Plasma and Dry Micro/Nanotechnologies
6. Micro/Nanofabrications

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Outline

6.1 Approaches in Micro/Nanofabrications

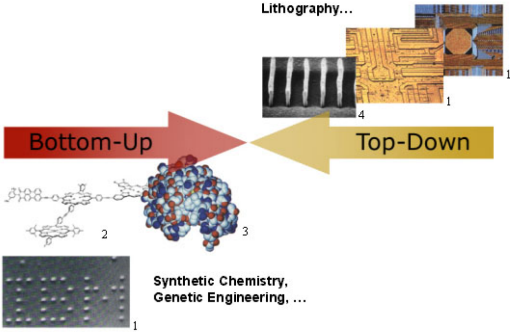
Two principle approaches can be used for micro/nanofabrication:

top-down approach:

- deposition of thin films
- doping
- etching/sputtering (lithography, i.e. through a mask, and nonlitographic fabrication)
- preparation of surfaces (cleaning, polishing, functionalization)

bottom-up

- building using nanoobjects (atoms, molecules),
- self-assempby of structures



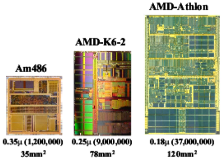
Fabrication of devices

- Microelectronics - requires fabrication of integrated circuits (ICs)
- MEMS/NEMS - borrows standard methods from ICs and adds other processes
- Sensors

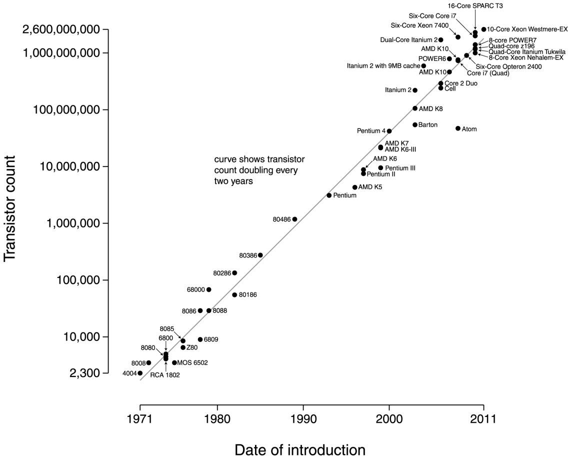
6.2 Fabrication of Integrated Circuits

Increase of integration:

- Small-Scale Integration (SSI) few transistors on chip,
- Medium-Scale Integr. (MSI) hundreds of transistors on chip (end of 60ties),
- Large-Scale Integration (LSI) 10 000 transistors on chip (70ties),
- Very Large-Scale Integr. (VLSI) 100 000 transistors on chip (begining of 80ties), 1 000 000 000 in 2007



Microprocessor Transistor Counts 1971-2011 & Moore’s Law



Source - www.wikipedia.org

Fabrication of Integrated Circuits

. . . multiple-step sequence of photolithographic and chemical processing steps during which electronic circuits are gradually created on a wafer made of pure semiconducting material. Silicon is almost always used, but various compound semiconductors are used for specialized applications.

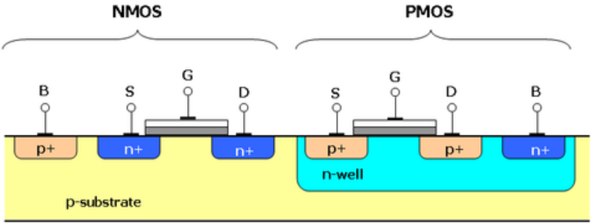
- **Front-end-of-line** (FEOL) is the 1st portion of IC fabrication where the individual devices (transistors, capacitors, resistors, etc.) are patterned in the semiconductor. FEOL generally covers everything up to (but not including) the deposition of metal interconnect layers.
- **Back-end-of-line** (BEOL) is the 2nd portion of IC fabrication - individual devices (transistors, capacitors, resistors, etc.) are interconnected with wiring on the wafer, the metalization layer (Cu, Al). BEOL includes contacts, insulating layers (dielectrics), metal levels, and bonding sites for chip-to-package connections.

Philips Chip Manufacturing Process
`https://www.youtube.com/watch?v=gBAKXvsaEiw` (start from 1')

Front-end-of-line (FEOL) Structure

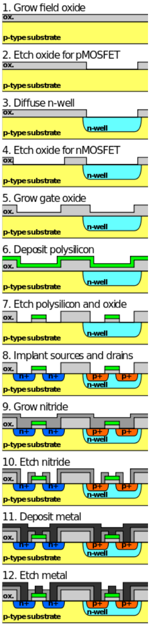
Today, **complementary metal-oxide-semiconductor** (CMOS) technology is the dominant semiconductor technology.

- uses complementary and symmetrical pairs of p-type and n-type metal oxide semiconductor field effect transistors (MOSFETs) for logic functions.

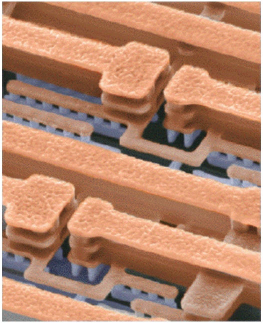


CMOS technology is used in microprocessors, microcontrollers, static RAM, and application specific integrated circuits (ASICs).

CMOS process flow
`https://www.slideshare.net/bhargavveepuri/cmos-process-flow`

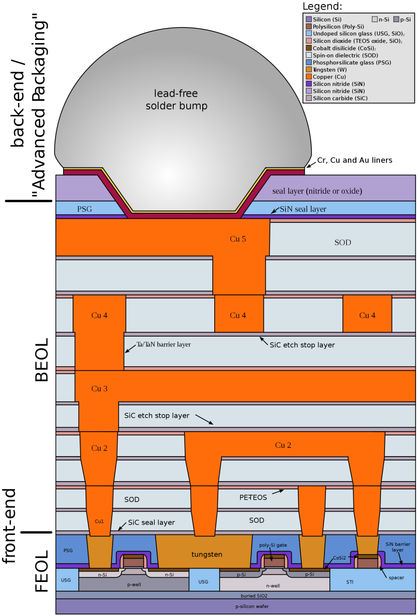


Back-end-of-line (BEOL) Structure



SEM view of three levels of copper interconnect metallization in IBM's CMOS integrated circuits

(Photograph courtesy of IBM Corp., 1997)



Technology Nodes in Microelectronics

Technology node - process sequence for manufacturing a chip

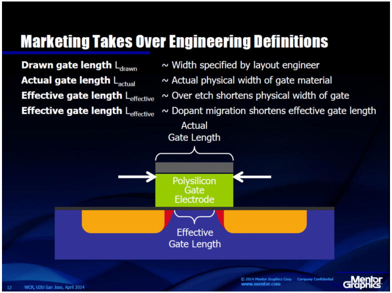
Pitch Counts

Year	Node	Half-pitch	Gate length*
2009[a]	32	52	29
2007[a]	45	68	38
2005[b]	65	90	32
2004[b]	90	90	37
2003[b]	100	100	45
2001[c]	130	150	65
1999[c]	180	230	140
1997[d]	250	250	200
1995[d]	350	350	350
1992[d]	500	500	500

* Here, gate width is defined as the physical gate length, which in recent years became smaller than the printed gate length.

[a] ITRS data 2008 update [b] ITRS data 2006 [c] ITRS data 2001
[d] ITRS data 1997

Note that each year skipped is identified on the ITRS as between nodes.



The device node - once equated to the half-pitch or spacing between the tightest metal lines then the minimum feature size in a chip and now a marketing term that continues to decrease linearly even if no feature on the chip can be found to match it.

6.3 Fabrication of MEMS/NEMS

What are MEMS/NEMS?
The acronym MEMS/NEMS (**micro / nanoelectromechanical systems**) originated in the USA. The term commonly used in Europe is microsystem technology (MST), and in Japan it is micro/nanomachines. Another term generally used is micro/nanodevices.

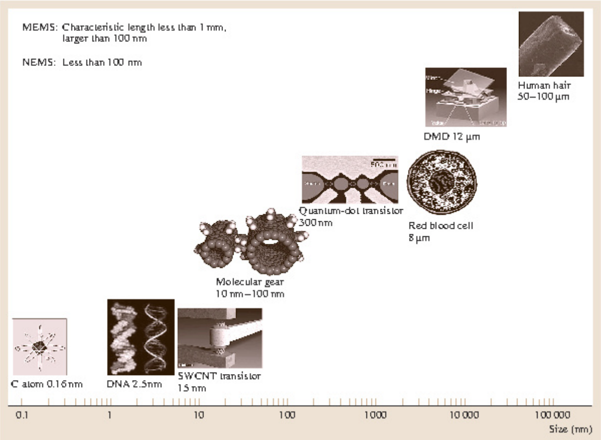
- MEMS - microscopic devices with characteristic length < 1 mm and > 100 nm
- NEMS - nanoscopic devices with characteristic length < 100 nm

MEMS/NEMS terms are also **now used in a broad sense** and include electrical, mechanical, fluidic, optical, and/or biological functions. They are referred to as intelligent miniaturized systems comprising e.g. sensing, processing and/or actuating functions.

MEMS/NEMS for

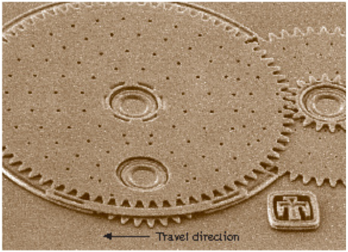
- optical applications -micro/nanooptoelectromechanical systems (MOEMS/NOEMS),
- electronic applications - radio-frequency-MEMS/NEMS or RF-MEMS/RF-NEMS.
- biological applications - BioMEMS/BioNEMS.

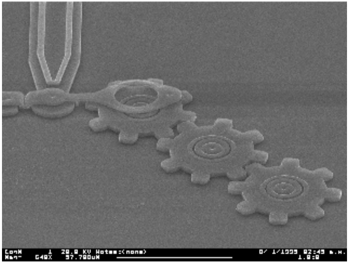
Dimensions of MEMS/NEMS in Perspective



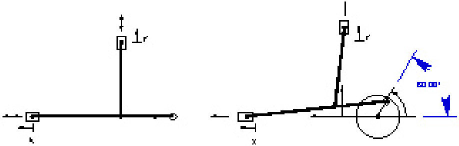
MEMS/NEMS examples shown are of a vertical single-walled carbon nanotube (SWCNT) transistor (5 nm wide and 15 nm high), of molecular dynamic simulations of a carbon-nanotube-based gear, quantum-dot transistor, and digital micromirror device (DMD *http://www.dlp.com*)

Examples of MEMS - gears/motors



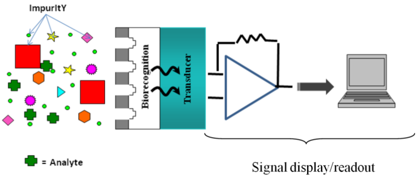


- MEMS motor was developped in lates 1980s using polycrystalline silicon (polysilicon) technology
- left-top photo shows micro-gears
  fabricated in mid-1990s using a five-level polysilicon surface micromachining technology (J. J. Sniegowski et al. IEEE Solid-St. Sens. Actuat. Workshop, 178–182 (1996)) -
  one of the most advanced surface micromachining fabrication process developed to date
- left-bottom SEM photo - microengine output gear and two additional driven gears
  gear extreme diameter is approximately 50 micrometers and gear thickness is 2.5 micrometers (J. J. Sniegowski et al.)

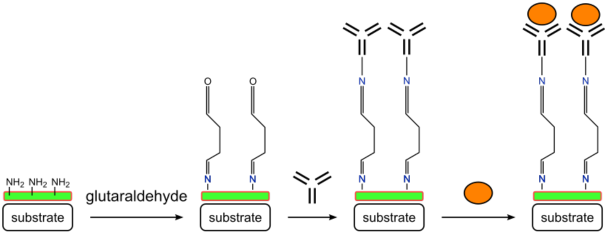


6.4 Biosensors

A **biosensor** is a transducer that incorporates a biological recognition component as the key functional element:



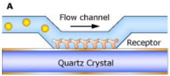
Analytical **immunosensors** are a subset of biosensors which utilize either antigen or antibody as the biospecific sensing element ⇒ Need of antibody/antigen immobilization at the surface, preferentially by covalent binding

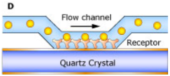


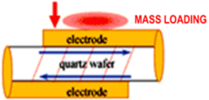
Immunosensing - Two Principles, Same Material Needs

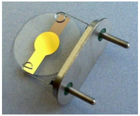
Different principles/transducers but same material is needed
- gold electrode coated with a functional film

Quartz crystal microbalance







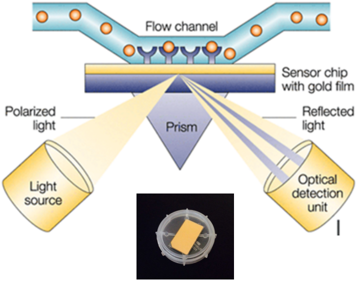


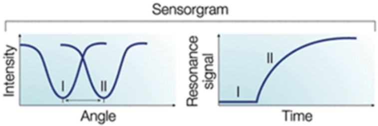
Sauerbrey equation for
change of oscillator frequency

$$\Delta f = 2.26 \times 10^{-6} f^2 \Delta m / A$$

f resonant frequency, A electrode area,
Δm mass change

Surface plasmon resonance



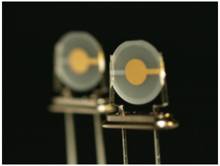


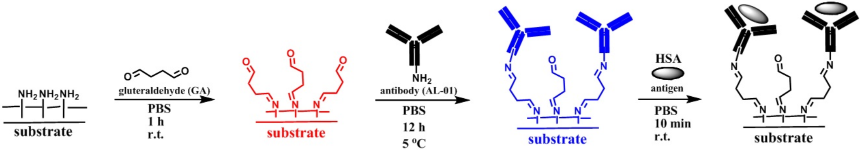
change of resonance angle / reflectance at given angle

6.4 Application of PP-CPA in Immunosensing

Human serum albumin (HSA) chosen for the demonstration of immunosensing application:

- Gold electrode of quartz crystal microbalance (QCM) coated by CPA plasma polymer ⇒ replacement of thiol-based self-assembled monolayer
- Covalent attachment of antibody AL-01 by 3 coupling methods, the most robust being glutaraldehyde (GA):





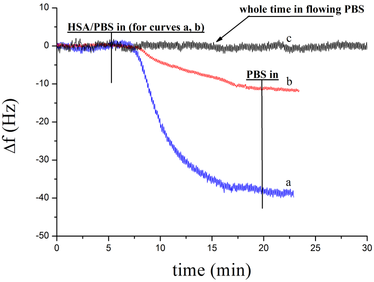
- Detection of HSA by change of QCM frequency
  - association phase: 15 min flow of HSA in PBS (50 mM phosphate buffer saline containing 150 mM NaCl, pH 7.0)
  - dissociation phase: 5 min of PBS buffer flow

A. Manakhov et al. Appl. Surf. Sci. 360(Part A) (2016) 28.

Sensor performance

sensor	reactor	W/F	C [at%]	N [at%]	O [at%]	thickn. loss [%]	$[NH_2]$ [at.%]
a	**R3, floating**	**high**	79.5	19.0	1.5	**18**	1.5
b	**R2, RF driven**	**high**	80.3	17.2	2.5	**2**	1.3

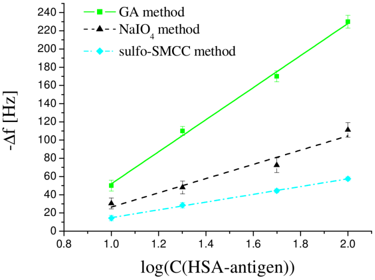
Response of both sensors to HSA (GA coupling of antibody Al-01):



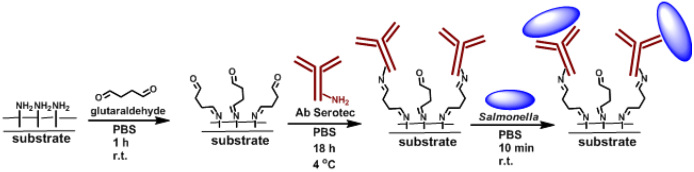
E. Makhneva et al. Surf Coat. Technol. 290 (2016) 116

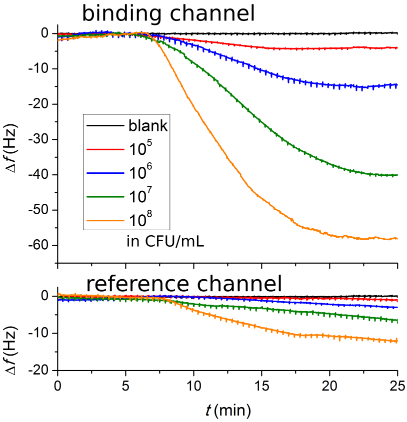
⇒ **Better response for the sensor (a)**, i. e. for polymer with lower cross-linking degree.

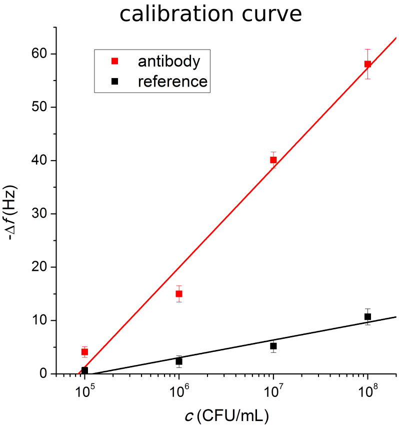
3 coupling methods used for sensor (a), callibration curves:



Real Immunosensing with PP-CPA - QCM Detection of Salmonella





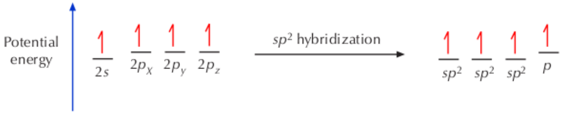


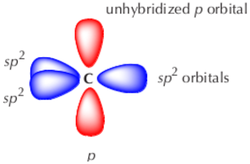
6.5 Examples of Bottom-Up Fabrication

Carbon-Based Nanomaterials - formed by sp^{2}C

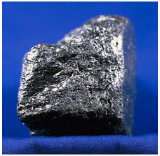
sp^2-C bonding (one valence electron in pure p state and the other three in hybrid orbitals) enables synthesis of several interesting carbon nanomaterials due to planar bond structure

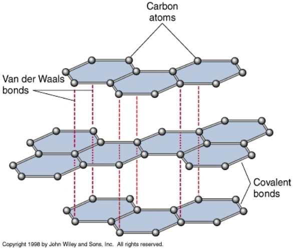
Formation of 3 sp^2 hybrid orbitals: combination of 1/3s and 2/3p - trigonal planar bonding directions with angles of 120°





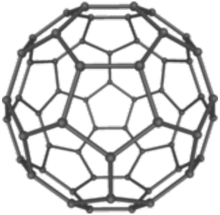
graphite, sp^2 bonded C





Carbon-Based Nanomaterials - formed by sp^{2}C

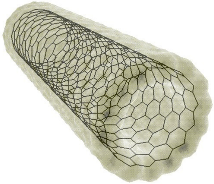
Fullerene - hollow sphere, ellipsoid *etc*.
Buckyballs - spherical fullerenes.



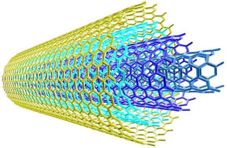
C60 - Buckminsterfuleren

prepared in 1985 at Rice University

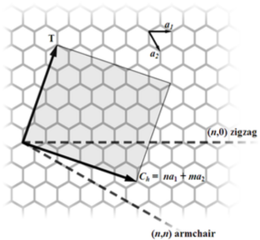
Single-walled carbon nanotube (SWCNT)

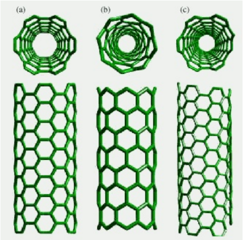


Multi-walled carbon nanotube (MWCNT)



- prepared 1991 by Iijima



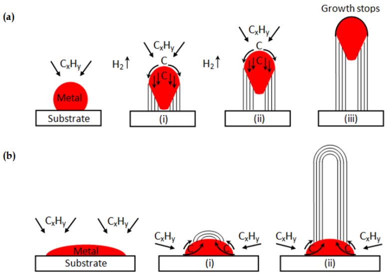


Different chirality of SWNT:

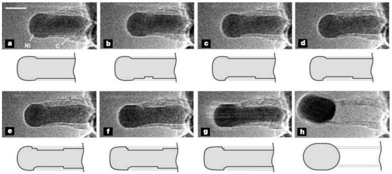
(a) armchair
(b) zigzag
(c) chiral (n,m)

Growth of Carbon Nanotubes

Widely-accepted growth mechanisms for CNTs: (a) tip-growth model, (b) base-growth model.



In situ HRTEM image sequence of a growing carbon nanofiber - images (a–h) illustrate one cycle in the elongation/contraction process.



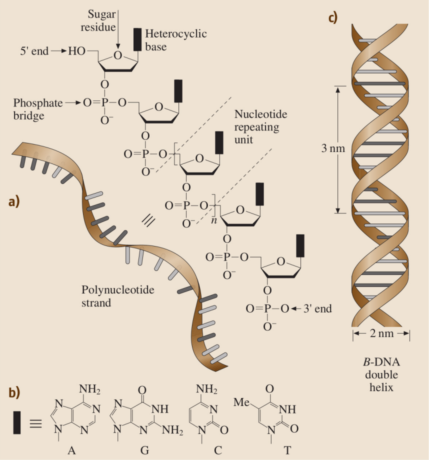
Drawings are included to guide the eye in locating the positions of mono-atomic Ni step-edges at the graphene–Ni interface. Scale bar = 5 nm. (Helveg et al., 2004. Nature 427, 426-429)

TEM video of growing CNTs
`https://www.youtube.com/watch?v=TaNCWcumeyg`

Mimicking Nature's Bottom-up Processes

Nature efficiently builds nanostructures by relying on chemical approaches:

- molecular building blocks: nucleic acids and proteins
- assembled in a variety of nanoscaled materials with defined shapes, properties, and functions.



example of **nucleic acids:**

- nucleic acids are large biomolecules (linear polymers) composed of **nucleotide repeating units** (Fig. a)
- nucleotides have 3 components: 5-carbon sugar, phosphate group, nitrogenous base.
- Chemical bonds between the phosphate of one nucleotide and the sugar of the next ensures the propagation of a polynucleotide strand from the 5' to the 3' end.

⇒ **main backbone of the polymeric strand**

- Every nucleotide carries **one of the four heterocyclic bases** shown in Fig. b.