

A Possible Roadmap for NEMS Sensors

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- Milestones of Nanotechnology Evolution
- From MEMS to NEMS
- Top-Down
- Bottom-Up
- Mixed Top-Down-Bottom-Up
- Honeywell contributions
- Conclusions

Visionary scientists :

1959 : **Richard Feynman** : “There is plenty of room at the bottom”

1965 : **Gordon Moore** : “IC complexity will double every 12 months”

1974 : **Norio Taniguchi**: “Nanotechnology”

1986: **Eric Drexler** : Engines of creation. The Coming Era of Nanotechnology”

Governmental plans:

2000+ : USA’s National Nanotechnology Initiative

2011-2020 : 6 EU FET Research flagship Initiatives (ex. “Guardian Angels”)

2011-2015 : Japan :The 4th S&T Basic Plan(2011-2015): basic research

*“Bottom-Up-Top-Down”- a synergetic interaction in S&T policy
Why nanotechnology is important ?*

Megatrends and Nanotechnology Honeywell

Ageing Population

Globalization

Health and environment awareness

Urbanization (smart-eco city)

Network organizing

Technology progress- Megatrends- Society Needs -Technology progress !

Mihail. C. Roco " US National Nanotechnology Initiative, 2000" and examples from us

1. Passive Nanostructures: GMR sensors
Ag nano-ink for bulk applications,
CNT in textile
Ultradeformable nanomaterial-medicine
TiO₂, ZnO in sunscreen
2. Active Nanodevices and Circuits: Nanoelectronics era after 2004
3. Complex Nanomachines : Advanced Research! Future Guardian Angel
4. Productive Nanosystems: Basic research ! Future Systems of nanosystems.

Today : 32 nm feature size for IC

What happened in the MEMS technology ? !

MEMS from idea to products

Honeywell

1954–Piezoresistive effect in silicon and germanium -Charles Smith

1964 –Suspended resonant gate FET-Harvey Nathanson

Pressure sensor

Inkjet head

Accelerometer (3 axis-iPhone 4)

Gyroscope (3 axis-iPhone 4)

Microphone (cell phone)

Microbolometer

Digital Light Processors

MEMS Oscillators –220 MHz

Future development : Sensors fusion, 3D-MEMS? : Accelero/Magneto combo

Successful top-down μ -technologies leading to commercial products !

“AppliedSensor”

MEMS gas sensor: Thick film SnO₂ deposited on micro-hot plate

VOC detection and its correlation with CO₂ for IAQ

Thin films-based integrated MEMS gas sensors still to come!

- NEMS are MEMS with at least one dimension below 0.1 micrometer.
- Possible realization technologies
 - Top-Down : Subtractive processing : material carving
 - Bottom-Up : Additive processing : molecular building blocks
 - Mixed Top-Down- Bottom-Up : Mix of Subtractive and Additive techniques
- Objective : Electro-Mechanical-Chemical-Bio Sensing Nanomachines reaching ultimate quantum limits of detection

Top-Down NEMS Systems

Source : M. Roukes, Caltech, Physics World, 2001,

- Ultra small mass and size of the resonator
- Ultrahigh natural resonance frequencies
- Ultrahigh sensitivities for force (zN), displacement (fm), additional mass (zg)
- Ultralow power consumption (1 pW for a s/n ratio= 10^6)
- Ultrafast response time to applied forces
- Ultralow power mechanical signal processing (mechanical computers)
- IC compatible : 10^6 on-chip NEMS resonator would consume $1\mu\text{W}$!
- New experimental discoveries at the quantum mechanics level
Caltech has proven the existence of the quantum of thermal conductance in 1999

Many of these advantages were proved in conditions of vacuum and cryogenic temp

Source: Michael Roukes, Physics World, 2001

- High Q-factor at nanoscale up to GHz frequencies
 - A nanobeam (100 x10x10) nm³ has 10% atoms located on the surface.
- On-chip actuation and detection
 - Sensing nano-capacitances can be much smaller than the parasitic ones at UHV
 - Present NEMS are using on-chip electrostatic actuation only up to 30 MHz
- Pico-meter accuracies in displacement reading at GHz frequencies
- NEMS sensing applications at 300K and 1 atm
- Nanolithography for feature size of 10 nm and below.
- The quanta of displacement jumps could be displayed by NEMS?
 - At 100 mK, only about 20 vibrational quanta appear to be excited.

NEMS resonators a fundamental tool for physics and future applications !

Source: Li, Tang, Roukes , Nature Nanotechnology 2007

- Status

- Encouraging resonant NEMS gas sensing at 127 MHz, 300K and 1 atm
 - Q factor of 400
 - Off-chip, piezoceramic actuation of the NEMS cantilever
 - On-chip piezoresistive detection in thin metallic film
 - 1 attogram (resolution 100 zg) of gas adsorbed on vibrating beam!

- Challenges

- Resonant NEMS at 1 GHz, 300K and 1 atm
- Sub-ppb sensitivities for gas sensitivities in the environmental air
- Selective functionalization of vibrating beams with width below 100 nm.

Fully integrated resonant NEMS gas sensors:

-A major scientific/technical target !

- High Q, in-plane nanomechanical resonators operated in air (Cornell Univ.)
- Quantum Electro-Mechanics (QEM) – Caltech-JPL
 - Integration of superconductor qubit to NEMS at cryogenic temp (Quantum computer-NEMS for future applications)
- From nanoscience to CMOS-based nanotechnology platform
 - CMOS powered VLSI-SOI-nanosystems (on-chip actuation, self-sustainable res)
 - Caltech-CEALETI
 - EU-FP-7-NEMSIC project leaded by EPFL
 - Target applications : Sensor arrays for gas and bio molecule detection
 - Single-Molecule Mass Spectrometry enabled by NEMS
 - Nanomechanical sensing: force, acceleration, rotation
- Nanomechanical circuits and computing (no transistor involved)-Berkeley
 - Integrated M/NEMS front-end RF circuits
 - Real-Time Frequency Gating Spectrum Analyzer
 - High efficiency on-chip power amplifiers and power converter circuits

NEMS- a powerful tool for molecular detection and novel computing science

Bottom -Up NEMS ?!

Fundamental bottom-up notions **Honeywell**

- Molecular self-assembly
- Molecular recognition
- Molecular electronics
- Positional molecular assembly
- Productive nanosystems
- Molecular nanotechnology
- Nanorobot

The next industrial revolution has started ?

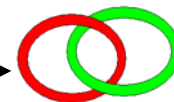
Molecular NEMS -Why?

Molecule is the place where the electronic processes take place !
(signal transduction, photosynthesis) and ultimate size scaling-down

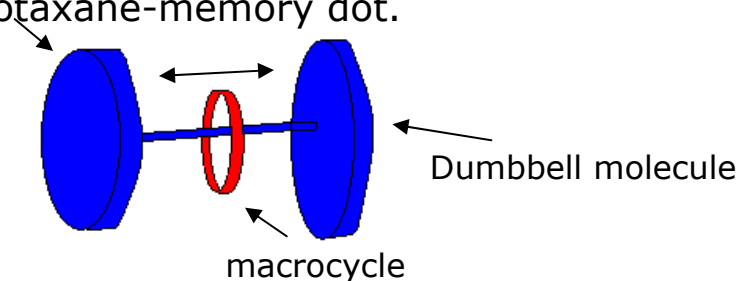
Status (James Heath, Caltech)

- Molecular electronics (ME) devices: switches, rectifier, computational circuits, memory
- Molecular machines (MM) based on dynamic stereochemistry, in the future?

-Mechanically-interlocked molecular architectures : rotaxane, knotane, catenane →



-Novel molecular memory concepts based on rotaxane-memory dot.



Reaching Molecular Intelligence

- Understanding the electrical conduction mechanism in complex molecules
- Reliable and reproducible fabrication of molecular building blocks of ME and MM
- Reliable interfaces between molecular blocks and outside world
- Novel molecular NEMS architectures for sensing and actuation arrays
- Integrated ME and MM?

- The electron transport mechanisms are determined by the localized nature of most of the molecular electronic states.
- In simpler molecules, there is a good understanding of the electron conduction in solid-state junctions as a function of its intramolecular transfer rate in solution, where the chemical synthesis was done.
- Theory of molecule-electrode contact is in the early stages.
- DNA is modeled as a wide band-gap semiconductor in its molecular junctions.
- Tuning of molecular energy level with respect to Fermi level of electrode is possible by adding the gate electrode. Thus, Kondo resonance in divanadium molecule junction was shown experimentally.
- A crossbar architectures was proposed for designing the molecular- electronics circuits, like 256 bit RAM, which are able to do the interface between very dense nanowire and the much wider metal lines performed lithographically.

Molecular electronics is paving the way to Molecular NEMS !

A Possible Roadmap of Bottom-Up NEMS

<p>Society's needs (need to be educated ?)</p>	<p>Ultimate, molecular-level miniaturized nanosystems and nanorobots for portable applications and health enhancement, and tools (productive nanosystems) for their large scale production</p>
<p>Potential Future Products</p>	<p>Productive nanosystem for large scale fabrication of nanorobot</p> <p>Molecular systems for nanorobot application</p> <p>Molecular systems for computing and sensing applications</p>
<p>Components</p>	<p>Molecular NEMS building blocs, sensors and actuators</p> <p>Molecular Memories and Computing and Outside Interfaces</p> <p>Single electron molecular transistor and gear</p> <p>Molecular Junction and Rectifier</p> <p>Molecular Switches</p> <p>Resistive molecular wires</p>
<p>Technologies</p>	<p>Molecular biotechnology</p> <p>Molecular recognition</p> <p>Molecular self-assembly and recognition, nanomanipulation techniques</p> <p>IC based interfacing technology</p>
<p>Enablers</p>	<p>Governmental support</p> <p>Quantum Physics and Chemistry</p> <p>Supramolecular Chemistry</p> <p>Material science</p> <p>Top down NEMS technology</p> <p>Classical top-down nanoelectronics, Molecular electronics</p>

time →

Mixed Top-down-Bottom-Up NEMS sensors

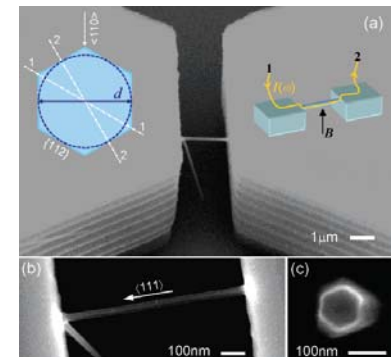
General characteristics

- A mix and match of classical top-down and 1D-Si, 1D and/or 2D carbon technologies
- On-chip grown carbon structures for making active devices and sensors
 - Vertical CNT obtained directly and selectively on Si substrate
 - Epitaxial Graphene obtained directly on SiC substrate
- Carbon structure manipulation/transfer to Si chip
 - Three axis piezoelectric nanomanipulators used to contact a W probe to CNT
 - CVD graphene sheets transferred to Si wafers

Carbon nanotechnologies are major players for "Beyond CMOS" and "More than Moore"

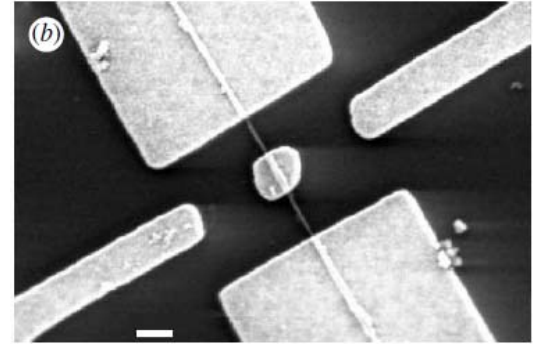
Source : Michael Roukes group, 2007-2008

- Suspended SiNW *grown atom by atom* using vapor-liquid-solid epitaxy
- SiNW resonator with magnetomotive transduction at $T=25$ K and vacuum (Lorentz force actuation and electromotive force detection)
 - Metalized SiNW ($L=1.6-3 \mu\text{m}$, $W=h=118-142 \text{ nm}$, $\text{Ti}=5\text{nm}$, $\text{Al}=30\text{nm}$)
 - Q factor of M-SiNW : 2000-2500 at 200 MHz
 - 10 pW power and 1 pW background (noise)
 - Sensitivity of 10 zeptograms
- Self-transducing SiNW-NEMS at 300K and vacuum (1 mtorr)
 - Piezoceramic actuation at 20-40 MHz and on-chip ELECTROSTATIC actuation !
 - Two-omega piezoresistive detection ($R=100 \text{ kohm}$) up to 100 MHz
 - Q factor of 800 (1200 at high stress in SiNW, but non-linear response!)
 - $Q=300$, at 100 torr and 30nm SiNW
 - Sensitivities of 500 yg (10^{-24}) (0.6 Da) for 30 nm SiNW, 75 MHz



Major efforts are done for reaching operation at 300K and 1 atm !

- CNT : discovered by Iijima in 1991.
diameter 1-50 nm, length : 10 nm-5 mm
high stiffness, strength, low density. Ultralow friction, self-repairing-MWNT
metallic, or "p" or "n" type semiconductor
- Out of chip CNT production:
Arc discharge from graphitic electrodes
Laser ablation of graphitic target
- On chip CNT deposition:
Catalytic decomposition on Fe layer of CH₄ in H₂, N₂
- Advanced applications (A. Kis and A. Zettl , Phil. Trans. R. Soc. A (2008), 366, 1591.



Nanomotor : Inner shell of MWNT is used as a shaft for a rotor plate.
(Fennimore et al, Nature 2003, vol. 424, pp 408-410)

CNT-based switches : Electrostatic Actuation for closing or opening the switch.

CNT-based memories : Reading of ON state with small voltage.

CNT-based oscillators : -Suspended CNT over SiO₂ trench excited by ac signal
Sazanova et al, 2004 applied on back gate. The sources-drain current
of CNT transistor is measured. (mixer approach).
-0.2 μm long CNT and 2 omega approach : 1.3 GHz in air!

CNT material :

- : High surface-to-volume ratio
- : Hollow structure
- : Excellent mechanical, optical and thermal properties
- : Excellent candidate for gas sensing

Gas sensing principles for CNT

- : Change in electrical resistance
- : Change in thermoelectric power
- : Change in local density of states

Types of CNT-based sensing layers

- : Pristine
- : Functionalized
- : Matrix nanocomposites incorporating CNT

Gases/Vapors detected by CNT-based sensors

- : CO, CO₂, H₂S, SO₂, NO₂, humidity,
- : Methanol, ethanol, 1-propanol, 2-propanol, 1-butanol, tertiary- butanol, 1-pentanol, 1-octanol NH₃

Challenges with CNT-based gas sensing

- : Synthesis of pure CNTs is costly;
- : Chemical and physical properties depend strongly on the preparation process;
- : Slow response and recovery time

- Graphene : One-atom-thick sheet of carbon atoms arranged in honeycomb lattice
- : constituent “unit monolayer” of graphite
 - : Unparalleled strength, stiffness and low mass per unit area
 - : Zero-gap material with high mobility limited by defect scattering
 - : $\mu_e = \mu_h$ of about $40000 \text{ cm}^2/\text{Vs}$, electrical ρ about $10^{-6} \Omega \text{ cm}$
 - : Compatible with 2D IC technology, lithographically patterned !
 - : Good signal-to-noise ratio with integrated readout
 - : Excellent candidate for mixed B-U-T-D NEMS resonators!

Preparation methods

- : Mechanical Exfoliation (best electrical and mechanical properties!)
- : CVD of CH_4 and H_2 on sacrificial Cu foil being transferred to Si wafer
- : Epitaxial growth by high temp sublimation of Si atoms from SiC surface

Resonator performances (Cornell University)

- : CVD Graphene adherent on perimeter of perforated Si_3N_4 membrane
- : Q increases with diameter of graphene membrane under tensile stress
- : Highest ever $R \cdot Q$ product (Surface/Volume ratio) $\times Q = 14000 \text{ nm}^{-1}$!)
- : Q of 2400 at 300K, for a graphene membrane diameter of $22.5 \mu\text{m}$
- : 300K, 6 mtorr, photothermal actuation, interferometric detection

Graphene is a very promising material for NEMS resonators

Johannes Svensson et al, Nano-letters, August 2011

Graphene suspended gate FET transistor as electron device

- CVD-SWCNT is manipulated by SEM to the right position above SiO₂/Si.
- EBL is used for Pd/Ti contacts to the SWCNT semiconductor tube.
- Graphene is mechanically exfoliated from graphite and suspended above SWCNT
- Electrical characterization in vacuum at 100K.
- The CNTFET has an On/Off ratio = 10^4 and a minimum resistance of 90k Ω .
- The 2.1 μm wide graphene gate has maximum resistance (4.7 k Ω) at Dirac point
- Subthreshold slope at 100K is 20 mV, i.e. higher than ideal, due to technology.

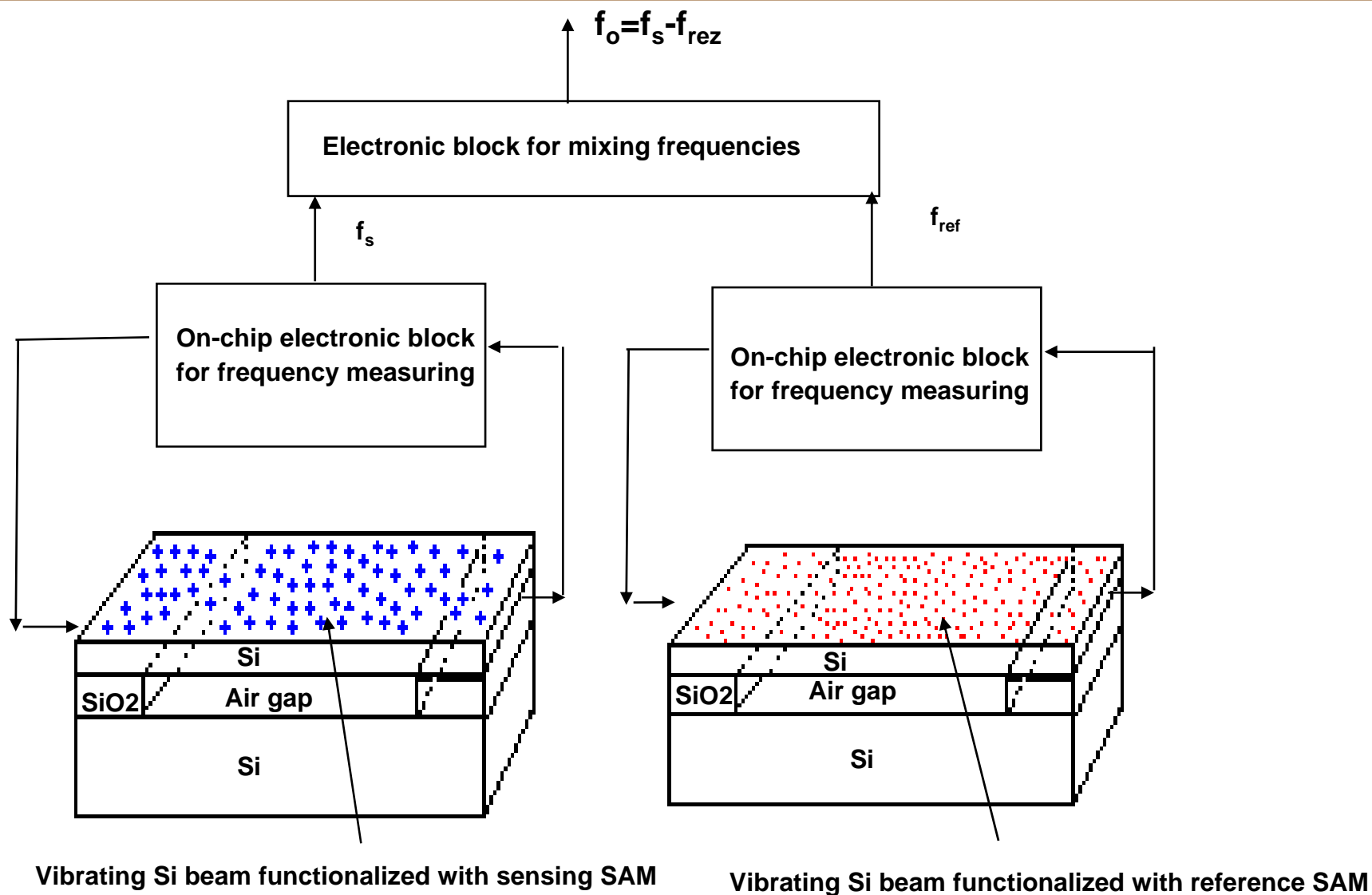
Graphene suspended gate FET as NEMS Resonator

- *Electrostatic* actuated graphene, as a movable gate for double gate CNT-FET !
- Electronic-tunable resonance frequency by driving a varying strain in the G-gate
- Non-linear multimode G-vibrations : mass and position sensing !
- FET as readout circuit with built-in amplification!

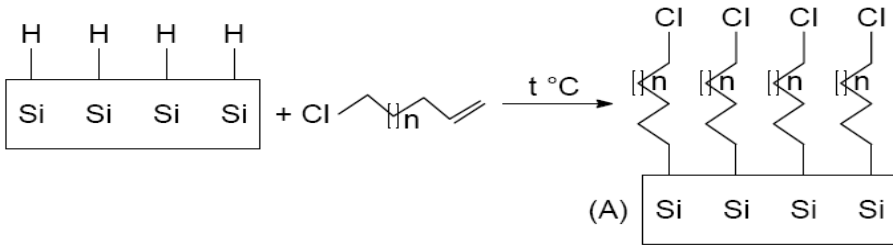
These devices are promising candidate for future NEMS sensors !

A possible roadmap of T-D-B-U NEMS sensors

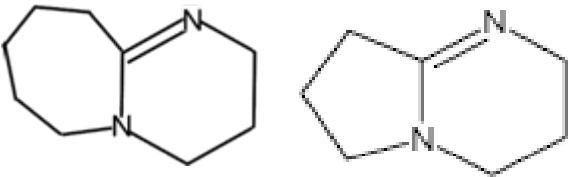
<p>Society's needs</p>	<ul style="list-style-type: none"> -Low cost/size/power-High sensitivity/selectivity gas sensors for air monitoring -High sensitivity biodetection for rapid response (<10 min) at nL sampling volume - Real-time detection-analysis-computing-wireless communication and feed-back
<p>Potential Future Products</p>	<p>Portable nanorobots with NEMS for sensing and RF Front End Wireless, on-chip NEMS resonant chemical sensor array, accelerometers, gyro NEMS resonant chemical sensors operating at 300K and 1 atm Mass Spectrometers for simultaneously mass and position detection NEMS resonators for on-chip clock, mechanical filtering in Front End RF, GHz (cell phone)</p>
<p>Components</p>	<p>Actuation and detection building blocks for resonant NEMS sensing systems Functionalized graphene nanobeams and or cantilever used as chemical sensors NEMS resonators based on suspended Graphene-gate SWCNT MOSFET as readout SWCNT FET transistor, Graphene Schottky diode and Graphene MOSFET transistor Pristine SiNW piezoresistor, Metallized SiNW, Graphene ultracapacitor</p>
<p>Technologies</p>	<p>Nanoscale functionalization processes (SAM) and tools (DPN) for chemical sensors SWCNT and Graphene manipulation tools (SEM, nanopiezoelectric probes, STM) CVD for Fe-catalyzed SWCNT selective deposition and Graphene Transfer Technologies SOI-CMOSFET based on Electron Beam Lithography, SLV epitaxy, graphene epitaxy</p>
<p>Enablers</p>	<p>Governmental support Carbon Allotrope Chemistry Material science, Quantum Physics and Chemistry Present and future Bottom-Up silicon, silicon carbide and carbon technology Classical top-down nanoelectronics and NEMS technologies</p>



1. Alkyl chloride chains bonded to Si-H



1,8 diazabicyclo[5,4,0] undec-7-ene (**DBU**)



The **DBU** structure

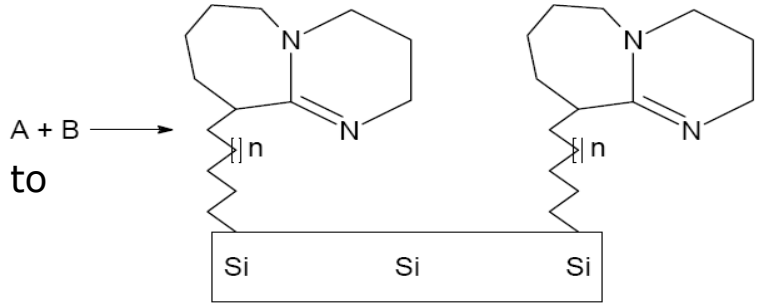
The **DBN** structure

2. Deprotonation of DBU

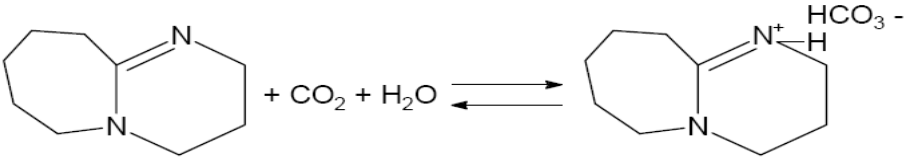


1,5 diaza [3,4,0]-non-5-ene (**DBN**).

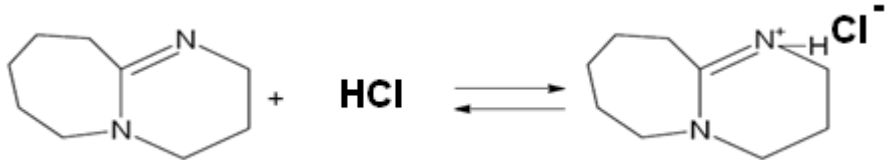
3. DBU reaction to alkyl chain



4. CO2 detection reaction on the sensing beam



5. Poisoning of CO2 sensing sites with HCl on reference beam



- 21st Century could belong to nanotechnology and its applications.
- Resonant NEMS is driving a large application platform from quantum fundamental science and single molecule detection, up to computer science and front end RF.
- Top-down, Bottom-up and Mixed top-down bottom-up are simultaneously developing towards similar target applications but with different time constants for reaching them.
- Tandem Graphene and CNT active devices are emerging as major candidates for both “Beyond CMOS” miniaturization and “More than Moore” diversification.
- Nanomanipulation tools for high accuracy positioning of CNT and graphene are the key challenge for a transition to a mass fabrication of NEMS.
- Bottom-up technologies are envisioning molecular devices and nanotools for their manipulation, with the long term goal of generating “productive nano-systems” as tools for the future industry of making nanosystems and systems of nano-systems.

Nanotechnology is the foundation of the next industrial revolution !