Aalto University
School of Chemical
Engineering

CHEM-E5125

Thin Film Technolgy - Introduction
Functional Materials Major

(5 credits)

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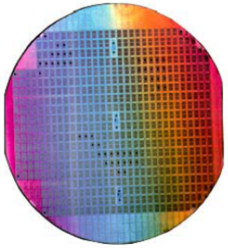
12.1.2021

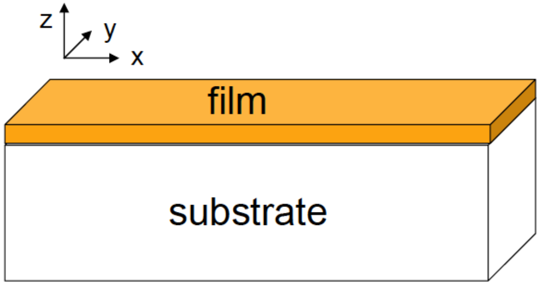
Contents

- Terminology
- Motivation: Why thin films?
- Applications
- Deposition methods – thin film process
- Examples
  - Microstructure
  - Composition
  - Properties – resistivity
  - Properties – Stress
  - Mechanical
- Interface

Terminology

- Film or coating is material which is restricted in one dimension
- Substrate is solid material supporting the film
- Thickness
  - Atomic level:
    - 2 – 5 atom layers on the surface (≈ 0.2 – 0.5 nm)
    - over 10 atomic layers (≈ 1 nm) is bulk
  - Technically
    - 1nm – 10 μm
    - Needed layer thickness, which is needed to:
      - protect substrate
      - Wanted functionality of the coating





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Motivations - why thin films?

- Interaction of materials (commonly) via surface
- Modification of material properties – added functionality
  - **Functional thin films**
- Market of thin films and coatings
  - volume about about 1% of GNP
  - common in all areas of industry
    - Electronics
    - Transport
    - Energy
    - Building
    - Bio-technology

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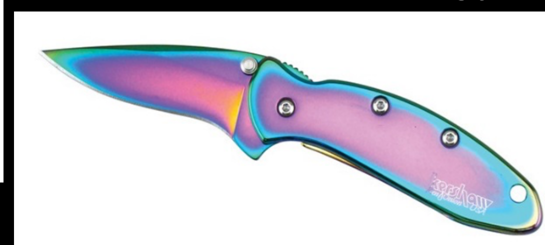
Hardness, protection and wear

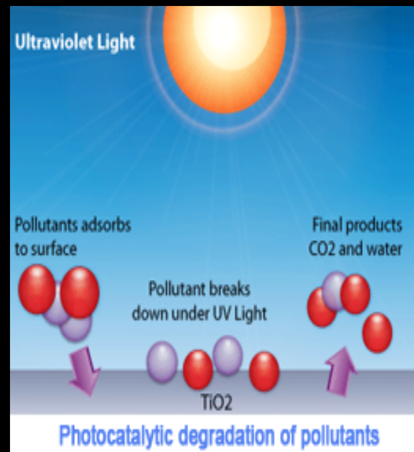
Diamond-like carbon

Art & Decoration



Titanium Nitride,
Titanium Dioxide

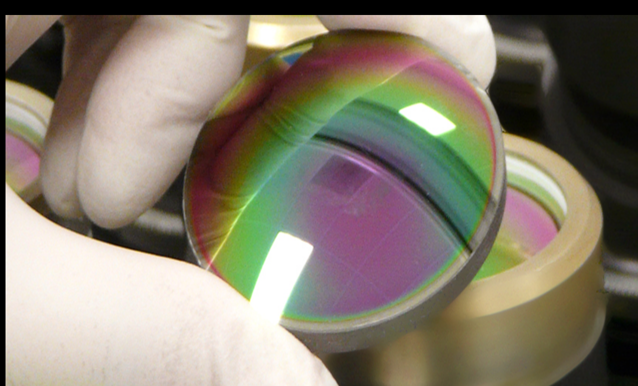
Function and utility

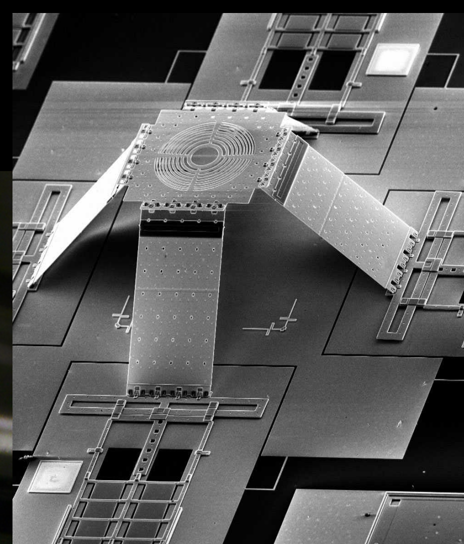


Titanium Dioxide: Photocatalytic activity

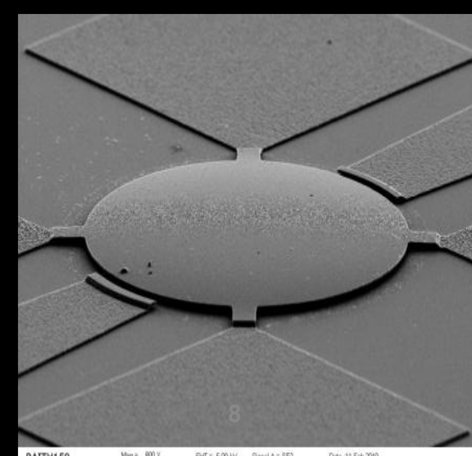
Indium Tin Oxide, ITO:
Defrosting coating

Optical systems, optical
MEMS





Microelectromechanical
systems, MEMS



Applications of thin films

- Electronic components
  - semiconducting, dielectric, insulating, conductors, barriers…
- Electronic displays
  - LCrystalD, LED, ELuminescent, Echorimc, transparent conductive…
- Photo voltaic
- Optical coatings
- Magnetic Films for Data Storage
- Optical data storage
- Antistatic coatings
- Hard protective coatings
- Decorative films
- Decorative and wear-resistant (decorative/functional) coatings
- Permeation barriers for moisture and gases
- Corrosion resistant films
- Coating of engine turbine blades
- Wear and erosion resistant (hard) coatings (tool coatings)
- Dry film lubricants
- Thin-walled freestanding structures
- etc.

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Coating technologies

Table 1.1: Vacuum deposition techniques [10]

Handbook of Deposition Technologies for Films and Coatings - Science, Applications and Technology (3rd Edition)
Edited by: Martin, Peter M. © 2010 William Andrew Publishing

Atomistic deposition	Particulate deposition	Bulk coatings	Surface modification
Electrolytic environment	Thermal spraying	Wet processes	Chemical conversion
Electroplating	Plasma spraying	Painting	Electrolytic
Electroless plating	D-gun	Dip coating	Anodization (oxide)
Fused salt electrolysis	Flame spraying	Electrostatic spraying	Fused salts
Chemical displacement	Fusion coatings	Printing	Chemical–liquid
Vacuum environment	Thick film ink	Spin coating	Chemical vapor
Vacuum evaporation	Screen printing	Cladding	Thermal
Ion beam deposition	Jet printing	Explosive	Plasma
Laser ablation	Enameling	Roll bonding	Leaching
Molecular beam epitaxy	Electrophoretic	Overlaying	Mechanical
Cathodic arc	Impact plating	Weld coating	Shot peaning
Vacuum polymer deposition			Thermal
Plasma environment			Surface enrichment
Sputter deposition			Diffusion from bulk
Activated reactive evaporation			Sputtering
Cathodic arc			Ion implantation
Plasma polymerization			Self-assembly
Ion plating			
Chemical vapor environment			
Plasma enhanced			
Atomic layer deposition			
Reduction			
Decomposition			
Spray pyrolysis			
Liquid phase epitaxy			

Coating technologies in this cource

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Reduction			
Decomposition			
Spray pyrolysis			
Liquid phase epitaxy			

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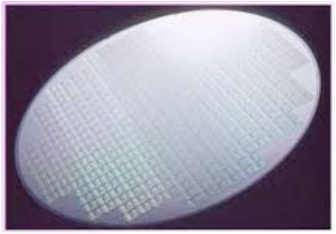
The thin film process

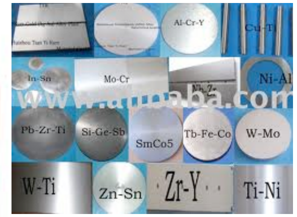
SOURCE solid
liquid
vapor
gas

SUBSTRATE

component
tool

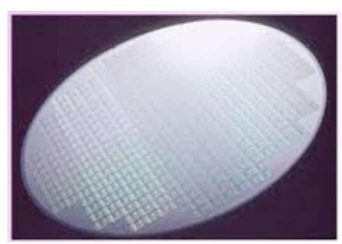


SOURCE
- solid
- liquid
- vapor
- gas



TRANSPORT
- gas phase
- vacuum
- liquid

SUBSTRATE
- component
- tool



SOURCE
- solid
- liquid
- vapor
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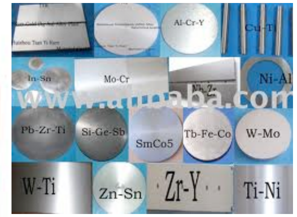


EXCITATION
- thermal
- plasma
- ion bombardment
- electron bombardment
- laser
- voltage
- chemical potential

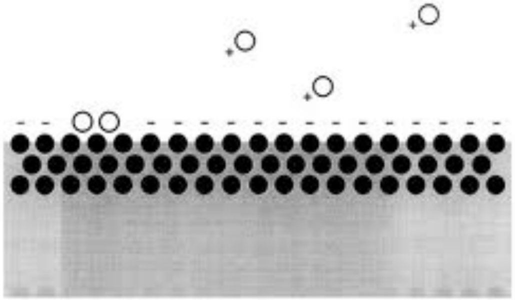
TRANSPORT
- gas phase
- vacuum
- liquid

SUBSTRATE
- component
- tool

SURFACE PROCESSES

- adsorption of film forming atoms
- desorption of film forming atoms
- film nucleation and coalescence
- impurity adsorption, desorption, incorporation

- ion bombardment
- energy from depositing specie
- external heating



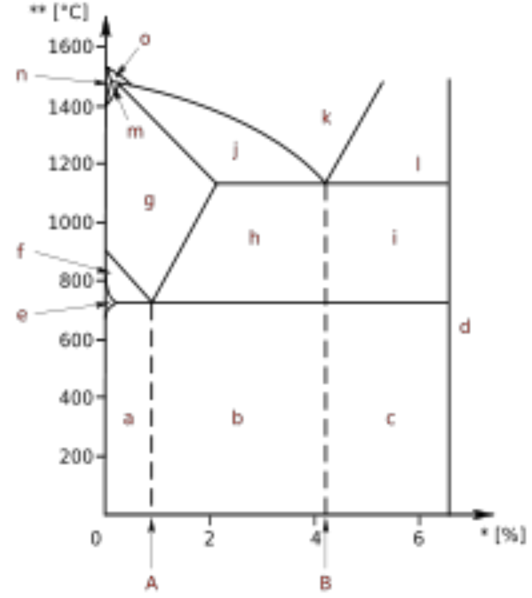
ANNEALING

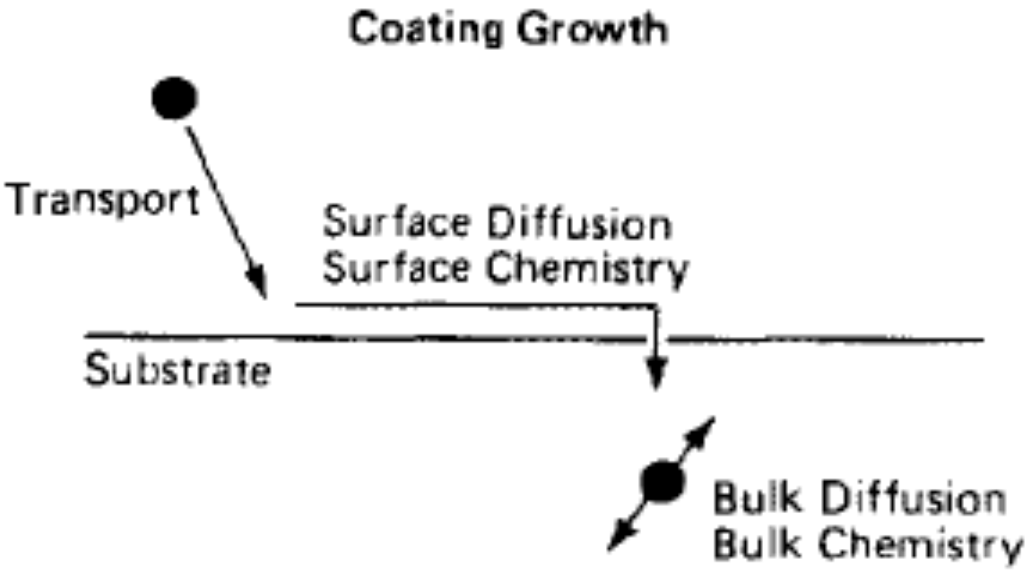
- inert atmosphere
- reactive atmosphere
- chemical reactions
- phycical reactions
- global vs. local

⇩

ANALYSIS

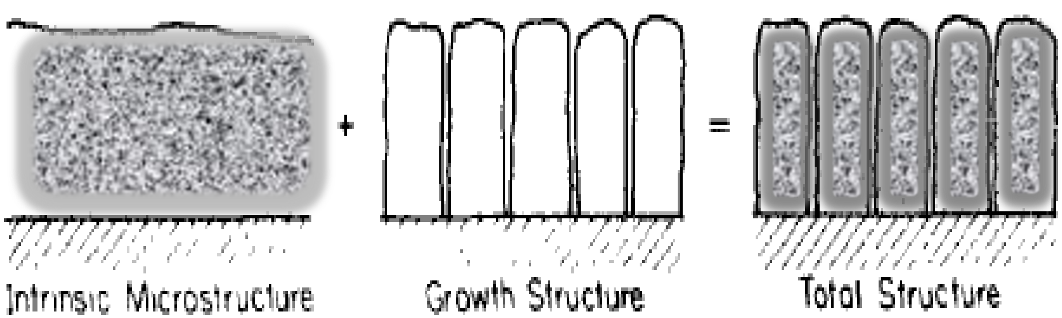
- physical
- chemical
- electrical
- optical





Deposition process

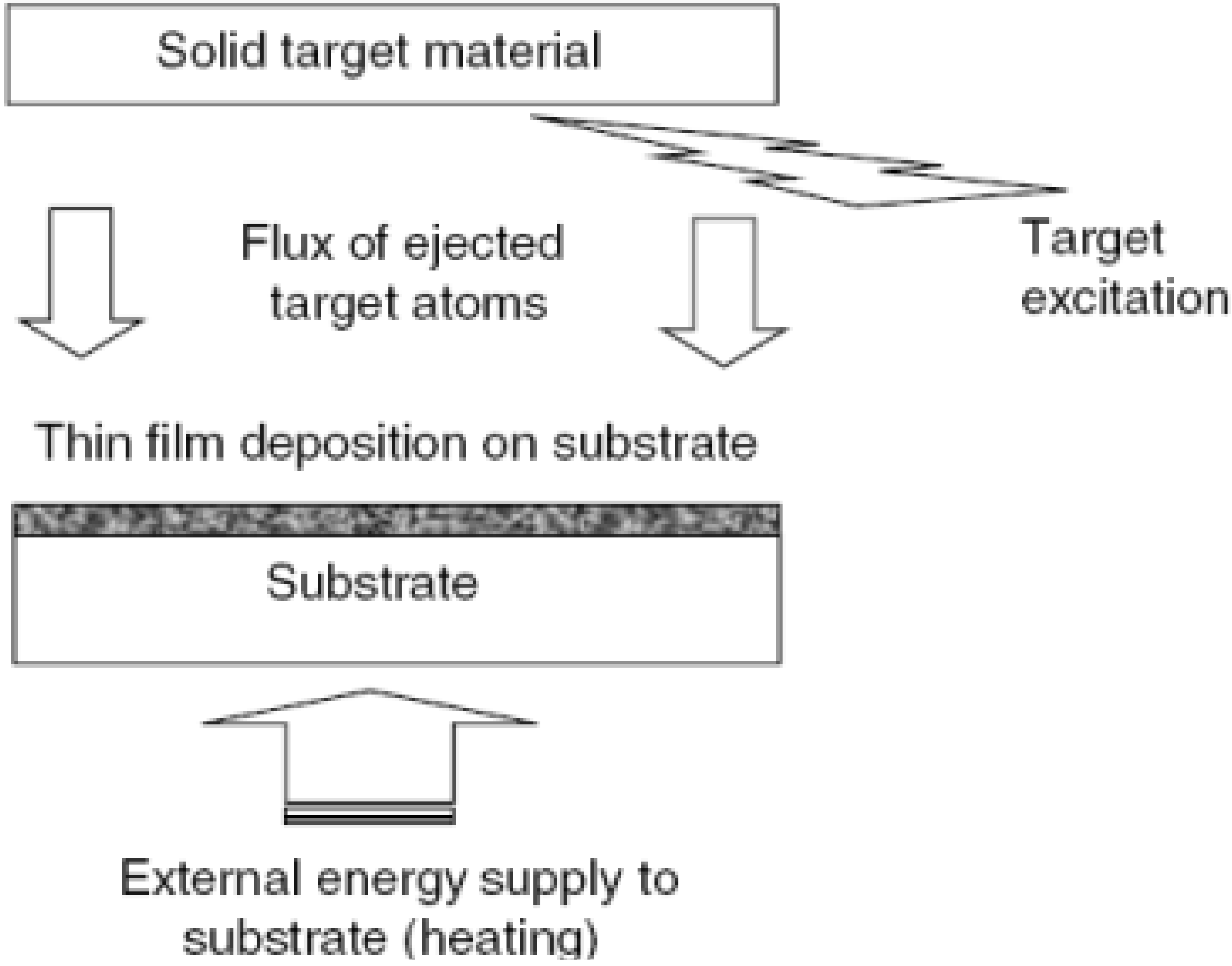
interaction



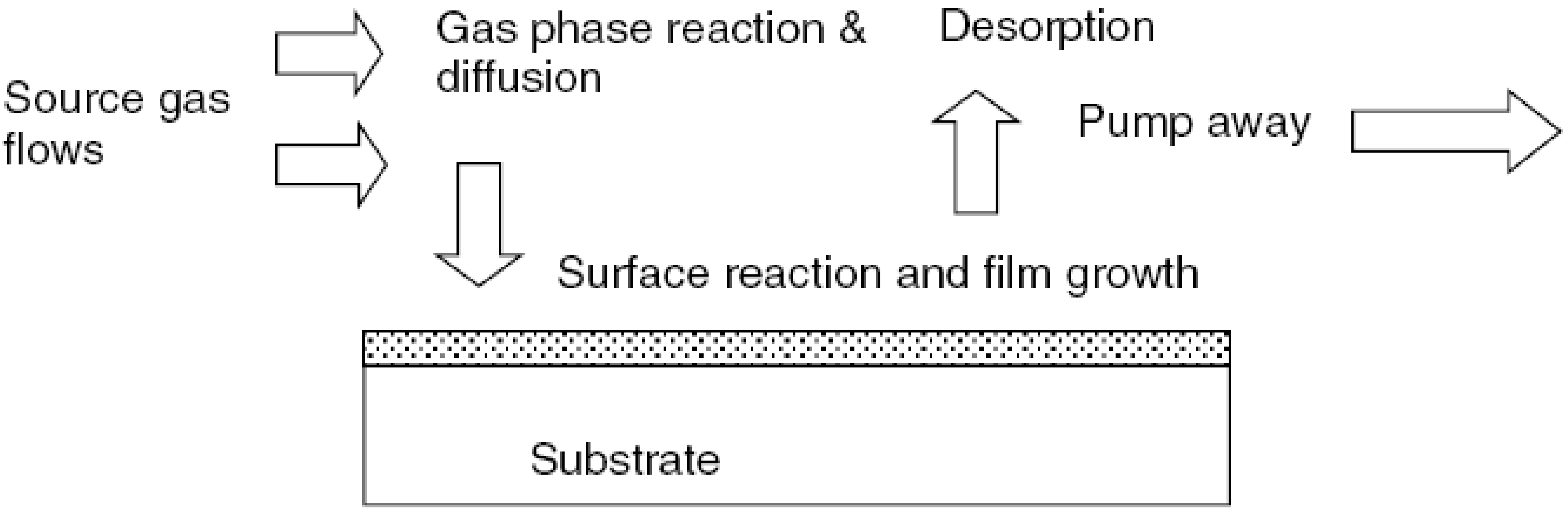
thin film structure

3059 J. Vac. Sci. Technol. A 4 (6), Nov/Dec 1986

PVD: Physical Vapor Deposition



CVD: Chemical Vapor Deposition



Deposition viewpoint: PVD

PVD activation methods:

• open resistive heating	→	evaporation (thermal)
• electron beam heating	→	evaporation (e-beam)
• equilibrium source heating	→	molecular beam epitaxy MBE
• argon ion bombardment	→	sputtering
• arc discharge	→	evaporation+ionization
• laser beam bombardment	→	ablation

Sputtering variables
Deposition of "optimal" AlN

Power supply	Power (kW)	Pressure (mTorr)	N_2 (%)	*d* (mm)	Temp. (°C)	Base P (Torr)	fwhm (°)
dc	2-6	1-5	100	?	500	1×10^{-8}	2-3
rf	1.0	3.4	33	50	315	1×10^{-8}	1
dc	?	2.7	?	?	?	3×10^{-9}	?
dc	0.2	1	100	40	200	?	2.3
rf	0.4	5	50	50	100	1×10^{-8}	3.3
rf	0.3	30	100	75	350	?	?
dc	0.1	6	100	35	250	8×10^{-6}	11
rf	0.2	3	50	40	50	?	2.5

Journal of The Electrochemical Society, **146** (2) 691-696 (1999)

Deposition viewpoint: CVD

- thermal CVD
- PECVD (a.k.a. PACVD) plasma enhanced
- MOCVD (metal organic)
- HDP-CVD (High Density Plasma)
- HW-CVD (Hot Wire)
- Photo-CVD
- LACVD (Laser Assisted)
- remote-PECVD
- low frequency (55 kHz; 400 kHz)
- µw-CVD (microwave)

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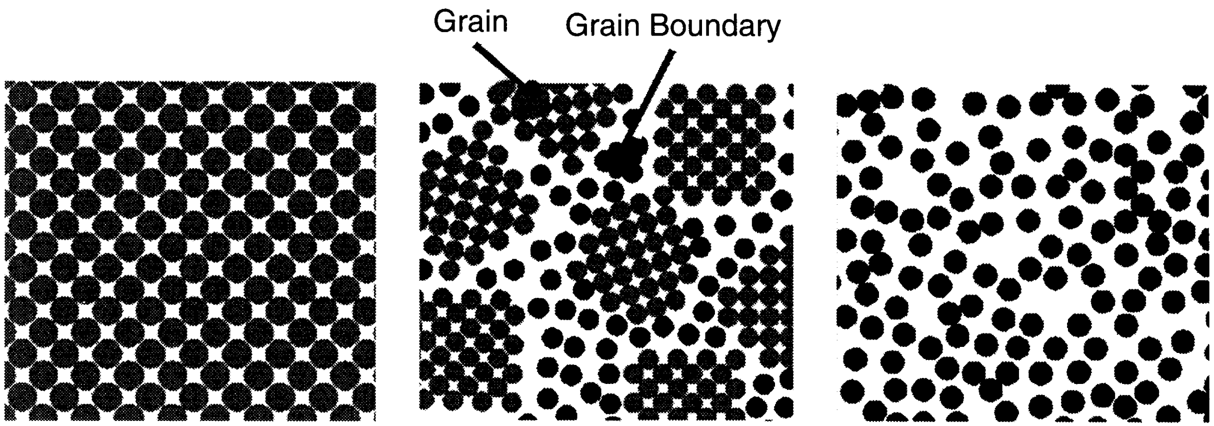
Film viewpoint

- amorphous
- nanocrystalline
- microcrystalline
- polycrystalline
- epitaxial
- textured



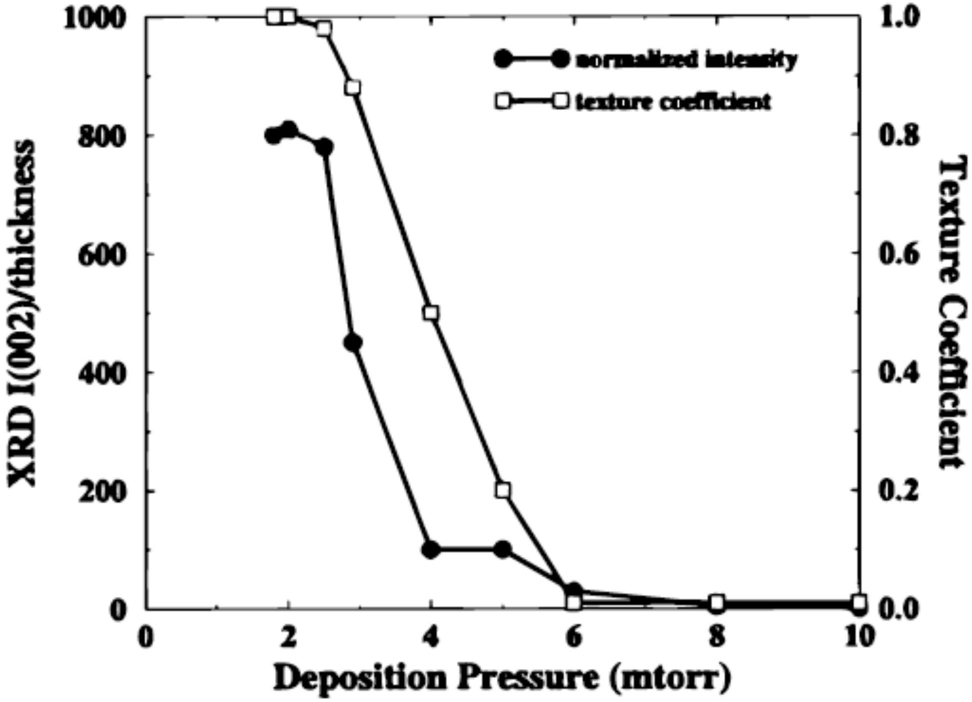
(a) Crystalline (b) Polycrystalline (c) Amorphous

Allen: MEMS

Texture coefficient TC

$$TC = \frac{I_{(002)}}{\sum I_{(hkl)}}$$

where $I_{(002)}$ is the XRD intensity of the (002) orientation and $I_{(hkl)}$ is the XRD intensity of the (*hkl*) orientation.



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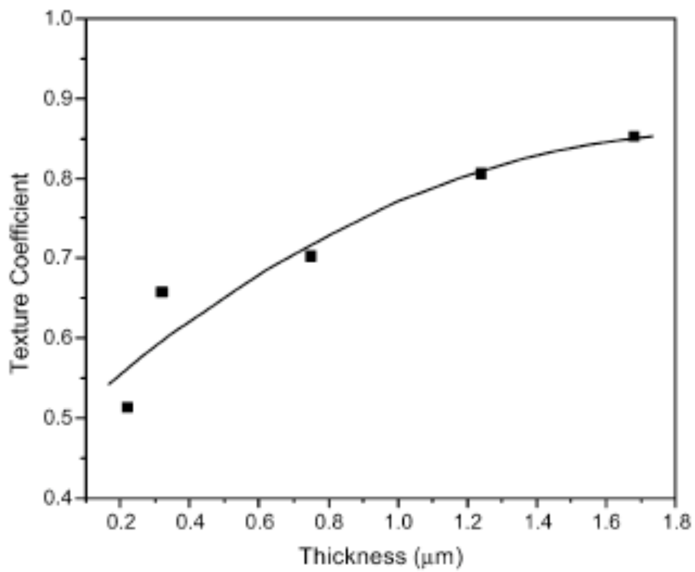
Film thickness and texture, TiN



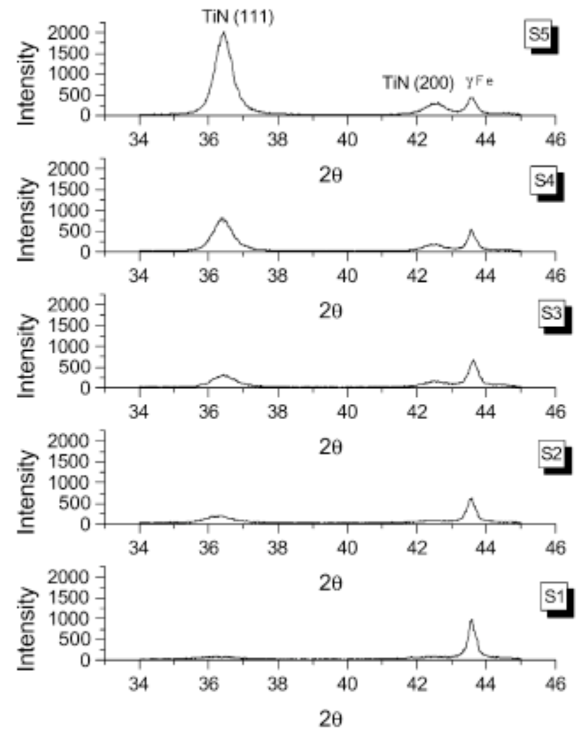


Fig. 5. The results of XRD, scanning from 2? = 34° to 45° with different thickness.

Specimen no.	Thickness μm
S1	0.22
S2	0.32
S3	0.75
S4	1.24
S5	1.68

W.-J. Chou et al. / Surface and Coatings Technology 149 (2002) 7–13

AlN structure

first experiment

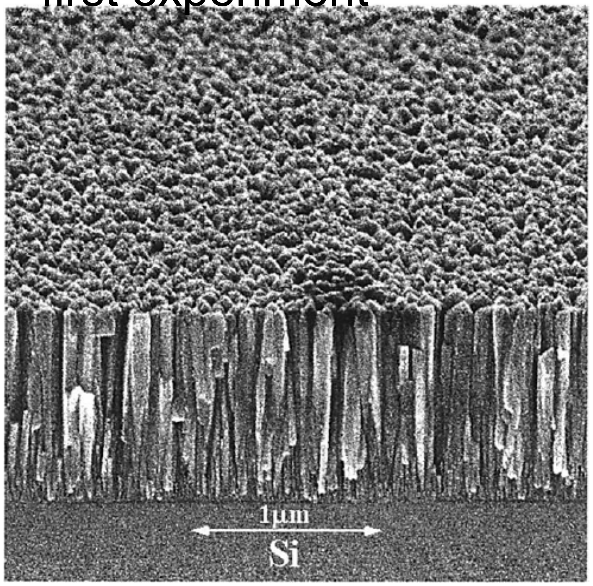
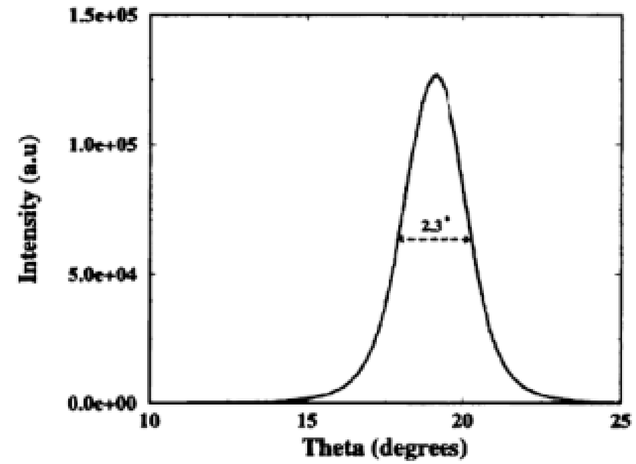


Figure 5. Cross-sectional SEM of initial AlN films on Si.



optimized

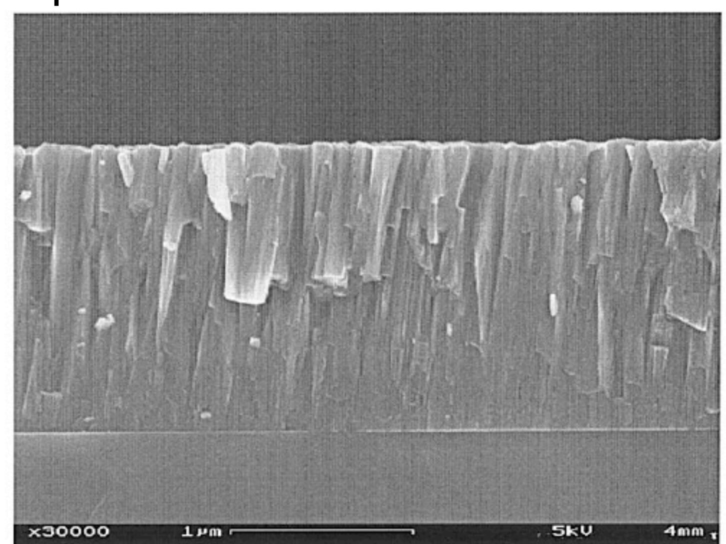
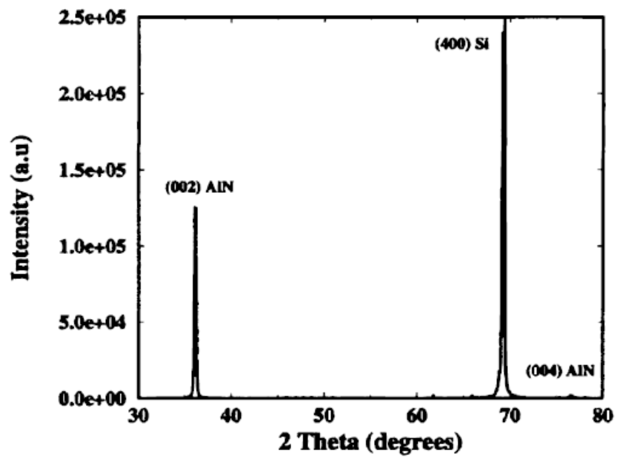


Figure 9. SEM cross section of an AlN film on Si deposited after the process and hardware modifications.



Journal of The Electrochemical Society, **146** (2) 691-696 (1999)

Film viewpoint cont'd

- stoichiometric
- hydrogenated
- porous/dense
- reacted
- doped

metals, oxides: 1-5% dopant

polysilicon: $10^{-3}...10^{-6}$ dopant

Doped oxides
SiO_xF_y

	FTMS	FTES	$TEOS/O_3$
Deposition rate (nm/min)	31	22	–
Fluorine concentration[a] ($\times 10^{21}$ atoms/cm^3)	5.4	5.3	–
Carbon concentration[a] ($\times 10^{21}$ atoms/cm^3)	1.1	2.0	–
Refractive index	1.390	1.403	1.451
Etching rate (nm/min) (1:30 buffered HF)	202	215	120
Si–O peak position (cm^{-1}) (FTIR spectra)	1083	1083	1075

[a] At the depth of 0.2 μm.

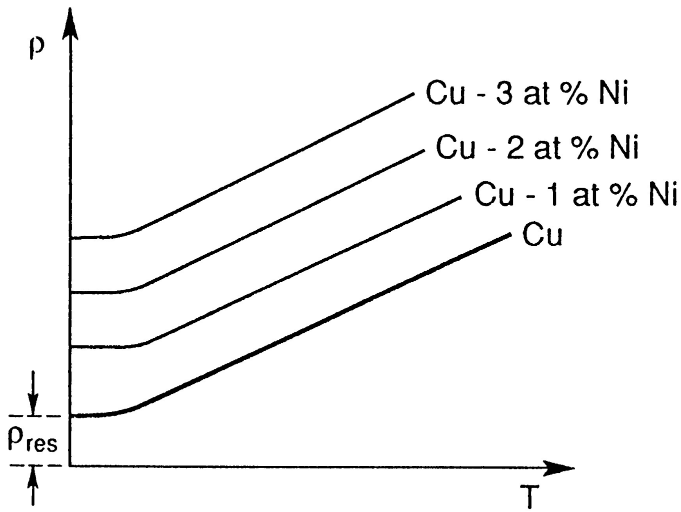
FTES fluorotriethoxysilane
FTMS fluorotrimethoxysilane
TEOS tetraethyl orthosilicate

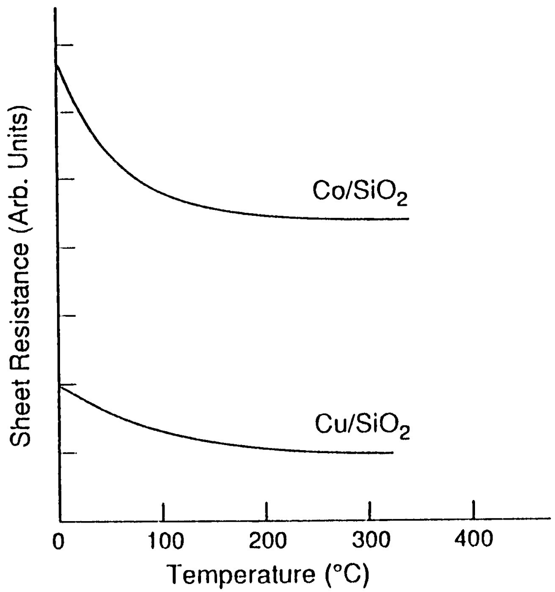
T. Homma / Materials Science and Engineering R23 (1998) 243–285

Film viewpoint cont'd

- low resistivity
- low impurity concentration
- low stress
- free of moisture absorption
- small surface roughness
- low shrinkage
- good step coverage

Resistivity





$\rho = \rho_{residual} + \rho_{temp}$

Linear TCR above Debye temperature (typically 200-400K)

Annealing defects at elevated temperature lowers resistance (no reaction with underlying film/substrate)

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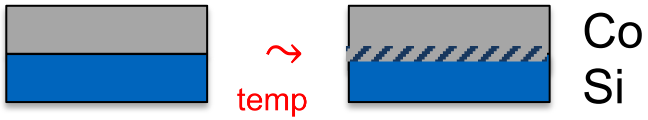
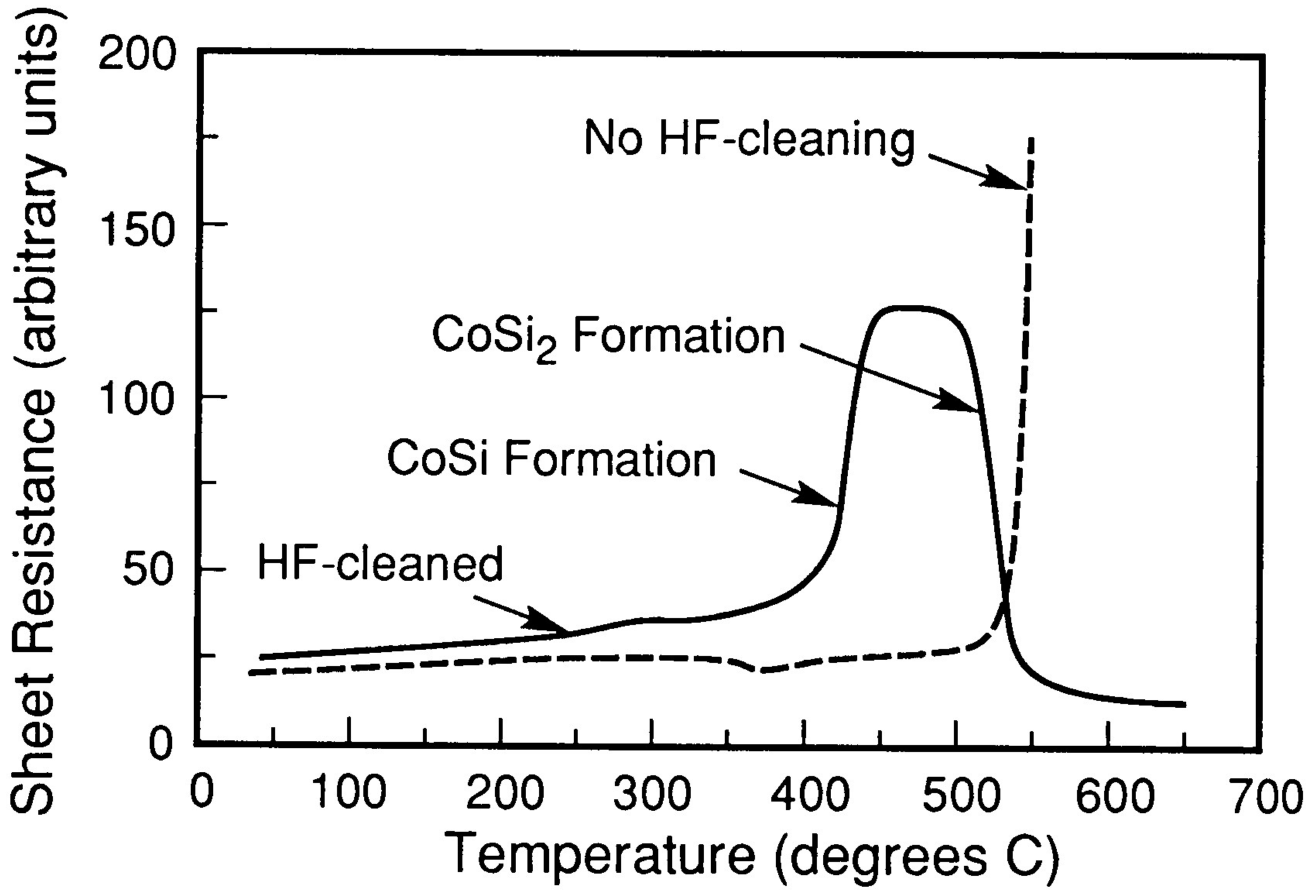
Thin film reaction: Co+Si





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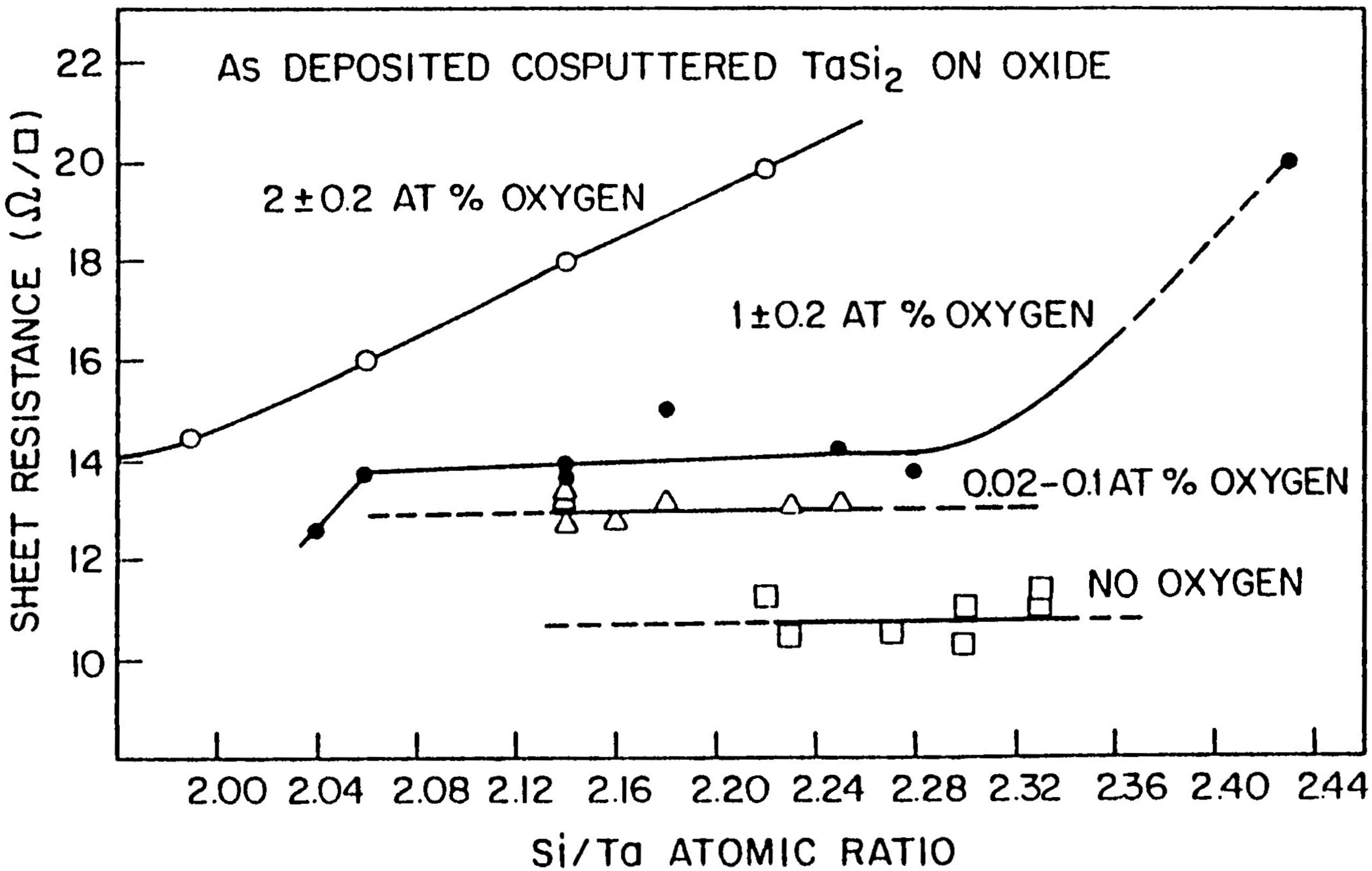
Resistivity: impurity effects



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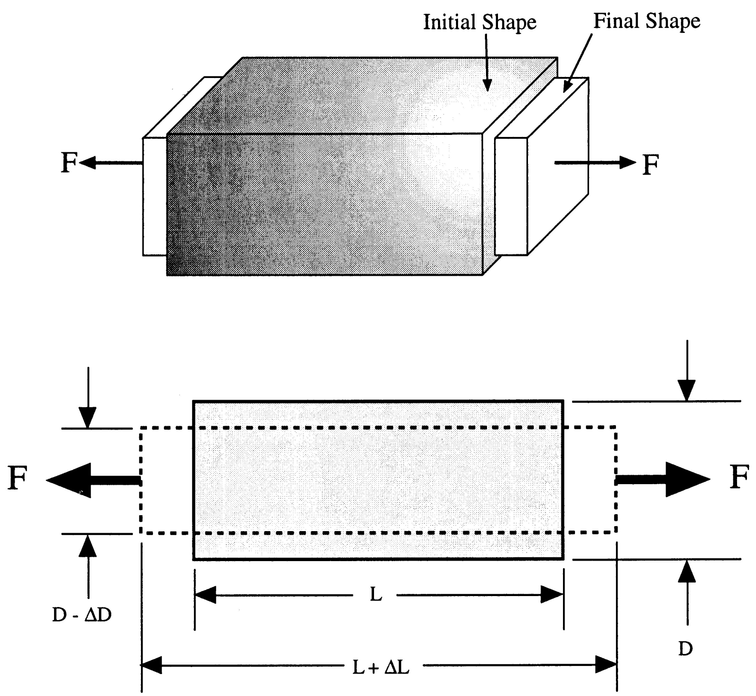
Stress and Poisson ratio



Stress $\sigma = F/A$

longitudinal strain $\varepsilon = \Delta L/L$

transverse strain $\varepsilon_t = \Delta D/D$

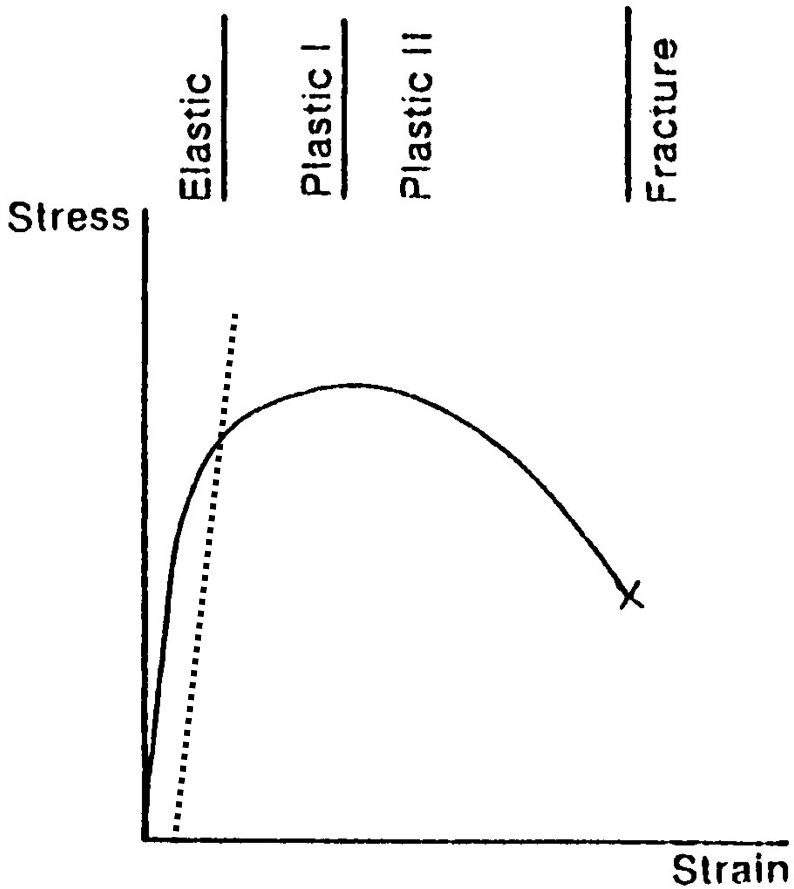
Young's modulus $E = \sigma/\varepsilon$

Poisson ratio $\nu = - \varepsilon_t / \varepsilon$

For many metals $\nu \approx 0.3$

Kovacs

Stress and strain



0.2%

Elastic/Linear region, Hooke's law valid: $\sigma = \varepsilon E$

Plastic I: permanent deformation

Yield strength: 0.2% shifted curve intersects stress-strain curve

Maximum stress = tensile stress

Plastic II: necking occurs

Toughness = area below stress-strain curve = energy absorbed

Hardness: resistance to plastic deformation

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Terminology 1

- Ductile materials (many metals) will bend before breaking. Tensile stress is greater than yield stress.
- Brittle materials (like silicon) will break suddenly and without warning. Tensile stress is roughly the same as yield stress

Sources of stress: $\sigma = \sigma_i + \sigma_{th}$

- intrinsic:
  - film microstructure (grain size, orientation)
  - defects and impurities in film
  - volume changes
  - lattice mismatch (important in epitaxy)
- thermal mismatch:

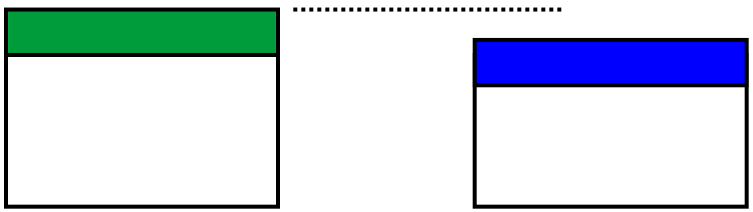
$$\sigma = E_f/(1-\nu) \times (\alpha_f - \alpha_s) \times \Delta T$$

Volume changes

$$xM + ySi \rightarrow M_xSi_y,$$

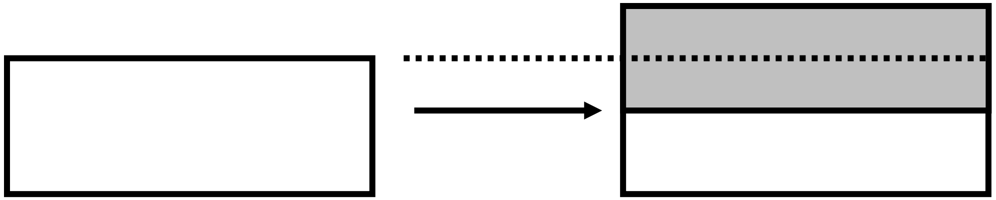
the volume change $\triangle V$ (%) is given by

$$\triangle V = \frac{(xV_M + yV_{Si}) - V(M_xSi_y)}{(xV_M + yV_{Si})} \times 100,$$

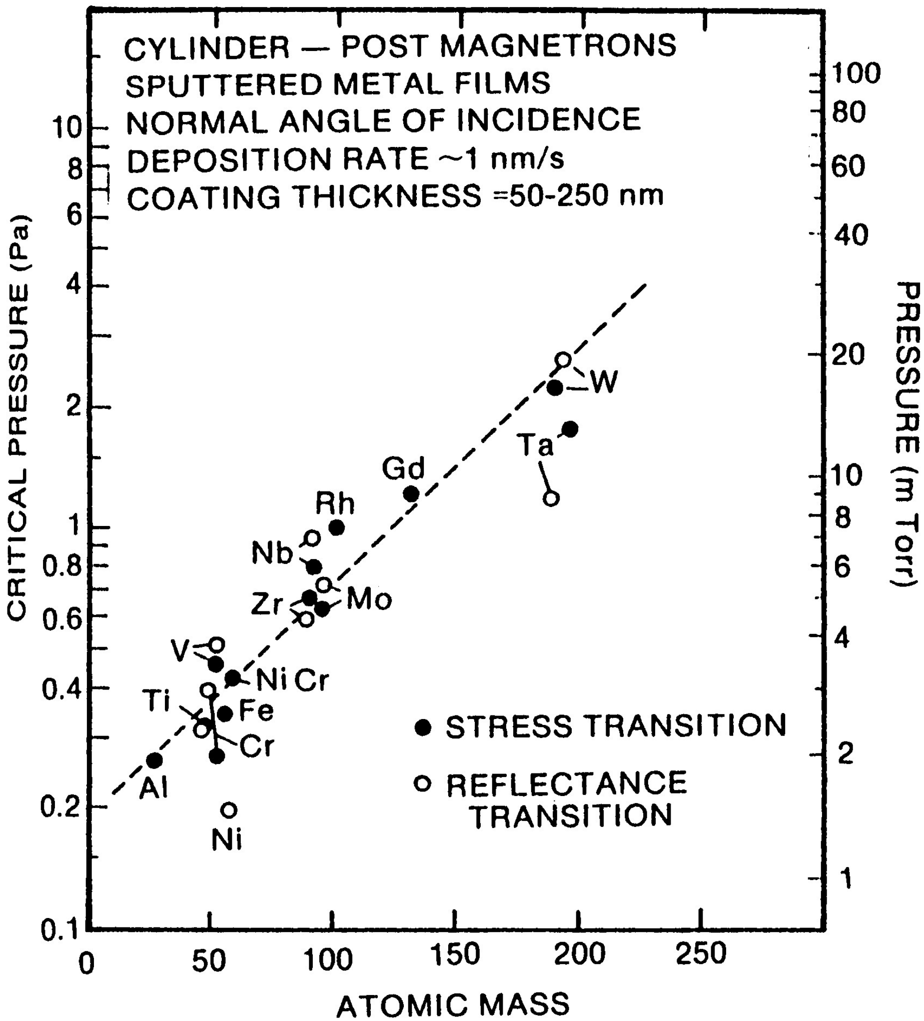


In silicide formation, negative volume change ➔ tensile stress

In thermal oxidation, positive volume change ➔ compressive stress



Sputtering pressure affects stress



At low pressures sputtered films are compressively stressed;

above critical pressure, tensile stressed

At low pressure there is large momentum transfer resulting in energetic argon atoms that will densify the film by knock-on (peening) or get implanted in the film

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Mechanical and tribological properties

Table 1
Mechanical and tribological properties of commercially available hard coatings.

	TiN	TiCN	TiC	TiAlN	CrN	Al_2O_3
Deposition method	PVD/CVD	PVD/CVD	CVD	PVD	PVD/CVD	CVD/PVD
Typical thickness (μm)	1–5	1–5	1–5	1–5	1–15	1–5
Hardness (HV 0.05)[a]	2300	3000	3100	3000	1900	2100 (HV 0.1)
Oxidation temperature (°C)[b]	> 450	> 350	> 350	> 700	> 600	
Friction coefficient[c]	0.5–0.7	0.5–0.7	0.5–0.7	0.6–0.8	0.5–0.8	0.7–0.9
Abrasive wear resistance	+ +	+ + +	+ + +	+ + +	+ +	+ +
Adhesive wear resistance against steel	+ +	+ / + +	+	+ +	+ +	+ + +
Resistance against wear by diffusion	+ +	+	+	+ + +	+ +	+ + +
Corrosion protection of base material[d]	+	+	+	+	+ +	+

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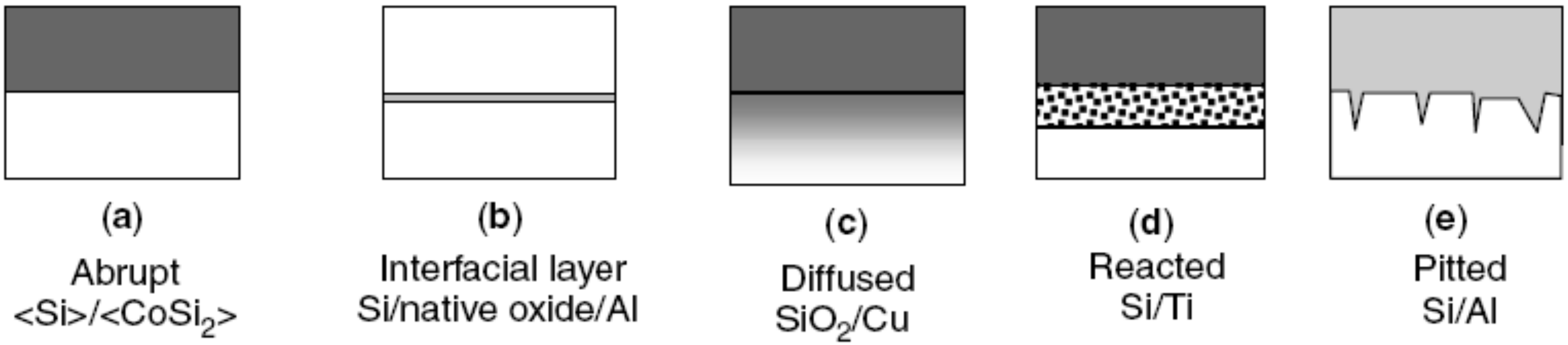
Mechanical and tribological properties cont'd

Table 2
Mechanical and tribological properties of MoS_2, diamond, and different DLC films.

	MoS_2	Me-DLC	DLC	Si-DLC	ta-C	Diamond
Deposition method	PVD	PVD	PECVD	PECVD	PVD	CVD
Thickness (μm)	0.1–1	1–5	1–5	1–5	1–3	3–10
Hardness (HV 0.05)[a]	< 500	800–1 800	1 500–3 500	600–1 000	3 000–7 000	10000
Typical values for compressive stress (GPa)		0.1–1	1–3	1	2–6	
Temperature of transformation (°C)[b]	350	350	400	500	450	> 600
Friction coefficient[c]	0.02–0.1	< 0.2	0.15–0.2	0.07–0.15	0.15–0.2	< 0.2
Abrasive wear resistance		+	+ + +	+	+ + + +	+ + + +
Adhesive wear resistance against steel		+ +	+ + +	+ +	+ + +	(+ + +) only with good cooling
Corrosion protection of base material[d]		+	+ + +	+ + +	+ + +	+ + +

Interfaces


(a)
Abrupt
<Si>/<$CoSi_2$>
(b)
Interfacial layer
Si/native oxide/Al
(c)
Diffused
SiO_2/Cu
(d)
Reacted
Si/Ti
(e)
Pitted
Si/Al