Fabricación de sensores nanométricos

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Disminuyendo el tamaño de los sensores hasta un tamaño comparable al molecular, aumenta la sensibilidad (es más eficiente la detección)

Eléctricos
Mecánicos
Ópticos

Nanomechanical devices

Nanomechanical devices functionality is based on exploiting the mechanical properties of nanostructures: elasticity, resonant behaviour

Operation modes can be static or dynamic. In static mode the quasi-static deflection is measured. In dynamic mode, the response of the oscillation modes is monitored

Nanomechanical resonant mass sensors allows to measure ultra-small amounts of mass. In comparison to quartz crystal microbalances, they present advantages in terms of mass sensitivity, spatial resolution and system integration

Read-out of the oscillation or deflection of a nanomechanical device is key issue for devices with small dimensions: optical, capacitive, piezoresistive, piezoelectric, ...
**Escuela de Nanofabricación Jaca. 6 y 7 de Julio de 2011**

**Nanofabricación de sensores**

**Sensores nanomecánicos**

*Sensores por detección de tensión superficial*

**G. Villanueva.**

**Sensores por detección de cambio de masa**

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**Simplest mechanical structure: cantilever**

\[ F = k \times x \]

\[ k = \frac{E \cdot t^3 \cdot w}{4 \cdot l^3} \quad (N/m) \]

\[ f_{res} = 0.162 \cdot \sqrt{\frac{E}{\rho} \cdot \frac{l}{t}} \quad (Hz) \]

**Elastic constant: \( k = F/x \)**

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**Effect of decreasing the dimensions of mechanical structures**

<table>
<thead>
<tr>
<th>( l ) (um)</th>
<th>( w ) (um)</th>
<th>( t ) (um)</th>
<th>( k ) (N/m)</th>
<th>( f_0 ) (Hz)</th>
<th>( m ) (gr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AFM</td>
<td>450</td>
<td>50</td>
<td>2</td>
<td>0.2</td>
<td>14 kHz</td>
</tr>
<tr>
<td>SiN</td>
<td>125</td>
<td>30</td>
<td>4</td>
<td>0.44</td>
<td>364 kHz</td>
</tr>
<tr>
<td>Nano</td>
<td>10</td>
<td>0.5</td>
<td>0.1</td>
<td>0.02</td>
<td>1.4 MHz</td>
</tr>
</tbody>
</table>

**Silicon cantilever**

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**From MEMS to Quasi 1D NEMS**

**MEMS**

**NEMS**

**SCNW & CNT NEMS**

- **Commercially available piezoresistive MEMS for sensing applications**
- **State-of-the-art piezoresistive NEMS**

- **Si NW prototype NEMS resonator**

- **Enhanced performance**
- **Novel functionalities**
- **New basic properties**
- **Highest structural quality to size ratio**
- **Self-assembled bottom-up fab.**
- **Unique electromechanical properties**
**SURFACE MICROMACHINING**

**PROCESS LAYERS DEPOSITED ON THE WAFER SURFACE**

A. Base material (Si)

B. Sacrificial Layer (SiO₂)

C. Structural layer (Si, PolySi, …)

D. Mobil structure

- A. Starting silicon wafer.
- B. Oxidation. Lithography. Wet etching
- C. Polysilicon deposition. Lithography. Reactive ion etching
- D. Wet etching to release the structure

**Critical process steps at nanometer scale**

I. Resist deposition

II. Lithography

III. Metal layer deposition

IV. Sacrificial layer etching

Nanolithography methods:

- AFM Lithography
- E-beam lithography
- FIB fabrication
- Nanostencil lithography

**Combination of e-beam and UV lithography**
**TOP DOWN:**

FIB Patterning by silicon doping and selective etching

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**Gal·lium implantation in Silicon by FIB**

![Implant profile without sputtering](image)

![Implant profile with steady state sputtering](image)

**Post-CMOS integration of nanomechanical devices by ion beam irradiation of silicon**

### HR-TEM characterization of implanted Si

**SEM**

**TEM**

**BF STEM**

- Crystallization of the Si in the substrate far away from the Ga+ implanted area.
- In the Ga+ implanted area, the material is amorphous.
- Next to the borders, the Si structure is damaged with rough areas of mixed amorphous and crystalline Si.

In collaboration with R. Guzmán, J. Arbiol. ICMAB/ICREA

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**Post-CMOS integration of nanomechanical devices by ion beam irradiation of silicon**

**HR-TEM characterization of implanted Si**

**BF TEM**

- Si-Ga+ amorphous
- Damaged Si

In collaboration with R. Guzmán, J. Arbiol. ICMAB/ICREA
Post-CMOS integration of nanomechanical devices by ion beam irradiation of silicon

**Fabrication of nanomechanical structures**

- **Starting substrate**
- **Structural layer (silicon)**
- **Sacrificial layer (silicon oxide)**
- **Substrate (silicon)**

**Lithography based process**
- Lithography and isotropic silicon etching

**FIB-exposure based process**
- FIB exposure
- Silicon oxide under-etching
- Anisotropic silicon etching

**Starting substrate**

**Lithography based process**

**FIB-exposure based process**

**Free standing nano-cantilever**
- Thickness: 25 nm
- Width: 200 nm

**Array of nanowires**
- Diameter: 25 nm

**Test platform for nano-mechanical characterization**
Coupled nanomechanical structures

Membrane with nano-holes

Excitación Electrostática para observar la resonancia

Post-CMOS integration of nanomechanical devices by ion beam irradiation of silicon
APLICACIONES

Fritz – Science – 2000

Tensión superficial

Chemisorption of thiol molecules on gold coated cantilever
Adsorption induces reduction of the interfacial stress.

Lavric – Review of scientific instruments - 2004

Medida de la tensión superficial

G. Villanueva.

Baller – Ultramicroscopy – 2000

Cantilever sensor array with polymer coatings
Ballard – Ultramicroscopy – 2000
DNA Hybridization detection

- **Basic idea:**
  - Coat each cantilever specifically to each protein / ssDNA
  - Expose to different analytes and observe bendings → **specific bindings**
  - Differential measurement to have reliable responses

![Diagram](image1.png)

Fritz – Science - 2000

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Frecuencia de resonancia: Medida de masa

![Diagram](image2.png)

<table>
<thead>
<tr>
<th>I (μm)</th>
<th>W (μm)</th>
<th>t (μm)</th>
<th>k (N/m)</th>
<th>( f_0 ) (kHz)</th>
<th>Sensitivity (g/Hz)</th>
</tr>
</thead>
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<tr>
<td>AFM</td>
<td>125</td>
<td>30</td>
<td>4</td>
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</table>

In collaboration with Dr. Jordi Fraxedas

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In-situ monitoring of the deposition of ultra-thin gold layers

![Diagram](image3.png)

AFM: 125 30 4 40 350 4.9·10^-14

“Nano” 10 0.5 0.1 0.02 1.4·10^3 4.2·10^-19
NEMS state of the art mass resolution

- State-of-the-art piezoresistive NEMS
  - 70-nm-thick 3C silicon carbide
  - 30 nm gold for piezoresistance
  - $F_{res}: 126$ MHz
  - $Q: 900$
  - Responsivity: 0.7 Hz·zg$^{-1}$
  - Resolution: 100 zg

- State-of-the-art CMOSNEMS
  - J. Verd et al., EDL (2008)
  - 300 nm width, 6.5 μm length polysilicon cantilever
  - $F_{res}: 11$ MHz
  - $Q: 3500$
  - Responsitivity: 15 Hz·ag$^{-1}$
  - Resolution: 90 zg

- State-of-the-art carbon nanotube NEMS
  - SWNT double clamped CNT
  - 900 nm length
  - $F_{res}: 120-140$ MHz
  - $Q$: 50 (300K); 865 (5K)
  - Responsivity: 1 Hz·yg$^{-1}$
  - Resolution: 25 zg (300K); 1.4 zg (5K)

1 atom mass sensitivity using carbon nanotubes


Out-of-plane vibrating quad-beams (QB)

- (6×6 μm$^2$ area, beams 10 μm × 500 nm, thickness= 450 nm)
- $\sim 50$ ag/Hz mass sensitivity
- $\sim 1.5$ MHz resonance freq.

- Evaporation of sessile droplets has implications in everyday life and industrial processes
- Determination of evaporation rate has been restricted to millimeter-size droplets due to available techniques
- Progress on Nanoscience has led to the possibility of manipulating micrometer size droplets

Nanomechanical mass sensors allow to study evaporation rate for femtoliter volume droplets, nine orders of magnitude below previous studies

J.C. Maxwell. Collected Scientific papers. 1890

CEMES-CNRS
**Experimental set-up**

Nanoscale dispensing (NADIS): hollow pyramidal-shaped AFM probes, milled at the apex by FIB

- NADIS tips with 300 nm holes
- Contact time to adjust droplet size ($\varnothing \sim 1 - 6 \mu m$)

**Droplets deposition process**

1. Approach of the tip, pre-loaded with a liquid
2. Adjustment of the position with the control table
3. Droplet deposition engaging the tip

**Glycerol droplet**

**Experimental determination of droplet evaporation**

Frequency response of the nanomechanical resonator

- Frequency shifts converted into mass using the calibration curve

Temporal evolution of the mass of droplets of different initial sizes (initial volumes ranging from 0.2 fL to 20 fL).

The inset plots the same data with logarithmic scale for the mass.

Resolution: $\sim 0.1 \text{ pg} \equiv 0.1 \text{ fL}$
Evaporation mechanism

Gas diffusion process: \[
\frac{dm}{dt} = -4\pi Dr(c_i - c_o) f(\theta) \Rightarrow \frac{dm}{dt} = -cm^{1/3}
\]

\(\theta\) = Contact angle
\(r\) = Droplet radius

At constant \(\theta\) (hydrophobic surface):

(i) a linear decrease with the same slope is observed for every droplet.

\[m^{2/3}(t) \text{ linear}\]

(ii) the total evaporation time depends on the initial mass \(m_0\) at power 2/3

\[t_{evap} \propto M_0^{2/3}\]

\[D = 5 \pm 1 \times 10^{-2} \text{cm}^2\text{s}^{-1}\]

Determination of diffusion coefficient

(Classical behavior is valid to model the evaporation rate.)

\(D = \frac{4\pi DM}{RT} \left(1 + \frac{1}{3}\frac{m_0^{2/3} - m(t)^{2/3}}{m(t)^{2/3}} \alpha t\right)^{-1/3}\)

\(\alpha = 1.64 \pm 0.07 \times 10^{-10} \text{g}^{2/3} \text{s}^{-1}\)

\(P_s = 0.08 \text{ mTorr}; \quad \theta = 60^\circ \pm 5^\circ\)

Need more sensitive devices and faster acquisition times
**SW CNT FETs as a new device, beyond CMOS technology limitations**

**Pros:**
- Advanced electrical properties
  - High mobility of the carriers
  - High carrier mean free path
  - High current density (up to 10^6 A/cm², local current density)
- Attractive chemical properties (each atom is in the surface)
- Outstanding physical and mechanical properties (due to bonds sp2 C-C)
- They are local 1-D systems

**State of the art:**
- Near zero Schottky contacts
- Allows high k dielectric for conductivity control
- Ballistic transport
- Self aligned geometries
- Ion=3.8 mA/μ at Ion/off = 10 (in TMOS hp90, Ion=0.5 mA !!)

Source: Prof. Emilio Lora-Tamayo

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**SENSORES BASADOS EN NANOTUBOS DE CARBONO**

**Determination of Salmonella infantis**

**Detection of xenoestrogenic compounds**

F. X. Rius, J. Riu, et al. URV

**Limite detección:** 2.19x10^-12 M (0.5 ppt).

**Detection of Bisphenol A in water**

**Funcionalización con receptor estrogénico**
**SENSORES BASADOS EN NANOTUBOS DE CARBONO**


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**Aproximación Bottom-up**

Crecimiento catalítico de nanotubos de carbono

- El CNT crece desde una partícula "catalizadora"
- La partícula determina la estructura del CNT
- Se puede seleccionar la posición donde crecerá el nanotubo

Deposición química des de fase vapor (CVD)

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**Fabricación approach 1: Electrón beam lithography**

CVD térmico

TEM: Single-Walled

Nanotube growth
Transistores de un nanotubo de carbono
fabricados mediante e-beam lithography

Batch fabrication of CNT-FET structures al wafer scale
Fast and cheap approach

More simple process: catalytic material deposition, CNT growth, contact definition

Optical lithography fabrication

Semiconductor nanotube selection
By passing an electrical current, metallic carbon nanotubes are eliminated

Simple process:
- catalytic material deposition,
- CNT growth
- contact definition
**Bottom-up assembly: Wafer-scale growth of CNTs**

- Large-scale manufacturing of CNT FETs for systematic testing of FET characteristics.
- High density CNT-modified microelectrodes for optimized electrical bio-interfaces.

**Technological process**

- 15 microelectronics standard steps
  - 3 Photolithographic processes
- 0. Si 4” wafer
- 1. Back gate contact
- 2. SWCNT selective synthesis:
  - Catalyst: Fe/Mo/Al\(_2\)O\(_3\)
  - CVD: 800°C, act.: H\(_2\), growth: H\(_2\)/CH\(_4\) (1:3)
- 3. Contact patterning

**Chip design**

- 15 x 15 mm\(^2\)
- 5,760 dev./chip = 16 dev./chip x 360 dev./des. (2,560 dev./cm\(^2\))

**Structure design parameters**

- Catalyst area: 1x1 / 2x2 / 4x4 / 5x5 μm\(^2\)
- Channel: 1 / 3 / 5 / 7 μm

**Massive fabrication**

- High yield
- Performance

**Bottom-up assembly: Wafer-scale growth of CNTs**

- 5,760 device chip = 138,240 device wafer
Fabricación masiva de transistores de nanotubo

Device performance as a function of CNT length

Maximum current decrease when the length increases
Linear dependence of the resistance with the CNT length
Inelastic scattering due to defects on the CNTs

Statistics attained over 32,751 devices that had been batch fabricated on a same wafer

Passivation of CNT-FET for biochemical measurements

Design of a passivated CNT-FET for electrochemical sensing

Fabrication of the CNT-FETs:
- Technology for the wafer scale fabrication of CNT-FETs

Passivation/depassivation procedure:
- PMMA could match the electrochemical passivation requirements
- An automatically aligned EBL process to match the resolution and accuracy needs
### Process for the passivation of the CNT-FETs

1. Wafer dicing:
   - Dicing saw (2x2 sensor chips)
2. PMMA deposition:
   - 950K PMMA, 200 nm
3. Automatic EBL:
   - Automatic alignment
   - Voltage: 5 kV*
   - Current: 120 pA
   - Dose: 100.000 µC/cm²
   - Development: MIBK
4. Depassivation of the pads:
   - Rub with acetone

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**Automatic alignment procedure**

1. First manual 3 point alignment
2. Automatic alignment at the by local automatic alignment marks

#### Results on the automatically aligned e-beam process

- Satisfactory alignment of the patterns
- No influence of e-beam on the IV characteristics of the CNT-FETs
- Process time: 20 min/sensor
- The time can be improved since alignment at every device is not necessary

#### Validation of the passivation procedure:

- The PMMA layer blocks the oxidation/reduction reactions at the electrode
- The leakage current due to electrochemical effects highly decreased after the electrode passivation

The sensors are now being evaluated for the bioelectrochemical detection of proteins

* M.J. Esplandiu, UAB-CIN2
Conclusiones

- Sensores nanométricos permiten obtener más sensibilidad debido a que se acercan más a las dimensiones de las moléculas.

- Existen diversas técnicas de nanofabricación que permiten el desarrollo de dichos sensores. Mezcla top-down y bottom-up es muy prometedora.
Interdigitated Electrodes (IDEs)

Electrochemical sensors, biosensors, nanoparticle detection, etc

Why nano-electrodes?

- Improved sensitivity for electrodes/gap with size similar to the target.
- Faster response.
- Less quantity of analyte.
- Miniaturization → Possibilities for Integration

Device performance

1. Voltamperometry: Electrochemical current coming from the redox reactions of the active species in the solution.
2. Impedance Spectroscopy: measurements of the impedance of the media as a function of the frequency. This is, the resistivity and capacitance.

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