

THALES



*Gas Sensor based on CNTFETs fabricated using
an Original Dynamic Air-Brush technique for SWCNTs deposition*

**Paolo Bondavalli
NANOCARB**

Unité mixte de Recherche Thales/CNRS

10/09/2010



- **Why CNT Transistors for sensing applications?**
- **Physics of Carbon Nanotubes sensors**
- **Our approach to fabricate CNTFETs**
- **Our approach for enhance selectivity**
- **Preliminary measurements**
- **Conclusions and Perspectives**



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Advantages :

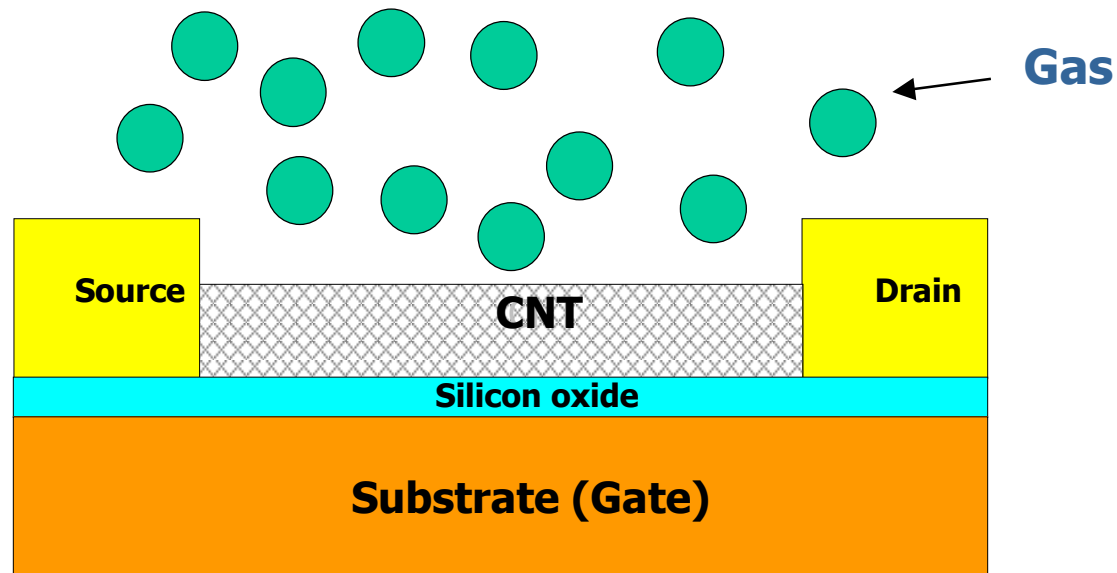
- **Fabrication of very compact devices (around some μms)**
- **High sensitivity :**
Less than one *ppm*, it can reach 100*ppt* (NO_2) it depends on the detection technique
- **Versatility :**
They could be used for different gas families and biological molecules (also using functionalization to improve selectivity)
- **Low Power consumption**
- **Very fast response and recovery time :**
The phenomenon physics concerns charges passage
Reset performed by heating, photo-desadsorption using UV light or by inversion of the Gate potential (CNTFET)
- **Room temperature utilization :**
they do not need high temperature to be effective
- **Technological steps compatible with CMOS technology and batch fabrication:**
Relatively low cost technology (potential for batch fabrication)



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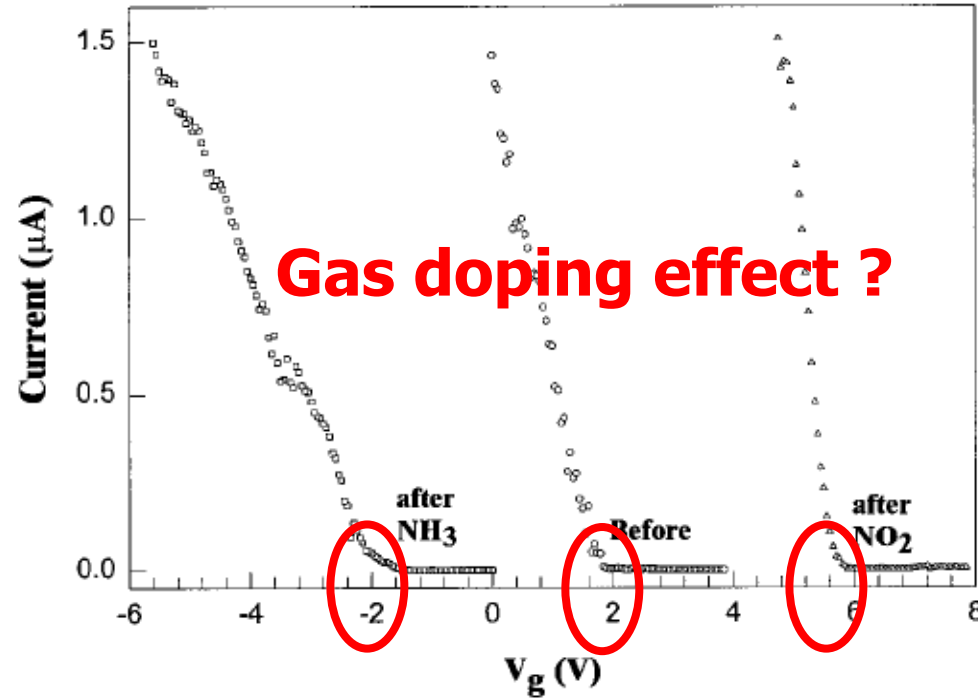
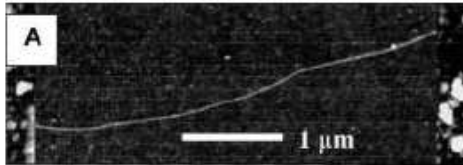
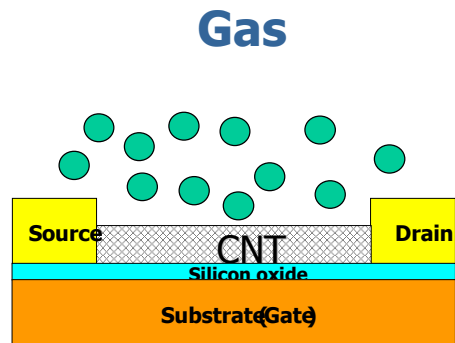


CNTFET = Carbon Nanotubes Field Effect Transistor



Carbon Nanotubes as the transistor channel (one single or a SWCNT mat)

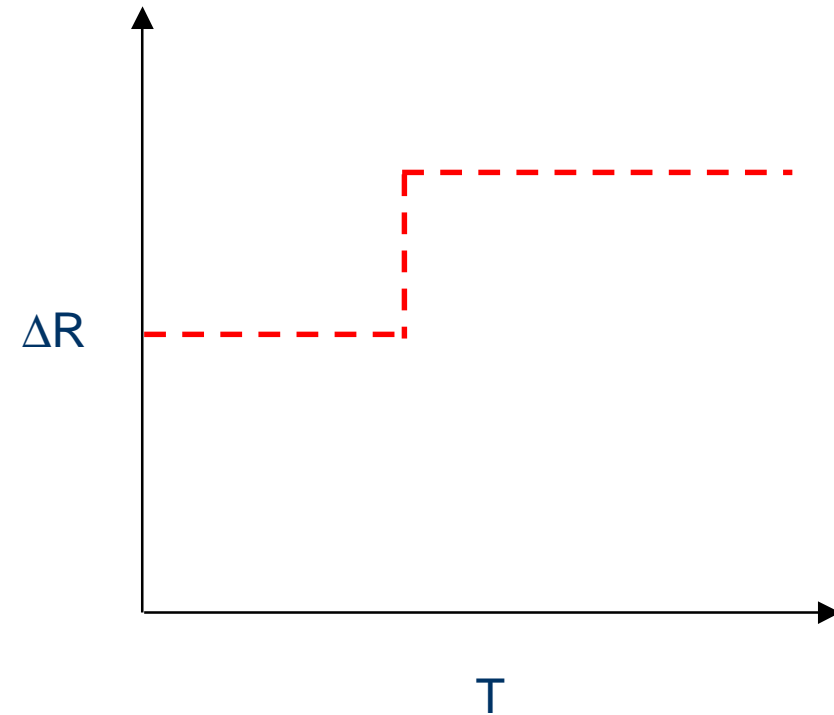
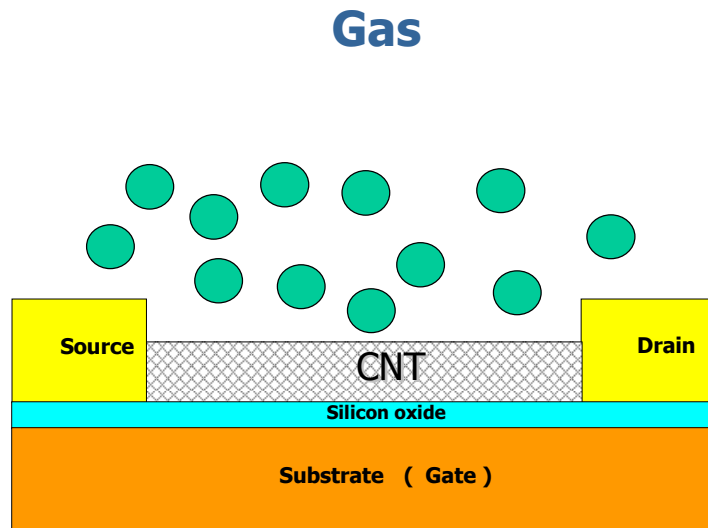
We analyze the change of the current between Source and Drain as a function of the Gate voltage (bottom gate configuration)



Jing Kong,^{1*} Nathan R. Franklin,^{1*} Chongwu Zhou,¹
Michael G. Chapline,¹ Shu Peng,² Kyeongjae Cho,² Hongjie Dai^{1†}

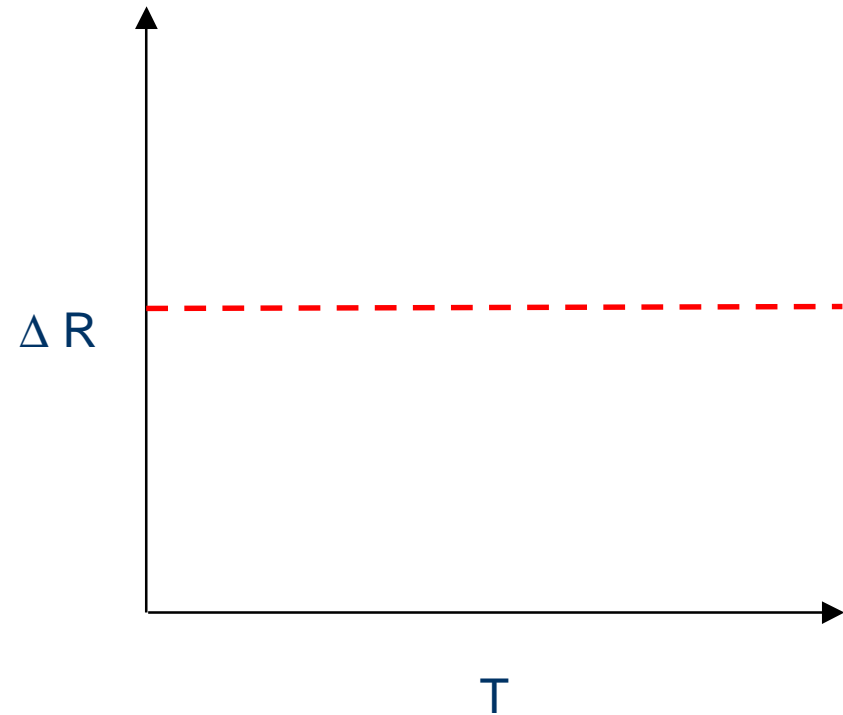
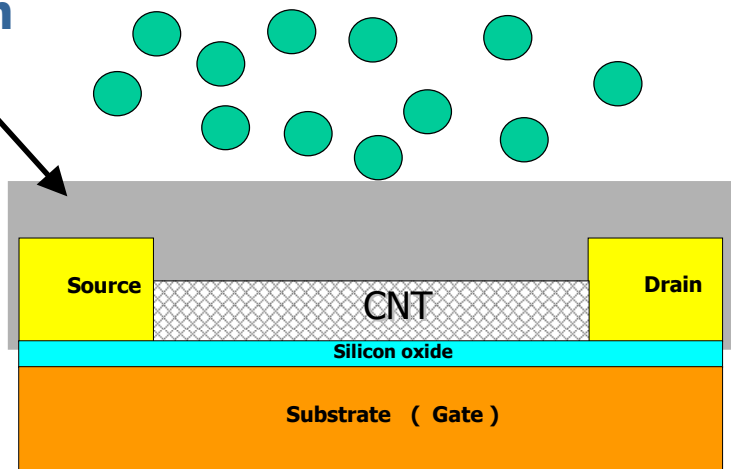
Stanford, 2000

The Turn-on voltage changes as a function of the gas



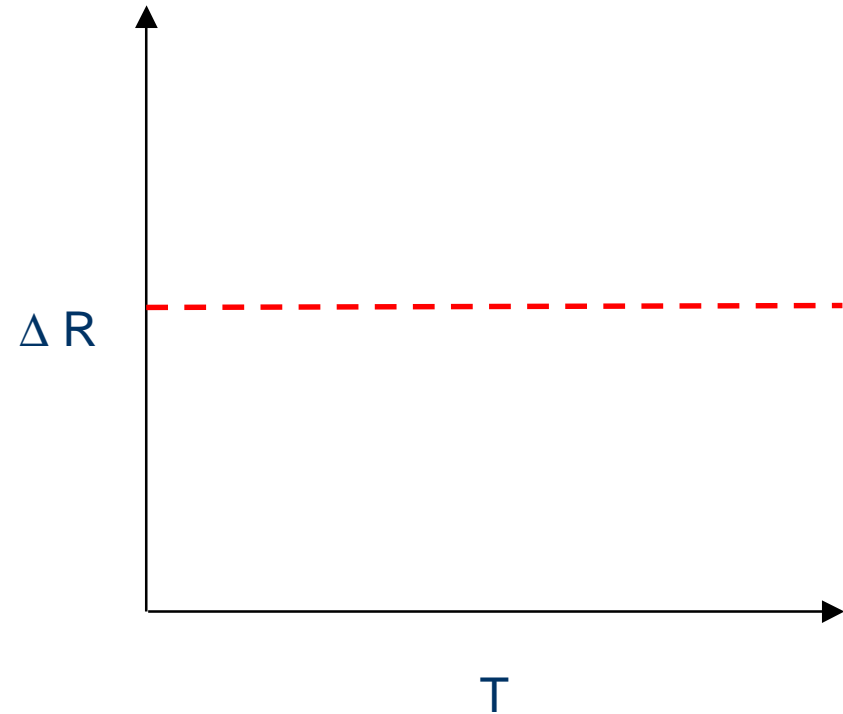
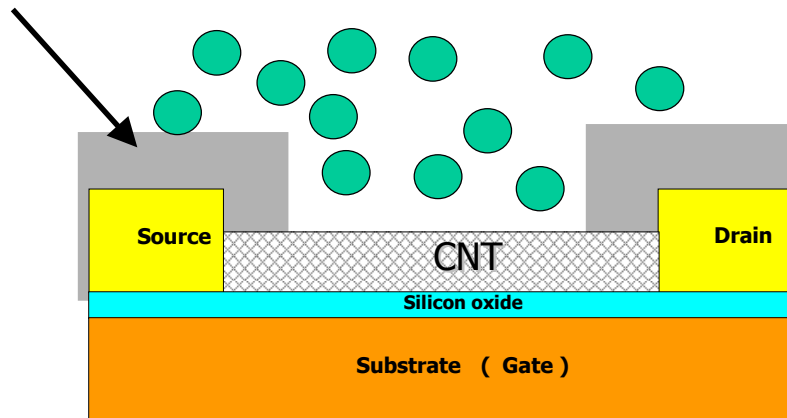


Resin





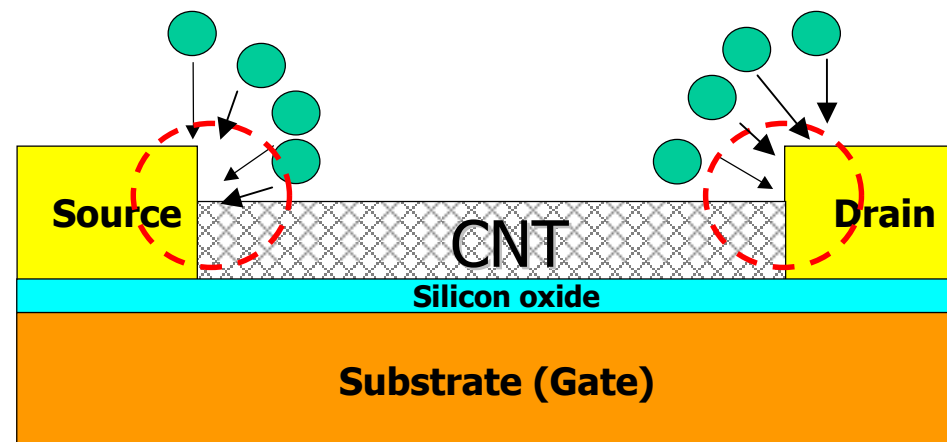
Resin



Ph.Avoiris (IBM, 1998) , H.Dai (Stanford, 2004) , J.Zhang (Georgetown University 2006),
Peng (2009)



The main interaction is at the Metal/CNT junction



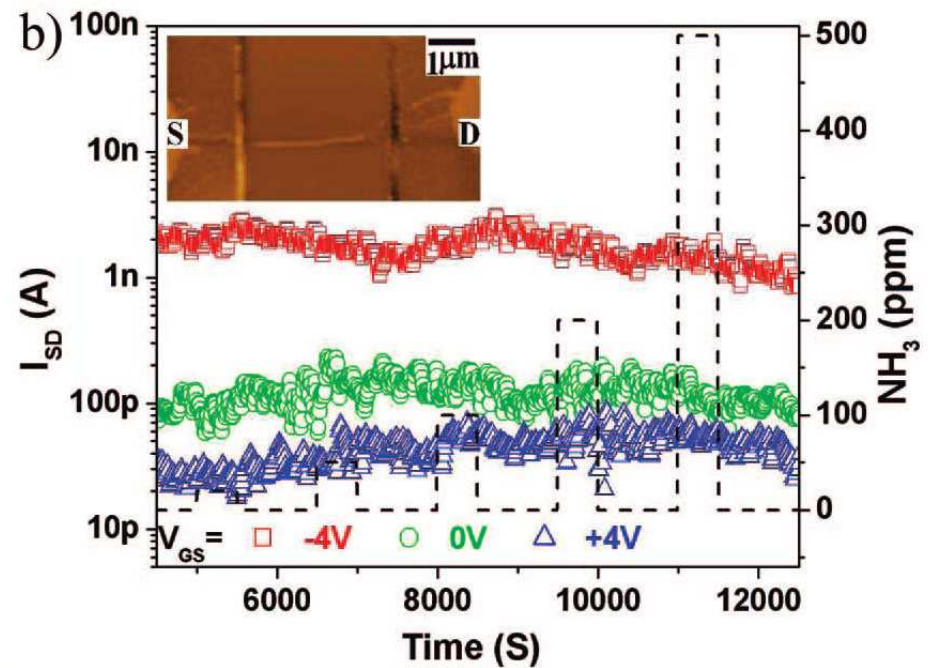
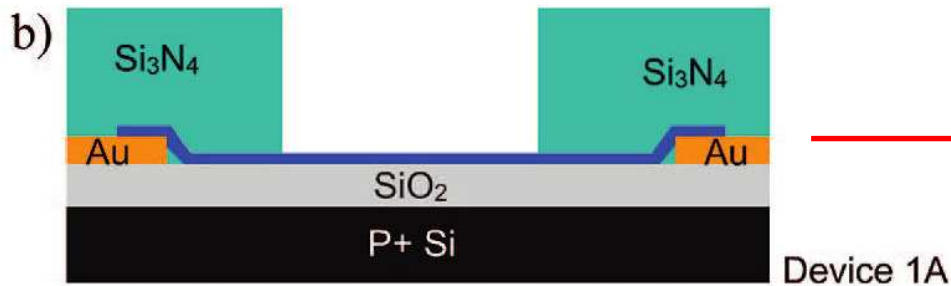
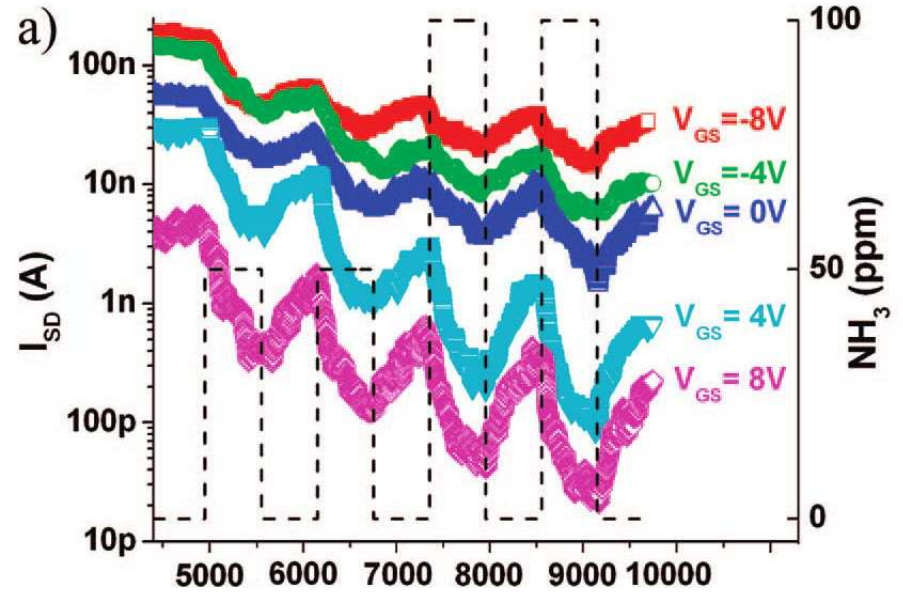
NOT A BULK PHENON

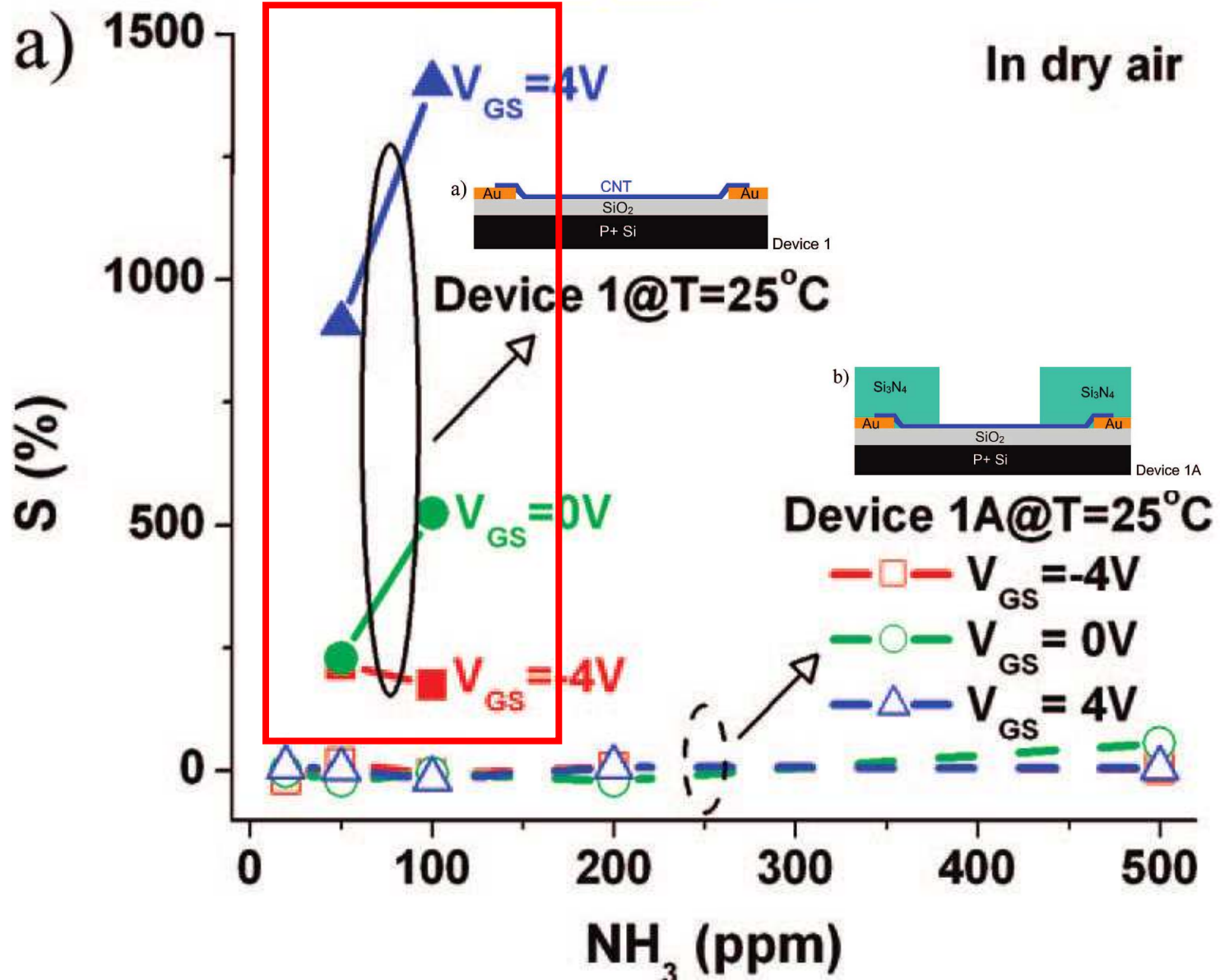
It seems to be not correlated to a doping effect

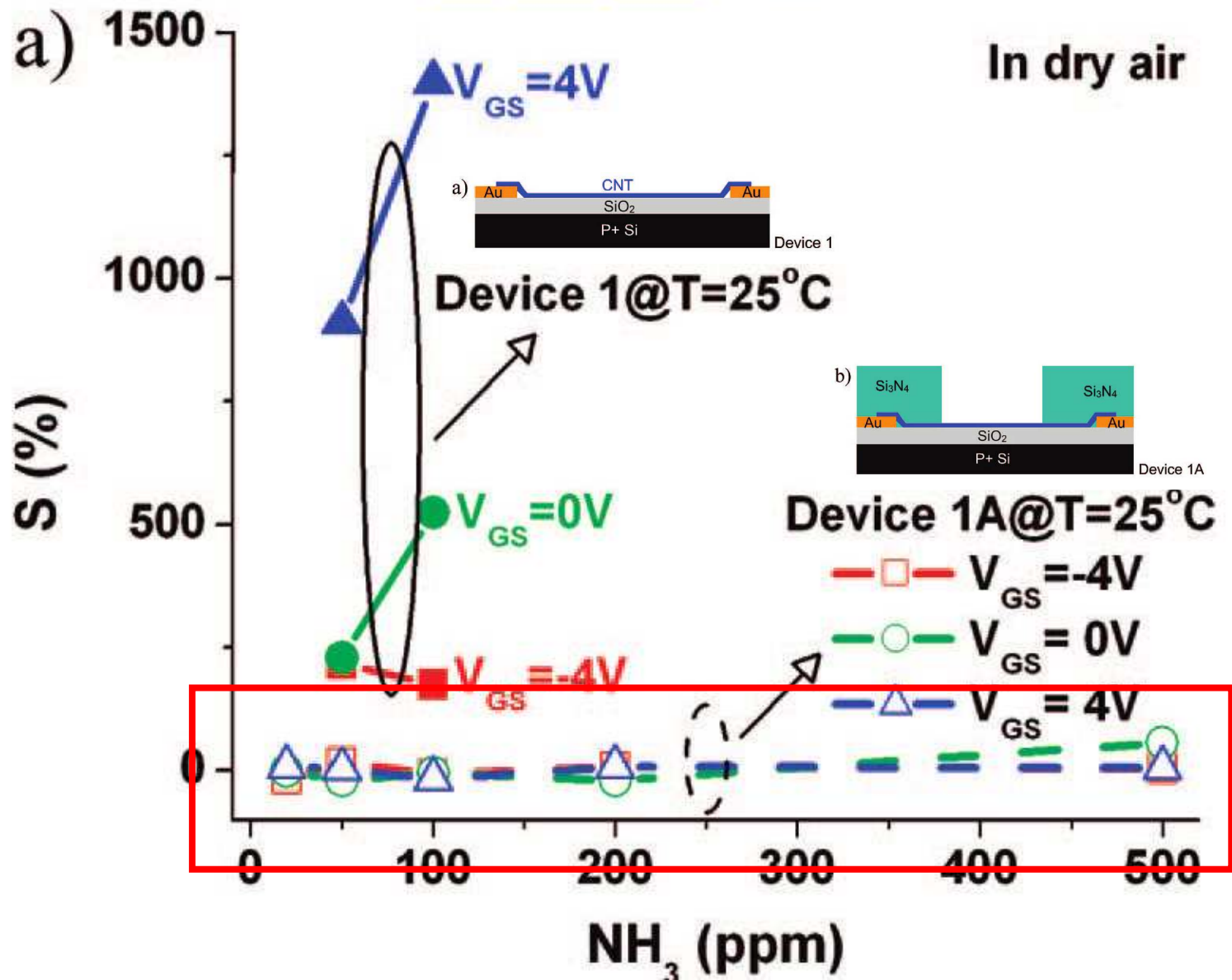
This seems to be true for short channel configuration $<100\mu\text{m}$



UCAM, MIT, Nanyang Technological University







Question :What actually happens at the contacts?



Example : junction Au/CNT

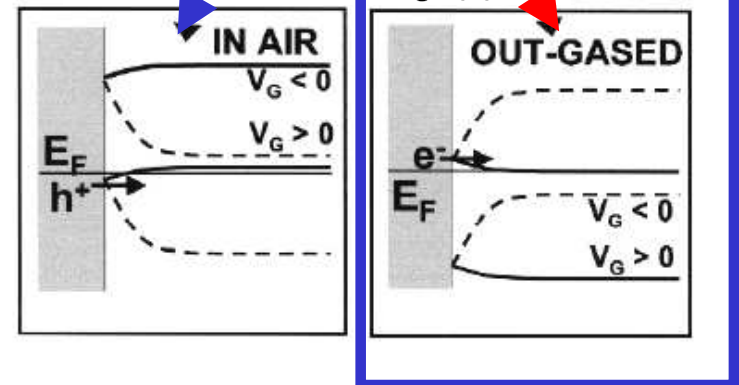
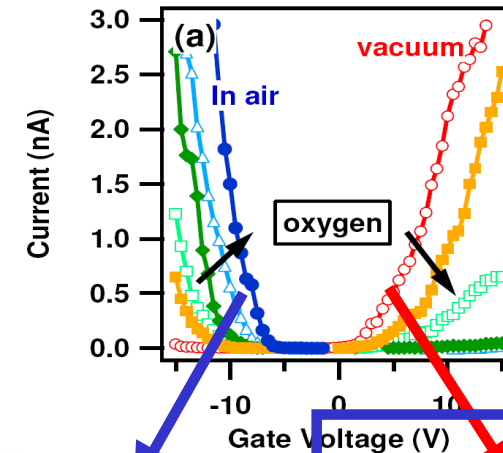
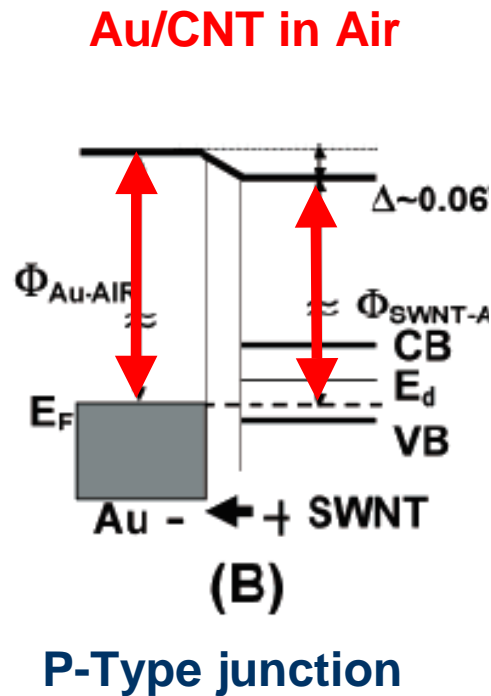
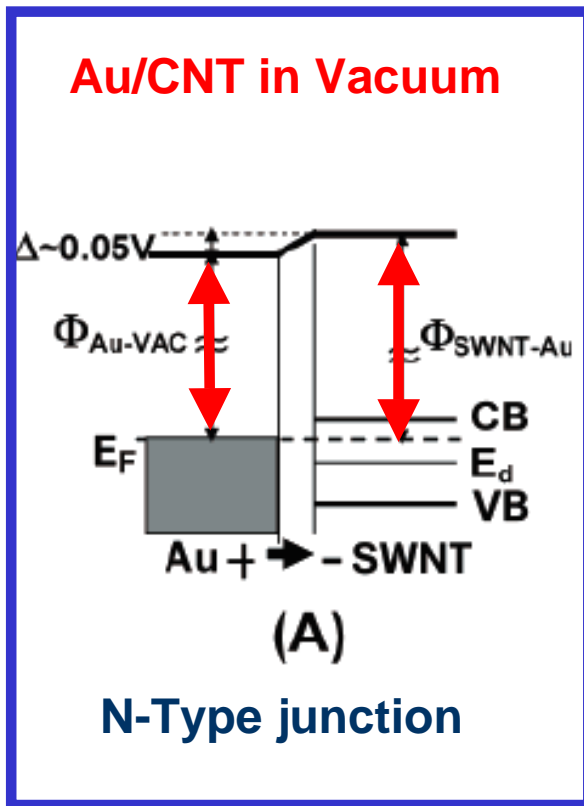


Fig. 13. Qualitative diagram showing the lineup of the valence and conduction bands of a CNT with the metal Fermi level at the source-CNT junction first in air and after annealing in vacuum.

Source Drain current change as a function of the oxygen concentration

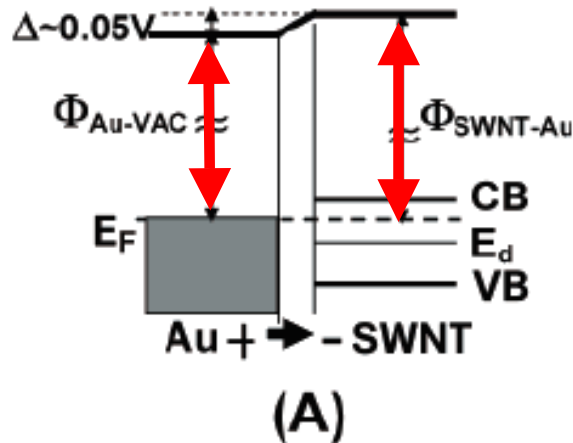
Ph.Avouris et al., Proceedings of the IEEE, Vol.91, n.11, 2003

What happens at the Metal/CNT junction?



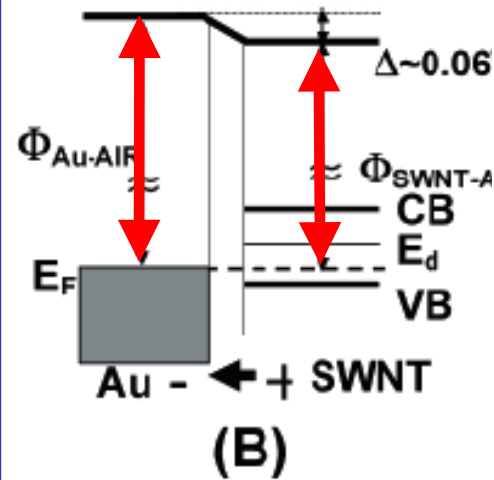
Example : junction Au/CNT

Au/CNT in Vacuum



N-Type junction

Au/CNT in Air



P-Type junction

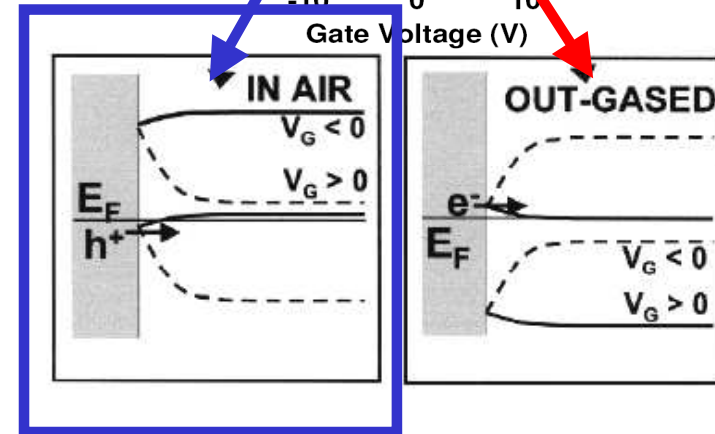
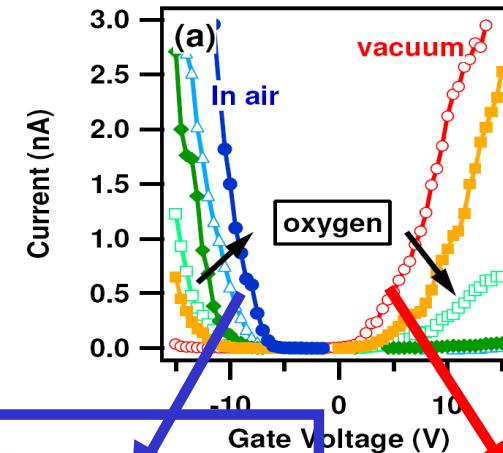


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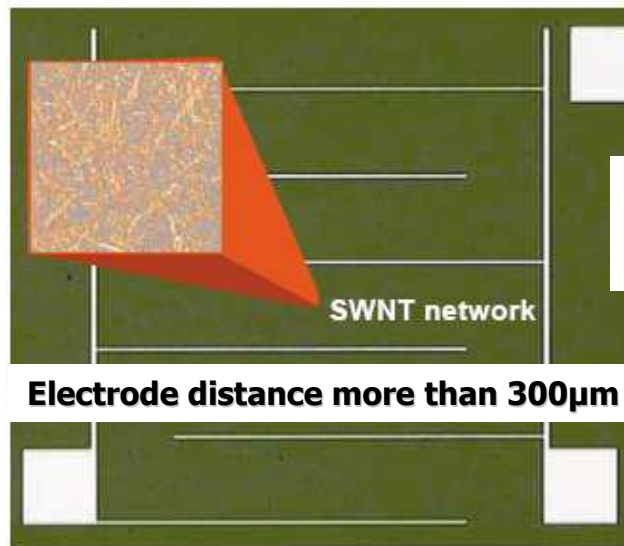
Ph.Avouris et al., Proceedings of the IEEE, Vol.91, n.11, 2003

What happens in case of very large channels?

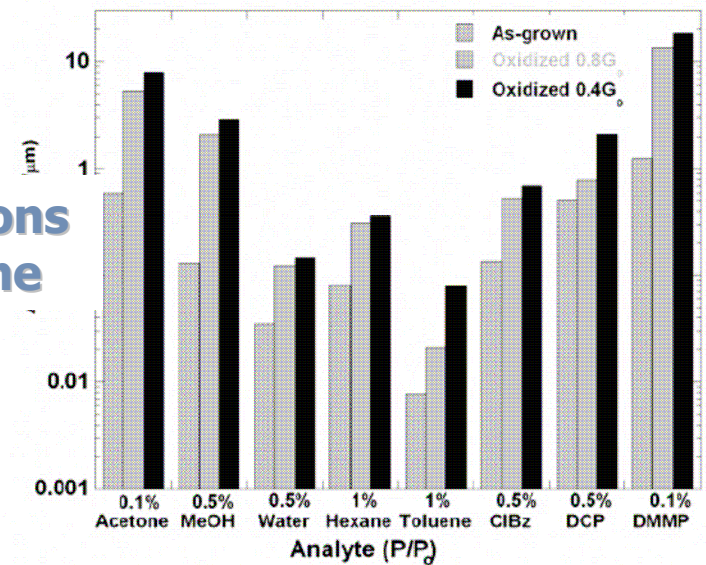


If Channel length is more than 100 μm the mat resistance can be compared to the contact resistance. In this case we can work in the so-called « resistive » configuration.

2mmx2mm



Quite high concentrations and high recovery time



Chemical vapor detection using single-walled carbon nanotubes†

E. S. Snow, F. K. Perkins and J. A. Robinson

Received 7th April 2006

First published as an Advance Article on the web 24th May 2006

DOI: 10.1039/b515473c

Role of Defects in Single-Walled Carbon Nanotube Chemical Sensors

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Received May 30, 2006; Revised Manuscript Received July 11, 2006



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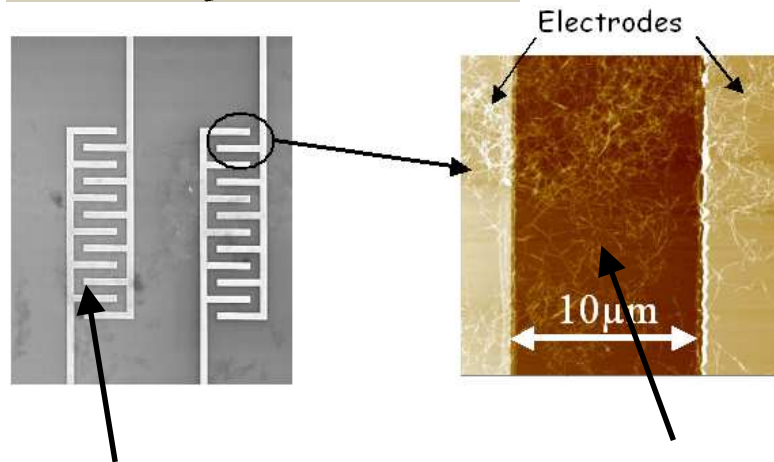
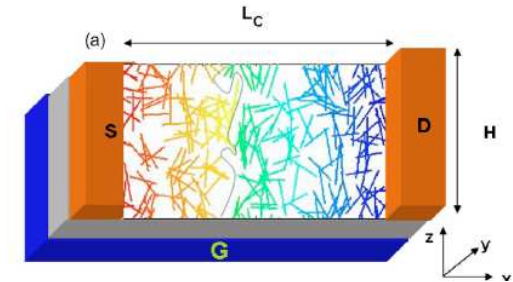
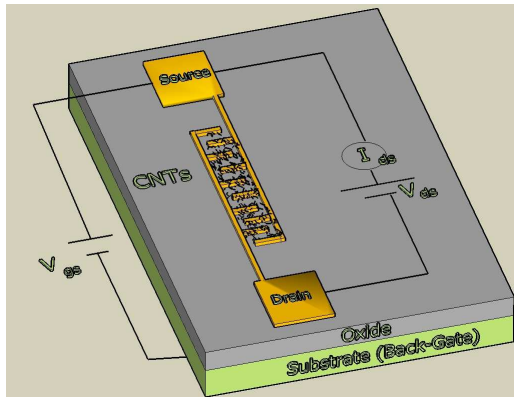


Advantages

- Strong fabrication time reduction (no need for AFM localization)
- Batch Fabrication (large surfaces reduction dramatically the cost)
- Better overall electrical control

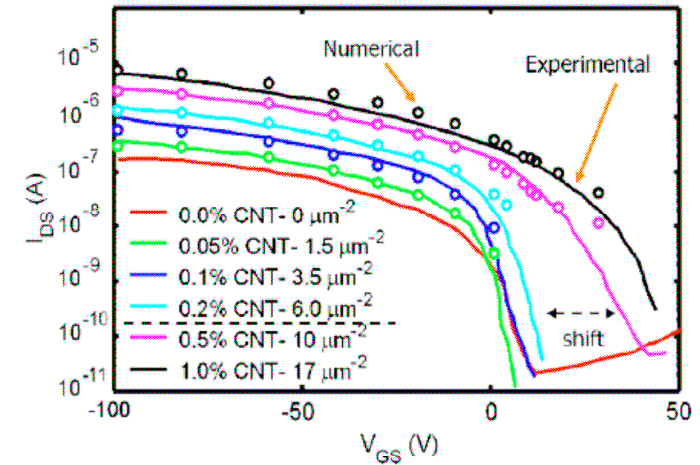
Overall semiconductor effect
(1/3 of the SWNTs are metallic)
SWCNT by COMOCAT ~90%

CNTFET



IDE electrodes

Carbon Nanotubes Chains



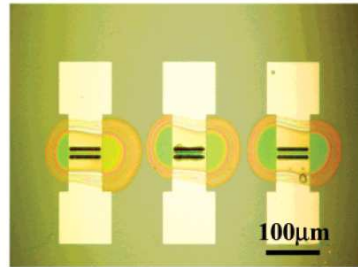
S. Kumar et al., Phys. Rev. Lett. 95, 066802 (2005)
S. Kumar et al., Applied Physics Letters, 88, 123505 (2006)



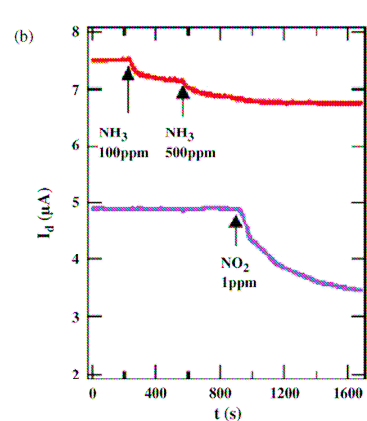
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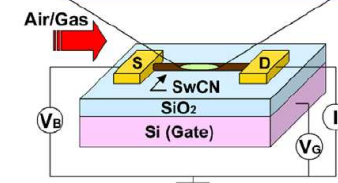
Stanford



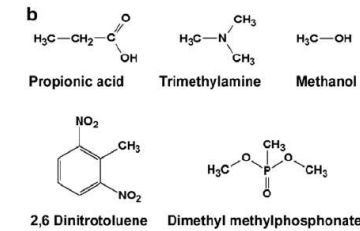
Polymer functionalization



Seq. 1 5' GAG TCT GTG GAG GAG GTA GTC 3'
Seq. 2 5' CTT CTG TCT TGA TGT TTG TCA AAC 3'

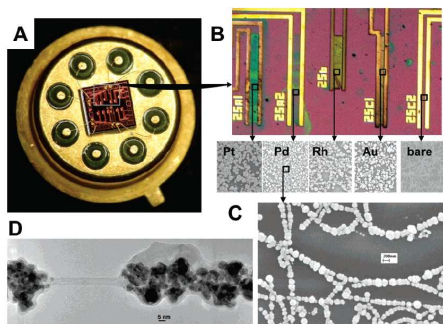


DNA functionalization



University of Pennsylvania

Nanomix



Metal particles mat decoration

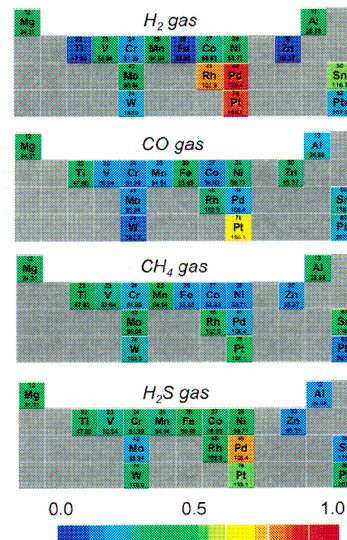
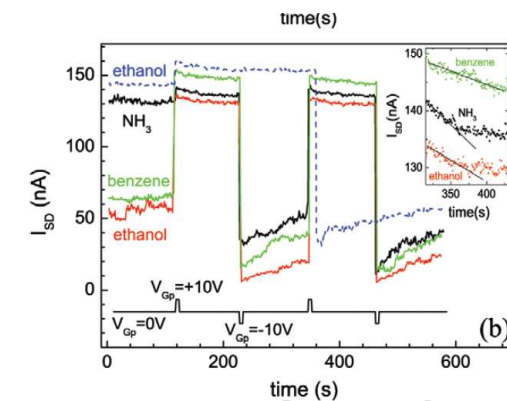


Figure 4. Correlation coefficients relating the conductance of devices decorated via metal evaporation with the gas profile of the tested gases, from 0 (no response) to 1 (maximal response). The catalytic metals were evaporated on carbon nanotube devices and tested for H₂, CO, CH₄, and H₂S gases as highlighted in the Periodic Table.

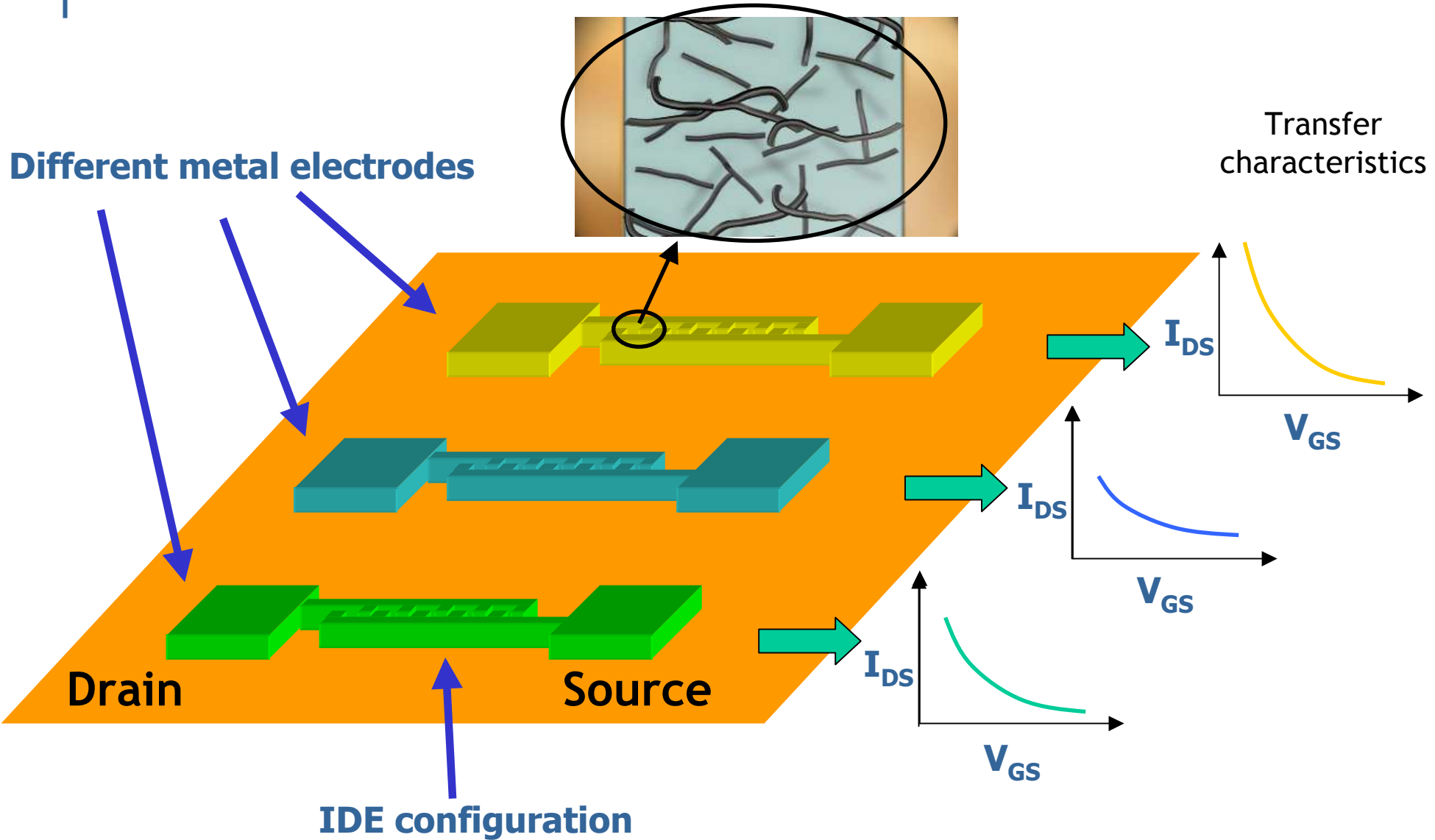
Desorption time



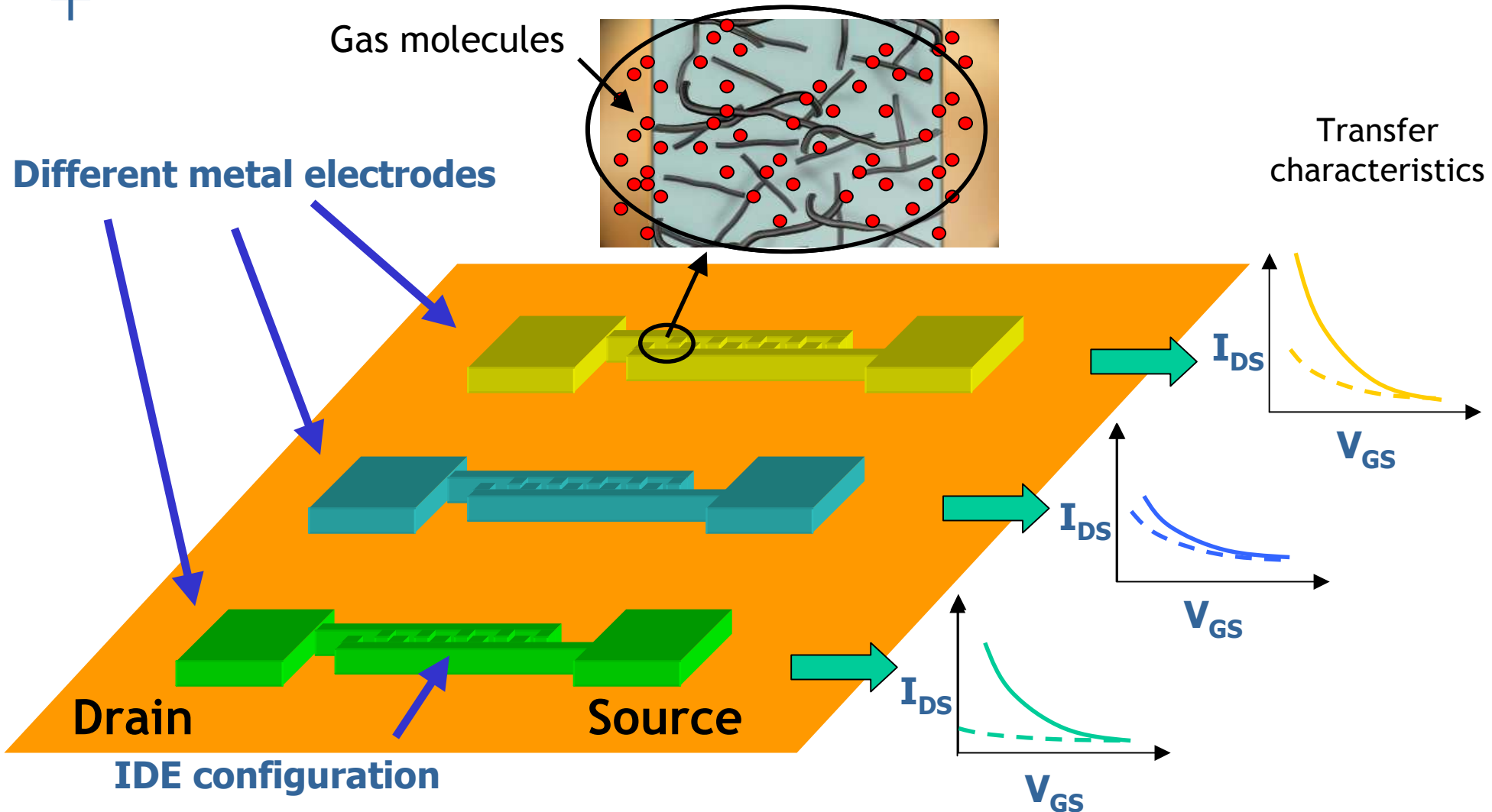
Yonsei University (South Korea)

THALES

Our Approach : Working Principle (fingerprinting concept)

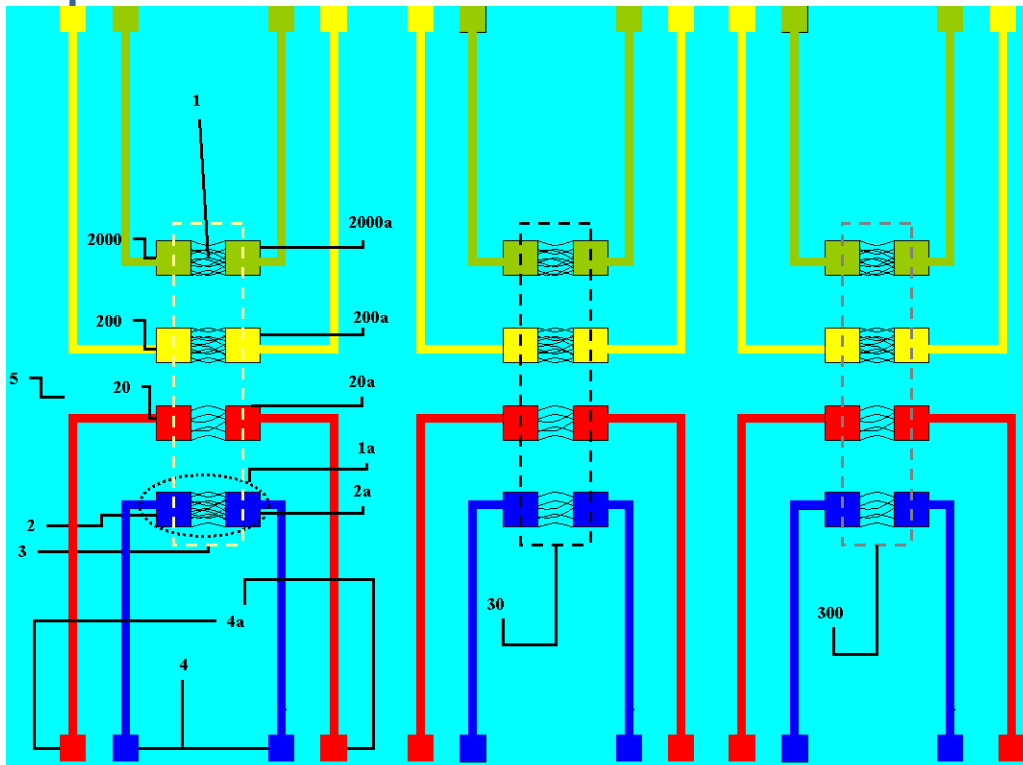


Our Approach : Working Principle (fingerprinting concept)



**The Selectivity is achieved using different metal electrodes :
We analyze the relative change of transfer characteristics for each gas**

Our Approach: gas fingerprinting using different metal/CNT junctions



Aim :
to obtain the electric
fingerprinting
of a specific gas

Patent owned by Thales (2006)
WO 2006/128828 A1

(54) Title: CONDUCTIVE NANOTUBE OR NANOWIRE FET TRANSISTOR NETWORK AND CORRESPONDING ELECTRONIC DEVICE, FOR DETECTING ANALYTES

(54) Titre : RESEAU DE TRANSISTORS FET A NANOTUBE OU NANOFIL SEMI-CONDUCTEUR ET DISPOSITIF ELECTRONIQUE CORRESPONDANT, POUR LA DETECTION D'ANALYTES

Principle:
**gas fingerprinting using CNTFETs with different
metal electrodes**



- **Introduction : Nanocarb Lab. presentation**
- **Why CNT Transistors for sensing applications?**
- **Physics of Carbon Nanotubes sensors**
- **Our approach to enhance selectivity**
- **Samples preparation**
- **Preliminary results using DMMP (simili-sarin gas)**
- **Conclusions and Perspectives**

Stable Carbon Nanotube solution using specific solvent



SWCNT
powder



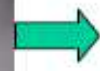
Sonication



Nanotubes
solution



CNT solution
before
centrifugation



Centrifugation
facility

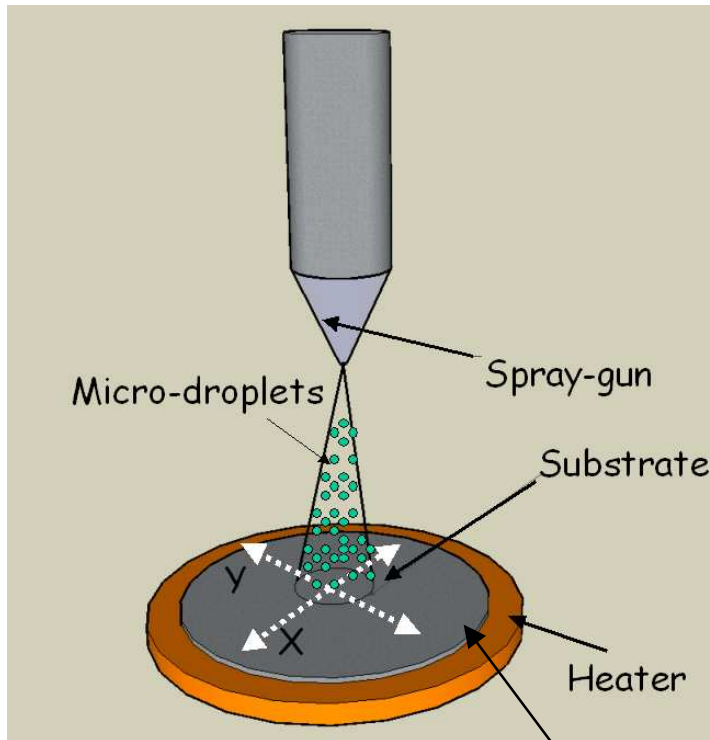


Supernatant after
centrifugation



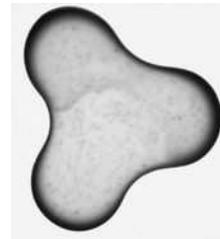
Final solution

CNT deposition using Air-Brush Technique



heated substrate ($\sim 200^{\circ}\text{C}$)

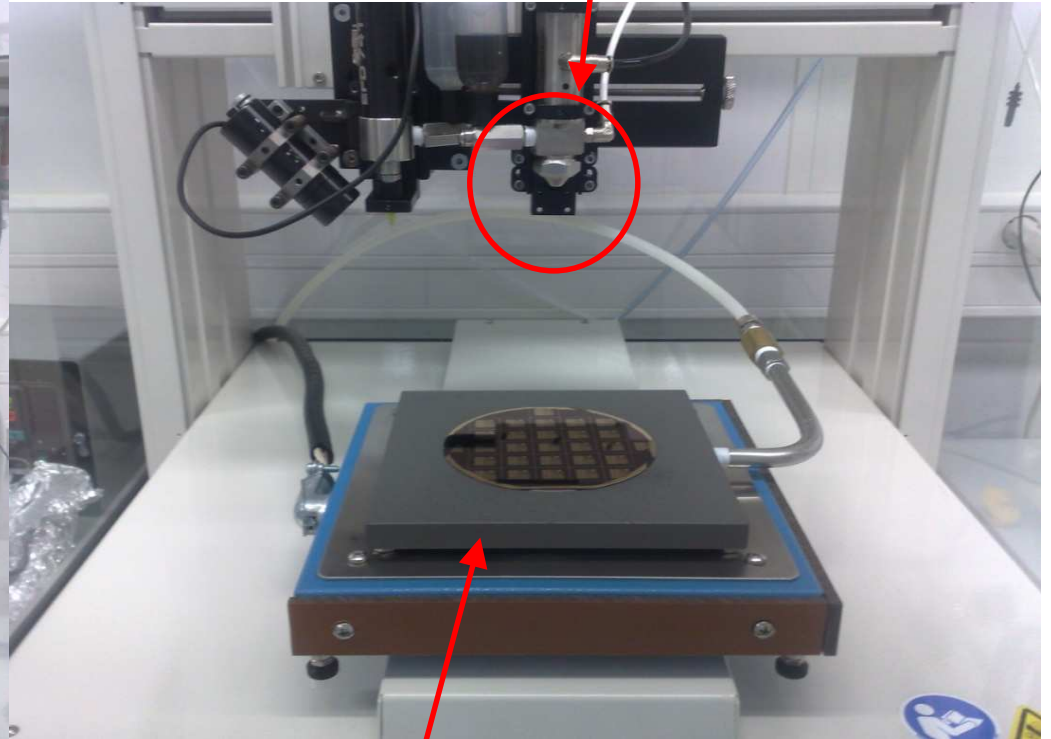
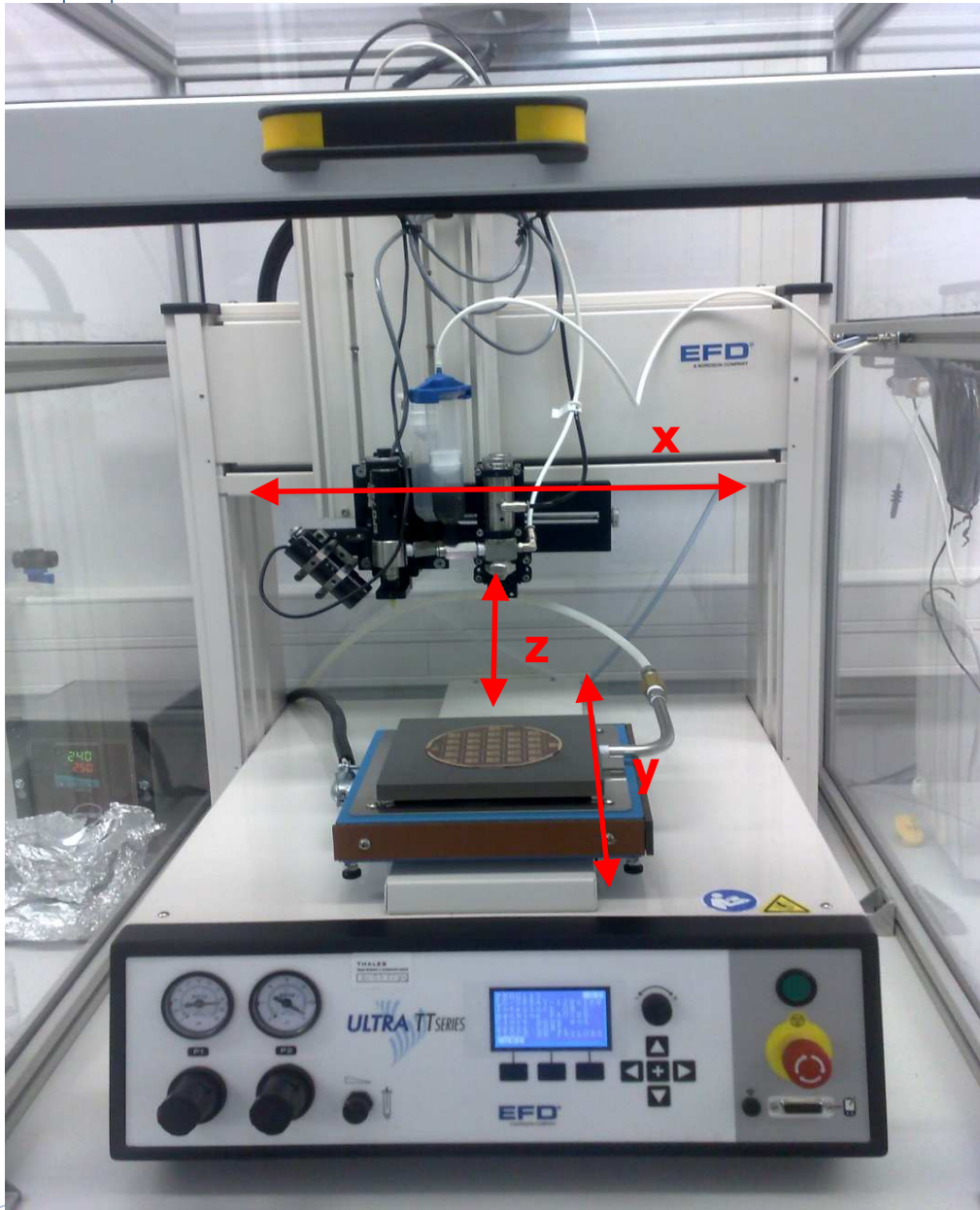
Not Uniform!!!
Not effective!!!
Not reproducible!!!
Not suitable for industrial application!!



100% of effective CNTFETs using Air-Brush Technique
Drop-Casting was $< 10\%$!!!



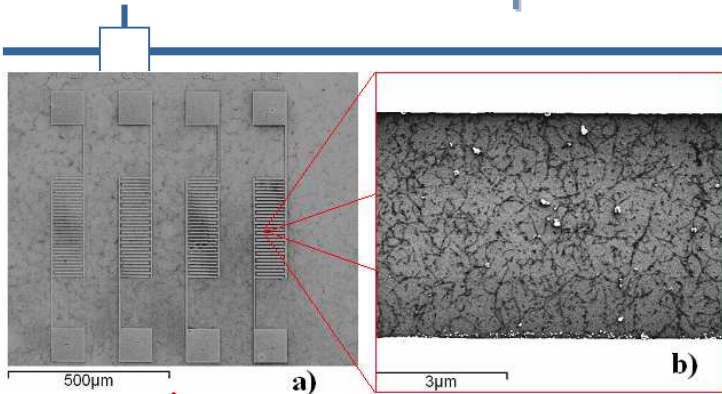
Deposition on 4 inches wafer but it could be used for larger surfaces!!!



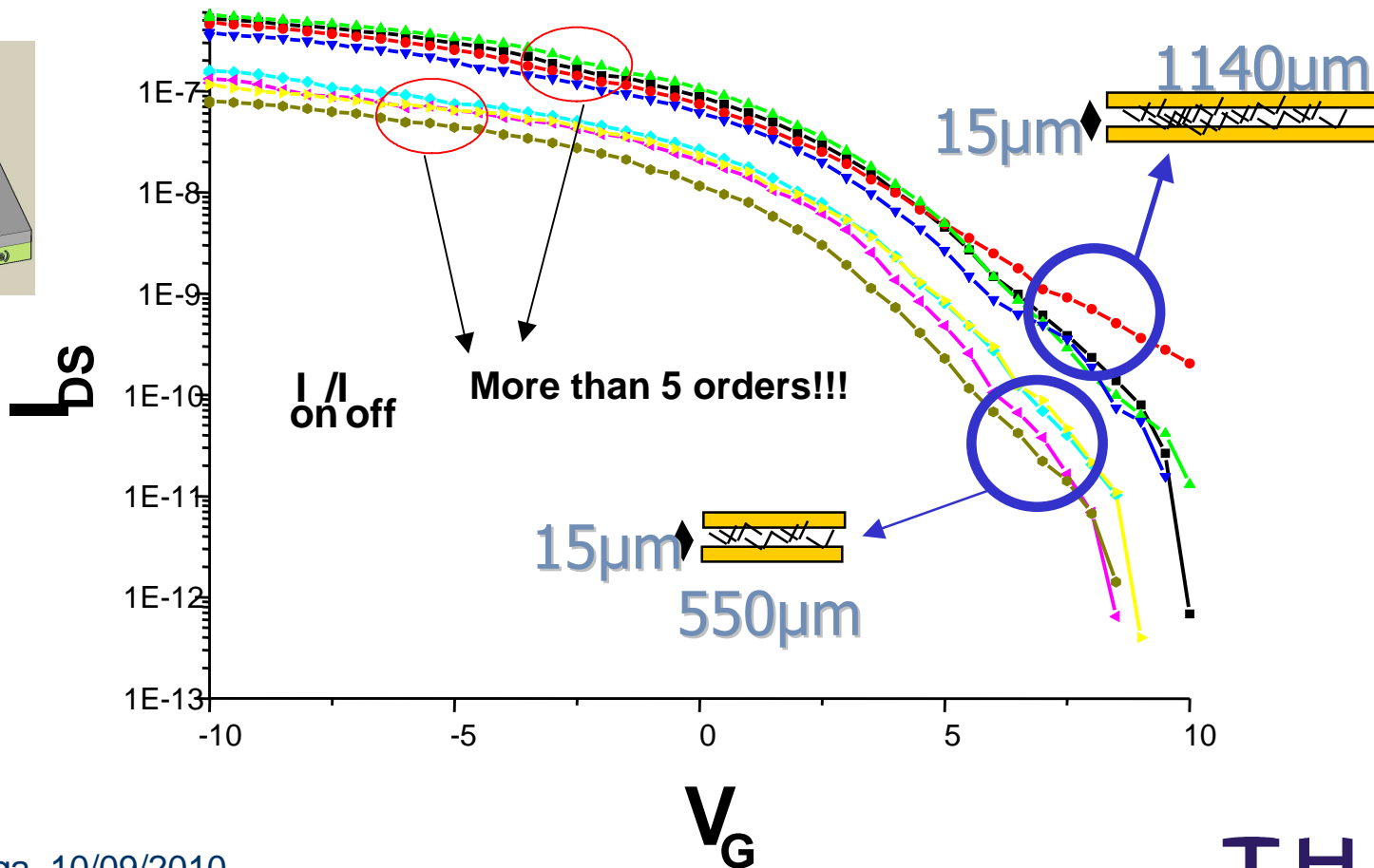
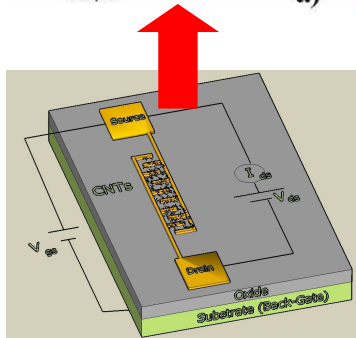
Spray-gun

Heating Platform

Reproducible Results with high Ion/Ioff ratio

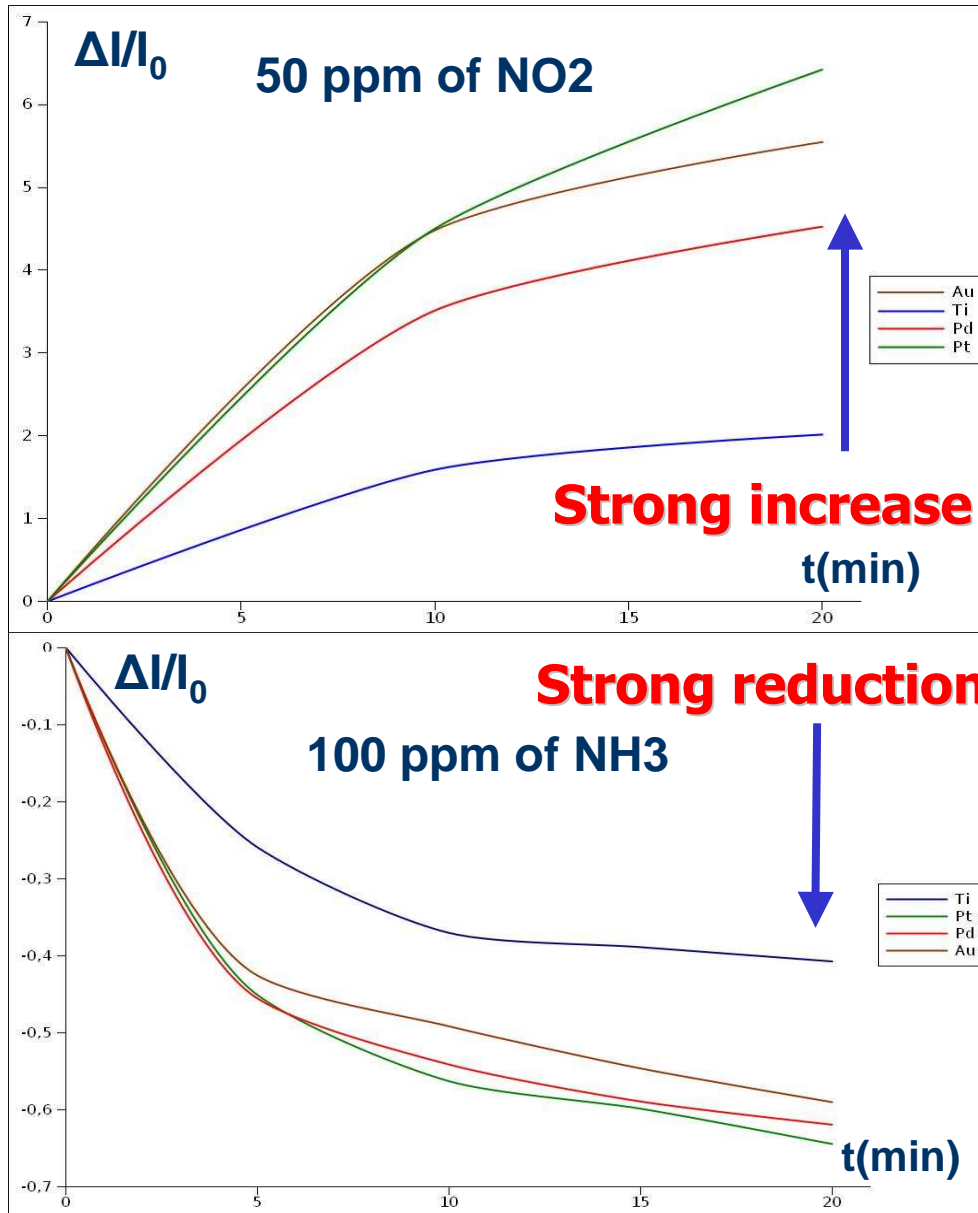


- 1 chip (1cm²)
- 32 transistors
- 4 series with electrodes distance of 2µm, 5µm, 10µm, 15µm
- for each electrode distance, two electrode lengths





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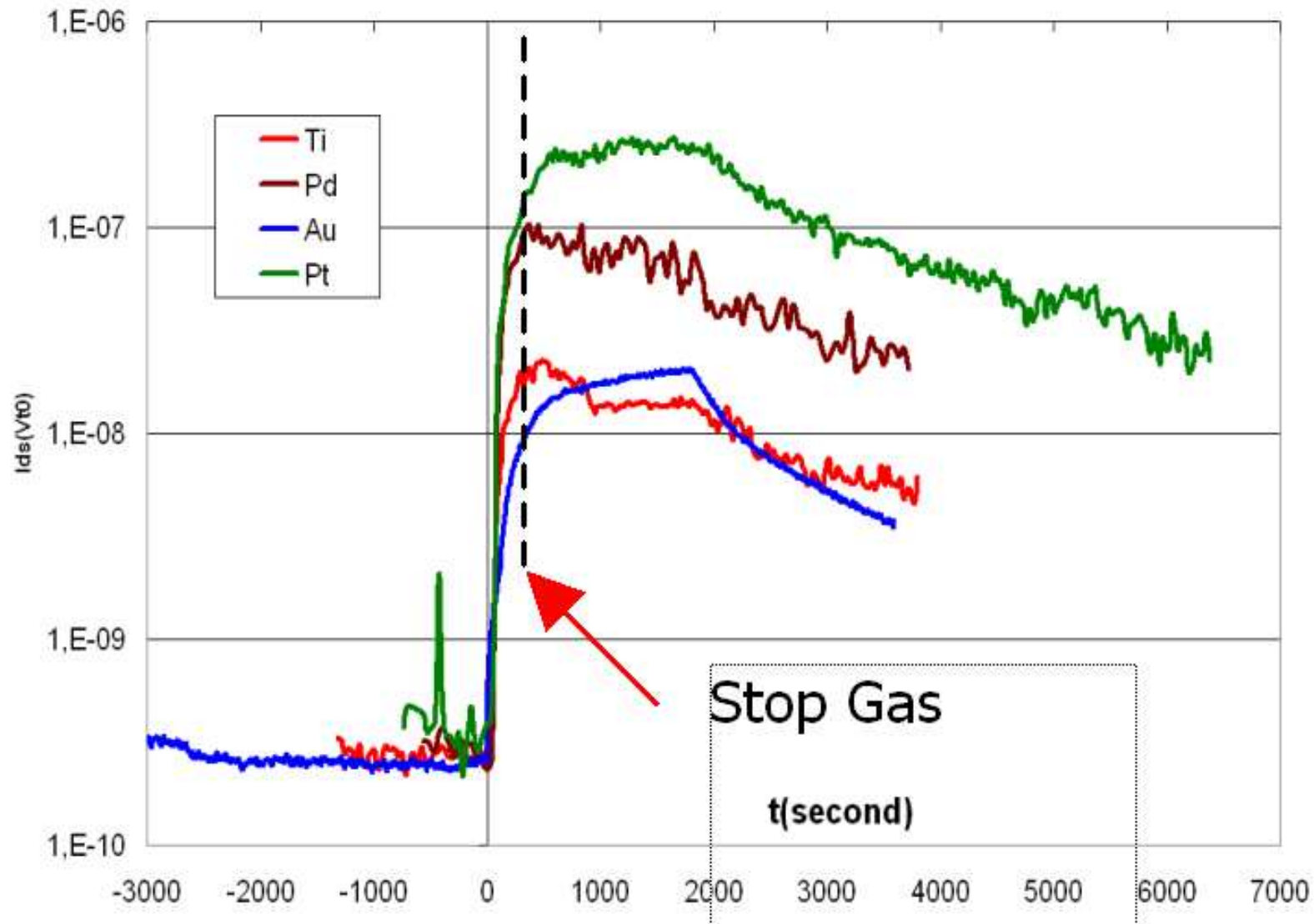


response

ΔI/I₀ After 10 minutes

	NO ₂ 50 ppm	NH ₃ 100 ppm
Au	448%	-49%
Ti	159%	-37%
Pd	351%	-54%
Pt	450%	-56%

Perform with the Help of CEA LITEN J.P. Simonato and L. Caillier for ANR PNANO-07 project NANOSSENSOFIN



Current change of 4 CNTFETs obtained using different metals after gas exposure ($NO_2, 50ppm$).



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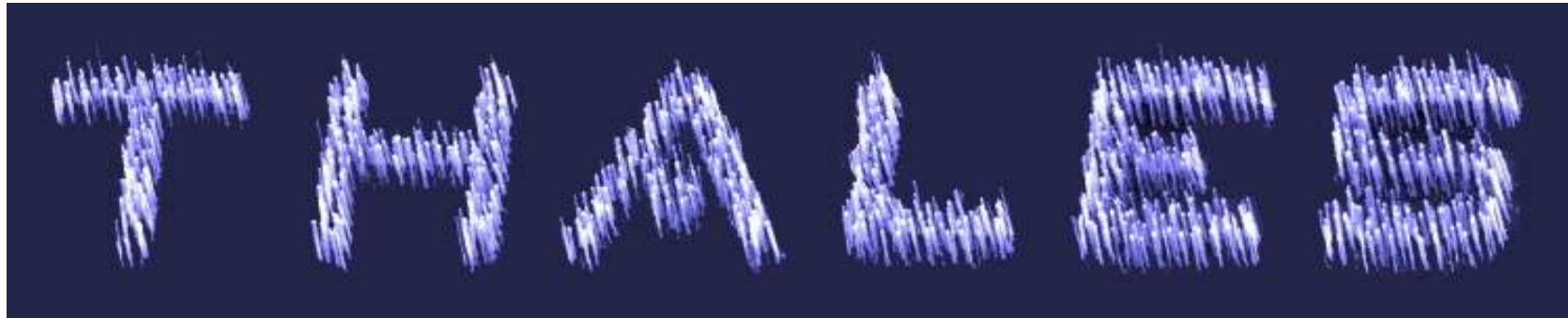
- **Effective and reproducible CNTFETs based on SWCNTs mat obtained through low cost Air-brush deposition technique : suitable technique for industrial fabrication**
- **These CNTFETs are suitable for gas sensor applications**
- **Results using NO₂ and NH₃ demonstrate the fingerprinting concept : Each gas interacts specifically with each metal electrode**

NEXT STEPS

- **To perform more systematic measurements using more gases using an optimized test bench and perform fusion and data analysis**
- **To reduce humidity effect using passivation of part of the SWCNTs mat (not the contacts)**



Thank you for your attention!



Recent publications

Carbon Nanotubes based transistors composed of single-walled carbon nanotubes mats as gas sensors : a review, P.Bondavalli, *Comptes Rendus de Physique*, in press (2010)

CNTFETs based gas sensors : patent review, P. Bondavalli, *Recent Patents on Electrical Engineering*, 3 (2010)

CNTFET based gas sensors : State of the art and critical review, P.Bondavalli, P.Legagneux and D.Pribat, *Sensors and Actuators B*, Volume 140, Issue 1, 18 June 2009, Pages 304-318