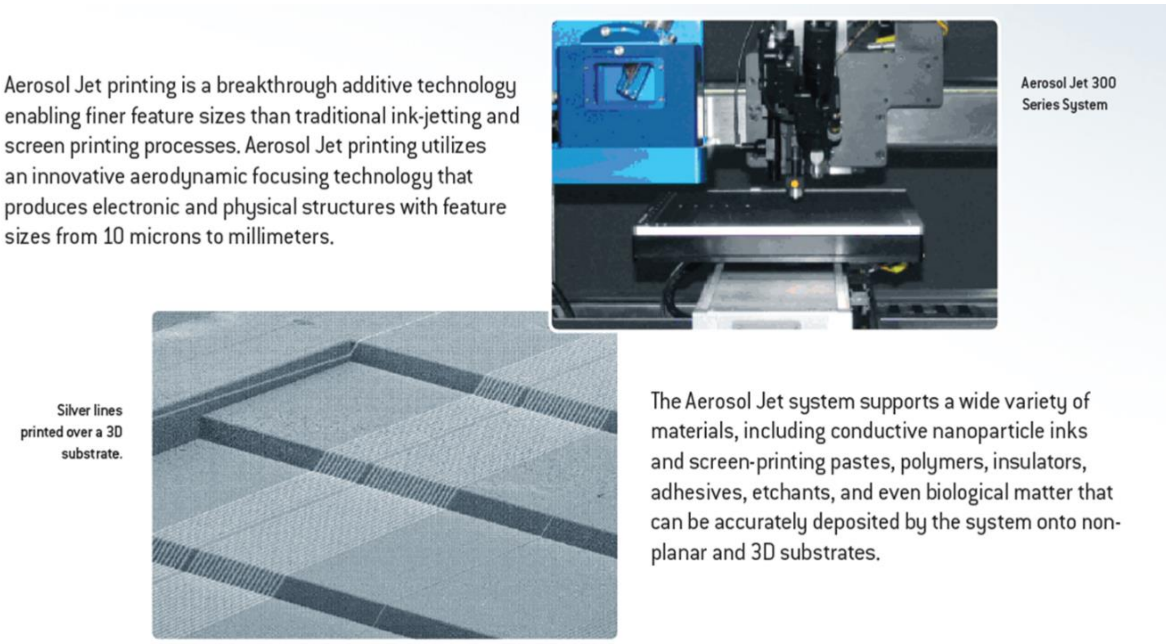


Figure 11 AJ_300 datasheet OPTOMEC.

Features	Aerosol Jet 300 Series Systems Details
Minimum line width	10 µm, 20 µm pitch (material and surface dependent)
Single Pass Layer Thickness	100 nanometers to 2+ µm
Print Speed	200mm/s max (100 mm/s typical) (linear speed)
Mechanical shutter	Response time 2 ms
Ink Viscosity Range Ultrasonic Atomizer Pneumatic Atomizer	 1 to 5 cP (Temperature stabilized water bath required- see below) 1 to 1000 cP (Heating may be used to reduce ink viscosity to achieve atomization of more viscous inks)
Pneumatic Atomizer heater/stirrer	Controls ink temperature, 25-60°C, Stirrer revolutions per minute, viscosity dependent
Platen (Standard)	300 mm x 300 mm; temp control up to 120°C
Platen (Optional)	370 mm x 470mm; temp control up to 120C
Laser (Optional)	700mW 830nm IR Multimode Laser System including Class I Laser Safe Hood
Droplet size	1-5 µm Ø
Stand-off height	Up to 5mm
Motion accuracy	+/- 6 µm for each axis
Motion repeatability	+/- 1 µm for each axis
CE Certifications	Fully compliant
Stand alone system dimensions	1020mm x 1375mmx 2240 mm(Does not include dimensions for ErgoArm and monitor)
Stand alone system weight	~795 kg
Electrical	110/220V, 50 or 60Hz, 30 Amps (10 Amp at continuous operation, typical)

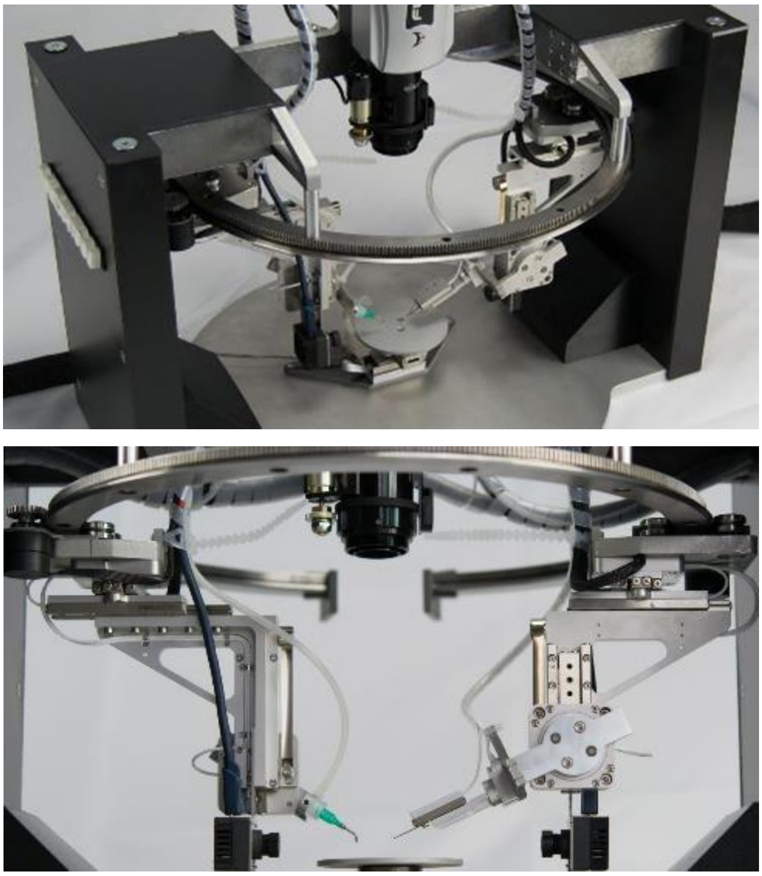


Figure 12 Solution of MICROW.

- Positioning: ≥ 100 nm
- Addressing range till 5 cm
- Degree of freedom (per tool arm): 6
- Working 3D range: 8 cm x 8 cm x 6 cm
- Size: 52 cm x 70 cm x 38 cm
- Weight: ca. 12 kg
- Operation: Gamepad, 6D mouse

Conclusions:

- 3D printing technologies have been identified
  → either the accuracy and the yield is to weak; or the functionality and speed to low
  → in general: 3D printer with needed resolution (<2µm) for high reproducibility are starting from ~100k€ → for 5 years depreciation 2000 custom sensors are needed per year for functionalization costs below 20€

Other process alternatives are required. For smaller requests dip-; droplet- and spin-coating technologies have been identified and established:

Experimental results for process alternatives – spectrometer on chip

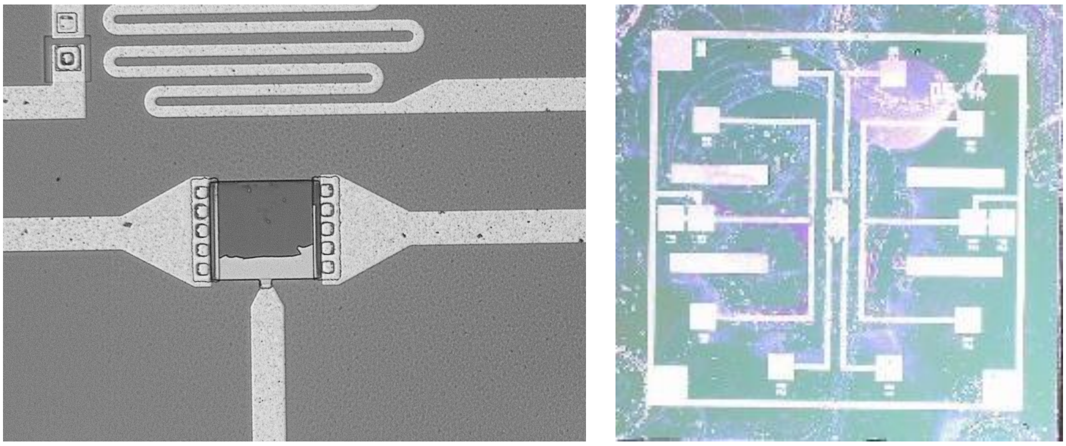


Figure 13 Images of spectrometer sensors after first functionalization runs.

Wafer level approach for custom process: Removal of function layer during development of Droplet-coating on chip level. The surface stress of the functional material (Fluor alcohol Polycarbosilanes) avoided reproducible results during curing process. Problems have been identified and procedure was established for stable polymer functionalization.

The functionalization of Cantilevers can be realized on wafer level (late stage in production but one sided functionalization) or on single Cantilever (both sides):

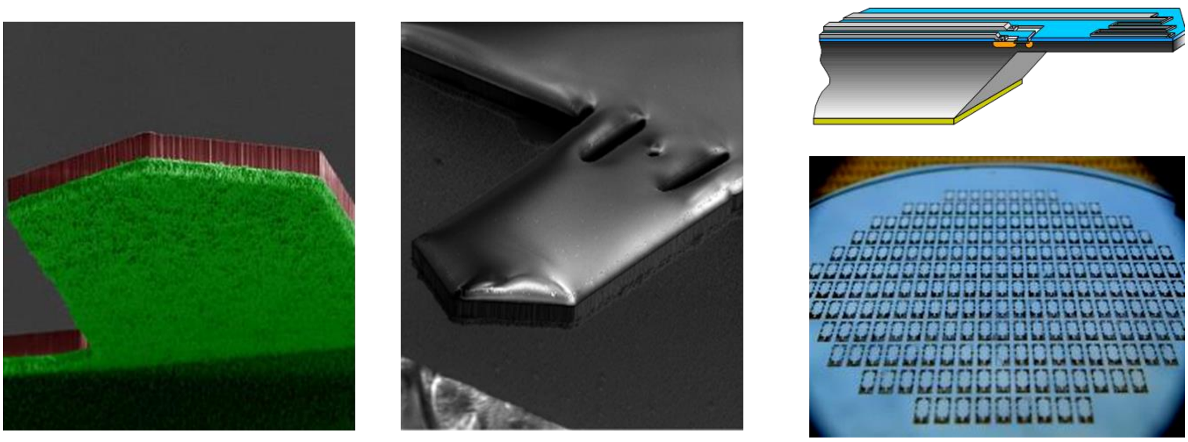
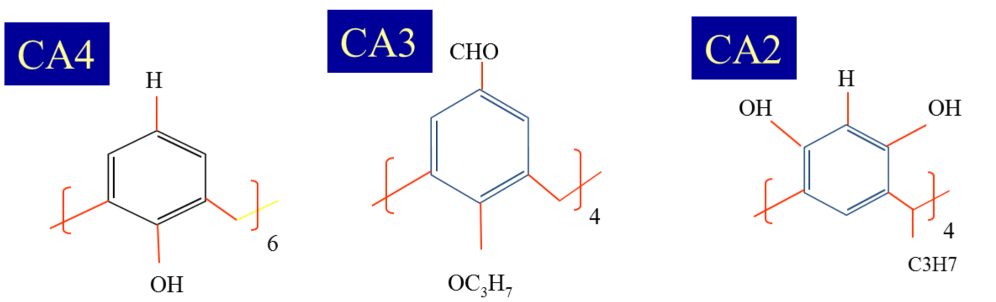


Figure 14 Active piezo-resistive functionalized cantilever. Single cantilevers on the left and wafer on the right.



Smallest feature is 10 nm wide, patterned at a dose of 2 µC/cm with 70 eV

Figure 15 Different calixarene compounds used for further functionalization.

Further investigations have been done on single cantilevers with Calixarenes ⇨ the cyclical phenol-formaldehyde oligomers and Calixarene molecules ⇨ spatial cavities of different size depending on number of including phenol rings.

Set-up for functionalization of single cantilever:

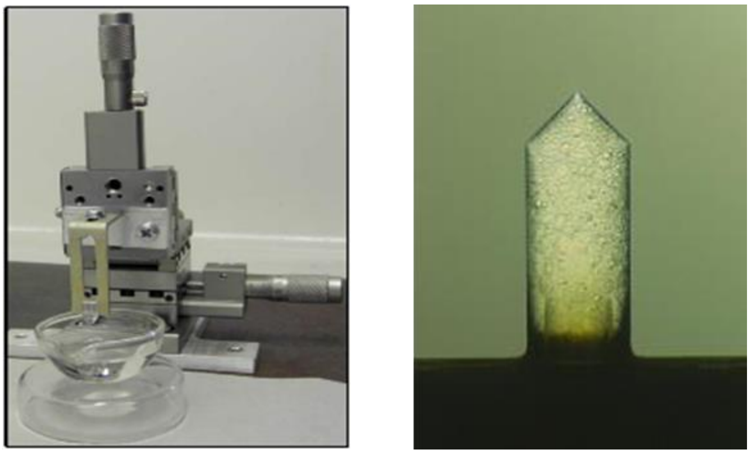


Figure 16 Single cantilever functionalization setup on the left and cantilever image after functionalization process on the right.

Single Sensor functionalization for cantilever

Dip-Coating set-up for precise

functionalization process

Needed improvement:

- Motorized approach
- Chemical resistant holder for faster exchange

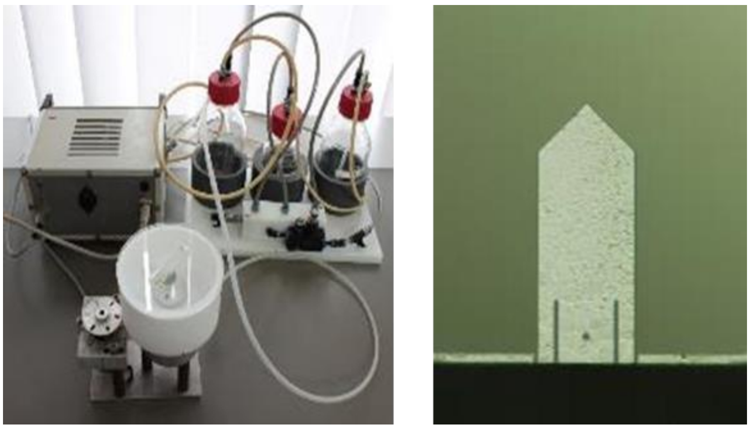


Figure 17 Spin-coating setup.

Spin-Coating set-up for precise

Control of layer thickness

Needed improvement:

- Experiments for double side coating
- Coating specs for different thickness

Functionalization of single spectrometer chips

Different functionalization materials on 2x n-Type and 1x p-Type spectrometer:

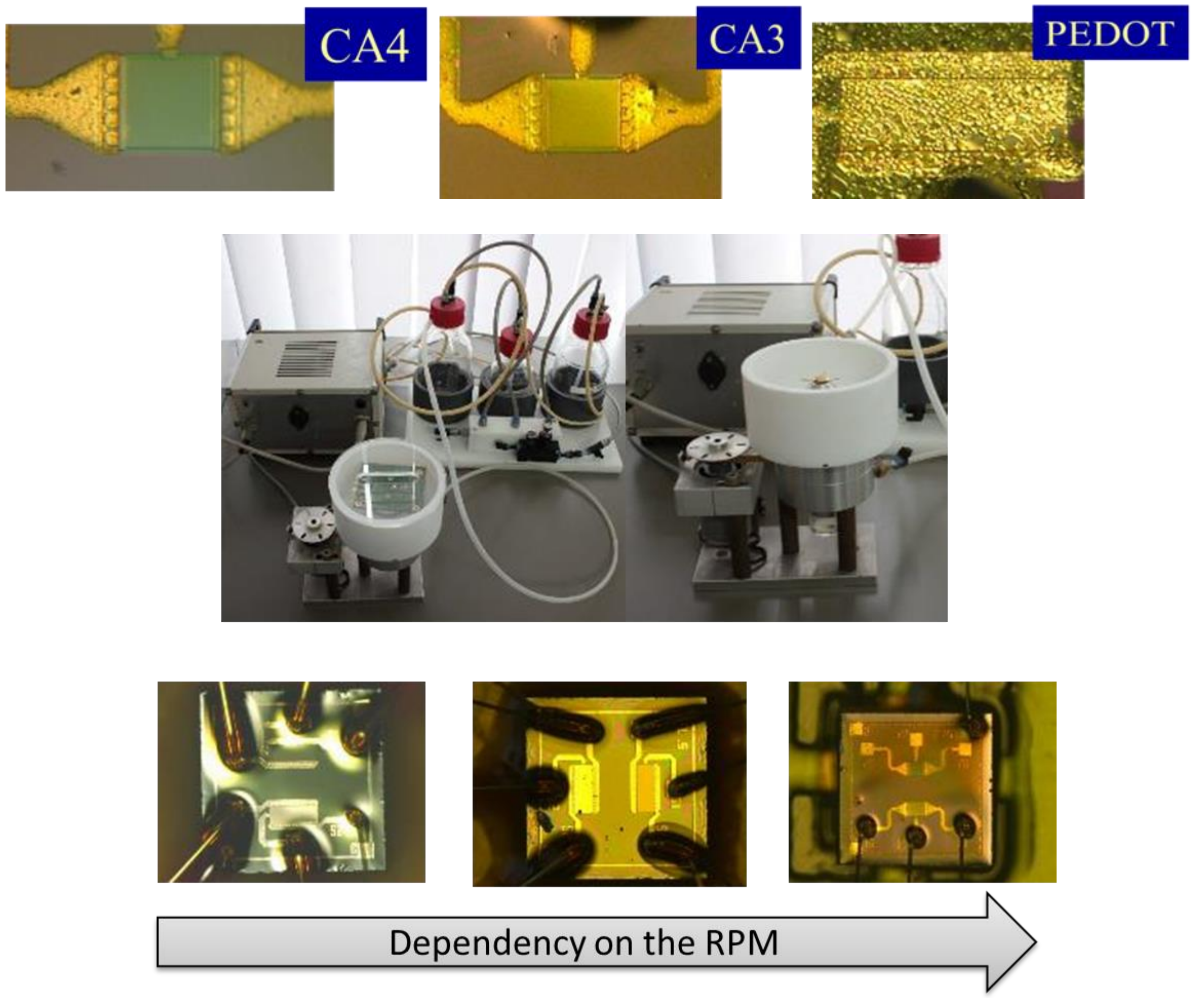


Figure 18 Spin coated of spectrometer samples with different calixarene compounds.

Experimental results:

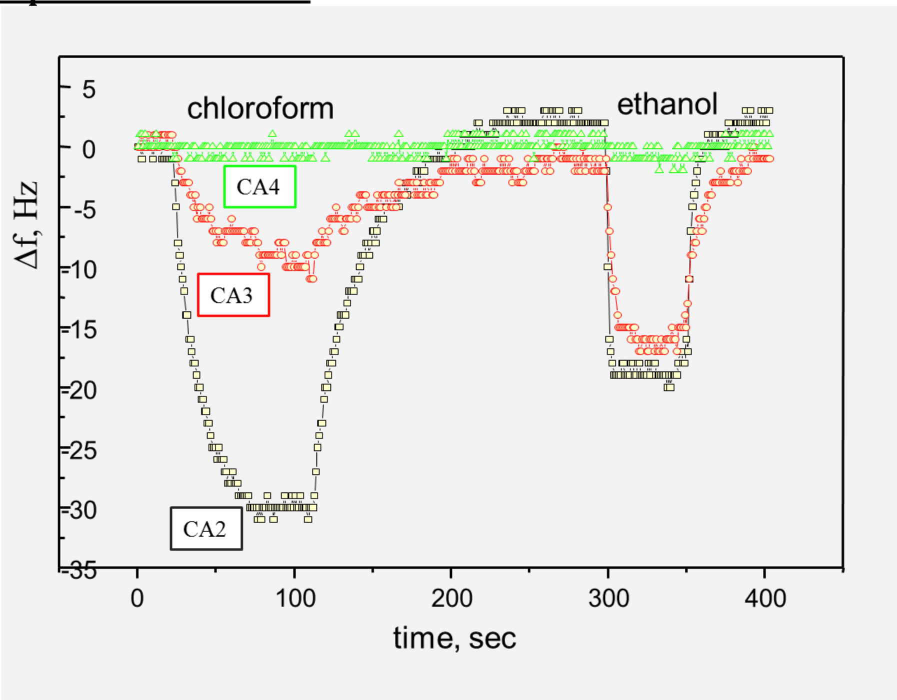


Figure 19 Active piezo-resistive cantilevers functionalized with calixarene compounds. responses.

Response to test coated cantilever with different calixarene types to injection of ~100 ppm chloroform and ethanol vapours. Demonstrate the molecule **Static selectivity effect** and the molecule related **Dynamic events.** Confirms the principle of cantilever network for selective detection and the injection/purge creating additional molecule identification events.

Deliverables

D7.1 “Report on the porting method and feasibility” – delivered in July 2016

D7.2 “3D porting method and feasibility” – delivered in July 2016

Deviations

No deviations with respect to achieved results.

Outcomes

- 3D printing technologies have been identified
  → either the accuracy and the yield is to weak; or the functionality and speed to low
  → in general: 3D printer with needed resolution (<2µm) for high reproducibility are starting from ~100k€ → for 5 years depreciation 2000 custom sensors are needed per year for functionalization costs below 20€
- Other process alternatives have been identified
- For smaller requests dip-; droplet- and spin-coating technologies have been identified and established