F4280 Technology of thin film deposition and surface treatment 1. Introduction

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Outline - chapter 1. In	roduction		

- 1.1 Field of Expertise, Suggested Literature
- 1.2 Overview of Material Processing
- 1.3 Introduction to Thin Film Deposition
- 1.4 Applications of Thin Films
- 1.5 Fabrication of microstructures/microdevices

1.1 Field of Expertise, Suggested Literature

What Expertise is Necessary?

Material processing requires knowledge of processes:

- gas kinetics (for processes from vapor/gas phase)
- film growth (general views like adsorption, desorption, utilization etc.)
- interaction of ions with solid (for ion beam and plasma techniques)
- chemistry (for chemical and plasmachemical methods)
- plasma-related phenomena, i.e. plasma physics, principles of electrical discharges, elementary processes in plasma, plasma-surface interation

The processes often takes places at decreased pressure. Therefore, a knowledge of **vacuum technology** is also required.

This information are then applied to master the material processing techniques:

- etching (physical sputtering, chemical etching, plasma etching)
- vacuum evaporation for thin film deposition
- magnetron sputtering for thin film deposition
- chemical vapor deposition (CVD)
- plasma enhanced chemical vapor deposition (PECVD)
- etc.

Handbooks of Technologies

- Handbook of Thin-Film Deposition Processes and Techniques, ed. K. K. Schuegraf, Noyes Publications 1988
- Handbook of Plasma Processing Technology (Fundametals, Etching, Deposition, and Surface Interaction), ed. S. M. Rossnagel, J. J. Cuomo a W. D. Westwood, Noyes Publications 1989
- Handbook of Ion Beam Processing Technology (Principles, Deposition, Film Modification and Synthesis), ed. J. J. Cuomo, S. M. Rossnagel, H. R. Kaufman, Noyes Publications 1989
- Handbook of Plasma Immersion Ion Implantation and Deposition, Wiley 2000
- Handbook of Thin Film Deposition Techniques (Materials and Processing Technology), by Krishna Seshan, (Noyes Publications 2002)
- Handbook of Nanotechnology (Springer 2010), B. Bushan

Books Focused on Specific Processes and Technologies

- Thin Films Phenomena, K. L. Chopra, McGraw-Hill 1969
- Thin-Film Deposition, Principles and Practice by Donald L. Smith, McGraw-Hill, 1995
- Chemical reactor, analysis and design, G. F. Froment and K. B. Bischoff, John Wiley 1990
- Ion-Solid Interactions, Fundamentals and Applications, M. Nastasi, J. W. Mayer and J. K. Hirvonen, Cambridge University Press 1996
- Principles of plasma discharges and materials processing, M. A. Lieberman and A. J. Lichtenberg, John Wiley 1994
- Lecture notes on principles of plasma processing, F. F. Chen and J. P. Chang, Kluwer Academic 2003

Books focused on Specific Materials

- Tribology of Diamond-like Carbon Films: Fundamentals and Applications, by Christophe Donnet and Ali Erdemir, Springer, 2008
- Carbon Nanotubes: Science and Applications, M. Meyyappan ed., CRC Press 2004
- The Science and Technology of Carbon Nanotubes, K. Tanaka, T. Yamabe, F. Fukui eds., Elsevier 1999
- Nanostructures & Nanomaterials: Synthesis, Properties & Applications by Guozhong Cao, Imperial College Press, 2004

Scientific Papers

There are several electronic information resources http://knihovna.sci.muni.cz/:

- databases of scientific publications that collect information independently on the publisher and often contain links to full texts
 - Web of Science
 - Scopus
 - ► INSPEC
- databeses of scientific publications from given publisher always connected with full texts but the download must not be for free (depends on the institutional domain, e.g. sci.muni.cz), some journals are "open access" (authors pay for the publication)
 - Science Direct
 - IOPscience
 - PROLA

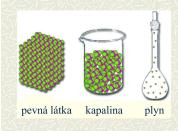
Related courses

- F4160 Vakuová fyzika 1 (jarní semestr, 1. roč. Bc)
- F6450 Vakuová fyzika 2 (podzimní semestr, 2. roč. Bc)
- F3180 Výboje v plynech (podzimní semestr, 2. roč. Bc)
- F5170 Úvod do fyziky plazmatu (podzimní semestr, 3. roč. Bc)
- F7241 Fyzika plazmatu 1 (podzimní semestr, 1. roč. Mgr)
- F3200 Fyzika materiálů a tenkých vrstev (podzimní semestr, 2. roč. Bc)
- F3370 Úvod do nanotechnologií (podzimní semestr, 2. roč. Bc)
- F3390 Výroba mikro a nanostruktur (podzimní semestr, 3. roč. Bc)
- F7360 Charakterizace povrchů a tenkých vrstev (jarní semestr 2022)
- atd.

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What is plasma? The 4th state of matter

Tři dobře známá skupenství hmoty:



✓ Tato skupenství se odlišují silou vazeb, které drží částice látky pohromadě – relativně silné v pevných látkách, slabé v kapalinách a téměř úplně chybí v plynech.

✓ Důležitou fyzikální veličinou je vnitřní kinetická energie (tepelná energie) částic látky, tj. její teplota. Rovnováha mezi touto tepelnou energií částic a vzájemnými vazebnými silami určuje skupenství látky.

✓ Zahříváním pevné nebo kapalné látky získávají její částice více tepelné energie až do okamžiku, kdy jsou schopné překonat vazebnou potenciální energii ⇒ dochází k fázovému přechodu při konstantní teplotě.

http://www.harcourtschool.com/activity/states_of_matter/

What is plasma? The 4th state of matter - ionized gas



✓ Dodáním dostatečné energie molekulárnímu plynu dochází k jeho disociaci na atomy v důsledku srážek těch částic, jejichž tepelná energie překračuje vazebnou energii molekuly.

✓ Ještě větší dodaná tepelná energie způsobí překonání vazebných sil elektronů k jádru ⇒ ionizace, tj. vznik volných elektronů a iontů ⇒ plazma - kvazineutrální systém nabitých částic (electronů - n_e , iontů - n_i), který obsahuje i neutrály (n_e)

stupeň ionizace: $\alpha = n_i / (n_i + n_g)$ plně ionizované plazma $\alpha \approx 1$ slabě ionizované plazma $\alpha \ll 1$

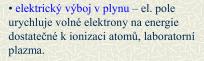
How to create plasma?

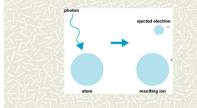
... by sufficient increase of temperature - then, the plasma is in thermodynamic equilibrium.

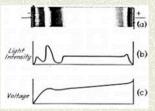
But the temperature should be extremely high $\Rightarrow\,$ many plasmas are created out of thermodynamic equilibrium

 \checkmark Plazma můžeme vytvořit i pomocí ionizačních procesů zvyšujících mnohonásobně stupeň ionizace nad jeho rovnovážnou hodnotu (po vypnutí zdroje ionizace dojde k dohasínání plazmatu díky rekombinaci):

 fotoionizace – ionizační potenciál např. atom. kyslíku je 13,6 eV ⇒ foton o vlnové délce 91 nm (daleká UV oblast). Ionosféra Země - přírodní fotoionizované plazma.







1.2 Overview of Material Processing

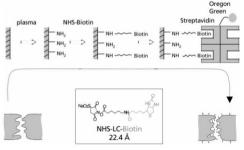
Surface Treatment

What can happen after surface treatment?

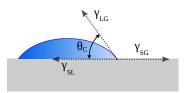
- change of surface roughness
- change of surface chemistry

What can be these changes used for?

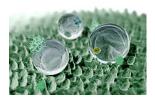
- change of surface free energy, i.e. wettability
- improved adhesion of further coatings
- immobilization of biomolecules



C. Oehr et al., Surf. Coat. Technol. 116-119 (1999) 25-35







Preparation of Films

Difference between thin-film and thick-film technology:

- thin-film technology: deposition of individual molecules, film thickness 10 nm-10 μm
- thick-film technology: involves deposition of particles (e.g. painting, silk screening, spin-on-glass coating, plasma spraying)

Plasmachemical methods compete with several other approaches on the field of thin film deposition and synthesis of nanostructures

Several aspects have to be taken into account:

- functional properties of the deposition
- uniformity of the processes
- step coverage
- conformality
- reproducibility
- simplicity
- price
- etc.

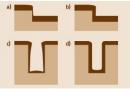


Fig. 8.3a-d Step coverage and conformality: (a) poor step coverage, (b) good step coverage, (c) nonconformal layer, and (d) conformal layer

Etching/Sputtering Processes

ion sputtering

- purely physical approach, removal by energy transfer
- slow process, no selectivity
- ions are directed by electric field, i.e. anisotropic process

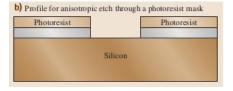
chemical etching

- purely chemical processes that requires aggressive chemicals and/or elevated temperature for reaction activation
- can be very fast, selective
- chemical reactions with surface are not directed, i.e. isotropic process

plasma etching

- combination of physical and chemical approaches
- directional process

Photoresist	Phot	presist
	Silicon	



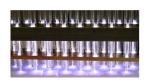
Unique Features of Plasma Technologies

- dry process, i.e. with low consumption of chemicals,
- offering replacement of toxic and explosive reactants
- environmentally friendly
- preparation of new materials

Why? Plasma of laboratory electrical discharge provides environment of

- ▶ hot electrons ($T \approx 10000$ K) \Rightarrow dissociation of molecules into reactive species
- ▶ positive ions that can be accelerated by ≈ 100 eV near solid surface ⇒ sputtering of targets, implantation, modification of surfaces and growing films
- ► cold neutral gas ⇒ highly energetic process can be kept in a vessel, heat sensitive materials can be treated (e.g. polymers, even polymer nanofibers)







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Plasma Processing Methods

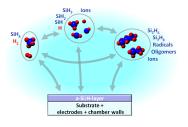
Plasma etching

anisotropic dry etching: combination of chemistry and effect of ions (reactive ion etching)



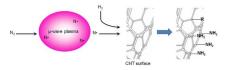
Plasma deposition of thin films

plasma enhanced chemical vapor deposition (PECVD)

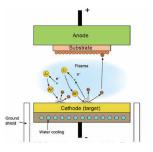


Plasma treatment in O2, NH3, CF4 ...

creation of surface chemical group



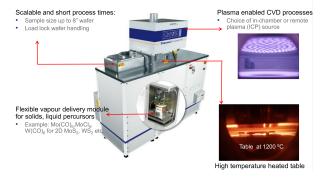
physical vapor deposition (PVD) - dc diode sputtering, magnetron sputtering



Commercial Plasma Reactors

Plasma reactors can also look very differently, like plastic boxes :-)





Oxford Instruments, PlasmaPro 100 - reactive ion etching Oxford Instruments, NanoFab

- high T (plasma enhanced) chemical vapor deposition for deposition of carbon nanomaterials and other 2D materials

1.3 Introduction to Thin Film Deposition

Thin-Film Deposition Process Steps

All thin-film processes contain the four (or five) sequential steps.

1. A source of film material is provided.

Solid, liquid, vapor or gas source. Solid materials need to be vaporized (by heat or energetic beam of electrons, photons, i.e. laser ablation, or positive ions, i.e. sputtering) - **physical vapor deposition (PVD)**. The methods using gases, evaporating liquids or chemically gasified solids are **chemical vapor deposition (CVD)** methods.

2. The material is transported to the substrate.

The major issue is uniformity of arrival rate over the substrate area. Transport in a high vacuum = straight travelling lines \rightarrow importance of geometry. Transport in a (gaseous) fluid = many collisions \rightarrow gas flow patterns, diffusion of source molecules through other gases present.

3. The film is **deposited** onto the substrate surface.

It is influenced by source and transport factors and the conditions at the deposition surface. Three principal surface factors: (i) surface condition (roughness, contamination, degree of chemical bonding with the arriving materials and crystallographic parameters in the case of epitaxy), (ii) reactivity of arriving material (sticking coefficient S_c from 1 to less than 10^{-3}) and (iii) energy input (substrate heating, photons, ions, chemical energy).

Thin-Film Deposition Process Steps

- 4. (Optionally, annealing takes place)
- 5. The final step is **analysis** of the film.

One level of analysis is the determination of functional properties important for given application and optimization of the deposition process for these processes (emphirical approach). A deeper level of analysis involves probing the film structure and composition (better understanding of the overall processes).

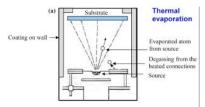
Analysis of the films after deposition - kind of final process monitoring. However, **monitoring** is important in all steps!

Overview of Deposition Methods I

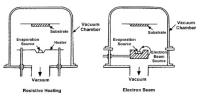
method/processes	specification				
evaporative techniques:					
thermal (vacuum) evaporation	resistive heating				
	flash evaporation				
	arc evaporation				
	exploding-wire technique				
	rf heating				
	electron-beam evaporation				
pulsed laser deposition (PLD)	·				
molecular beam epitaxy (MBE)					
liquid-phase ch	nemical techniques:				
electro processes	electroplating				
	electrolytic anodization				
mechanical techniques	spray pyrolysis				
liquid phase epitaxy					
gas-phase ch	emical techniques:				
chemical vapor deposition (CVD)	CVD epitaxy				
	metalorganic CVD (MOCVD)				
	low-pressure CVD (LPCVD)				
	atmospheric-pressure CVD (APCVD)				
atomic layer deposition (ALD)	,				
gas-phase physica	al-chemical techniques				
	na and ion beam):				
modifications of CVD	hot filament CVD (HFCVD)				
	laser-induced CVD (PCVD)				
	photo-enhanced CVD (PHCVD)				
	electron enhanced CVD				

Overview of Deposition Methods I - evaporative methods

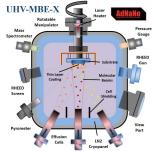
vacuum evaporation



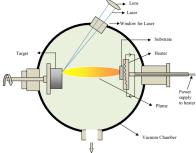
vacuum evaporation (resistive and electron beam



molecular beam epitaxy



pulsed laser deposition

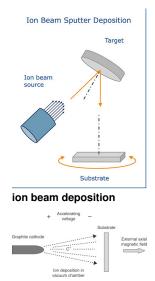


Overview of Deposition Methods II

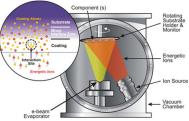
method/processes	specification
p	lasma techniques:
sputter deposition	dc sputtering
	rf diode sputtering
	magnetron sputtering
PECVD in low temperature	dc discharge
discharges	rf capacitively coupled plasma (CCP)
	rf inductively coupled plasma (ICP)
	microwave ECR deposition
	microwave resonantor reactor
	atmospheric pressure dielectric barrier discharge (DBD)
	atmospheric pressure glow discharge (APGD)
	atmospheric pressure surface barrier discharge
	etc.
plasma processing in high temperature	vacuum arc
discharges	dc torch
	microwave torch
	etc.
	n beam techniques:
sputter deposition	ion beam sputter-deposition
	reactive ion beam sputter-deposition
ion deposition	ion beam deposition
	ionized cluster beam deposition (ICB)
dual processes	ion beam assisted deposition (IBAD)
	dual ion beam deposition

Overview of Deposition Methods II - ion beam

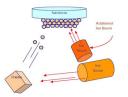
ion beam sputter-deposition



ion-beam assisted deposition (IBAD)



dual ion-beam deposition



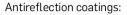


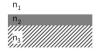
1.4 Applications of Thin Films

Overview of Applications Related to Particular Properties

- Optical properties
 - Antireflection coating
 - Filters (interference coatings)
 - Decoration (color, color effects)
- Thermomechanical properties
 - Scratch resistant coatings (hardness)
 - Thermal protection/heat barriers
 - Tribology (friction control, wear resistant films)
- (Bio)chemical properties
 - Corrosion resistant coatings
 - Permeation barriers
 - Biocompatible surfaces, not-fouling surfaces
- (Photo)Electrical properties
 - Conductors
 - Insulators
 - Semiconductor devices (microelectronics)
 - Photovoltaic materials (sollar cells)
- Magnetic properties
 - Magnetic storage devices

Thin Films for Optical Applications





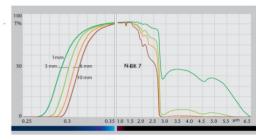
$$r = \frac{r_{12} + r_{23}e^{-\imath 2\Delta}}{1 + r_{12}r_{23}e^{-\imath 2\Delta}}$$

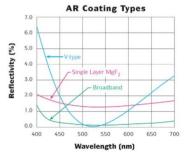
with
$$n_2 d = rac{\lambda}{4}$$
 and $lpha$ = 0:

$$R = \left(\frac{n_1 n_3 - n_2^2}{n_1 n_3 + n_2^2}\right)^2$$

with $\mathbf{n}_1 = \mathbf{1}$ (air) and $n_2 = \sqrt{n_3}$:



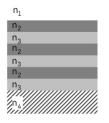




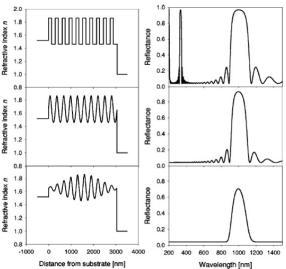
Thin Films for Optical Applications

Interference filters and mirrors:

multilayer structure

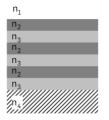


Important – control of film thickness, roughness (interface) and refractive index



Thin Films for Optical Applications

Interference filters and mirrors: multilayer structure



Important – control of film thickness, roughness (interface) and refractive index

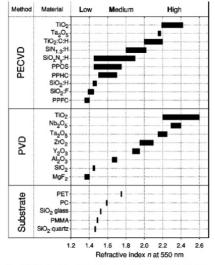


FIG. 2. Refractive index (at λ =550 nm) of different PECVD optical film materials; comparison with selected substrate and PVD materials.

L. Martinu and D. Poitras J. Vac. Sci. Technol. A, Vol. 18 2619

Thin Films for Mechanical Protection

Cutting tools:

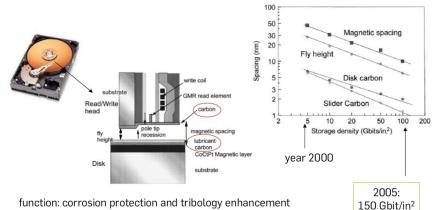
Which properties can be improved? What do we achieve with it? What are the challenges?



Hardness - wear resistance, range of materials Friction - wear resistance, cutting speed Thermal stability - cutting speed Heat conductivity - cutting speed Chemical stability - cutting speed and range of materials Color - more attractive for customer

Challenges: adhesion, cohesion, thermal expansion, chemical stability Complex shape of the object

Thin Films for Mechanical Protection



function: corrosion protection and tribology enhancement Important – control of film thickness, roughness and uniformity Challenge – measurement of film properties at thickness < 3 nm

Thin Films for Mechanical Protection

Melting or Decomposition Temperature Material (°C)			$H = H_0 e^{-aT}$ (Eq. 12-4)		Density (g-cm ⁻³)	Young's Modulus (kN-mm ²)	Thermal Expansion Coefficient (10 ⁻⁶ K ⁻¹)	Thermal Conductivity (Wm ⁻¹ K ⁻¹)	Fracture Toughness (MPa-m ^{1/2})
	Hardness (kg-mm ⁻²)	<i>H</i> ₀ (kg-mm ⁻²)	a (10 ⁻⁴ C ⁻¹)						
Ionic									
Al ₂ O ₃	2047	2100	2300	7.85	3.98	400	6.5	~ 25	3.5
TiO,	1867	1100	1250	5.99	4.25	200	9.0	9	
ZrO,	2710	1200			5.76	200	8.0	1.5	4-12
SiO	1700	1100			2.27	151	0.55	2	< 1
Covalent									
C (Diamond)	3800	~ 8000			3.52	1050	1	1100	
B ₄ N	2450	~ 4000			2.52	660	5		
BN	2730	~ 5000			3.48	440			
SiC	2760	2600	2800	0.90	3.22	480	5.3	84	3
Si ₃ N ₄	1900	1700	1900	2.79	3.19	310	2.5	17	4
AIN	2250	1200	1100		3.26	350	5.7		
Metal									
Compounds									
TiB ₂	3225	3000	3500	18.9	4.5	560	7.8	30	
TIC	3067	2800	3300	18.3	4.9	460	8.3	34	0.46
TIN	2950	2100	2100	23.5	5.4	590	9.3	30	
HIN			2000	8.57			6.9	13	
HfC	3928	2700	3000	14.7	12.3	460	6.6		
TaC	3985	1600	1800	6.75	14.5	560	7.1	23	
WC	2776	2300	2350	3.62	15.7	720	4.0	35	
Substrate									
Materials									
High-Speed									
Steel	1400	900			7.8	250	14	30	50-170
WC-6%Co		1500				640	5.4	80	11.4
Ti	1667	250			4.5	120	11	13	80
Ni Superalloys		200			7.9	214	12	62	> 100

M. Ohring, The Materials Science of Thin Films

Alloys can have properties superior to each component

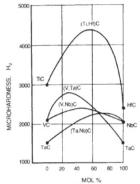
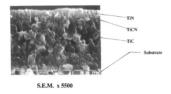
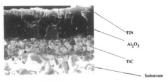


Figure 12-5. Microhardness of mixed carbides due to solid solution and precipitation hardening (From Ref. 3).

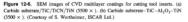
M. Ohring, The Materials Science of Thin Films

Multilayer structures can combine properties of different compounds





S.E.M. x 3500



Thin Films as Barrier Protection

Barrier coatings - permeation barriers



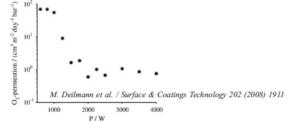


Fig. 5. Permeation rates of 60 nm thick SiO_x films for various pulse powers 600 W $\leq P \leq$ 3000 W at plasma conditions $\Phi_{\rm HMDSO}$ =4 sccm, $\Phi_{\rm O2}$ =400 sccm, p=30 Pa, t_{on}=4 ms and t_{off}=40 ms.

1.4 Applications of Thin Films

Lenka Zajíčková

Thin Films as Barrier Protection

Barrier coatings - permeation barriers

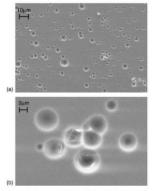


Figure 7. SEM micrographs of SiO_x films on PET after 5 h etching in CCP oxygen plasma.

Practical problem: Bottels are filled at pressure of ~ 6 bar!



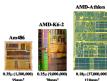
Important: adhesion, microstructure (defects), elasticity, biocompatibility

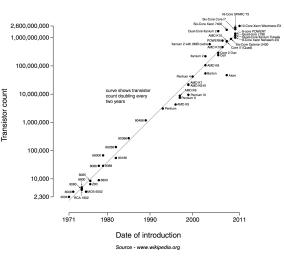
1.5 Fabrication of microstructures/microdevices

Microelectronics - 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

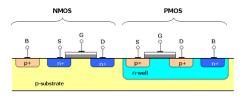




Microprocessor Transistor Counts 1971-2011 & Moore's Law

Microelectronics - Fabrication of Integrated Circuits

Front-end-of-line (FEOL) structure: complementary metal-oxide-semiconductor (CMOS) technology is the dominant semiconductor technology for microprocessors, microcontrollers, static RAM and other ICs

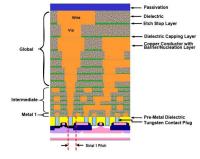


CMOS uses complementary and symmetrical pairs of p-type and n-type metal oxide semiconductor field effect transistors (MOSFETs) for logic functions.

Back-end-of-line (BEOL) structure: interconnect metallization, Cu instead of AI and low-k materials are used to decrease the R and C, i.e. BEOL delay.



SEM view of three levels of copper interconnect metallization in IBM's CMOS integrated circuits (Photograph courtesy of IBM Corp., 1997.)



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.

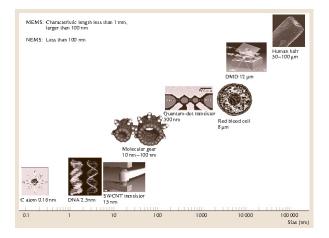
- ▶ MEMS microscopic devices with characteristic length < 1 mm and > 100 nm
- NEMS nanoscopic devices with characteristic length < 100 nm</p>

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

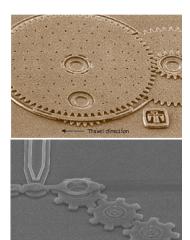
- optical applications -micro/nanooptoelectromechanical systems (MOEMS/NOEMS),
- electronic applications radio-frequency-MEMS/NEMS or RF-MEMS/RF-NEMS.
- biological applications BioMEMS/BioNEMS.

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.)

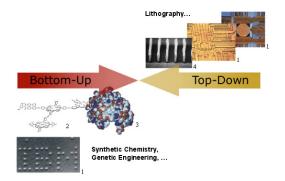


Approaches in Micro/Nanofabrication

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) anisotropic etching of Si
- preparation of surfaces (cleaning, polishing, functionalization)



bottom-up

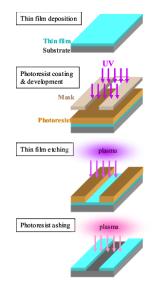
- building using nanoobjects (atoms, molecules),
- self-assemply of structures

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Lithography - process flow

Microlithography is a technique that creates microstructures after given geometrical template:

- Lithography is usually applied to shape a thin film ⇒ deposition of thin film
- Photosensitive material (resist) is coated on the material that should be shaped
- Resist is irradiated through a mask, by projection of UV image or by directed electrons (photolitography or electron lithography)
- Resist development:
 - positive resist: soluble in developper at the irradiated places
 - negative resits: unsoluble in developper at the irradiated places
- Etching of the film through photoresist pattern
- Rest of the resist is removed



lithography patterning with positive resist