Novel Concepts for CO_2 Detection by Differential Resonant Nanosensing

Cornel Cobianu and Bogdan Serban

Sensors Laboratory Bucharest,

Honeywell Romania SRL

16th March 2010

9th Romanian Seminar- Nanoscience and Nanotechnology

Honeywell

Outline

Honeywell

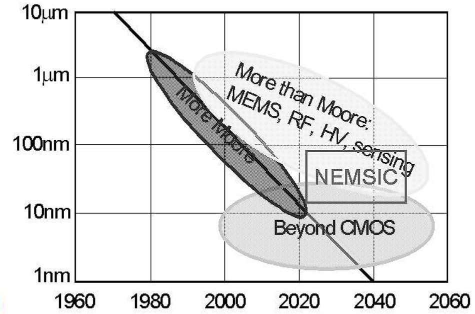
- EU-FP-7-"NEMSIC" project presentation
- State of the art –NEMS/MEMS resonant differential chemical sensors
- Honeywell concept
- Chemical sensing at nano-scale by numbers
- Novel concepts-All differential resonant chemical sensor
- Novel concept for CO_2 detection by all differential resonant approach
- Conclusions

EU-FP-7 "NEMSIC" project

Honeywell

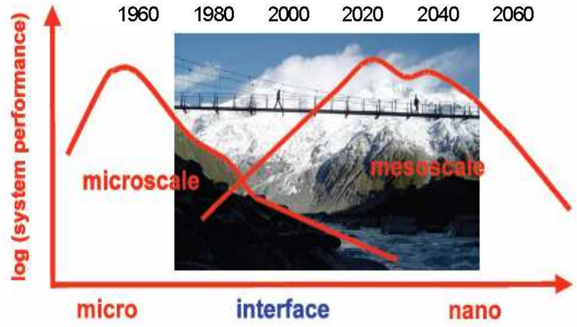
About NEMSIC

•"NEMSIC" was ranked no 1 out of 160 EU proposals on Nanotechnology-2008
• "Hybrid Nano-Electro-Mechanical/Integrated Circuit Systems for Sensing and Power Management Applications"
•Project coordinator : Prof. Adrian Ionescu-EPFL



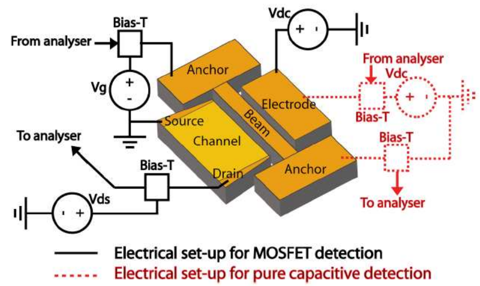
Strategic objective

•Nanoelectronics with enhanced functionality (CO_2, NO_2, SO_2, DNA, proteins)
"More than Moore" nanosystems for gas/bio sensing
Novel NEM-FET switches for power management



Technical objectives

•NEMS-SOI-CMOSFET as a sensing technology platform
• Vibrating gate/Si body FET as a resonant nanosensor
•Ultra-high gas/bio sensitivities at room temperature operation

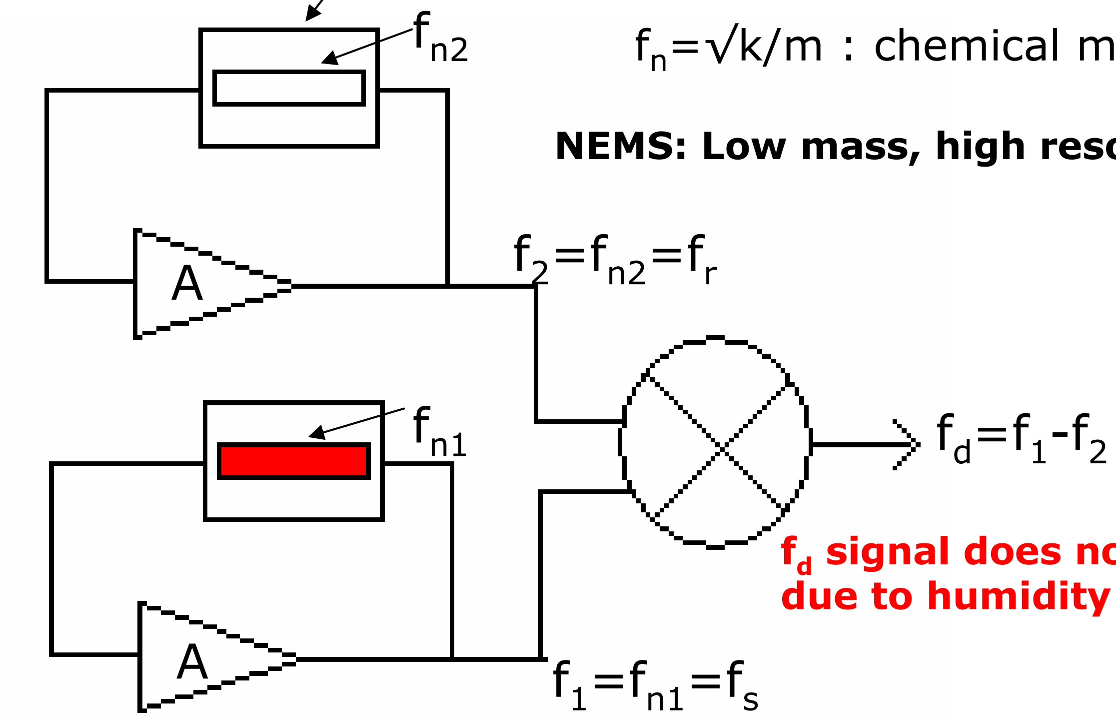


State of the art
MEMS/NEMS resonant chemical sensor

Honeywell

Differential resonant sensing: detected measurand shifts the resonance frequency

Uncoated vibrating MEMS beam in the feed-back loop of an amplifier



$f_n=\sqrt{k/m}$: chemical measurand increases mass loading

NEMS: Low mass, high resonant frequency and sensitivities

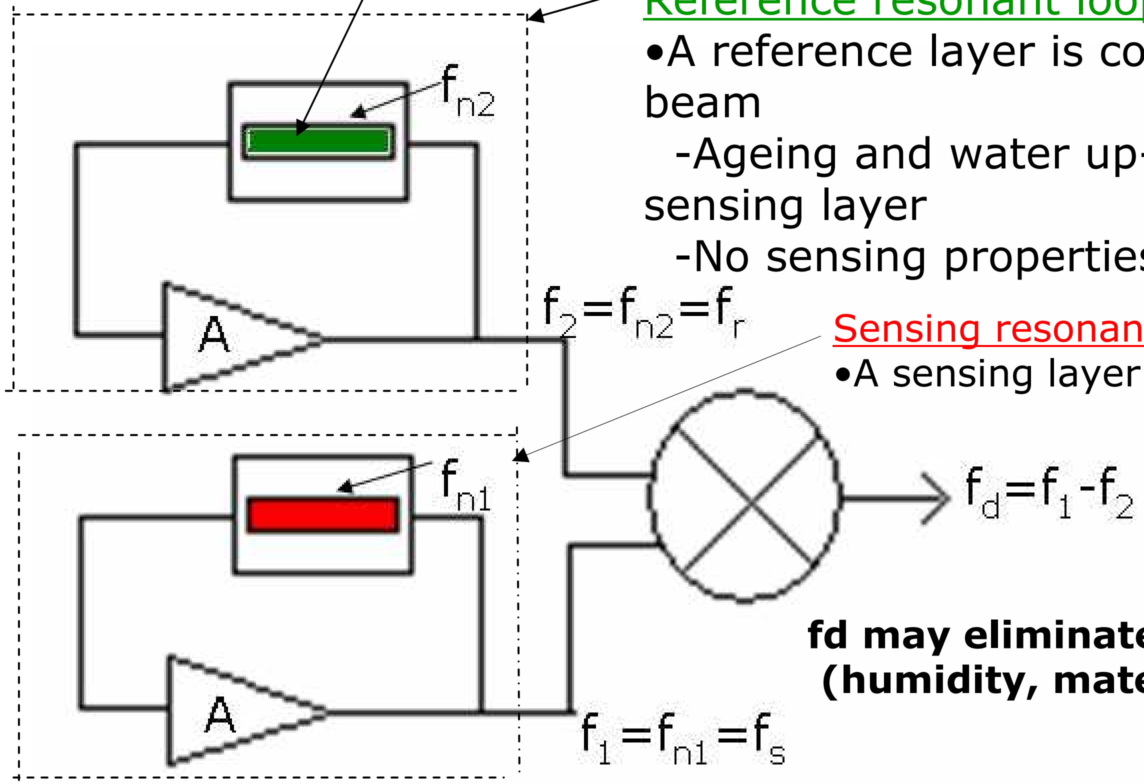
f_d signal does not eliminate sensor response drift due to humidity and ageing effects!

f_{n1} : mechanical resonance frequency of coated sensing beam
f_{n2}: mechanical resonance frequency of uncoated reference beam
f_1: operating frequency of the sensing oscillator
f_2: operating frequency of the reference oscillator
f_d: output frequency of the mixer providing sensor response to a chemical measurand

Honeywell's concept*

Honeywell

<u>Coated</u> vibrating MEMS/NEMS beam



<u>Reference resonant loop (non-sensing)</u>

- A reference layer is coating the reference vibrating beam
  - -Ageing and water up-taking properties as for sensing layer
  - -No sensing properties !

<u>Sensing resonant loop</u>

- A sensing layer is coating the sensing beam

fd may eliminate the "common mode" signals! (humidity, material ageing, etc)

f_{n1} : mechanical resonance frequency of <u>coated</u> sensing beam
f_{n2}: mechanical resonance frequency of <u>coated</u> reference beam (non-sensing layer)

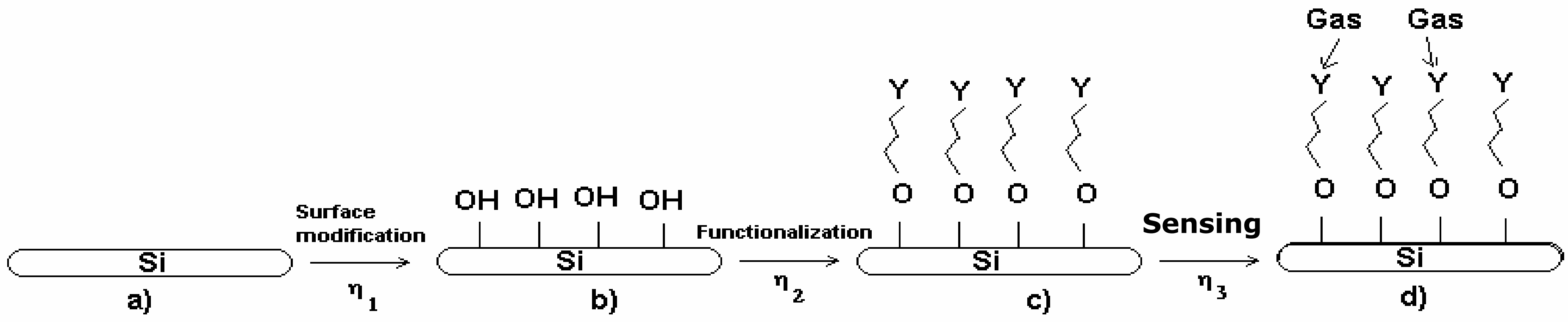
**Cornel Cobianu, Bogdan Serban, "All-differential resonant nanosensor apparatus and method", U.S patent application, Application number: 12/617,893, Filing date: 11/13/09*

Chemical sensing at nano-scale

Honeywell

- Sensing mono-layers should preserve low inertial mass of beam: m=(1-20) fg

(L=2 μm, W=100 nm, H=40nm; S_A=56 x 10^{-10} cm^2)



Mass loading estimations for an optimistic scenario

Mass of vibrating beam: m=18 fg

M_{NO2} = 46 g/mole;

Ds=10^{15} cm^{-2}

N_A = 6.023 x 10^{23} molecules/mole

$$\delta m_{gas} = Ds \cdot S_A \cdot \eta_1 \cdot \eta_2 \cdot \eta_3 \cdot \frac{M}{N_A}$$

$\eta_1=\eta_2=\eta_3=1/2$

δm_{gas} = 5.3 x 10^{-17} g=53 ag

$$\frac{\delta m}{m} = \frac{5.3 \cdot 10^{-17}}{1.8 \cdot 10^{-14}} = 3 \cdot 10^{-3} = 2\frac{\delta f}{fo}$$

δm/m could easily be in the range of 10^{-6} for ultra low gas concentrations !

C. Cobianu et al., CAS Conference 2009, Sinaia

Functionalization - General approach

Honeywell

- Clean Si surface is functionalized for CO_2 sensing.

- Self assembled monolayers (SAMs) with suitable sensing terminal groups at the surface of silicon are used.

- Design and/or selection of sensing materials were performed according to acid-base interaction (in the terms of Bronsted-Lowry theory or Hard-Soft Acid Base –theory).

- Functionalized sensing layer-in the sensing loop

- Functionalized reference layer-in the reference loop*.

**Cornel Cobianu, Bogdan Serban, "All-differential resonant nanosensor apparatus and method", U.S patent application, Application number: 12/617,893, Filing date: 11/13/09*

Functionalization for CO_2 – First approach(1/4)

Honeywell

- Self-assembled monolayers (SAMs) have been used for the **functionalization** of the **silicon surface** for CO_2 sensing.

- The selection of the sensitive terminal groups which are incorporated in the SAMs was based on the **Hard Soft Acid Base (HSAB) rule**. According to the HSAB rule, since CO_2 is a hard acid, a hard base should be suitable for sensing it.

- **We have chosen amino-groups for the interaction with CO_2.** This interaction is an acid-base equilibrium, which is reversible and leads to the formation of carbamates.

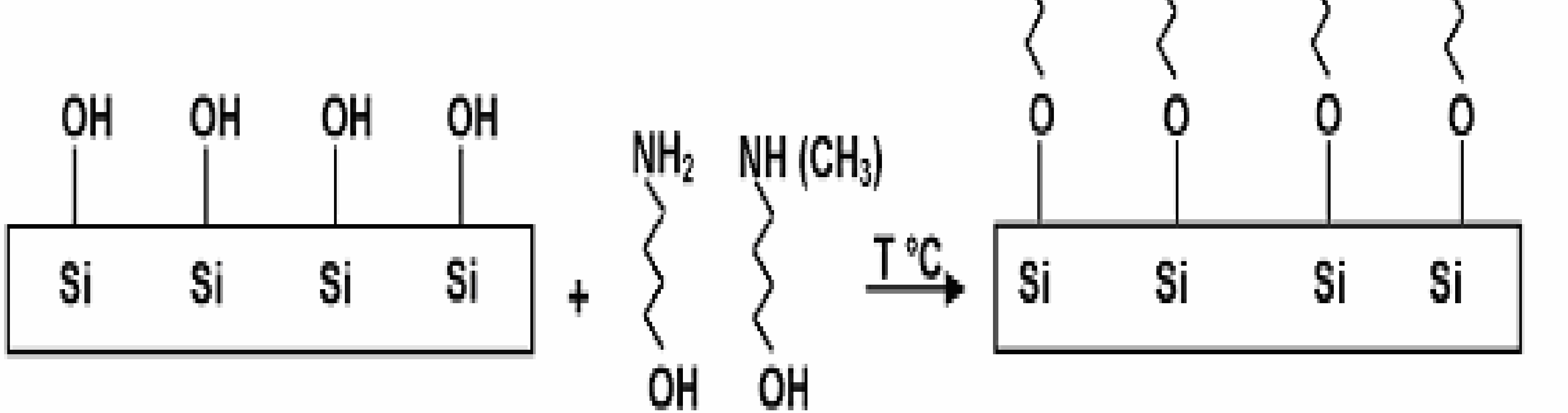
Functionalization for CO2–First approach(2/4)

Honeywell

- Amino-alcohol compounds to be used*

•**Bogdan Serban, Cornel Cobianu, Mihai N. Mihaila, Viorel Georgel Dumitru, "Functionalized monolayers for carbon dioxide detection by a resonant nanosensor", U.S patent provisional application, Application number: 61/262,702, Filing date: 11/19/2009*

- Polycondensation of hydroxyl terminated silicon surface with 4 amino-1 butanol and 4- N-methyl amino- 1 butanol

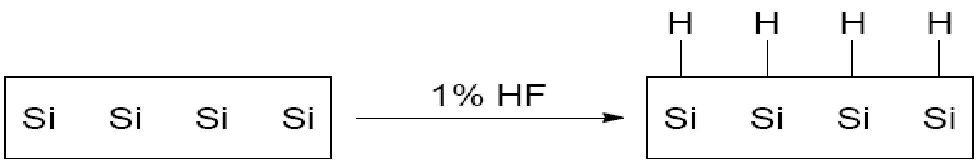


Functionalization for CO_2 – First approach(3/4)

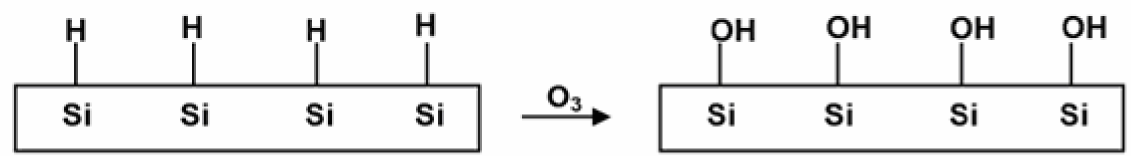
Honeywell

– Processed Si wafer cleaning in isopropyl alcohol and DI Water

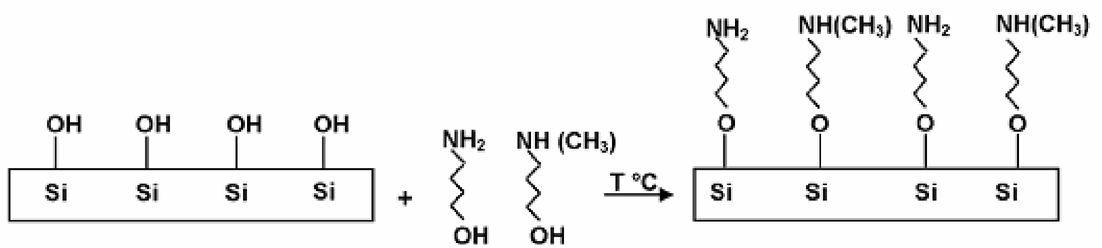
– Native oxide removal from the Si wafer and formation of Si-H bonds on Si surface



– Ozone exposure in order to obtain a hydroxyl terminated surface



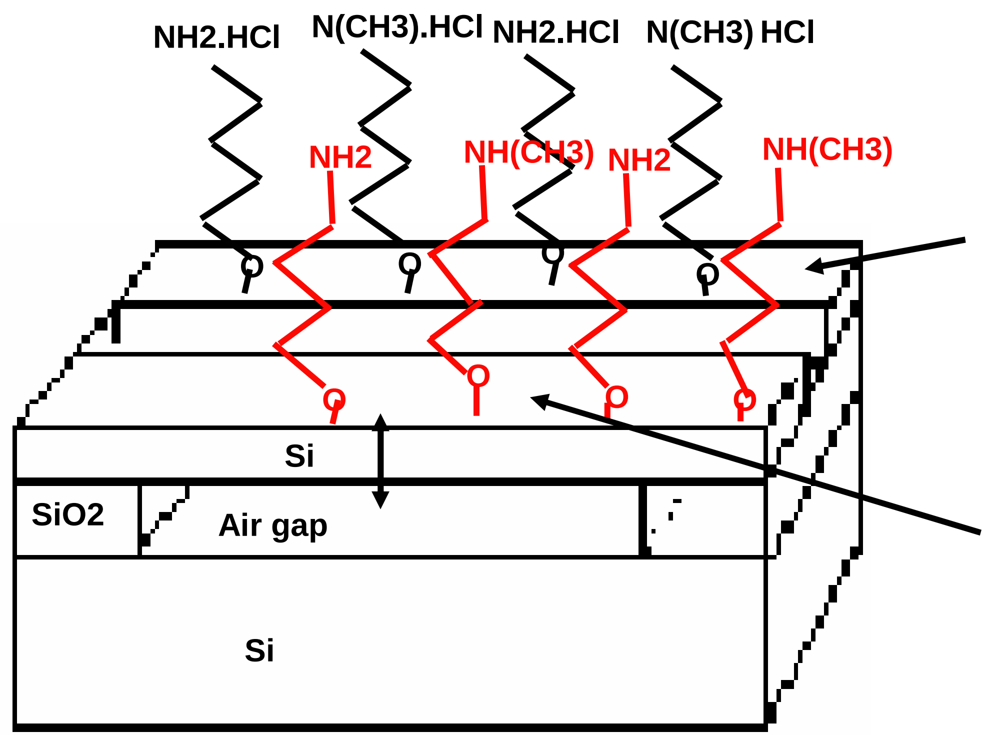
- Immersion in a sealed flask containing 4 amino- 1 butanol and 4- N-methyl amino- 1 – butanol



Reference layer functionalization 4/4

Honeywell

-Reaction of the above layer with HCl to get a reference layer <u>on the reference beam</u>



Vibrating beam with reference SAM based on hydrochlorides terminal groups connected to Si surface by oxygen atom

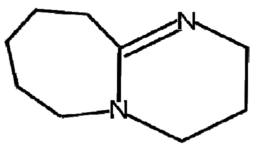
Vibrating beam with sensing SAM based on NH2 group for CO2 detection Connected to Si surface by oxygen atom

Functionalization for CO_2 – Second approach (1/3)

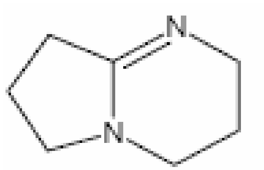
Honeywell

- Self-assembled monolayers (SAMs) have been used for the functionalization of the silicon surface for CO_2 sensing. The sensing layers contain CO_2 sensitive terminal groups, such as 1,8 diazabicyclo[5,4,0] undec-7-ene (DBU) or 1,5 diaza [3,4,0]-non-5-ene (DBN)*.

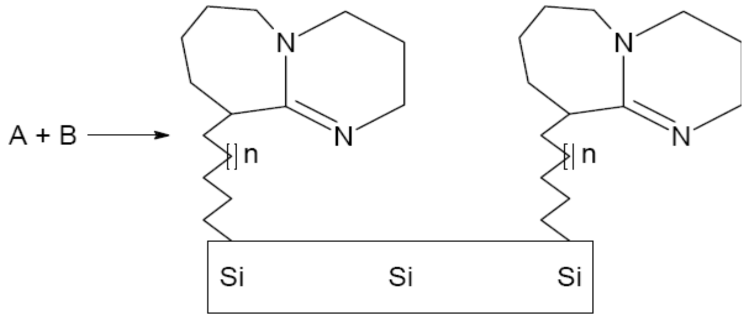
* *Bogdan Serban, Cornel Cobianu, Mihai Mihaila, Viorel Dumitru, "Amidines-based monolayers for CO2 detection by resonant silicon nano-sensors", Docket Number: H0024790, Filing date: 12/11/2009*



- The **DBU** structure

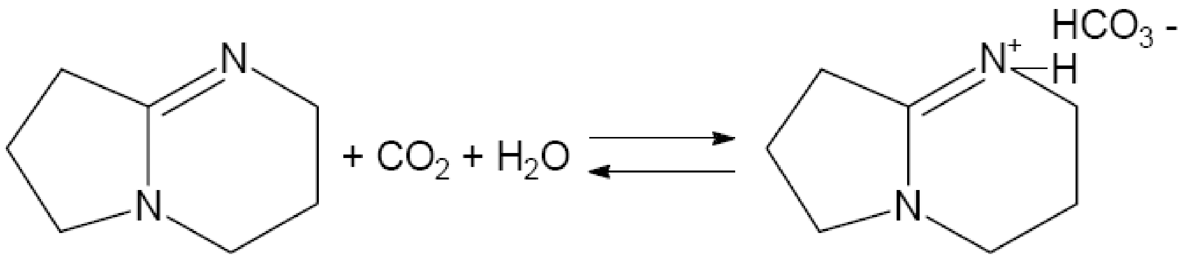


- The **DBN** structure



- Functionalization of silicon surface with **terminal – DBU moieties** for CO_2 sensing

- The chemical reaction responsible for CO_2 sensing

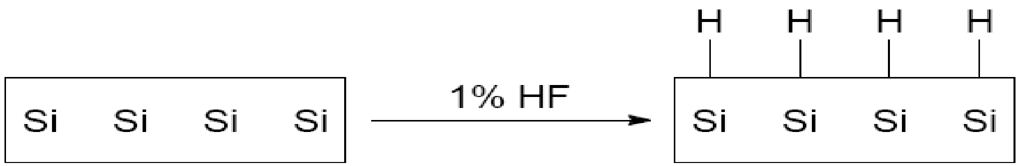


Functionalization for CO_2 – Second approach (2/3)

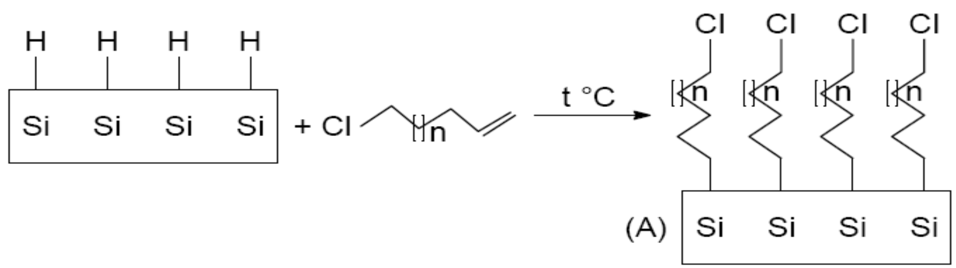
Honeywell

- Wafer cleaning avoiding the sticking of the suspended membrane to the substrate

- Native oxide removal from suspended Si beam in 1% HF for obtaining H-terminated Si beam surface



- Immersion of Si-H terminated wafers in a flask containing unsaturated alkyl halide, such as alkyl chloride and toluene, followed by heating the sealed flask for getting a monolayer of this alkyl chloride connected to the Si surface by carbon atoms

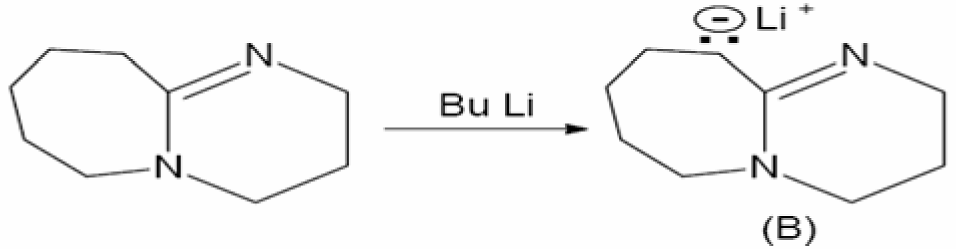


Functionalization for CO_2 – Second approach (3/3)

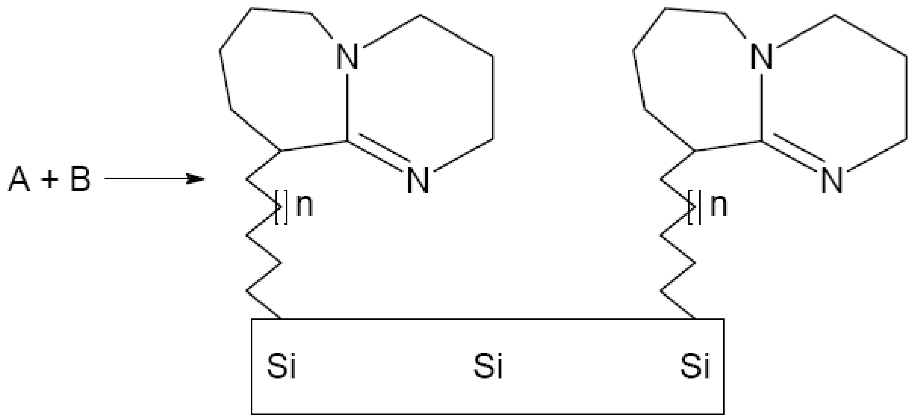
Honeywell

- Rinsing the wafers in isopropyl alcohol, followed by their cleaning and drying, so as to avoid the suspended beam sticking to the substrate

- Deprotonation of the DBU in the presence of butyl lithium



- Reaction of deprotonated DBU with alkyl chloride monolayer from the silicon surface



-Reaction of above structure with HCl on the reference beam to get reference layer

Conclusions

Honeywell

- NEMS chemical sensing is able to detect ultra low gas concentrations
- All-differential resonant chemical sensing is proposed as a step forward in NEMS chemical sensing.
- Functionalized sensing layer and reference layer in a differential approach are expected to minimize drift in the response of NEMS chemical sensors.
- Two novel chemical routes are proposed for the all-differential detection of CO_2

Acknowledgements :

EU-FP-7 program and Honeywell International are greatly acknowledged for their support in developing this research, within the Grant Agreement 224525