F4280 Technology of Thin Film Deposition & Surface Treatments

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Outline - 1. Introduction

- 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. Field of Expertise, Suggested Literature

What Expertise is Necessary?

Dry material processing requires knowledge of

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

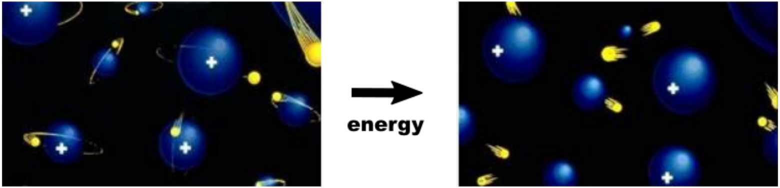
The processes often takes places at decreased pressure. Therefore, a knowledge of **vacuum technology** is also required.

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.

What is Plasma? How to create it?

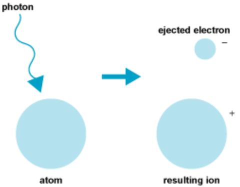
Plasma is created from gas by adding sufficient energy (**4th state of matter**). Added energy leads to **ionization of neutral gas**, i. e. generation of electron-ion pairs:



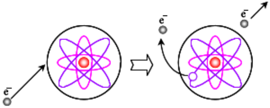
Plasma in thermal equilibrium has extremely high temperature (thermal plasma: fusion, sun)

$\Rightarrow$ many plasmas are created out of thermodynamic equilibrium by increasing **ionization degree** $\alpha = n_i/(n_i + n_g)$ above the equilibrium value with an **additional ionization source**

photoionization (Earth's ionosphere)



electron impact ionization (laboratory electrical discharges - electric field accelerates electrons)

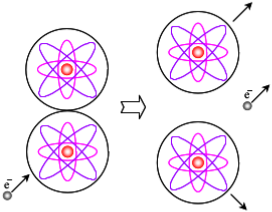


Why Plasma in Material Processing?

Low temperature plasma of gaseous discharges provides unique environment for material processing:

- **hot electrons** (T_e few eV, 1 eV = 11 600 K)
  $\Rightarrow$ dissociation of molecules into reactive species

$$\mathrm{e}^- + \mathrm{AB} \longrightarrow \mathrm{A} + \mathrm{B} + \mathrm{e}^-$$



- **positive ions** that can be **accelerated** to hundreds of eV near a solid surface (in the **plasma sheath**)
  $\Rightarrow$ sputtering of targets, implantation, modification of surfaces and growing films
- **cold neutral gas**
  $\Rightarrow$ highly energetic process can be kept in a vessel, heat sensitive materials can be treated (e. g. , polymers)

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

1.2 Overview of Material Processing

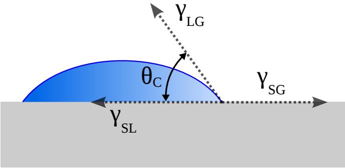
Surface Treatment

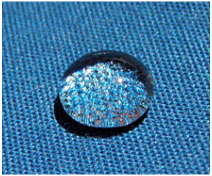
What can happen after surface treatment?

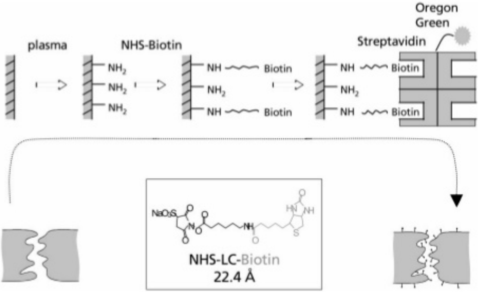
- change of surface roughness
- change of surface chemistry

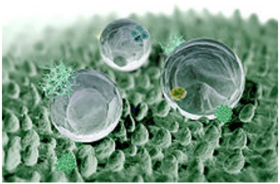
What can be these changes used for?

- 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.

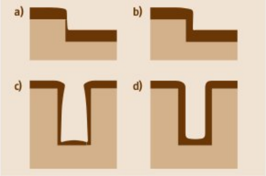


Fig. 8.3a–d Step coverage and conformality: (a) poor step coverage, (b) good step coverage, (c) nonconformal layer, and (d) conformal layer

Etching/Sputtering Processes

ion sputtering

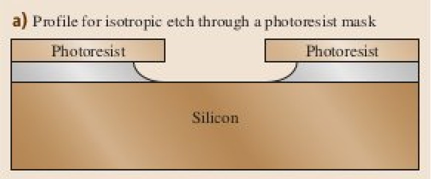
- purely physical approach, removal by energy transfer
- slow process, no selectivity
- ions are directed by electric field, i.e. anisotropic process

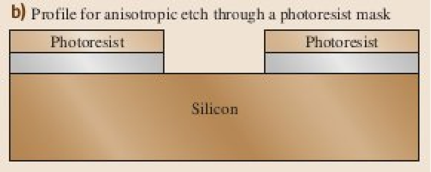
chemical etching

- 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



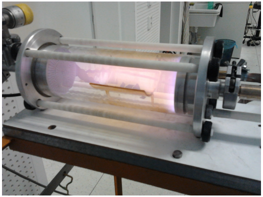


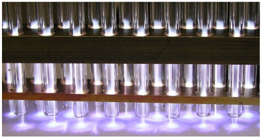
Unique Features of Plasma Technologies

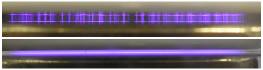
- dry process, i.e. with low consumption of chemicals,
- offering replacement of toxic and explosive reactants
- environmentally friendly
- preparation of new materials

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 $\Rightarrow$ sputtering of targets, implantation, modification of surfaces and growing films
- **cold neutral gas** $\Rightarrow$ highly energetic process can be kept in a vessel, heat sensitive materials can be treated (e. g. polymers, even polymer nanofibers)



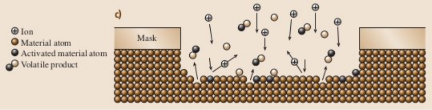




Plasma Processing Methods

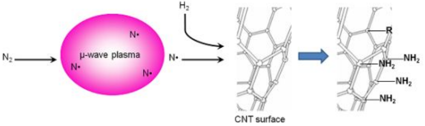
Plasma etching

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



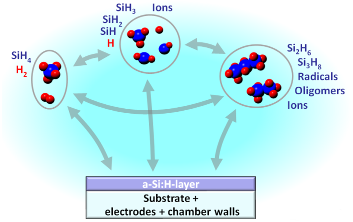
Plasma treatment in O2, NH3, CF4 . . .

creation of surface chemical group

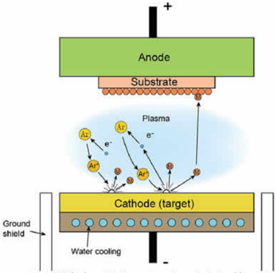


Plasma deposition of thin films

plasma enhanced chemical vapor deposition (PECVD)



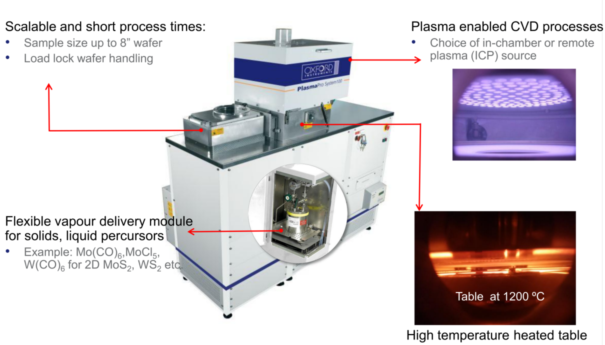
physical vapor deposition (PVD) - dc diode sputtering, magnetron sputtering



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).

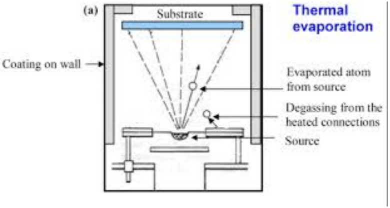
Analysis of the films after deposition - kind of final process monitoring. However, **monitoring** is important in all steps!

Overview of Deposition Methods I

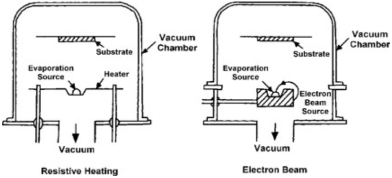
method/processes	specification
evaporative techniques:	
thermal (vacuum) evaporation	resistive heating
	flash evaporation
	arc evaporation
	exploding-wire technique
	rf heating
	electron-beam evaporation
pulsed laser deposition (PLD)	
molecular beam epitaxy (MBE)	
liquid-phase chemical techniques:	
electro processes	electroplating
	electrolytic anodization
mechanical techniques	spray pyrolysis
liquid phase epitaxy	
gas-phase chemical techniques:	
chemical vapor deposition (CVD)	CVD epitaxy
	metalorganic CVD (MOCVD)
	low-pressure CVD (LPCVD)
	atmospheric-pressure CVD (APCVD)
atomic layer deposition (ALD)	
gas-phase physical-chemical techniques (except plasma 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

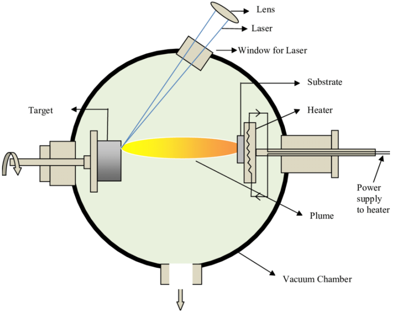
vacuum evaporation



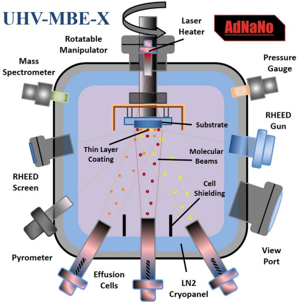
vacuum evaporation (resistive and electron beam



pulsed laser deposition



molecular beam epitaxy

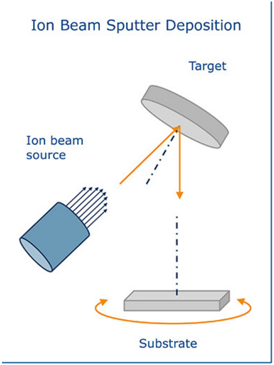


Overview of Deposition Methods II

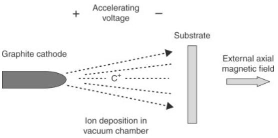
method/processes	specification
	plasma techniques:
sputter deposition	dc sputtering
	rf diode sputtering
	magnetron sputtering
PECVD in low temperature discharges	dc discharge
	rf capacitively coupled plasma (CCP)
	rf inductively coupled plasma (ICP)
	microwave ECR deposition
	microwave resonantor reactor
	atmospheric pressure dielectric barrier discharge (DBD)
	atmospheric pressure glow discharge (APGD)
	atmospheric pressure surface barrier discharge
	etc.
plasma processing in high temperature discharges	vacuum arc
	dc torch
	microwave torch
	etc.
	ion 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

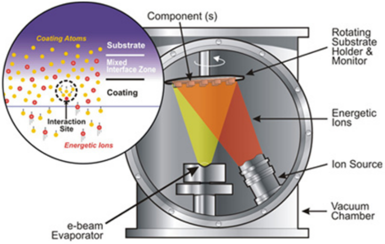
ion beam sputter-deposition



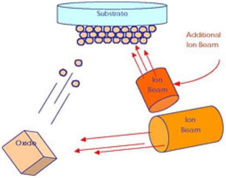
ion beam deposition



ion-beam assisted deposition (IBAD)



dual ion-beam deposition

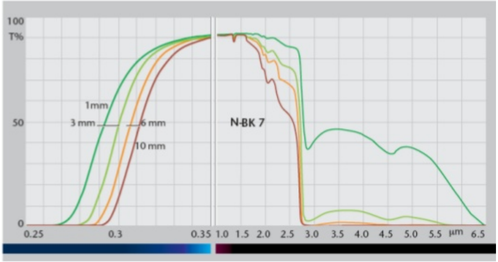


1.4 Applications of Thin Films

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



Antireflection coatings:

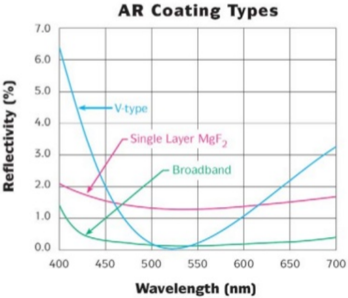
$$r = \frac{r_{12} + r_{23} e^{-i2\Delta}}{1 + r_{12} r_{23} e^{-i2\Delta}}$$

with $n_2 d = \frac{\lambda}{4}$ and $\alpha = 0$:

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

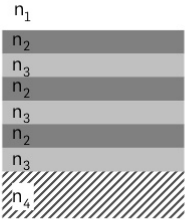
with $n_1 = 1$ (air) and $n_2 = \sqrt{n_3}$:

→ R = 0!

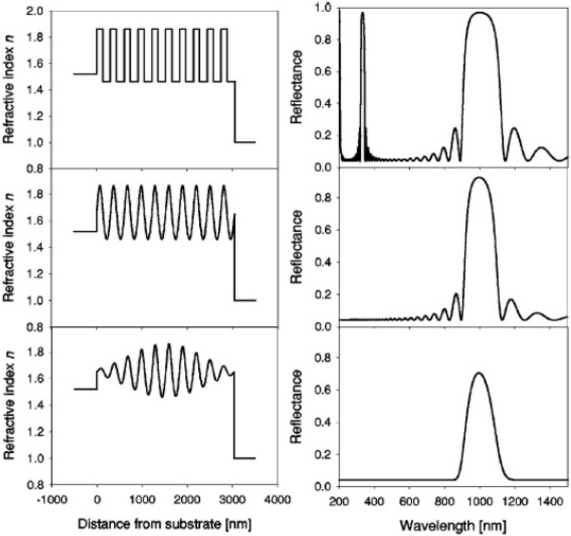


Thin Films for Optical Applications

Interference filters and mirrors:
multilayer structure

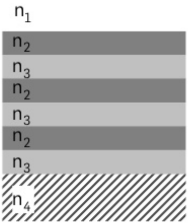


Important – control of film thickness, roughness (interface) and refractive index



Thin Films for Optical Applications

Interference filters and mirrors: multilayer structure



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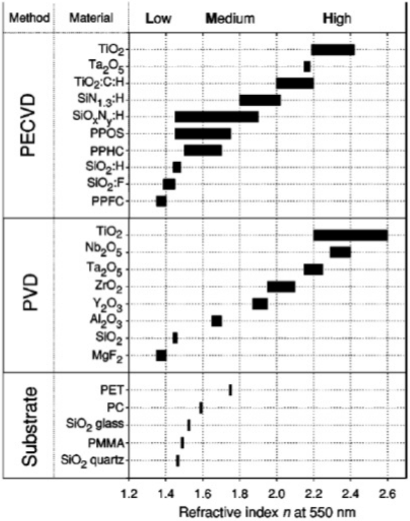


FIG. 2. Refractive index (at $\lambda = 550$ nm) of different PECVD optical film materials; comparison with selected substrate and PVD materials.

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

Thin Films for Mechanical Protection

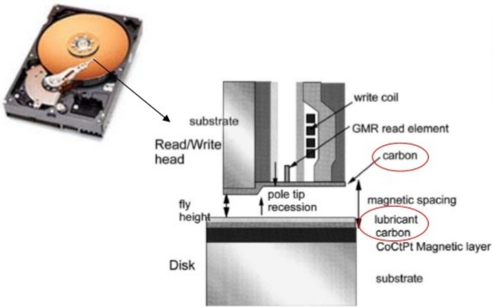
Cutting tools:

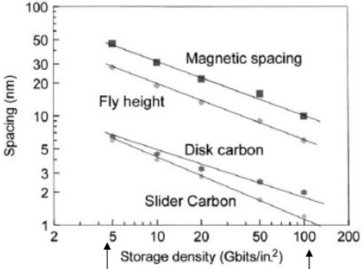
Which properties can be improved?
What do we achieve with it?
What are the challenges?

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





year 2000

2005:
150 Gbit/in^2

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

Table 12-1. Mechanical and Thermal Properties of Coating Materials

Material	Melting or Decomposition Temperature (°C)	Hardness (kg-mm^{-2})	$H = H_0 e^{-aT}$ (Eq. 12-4) H_0 (kg-mm^{-2})	a (10^{-4} C^{-1})	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$^{1/2}$)
Ionic									
Al_2O_3	2047	2100	2300	7.85	3.98	400	6.5	~ 25	3.5
TiO_2	1867	1100	1250	5.99	4.25	200	9.0	9	
ZrO_2	2710	1200			5.76	200	8.0	1.5	4–12
SiO_2	1700	1100			2.27	151	0.55	2	< 1
Covalent									
C (Diamond)	3800	~ 8000			3.52	1050	1	1100	
B_4N	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_3N_4	1900	1700	1900	2.79	3.19	310	2.5	17	4
AlN	2250	1200			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	
HfN			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	1280				7.9	214	12	62	> 100

M. Ohring, The Materials Science of Thin Films

Thin Films for Mechanical Protection

Alloys can have properties superior to each component

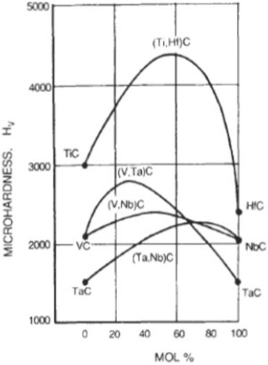


Figure 12-5. Microhardness of mixed carbides due to solid solution and precipitation hardening (From Ref. 3).

M. Ohring, The Materials Science of Thin Films

Multilayer structures can combine properties of different compounds

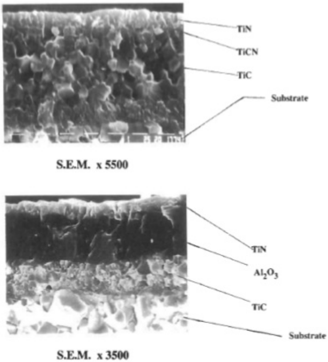


Figure 12-6. SEM images of CVD multilayer coatings for cutting tool inserts. (a) Carbide substrate/TiC/TiCN/TiN (5500 ×). (b) Carbide substrate–TiC–Al_2O_3–TiN (3500 ×). (Courtesy of S. Wertheimer, ISCAR Ltd.)

Thin Films as Barrier Protection

Barrier coatings – permeation barriers

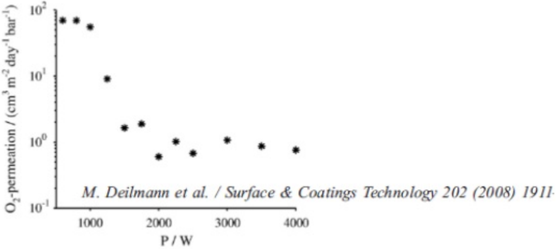


Fig. 5. Permeation rates of 60 nm thick SiO_x films for various pulse powers $600\ W \leq P \leq 3000\ W$ at plasma conditions $\Phi_{HMDSO}=4$ sccm, $\Phi_{O2}=400$ sccm, $p=30$ Pa, $t_{on}=4$ ms and $t_{off}=40$ ms.

Thin Films as Barrier Protection

Barrier coatings – permeation barriers

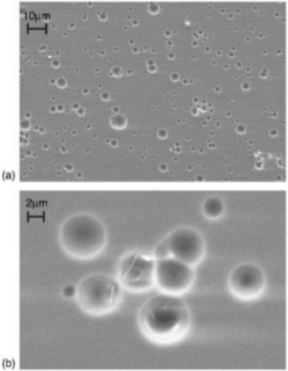


Figure 7. SEM micrographs of SiO_x films on PET after 5 h etching in CCP oxygen plasma.

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

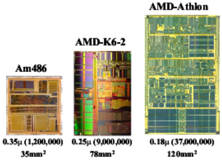
Important: adhesion, microstructure (defects), elasticity, biocompatibility

1.5 Fabrication of microstructures/microdevices

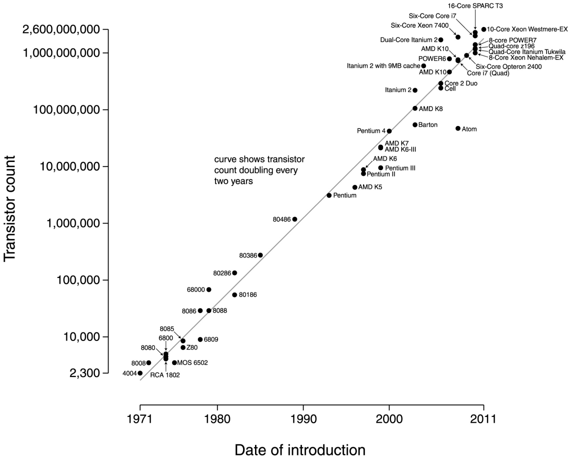
Microelectronics - Fabrication of Integrated Circuits

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



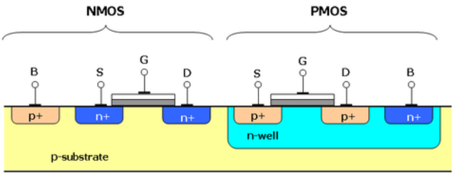
Microprocessor Transistor Counts 1971-2011 & Moore's Law



Source - www.wikipedia.org

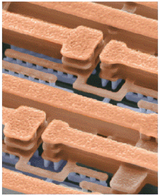
Microelectronics - Fabrication of Integrated Circuits

- **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

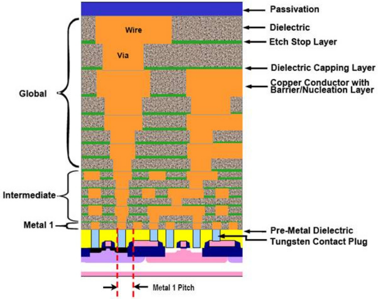


CMOS uses complementary and symmetrical pairs of p-type and n-type metal oxide semiconductor field effect transistors (MOSFETs) for logic functions.

- **Back-end-of-line (BEOL)** structure: interconnect metallization, Cu instead of Al 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.

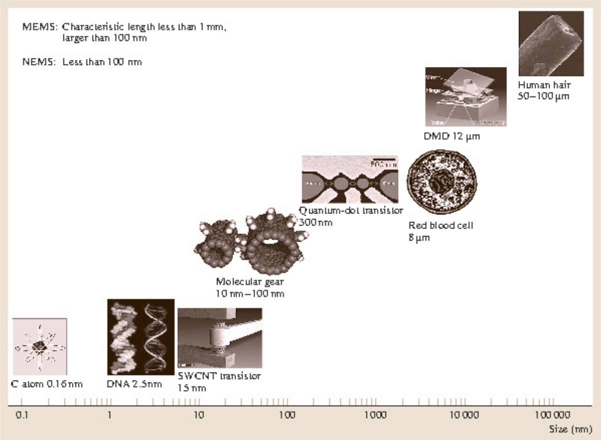
- MEMS - microscopic devices with characteristic length < 1 mm and > 100 nm
- NEMS - nanoscopic devices with characteristic length < 100 nm

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

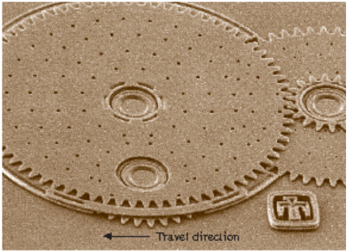
- optical applications -micro/nanooptoelectromechanical systems (MOEMS/NOEMS),
- electronic applications - radio-frequency-MEMS/NEMS or RF-MEMS/RF-NEMS.
- biological applications - BioMEMS/BioNEMS.

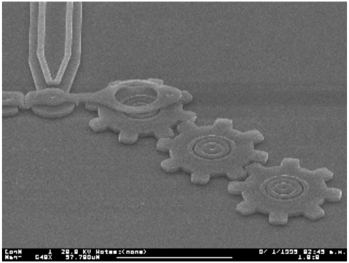
Dimensions of MEMS/NEMS in Perspective



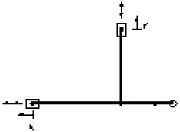
MEMS/NEMS examples shown are of a vertical single-walled carbon nanotube (SWCNT) transistor (5 nm wide and 15 nm high), of molecular dynamic simulations of a carbon-nanotube-based gear, quantum-dot transistor, and digital micromirror device (DMD *http://www.dlp.com*)

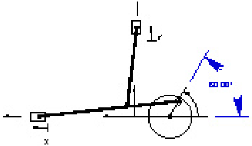
Examples of MEMS - gears/motors





- 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

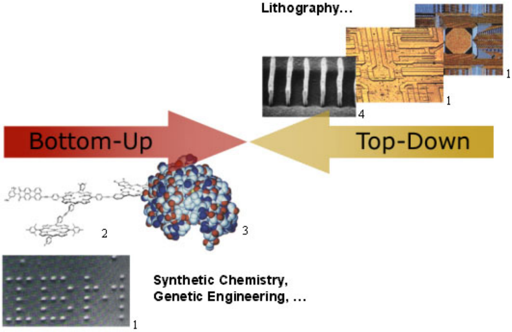
Two principle approaches can be used for micro/nanofabrication:

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

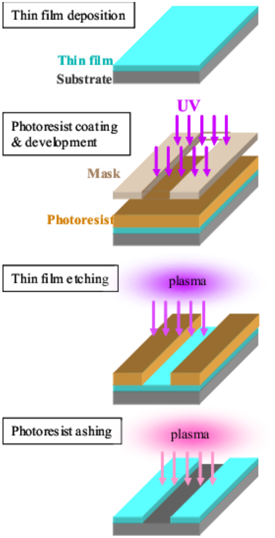


mohla

Lithography - process flow

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

- Lithography is usually applied to shape a thin film $\Rightarrow$ 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