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Multilayers and interfaces

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Why multilayers ?

More functionality and performance

Single layer ARC vs. $\lambda/4$ filter

Grain size and orientation are affected by underlayer

More reliability

If aluminum broken because of electromigration, but TiN conducts still

Adhesion layers & barriers

SiO_x/SiN_x passivation: films complement each other

More process robustness

Etch stop layer, no timed etching needed

TiN on Al reduces reflectivity and eases lithography

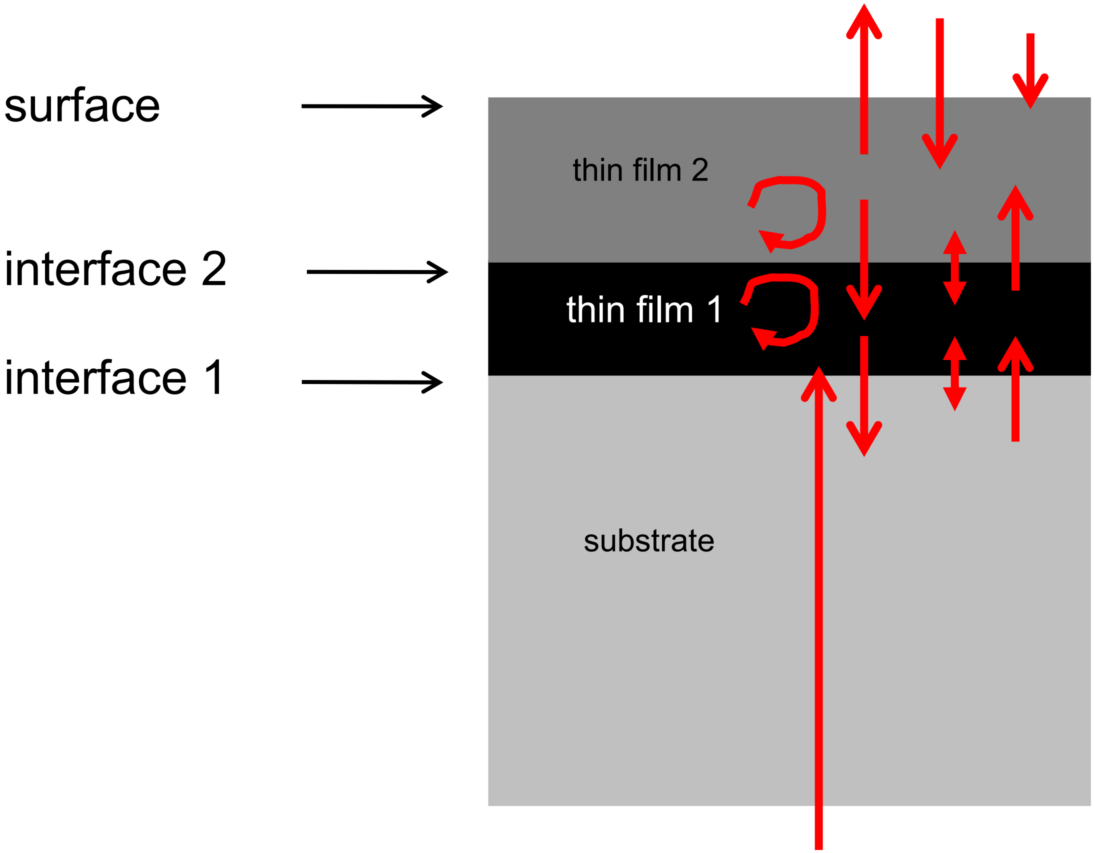
Why not multilayers ?

More complex deposition equipment needed
e.g. Multiple targets, multiple chambers

Deposition thruput compromised
esp. if thickness or nature of films very different

Each new interface is a potential problem

This lecture deals with phenomena during processing



surface

interface 2

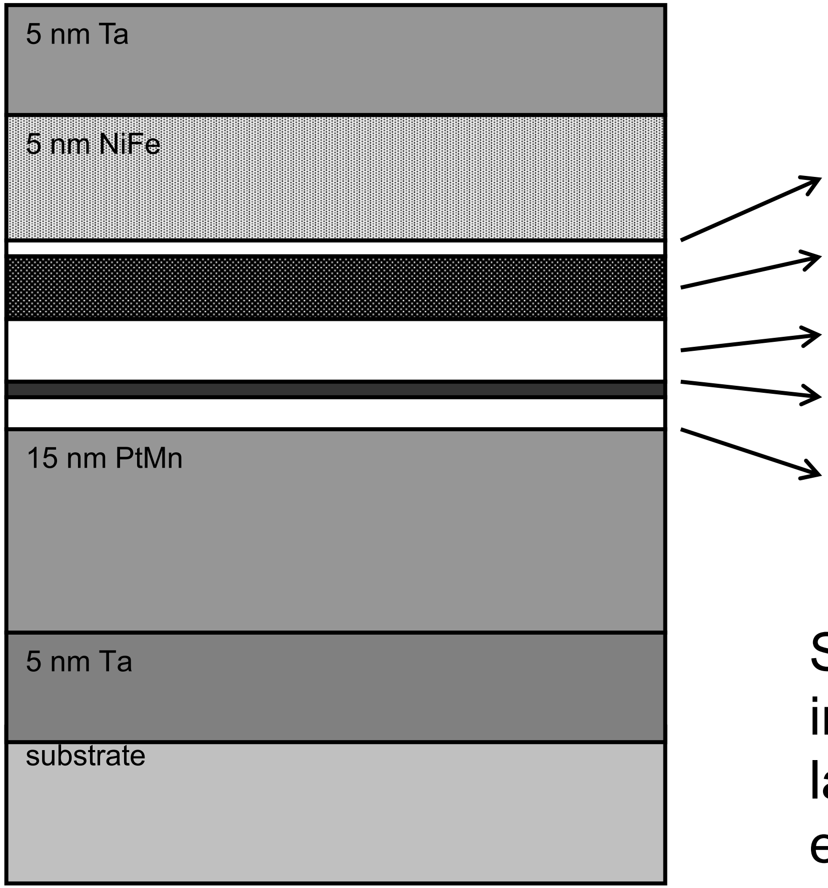
interface 1

thin film 2

thin film 1

substrate

Magnetic multilayers



1 nm CoFe

2.6 nm Cu

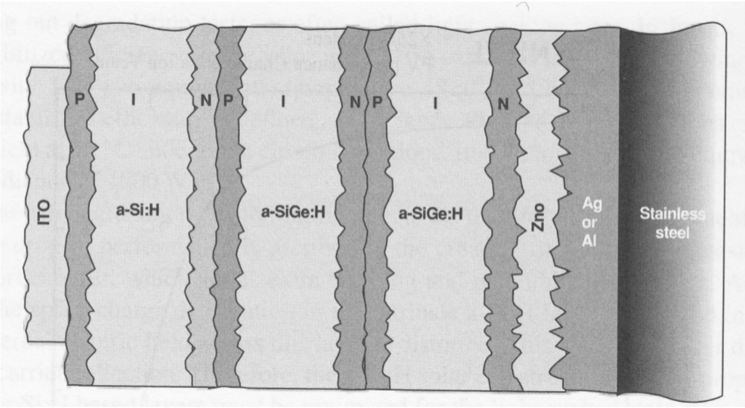
2.5 nm CoFe

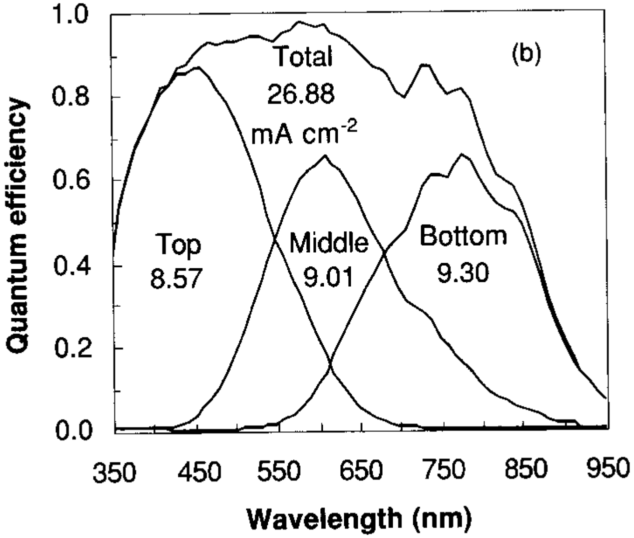
0.8 nm Ru

2 nm CoFe

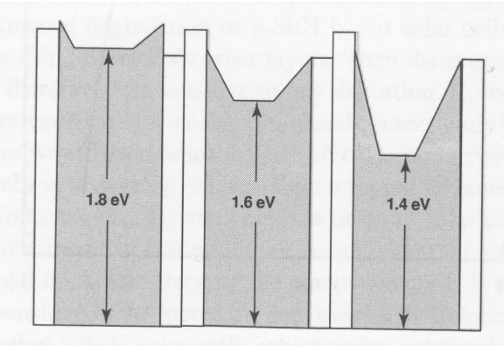
Surface roughness must not increase with each successive layer !! Otherwise deposition of extremely thin films becomes impossible.

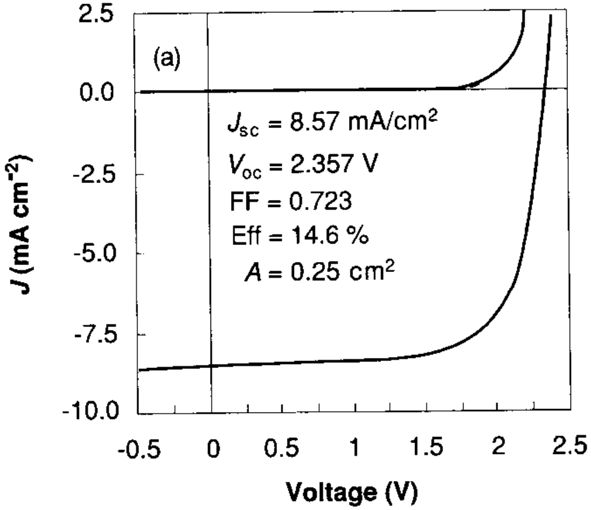
Multiple junction solar cell





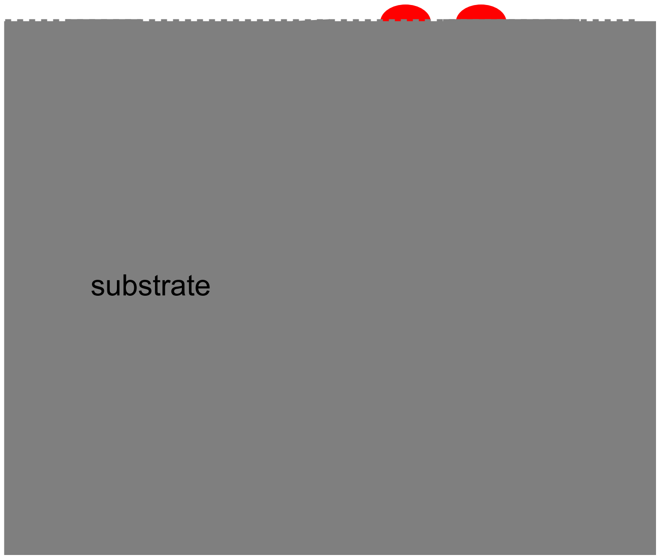
Si:Ge ratio modifies bandgap





Poortmans: Thin Film Solar Cells, p. 214

Substrate surface



Adsorbed water

Carbon & other impurities

Particles

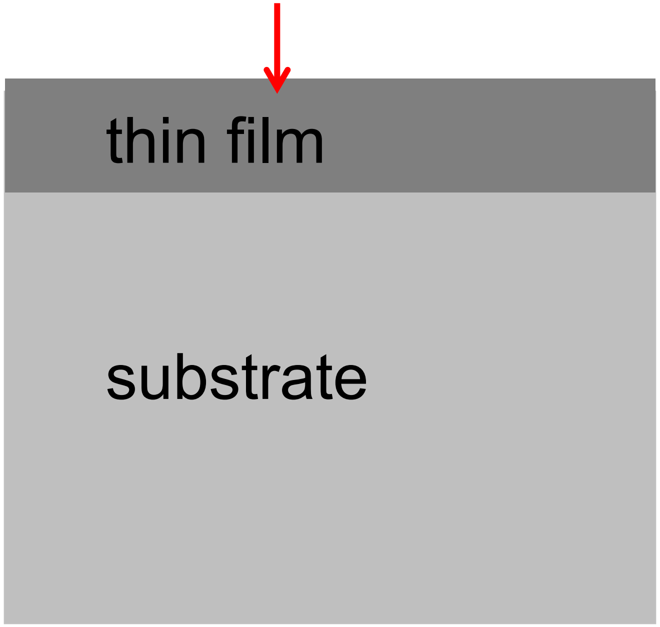
Roughness

Crystal structure

Crystalline defects

Dangling bonds

Surface reactions

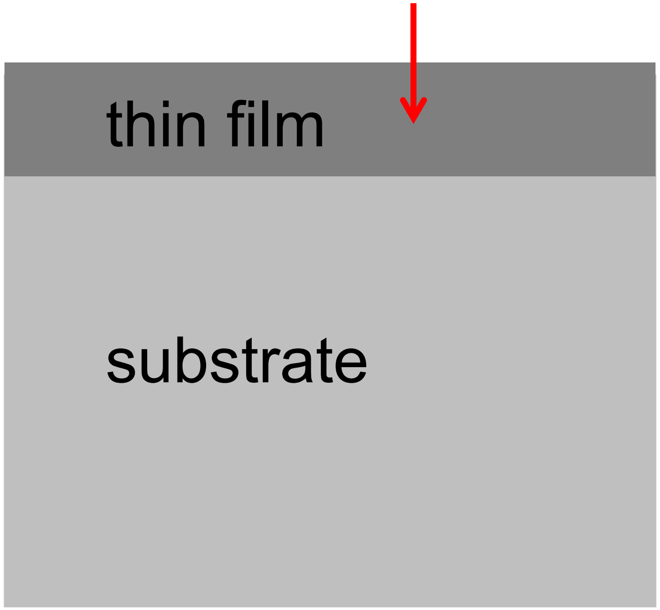


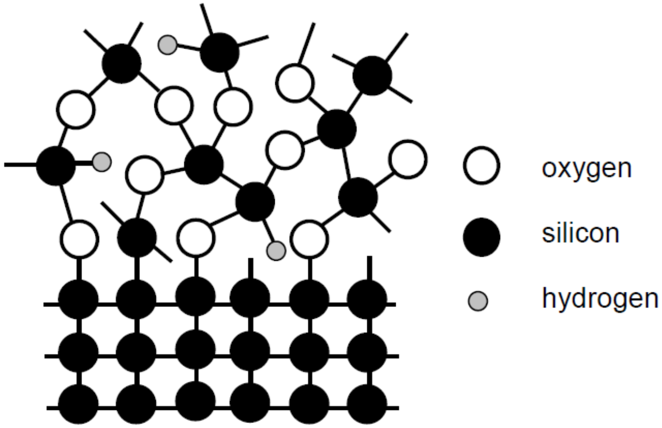
Native oxide formation e.g.
Si, Ti, Cu, Cr

But CrO is conductive, others insulators.

Nitridation:
difficult, needs either
    -ammonia exposure
    -high temperature
TiN formation is an exception

Ambient gases into film





Oxygen:
stoichiometry finetuning: Ta_2O_5

Water:
-into pores
-into PSG (hygroscopic film)

Nitrogen:
Grain boundary stuffing,
TiW:N, W:N

Hydrogen (N_2:H_2 in practice)
Dangling bond passivation

PSG

CVD oxides have unfortunately many names:

USG = undoped silica glass (=CVD SiOx, x ≈2)

PSG = phosphorous doped silica glass (=CVD oxide, which had P2O5 flow during deposition ➔ phosphorous incorporated into film)

PSG typical: 5 wt% phosphorous
excellent gettering agent for Na+ ions
hygroscopic if too much P
Note: in metals and oxides: 1-5% dopant/alloying element
in semiconducotrs parts per million (10^{-6}) dopant

Interfaces

(a) Abrupt $\langle Si\rangle/\langle CoSi_2\rangle$

(b) Interfacial layer Si/native oxide/Al

(c) Diffused SiO_2/Cu

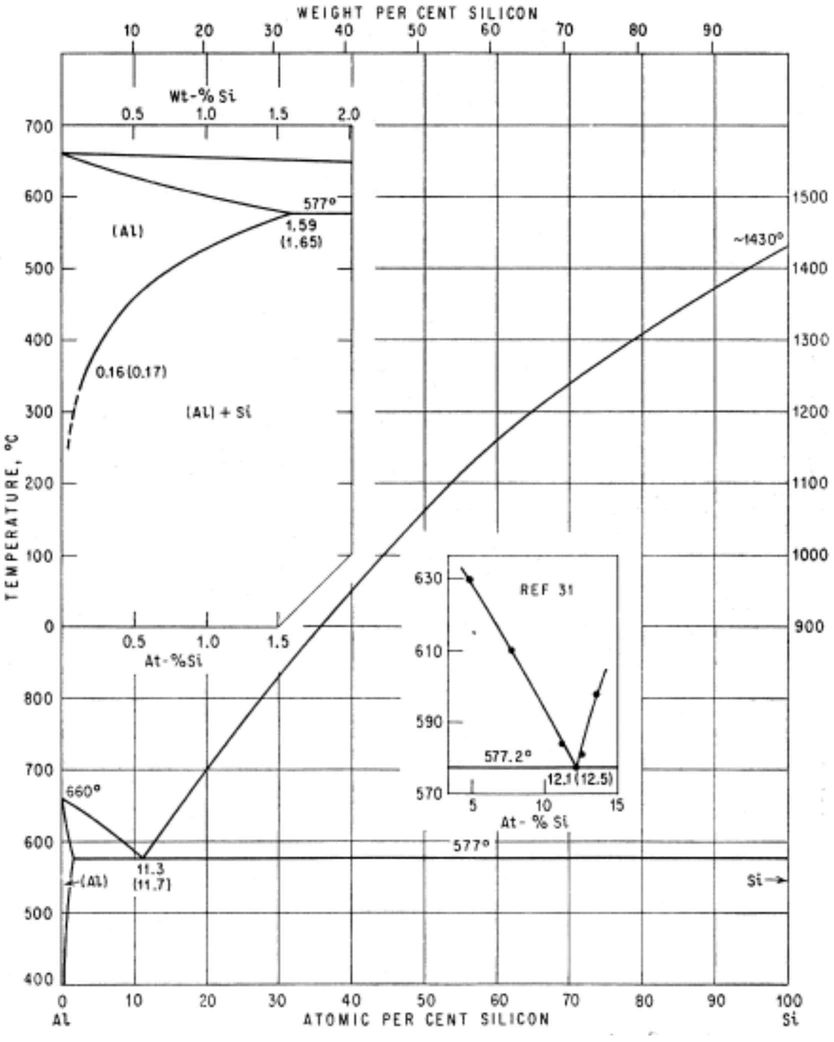
(d) Reacted Si/Ti

(e) Pitted Si/Al

Stability of interface in subsequent processing and during use ?

Barrier layers: extra films to stabilize interfaces

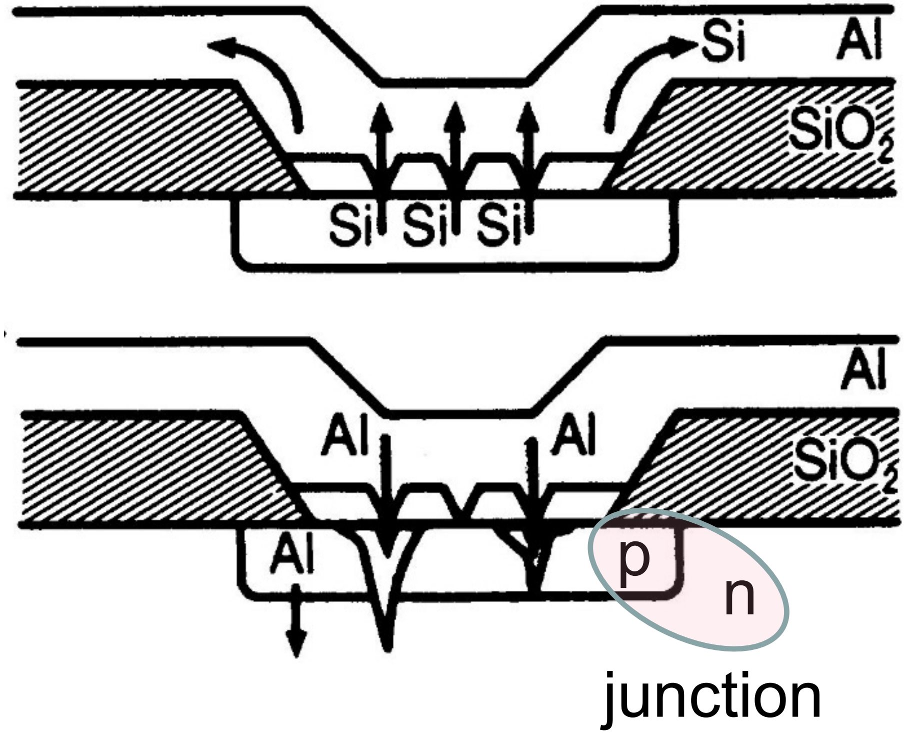
Al-Si phase diagram



A little silicon is soluble in aluminum at 400^{o}C, ca. 0.3 at%

➔ Al to Si interface is unstable at 400^{o}C

Junction pitting



Silicon dissolves into aluminum

Aluminum diffuses into silicon via the vacancies left by removed silicon

If aluminum diffusion deep, it will extend to pn-junction

➔ No pn-junction anymore

Ohring

Interface stability: ΔG

Change in Gibbs free energy is given by:

$$\Delta G = G_{products} - G_{\mathrm{reactants}}$$

ΔG positive = stable pair; ΔG negative = films react

For reaction titanium reaction with silicon dioxide:

$Ti + SiO_2 \rightarrow TiO_2 + Si$

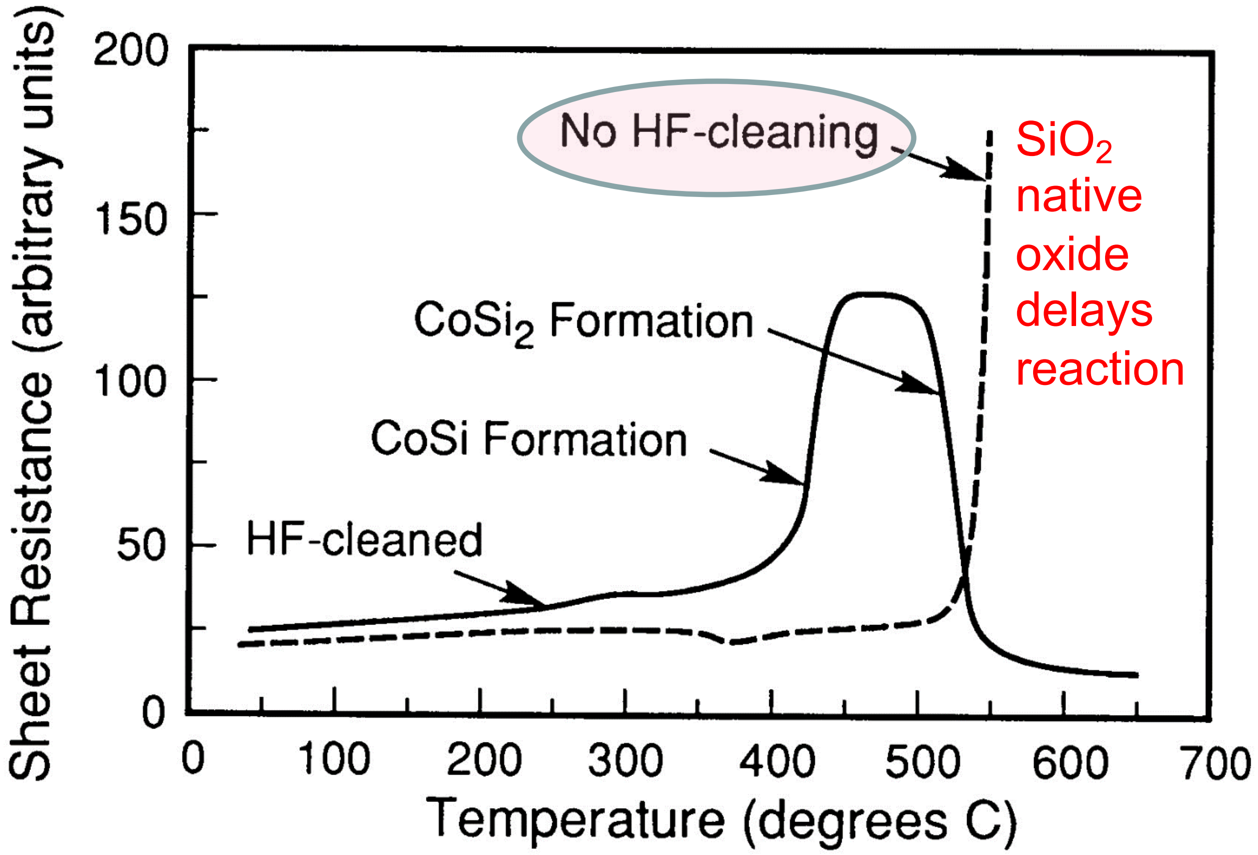
$\Delta G = G_{TiO2} - G_{SiO2}$ = (160 – 165) Kcal = -5 Kcal, indicative that the reaction can take place.

For $Co + SiO_2 \rightarrow CoSi_2 + Si$ $\Delta G > 0$, no reaction.

Reaction Co+Si

$Co + Si \rightarrow CoSi$

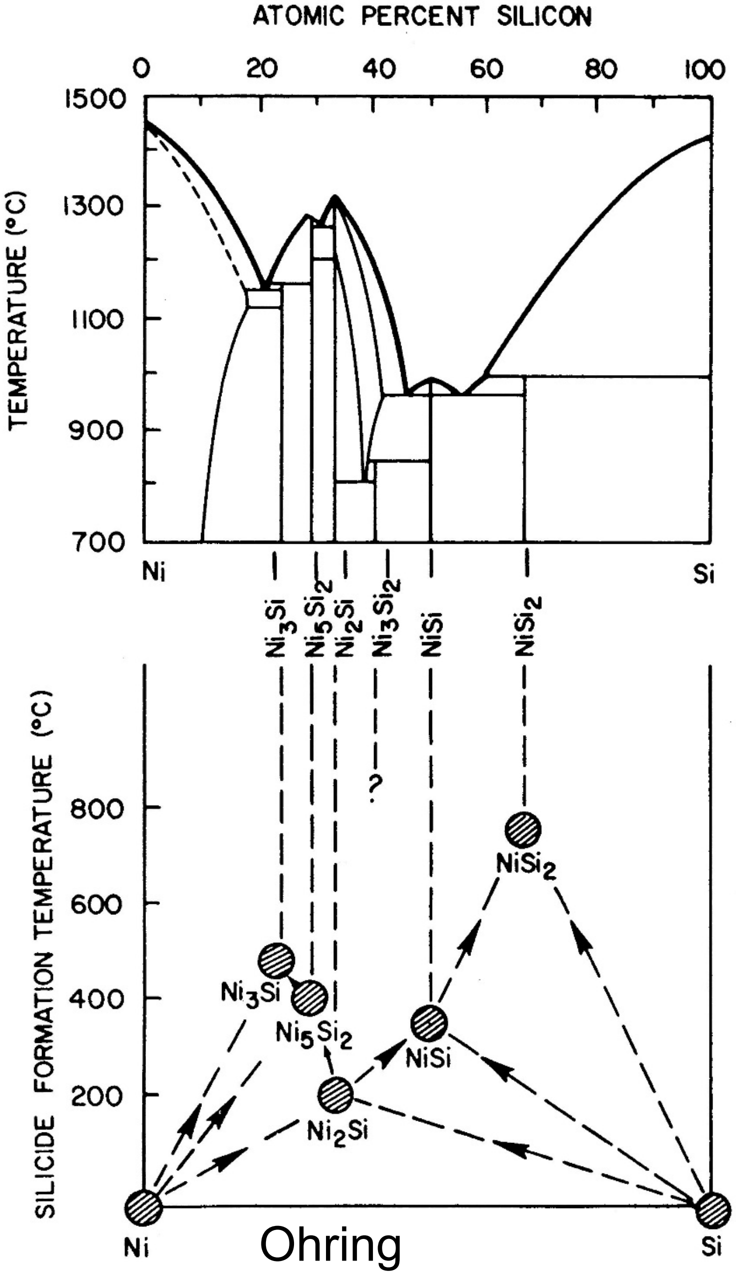
$CoSi + Si \rightarrow CoSi_2$ at higher temperature



At high enough temperature the native oxide breaks down, and Co+Si reaction can take place.

Murarka

Nickel silicide formation



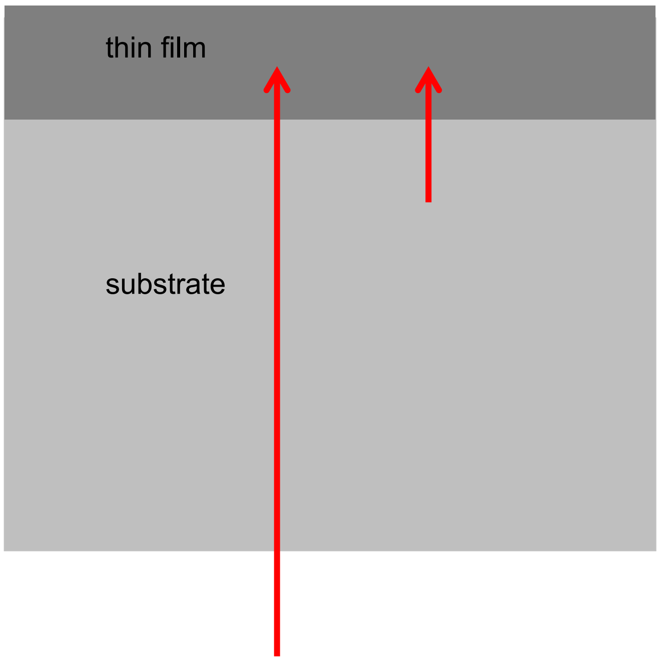
Ohring

It is not always the case that the silicide that will form is the technologically interesting one !

NiSi is the desired low resistivity material;

$NiSi_2$ is the stable phase that tends to form.

From substrate into film

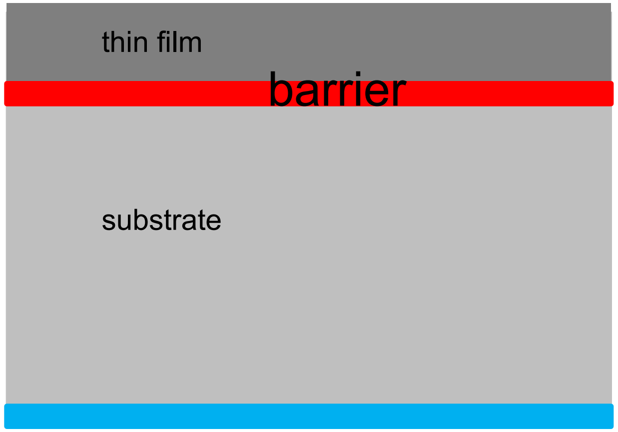


Steel substrates are a source of metals

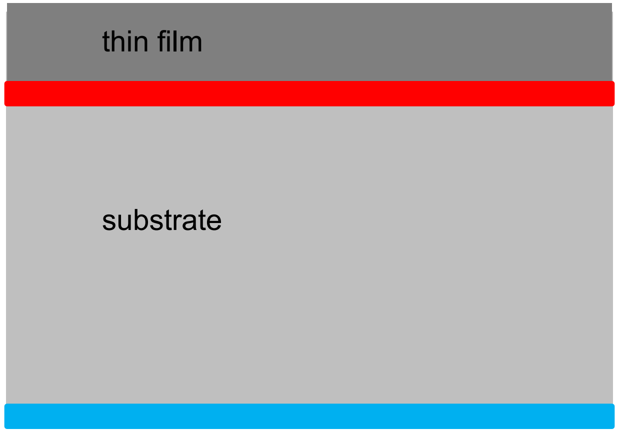
Glass substrates are sources of sodium

Polymer substrates are permeable to water vapor and oxygen

➔ Need barrier(s)



Barriers



Atom barrier: blocks atom movements.

Ion barrier: blocks ions.

Total barrier: no atoms, no electrons pass thru.

Barrier can simultaneously act as smoothing layer. This is important if e.g. stainless steel is used. Spin-on glasses !

Examples of barriers

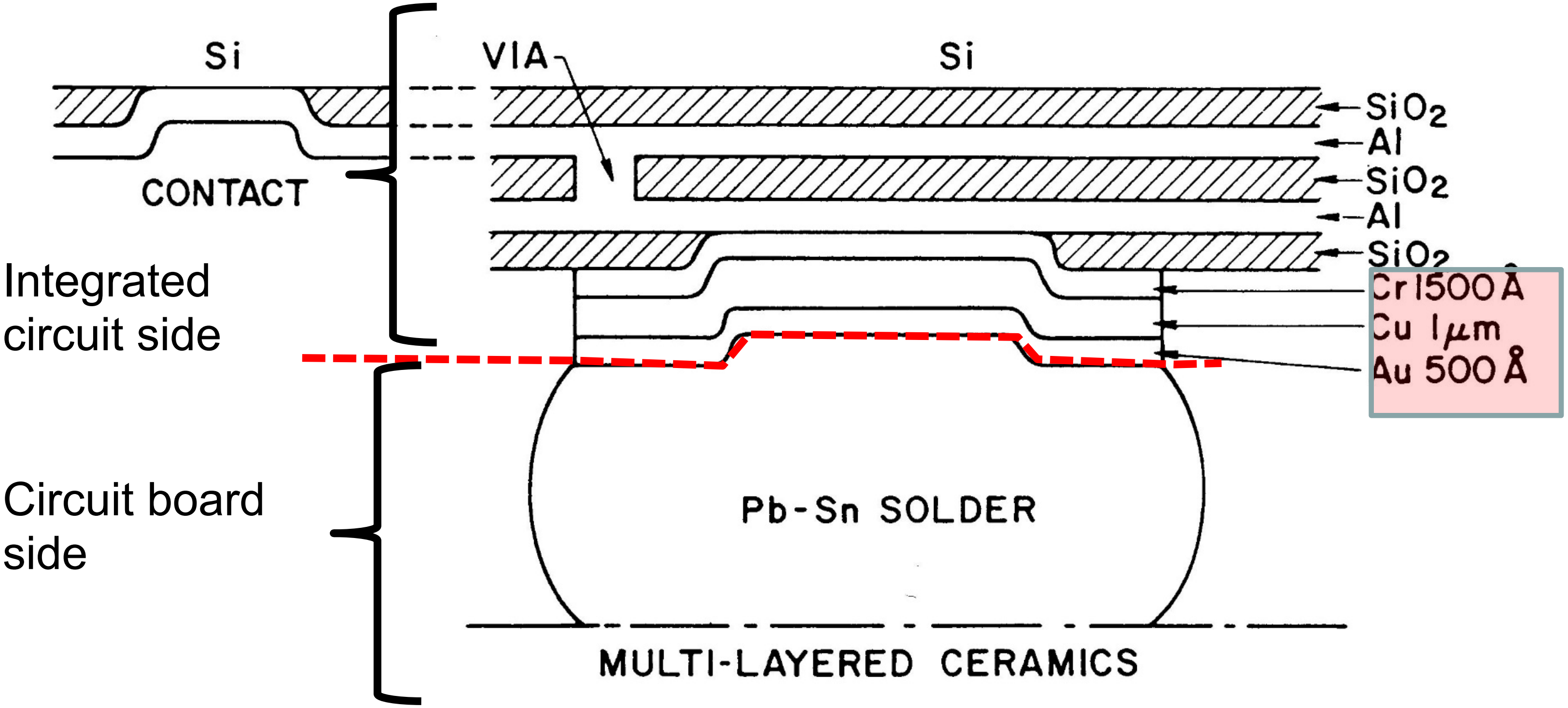
Diffusion barrier: <Si>/TiW/Al in IC metallization

Improved diffusion barrier, stuffing: <Si>/TiW:N/Al

Dielectric barrier: SiO_2/SiN_x/Cu

Ion barrier: glass/Al_2O_3/ZnS in electroluminescent displays

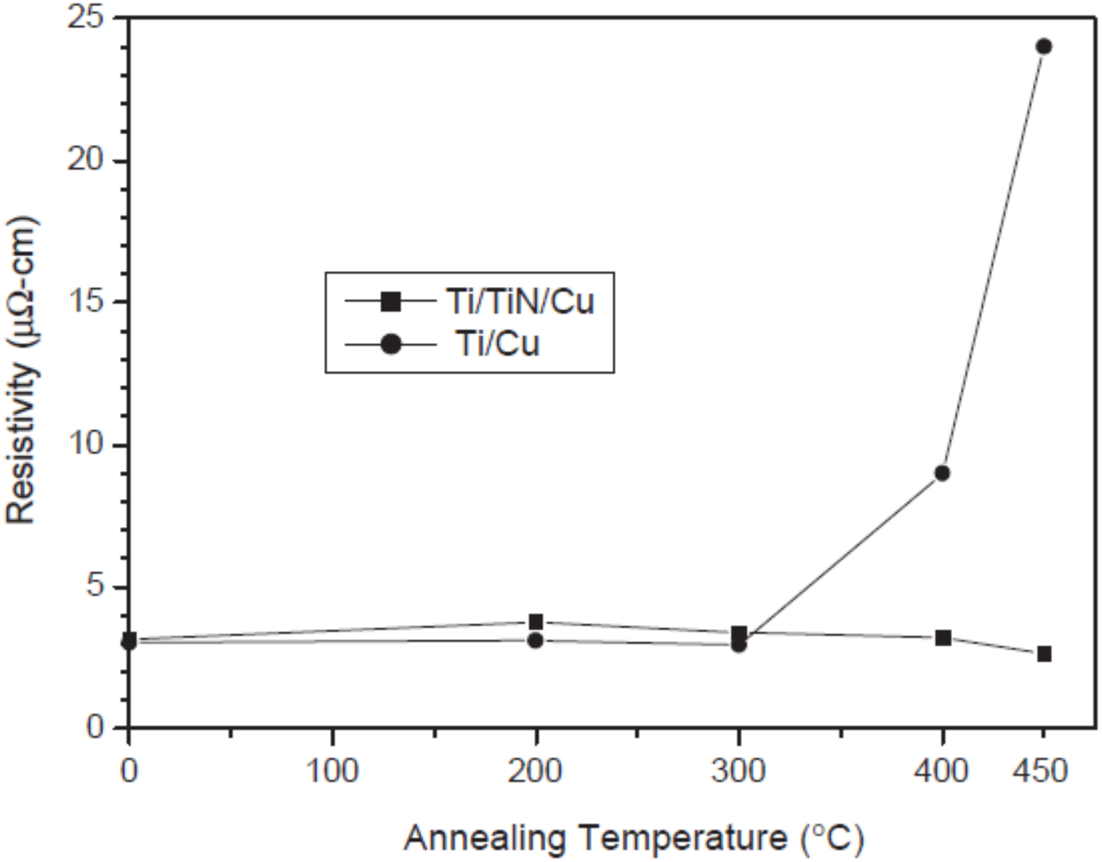
Solder joint

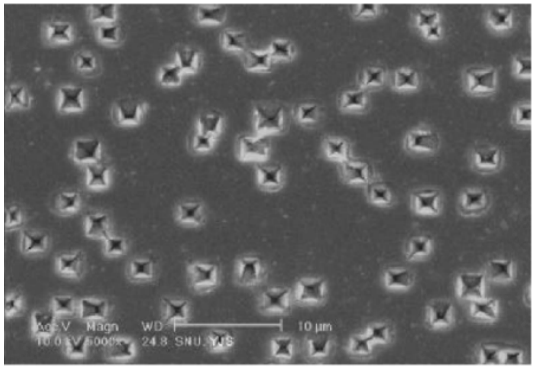


Pb-Sn will react with aluminum, therefore a barrier (Cr/Cu/Au) is needed.
The alternative strategy of lower temperature does not work because solder has to flow.

Ohring

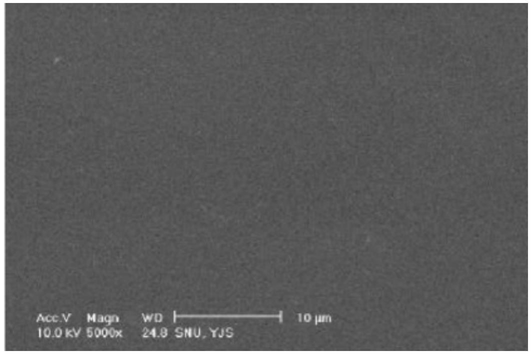
Stability of metallization





Ti barrier

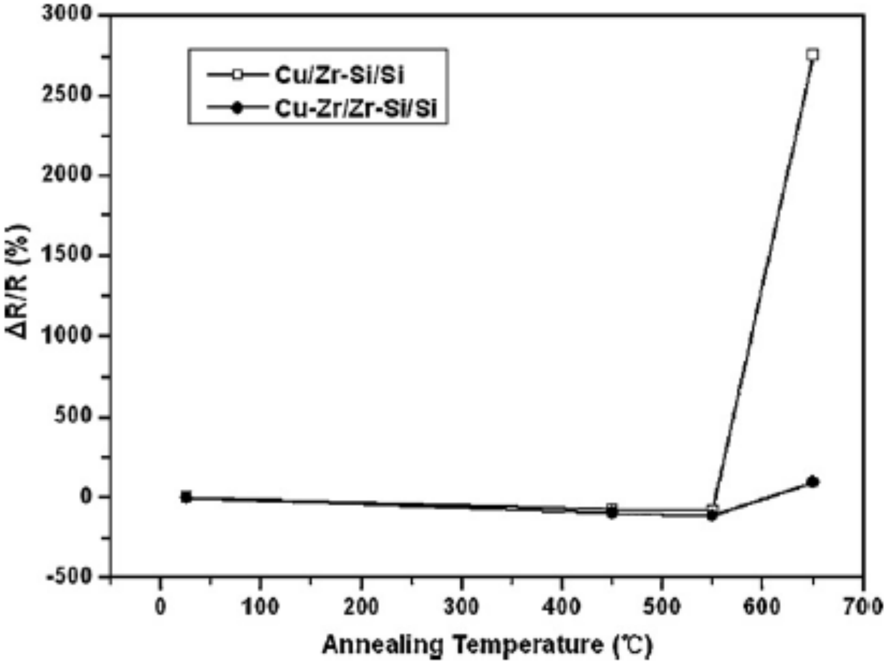
Ti/TiN barrier



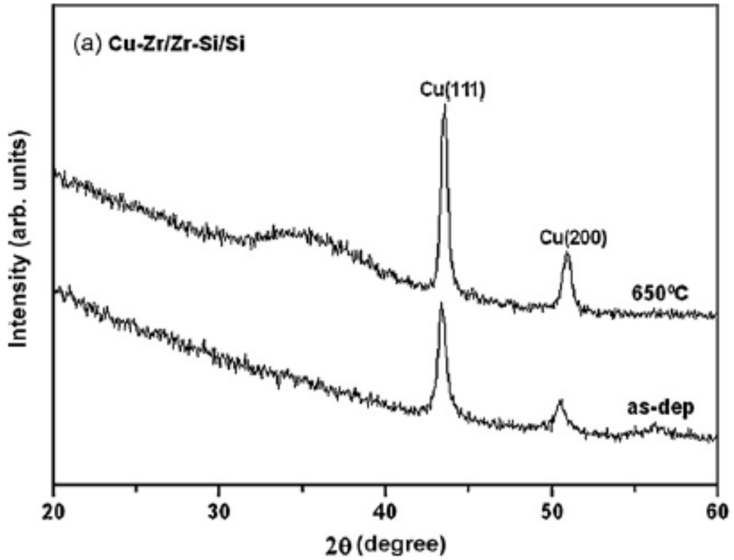
J. You et al. / Solar Energy Materials & Solar Cells 79 (2003) 339–345

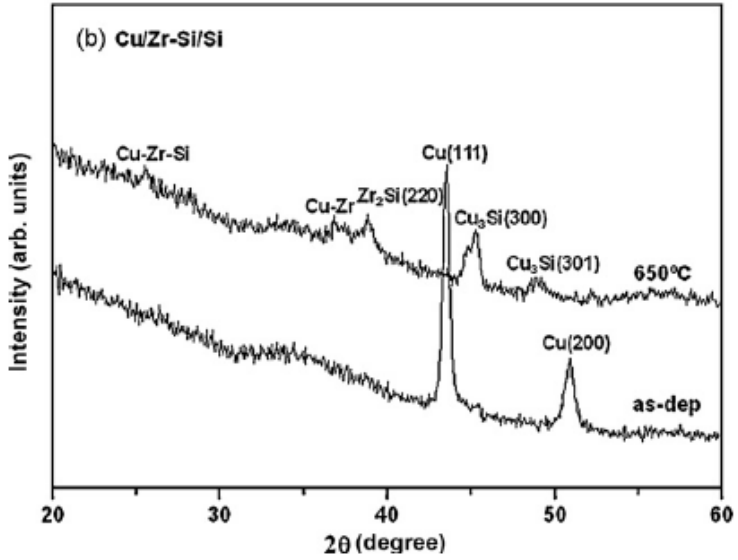
Alloying effect

Zirconium at grain boundaries acts as an extra barrier, preventing formation of high resistivity Cu_3Si

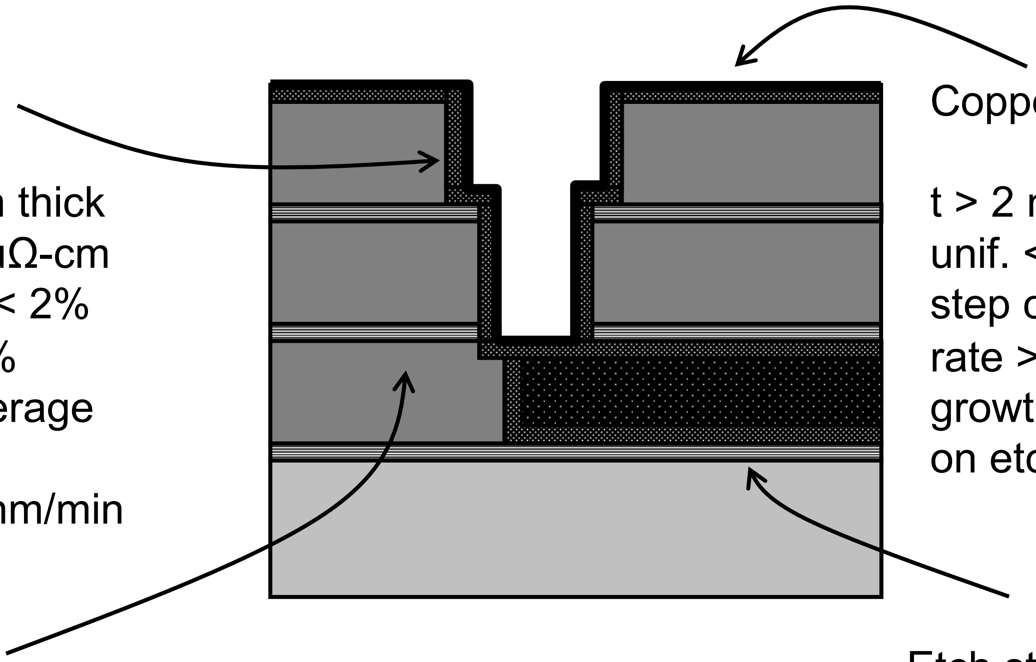


Y. Wang et al. / Journal of Alloys and Compounds 486 (2009) 418–422





Copper for IC metallization



Barrier:

t < 10 nm thick
ρ < 500 μΩ-cm
Cl conc. < 2%
unif. < 2%
step coverage >90%
rate > 3 nm/min

Copper seed

t > 2 nm
unif. < 2%
step coverage ~100%
rate > 10 nm/min
growth and adhesion on etch stopper

Low-k:

CMP compatible
$T_{depo} < 400^{o}C$
adhesion on etch stopper

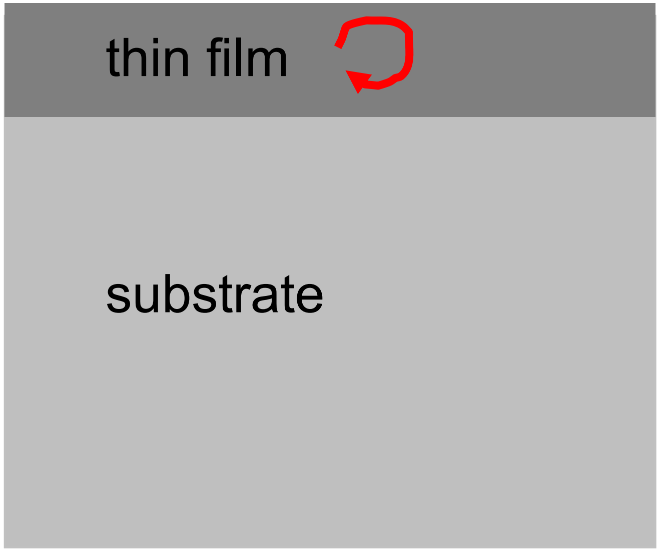
General:

low variation
low particle generation
large process window

Etch stopper:

growth and adhesion on dielectric
growth and adhesion on barrier

Inert annealing changes in film



Crystallization

Grain growth

Bond formation: e.g. Si-N bonds formed in PECVD nitride

Annealing: bond formation

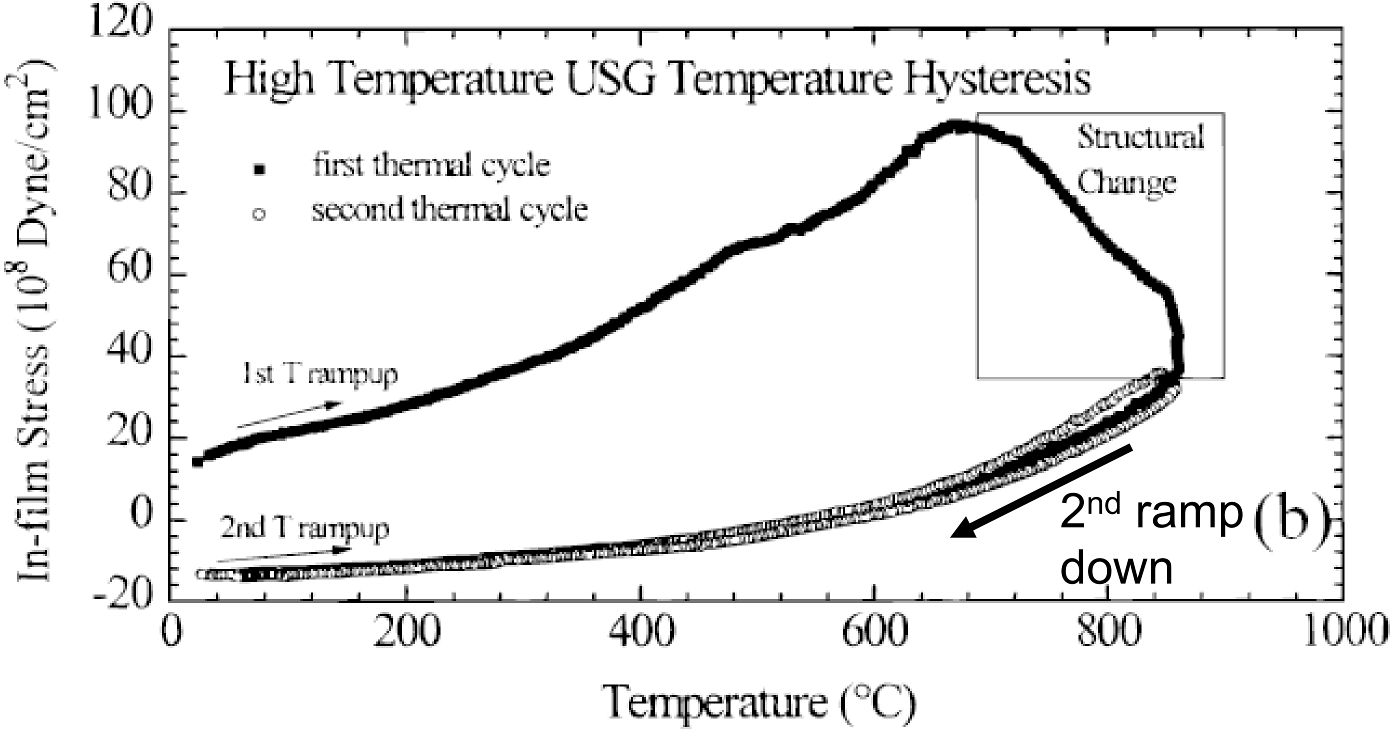
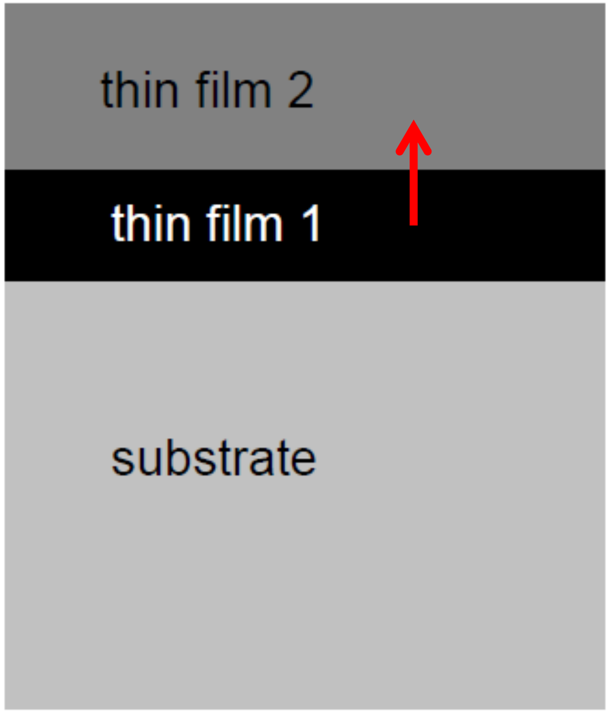


Figure 2. The effect of annealing on USG film properties: (a) film stress temperature variation at two consecutive thermal cycles, showing strong hysteresis for the first cycle only; (b) bonding structure change shown by FTIR, indicating increase in Si–O stretching mode. The deposition temperature is 550°C.

Journal of The Electrochemical Society, **146** (3) 1181-1185 (1999)

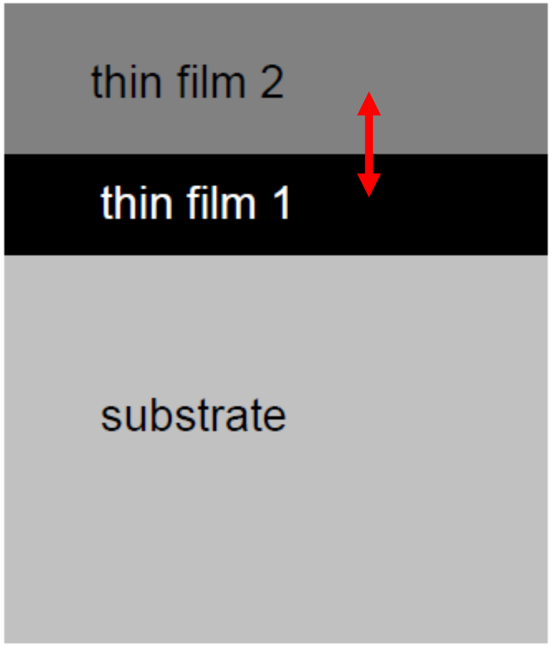
Film poisoning during 2nd deposition



If film 1 is porous or incompletely reacted, it can release atoms and poison film 2.

e.g. film 1 is spin-on-glass, and oxygen or water vapor from it penetrate into aluminum, leading to increased resistivity (and in extreme case, Al_2O_3 formation).

Film-to-film modification

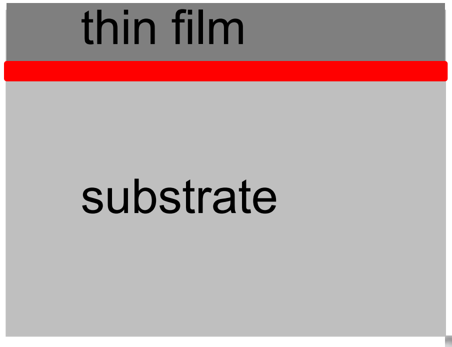


During annealing atoms from one film move to the other.

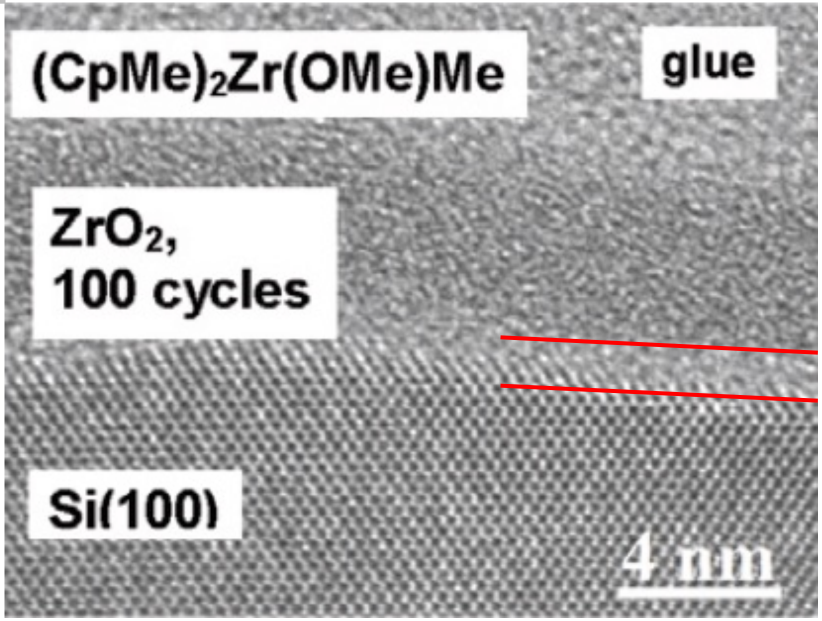
e.g. Film-2 is phosporous-doped oxide, and film-1 is polysilicon, then polysilicon will be doped n-type by phosphorous.

e.g. Film-2 is PECVD nitride, film-1 is a-Si or poly, then during annealing hydrogen from nitride will passivate dangling bonds in silicon.

Substrate oxidation



If thin film precursor is oxygen or water vapor, silicon is easily oxidized, e.g. ALD ZrO_2 with O_2 pulses.



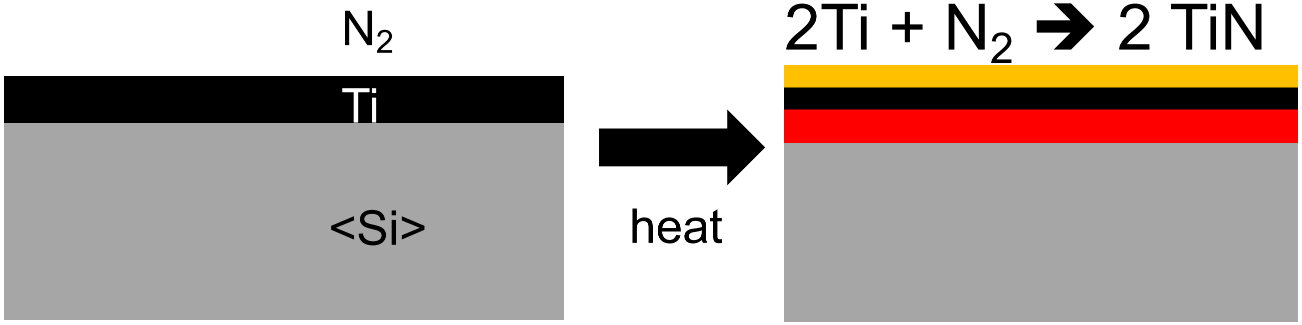
SiO_2 ca. 2 nm

Annealing: chemical reactions

Surface reaction:

Titanium nitride formation

$2Ti + N_2 \rightarrow 2\ TiN$



Interface reaction:

Titanium silicide formation

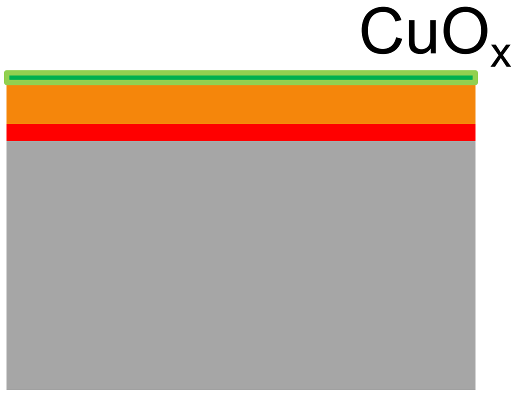
$Si + 2\ Ti \rightarrow TiSi_2$

Solution: anneal in argon

Annealing: chemical reactions

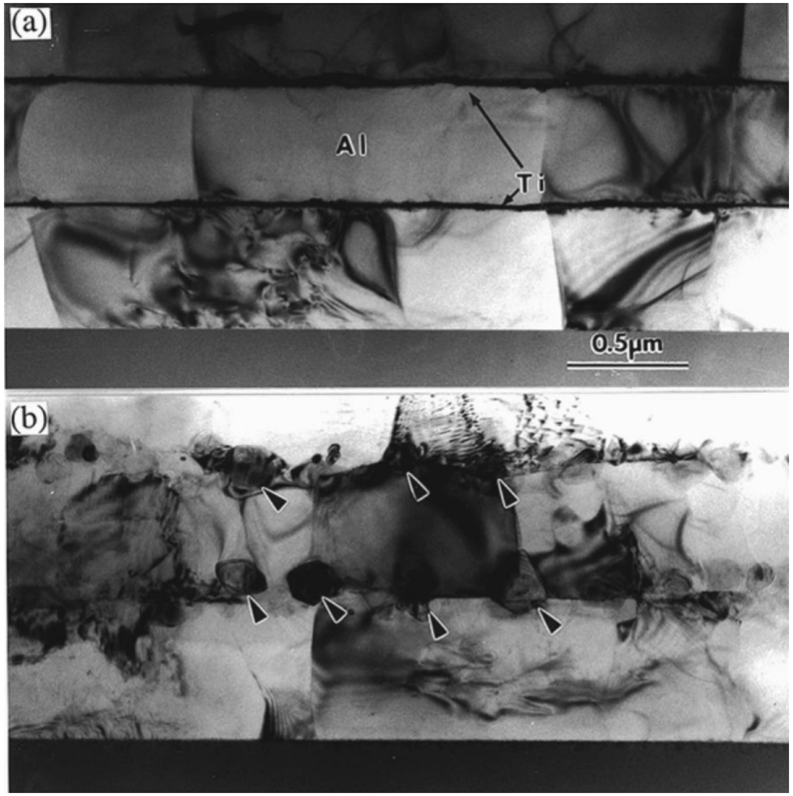
$Cu + Si \rightarrow CuSi_x$

$CuSi_x$ is a high resistivity material



Annealing atmosphere: Even tiny oxygen contamination will lead to copper surface oxidation.

Precipitates



10 nm Ti/500 nm Al,
Annealed 550^{o}C, 1 h in N_2

Arrows indicate Al_3Ti precipitates

Pure Al yield strength 95 MPa
Al-1%Ti yield strength 175 MPa

Al_3Ti precipitates formed during 550^{o}C anneal.
Al_3Ti has an elastic modulus of 210 GPa, is much stiffer than pure Al (60 GPa).

Stiff precipitates block dislocation movement through a soft matrix and thereby increase the yield strength.

One can improve the strength of an Al membrane while only slightly diminishing its conductivity.

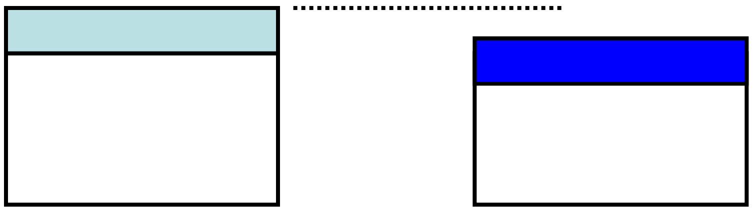
Lee, Appl. Phys. Lett., Vol. 76, p. 3415

Volume changes

$$xM + ySi \rightarrow M_xSi_y,$$

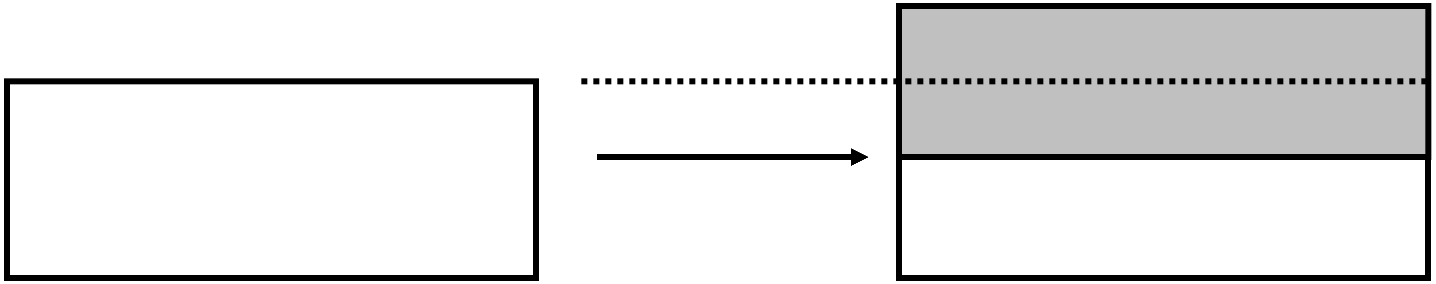
the volume change $\triangle V$ (%) is given by

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



In silicide formation, negative volume change ➔ tensile stress

In thermal oxidation, positive volume change ➔ compressive stress



Annealing multilayers

Top surface reaction
-e.g. oxidation

Film-film reaction
-e.g. $Ti + 3Al \rightarrow TiAl_3$

Film-substrate reaction
-e.g. $Ti + 2Si \rightarrow TiSi_2$

Texture inheritance

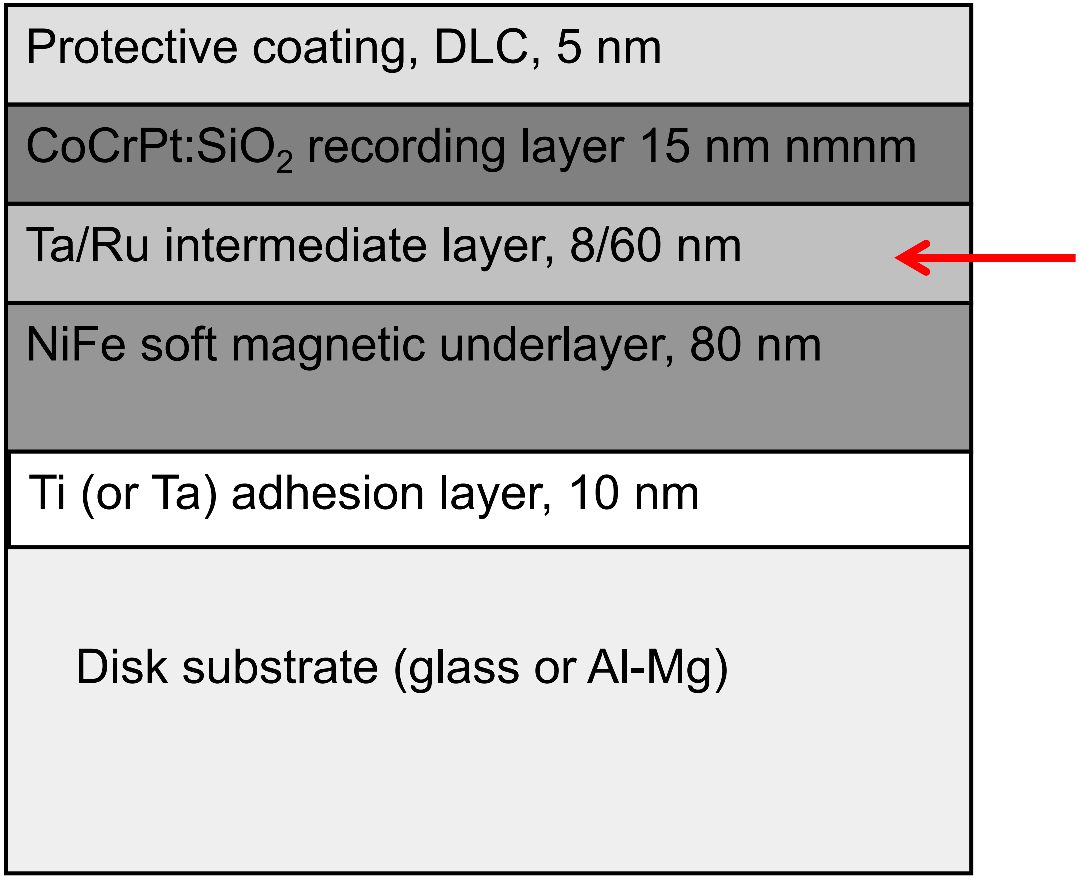
Film 2 will register the crystal structure of film 1.

Choosing film 1 to be either amorphous (like SiO_2) or polycrystalline (like TiW), will result in different film2 texture and properties.

Molybdenum as film2:

Mo thickness	**Film 1**	**Film 2 resistivity**
300 nm	SiO_2	12 µOhm-cm
300 nm	TiW	9 µOhm-cm

Texture inheritance (2)



Protective coating, DLC, 5 nm

$CoCrPt{:}SiO_2$ recording layer 15 nm nmnm

Ta/Ru intermediate layer, 8/60 nm

NiFe soft magnetic underlayer, 80 nm

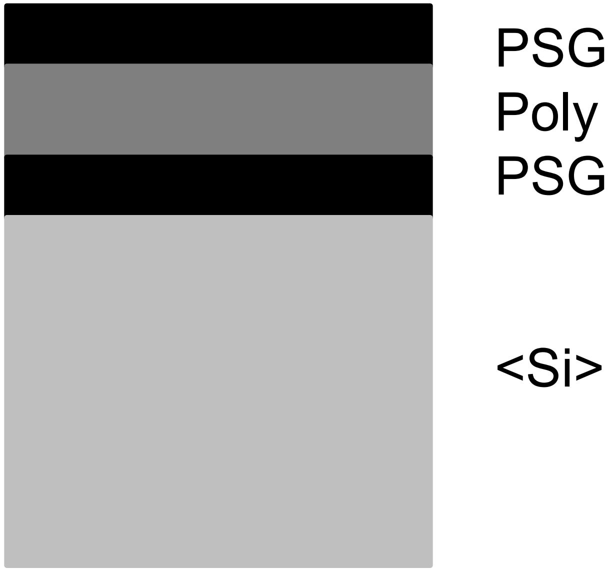
Ti (or Ta) adhesion layer, 10 nm

Disk substrate (glass or Al-Mg)

Ta/Ru film will induce suitable crystallinity in the magnetic data storage layer $CoCrPt{:}SiO_2$

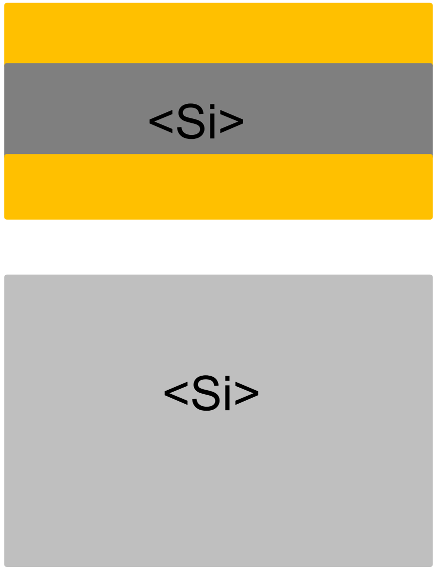
Terminology: $CoCrPt{:}SiO_2$ means that CoCrPt films contains small SiO_2 crystals.

Symmetric 3-layer

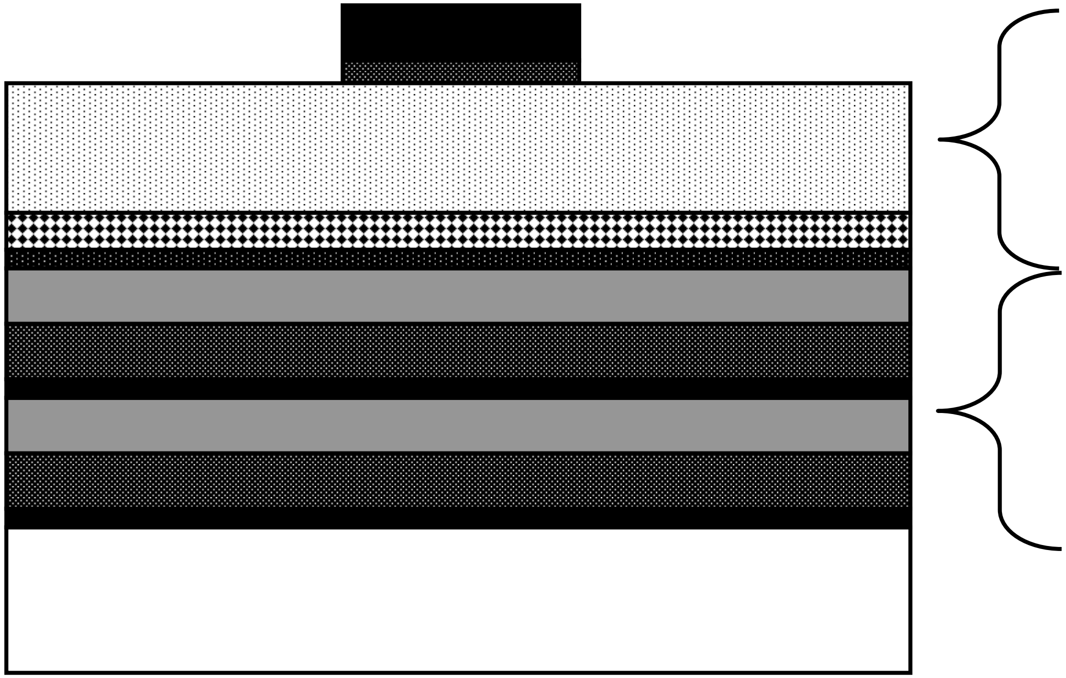


Poly will be doped by PSG (phosphorous doped silica glass) symmetrically.

Au/<Si>/Au mirror planarity assured by a symmetric metallization.

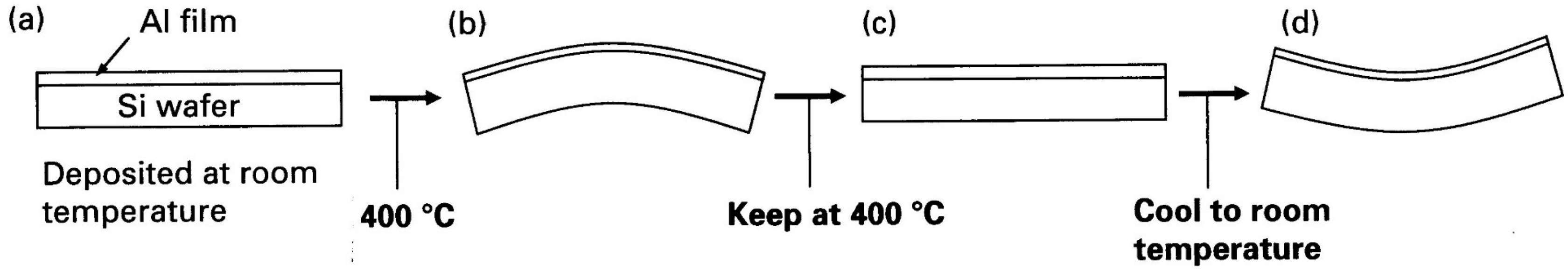


Acoustic $\lambda/4$ multilayers



Al	(300 nm)
Mo	(50 nm)
ZnO	(2300 nm)
Au	(200 nm)
Ni	(50 nm)
SiO_2	(1580 nm)
W	(1350 nm)
TiW	(30 nm)
SiO_2	(1580 nm)
W	(1350 nm)
TiW	(30 nm)
glass wafer	

Stress evolution



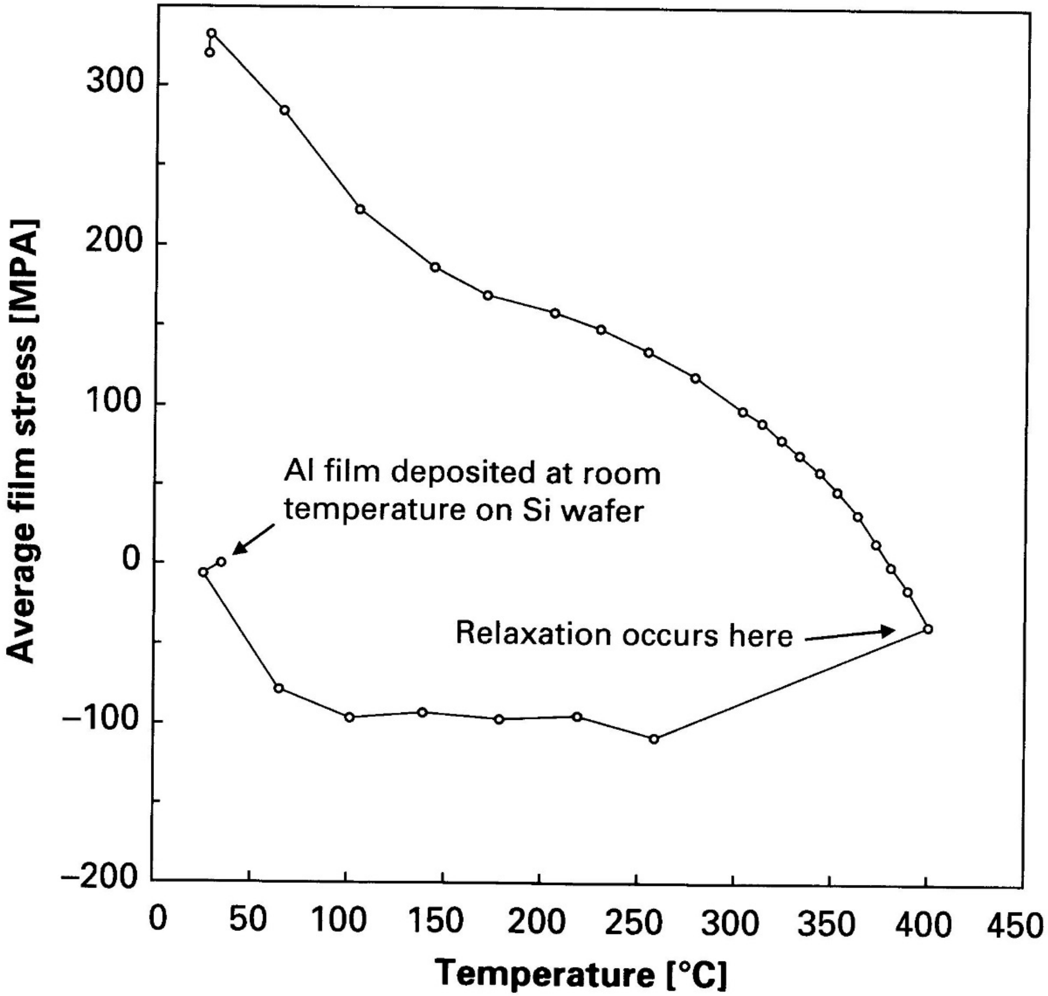
Much more extensive relaxation takes place in the Al thin films than in bulk.

Thin film grain size, typically ~1 μm vs. ~ 100 μm for bulk, would enable much more extensive grain boundary sliding and hence greater stress relaxation.

Hoo-Jeong Lee,a) Guido Cornella, and John C. Bravman: Appl. Phys. Lett., Vol. 76, p. 3415

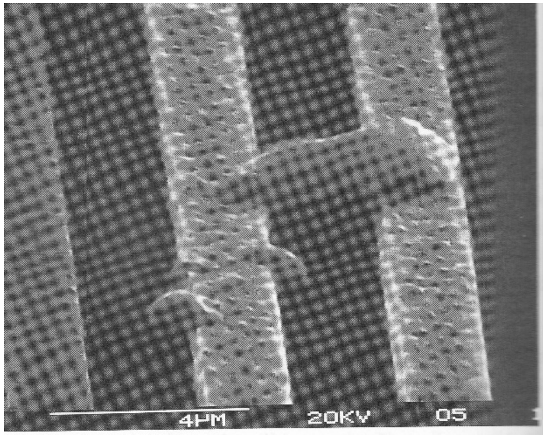
King Tu, p. 131

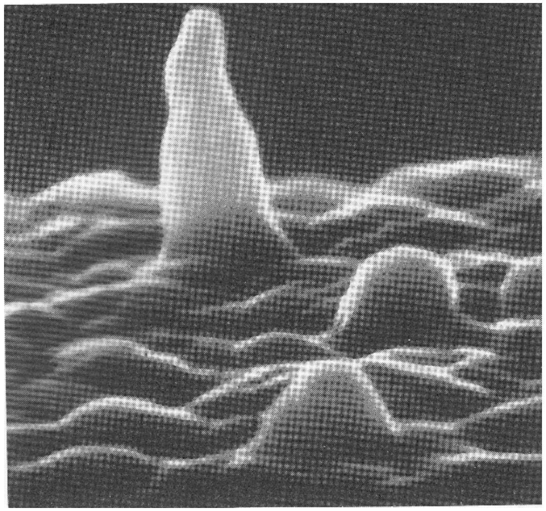
Stress relaxation (1)



King Tu, p. 133

Hillock generation





Compressive stress is relieved by hillock growth.

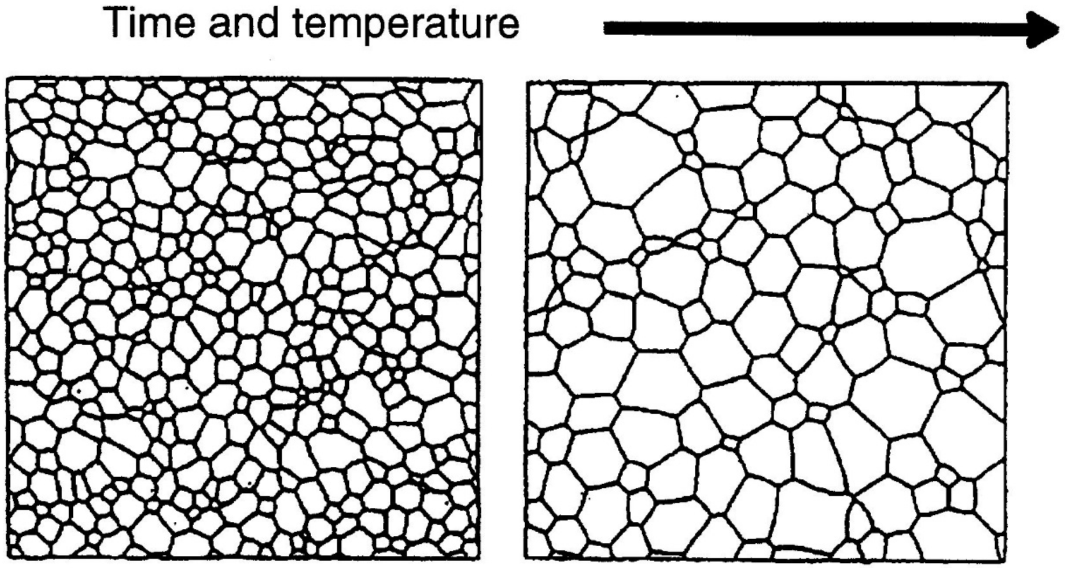
If surface is free (as in high vacuum), the surface acts as a sink for vacancies and extra atoms are uniformly distributed over the surface.

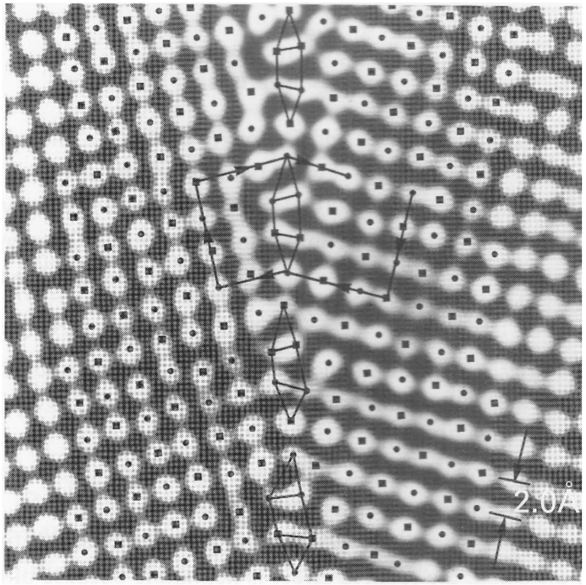
Oxide covered surface breaks randomly and hillocks are formed.

Hillocks are same size as microlithographic structures and film thicknesses.

➔ Hillocks can short two neighboring lines or two films.

Grain growth



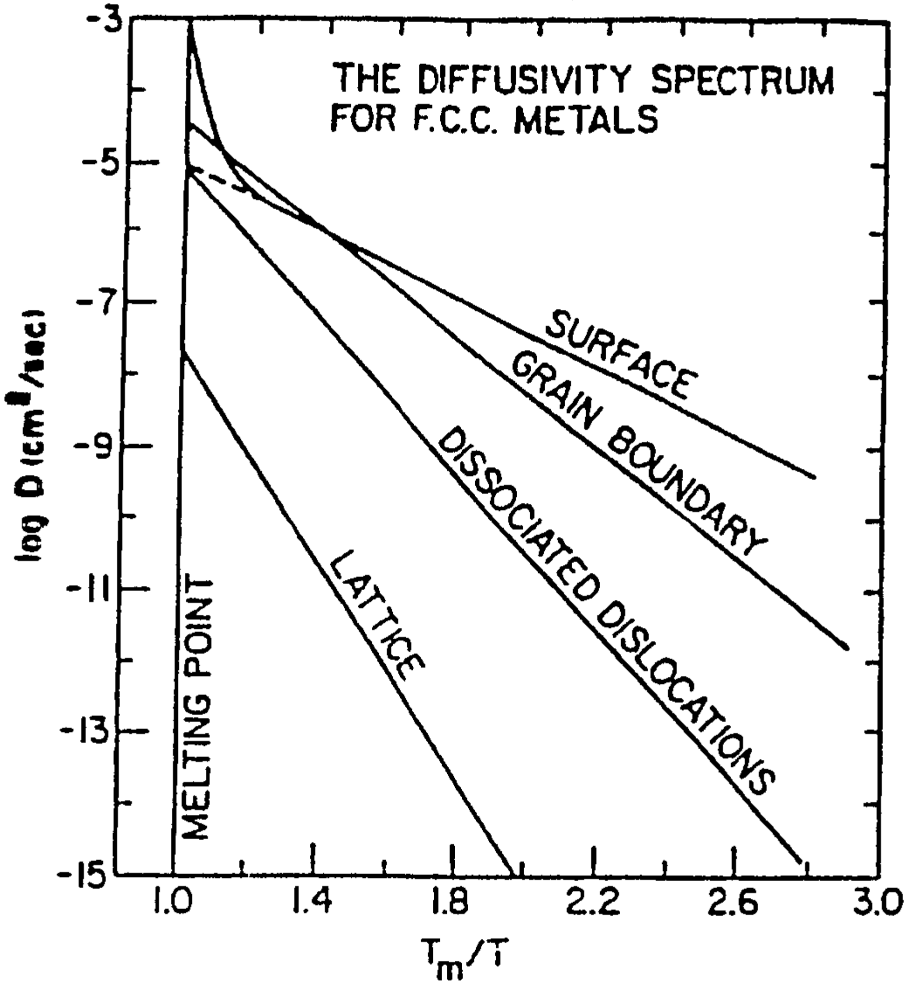


Grain boundaries important because they:

- -act as nucleation sites for growth of new phases
- -act as sites of enhanced reaction rates
- -act as fast diffusion paths
- -act as precipitation sites

King Tu, p. 193

Grain boundary vs. bulk diffusion



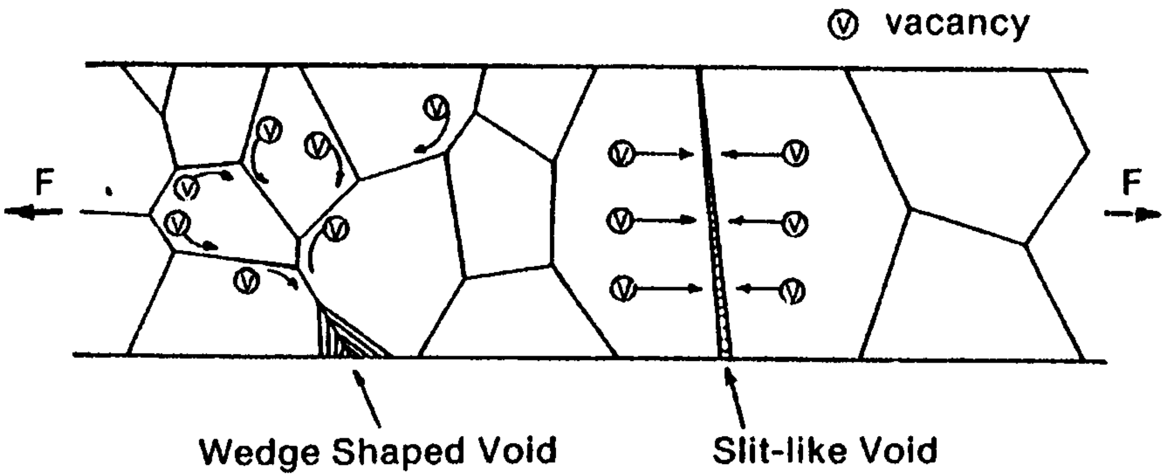
Grain boundaries and dislocations are paths of rapid diffusion (below 0.65 T_m).

Impurities and dopants are easily trapped and precipitated at defects and grain boundaries ➔ fast diffusion paths blocked ➔ improved resistance against processes that rely on them.

Murarka p. 93

Stress voiding

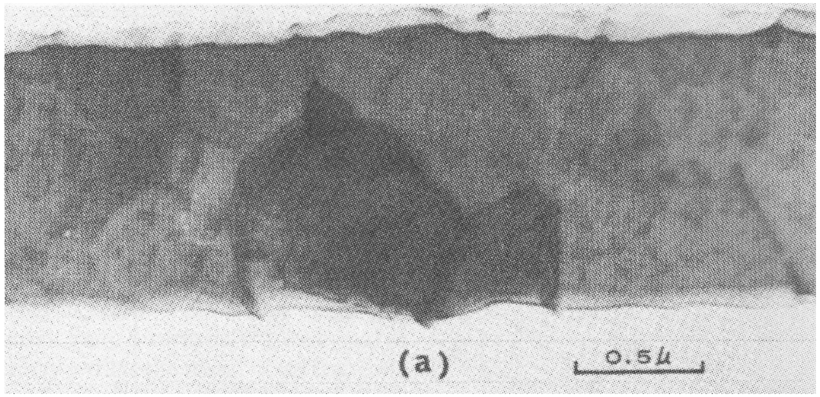
In order to relieve stress, vacancies diffuse.



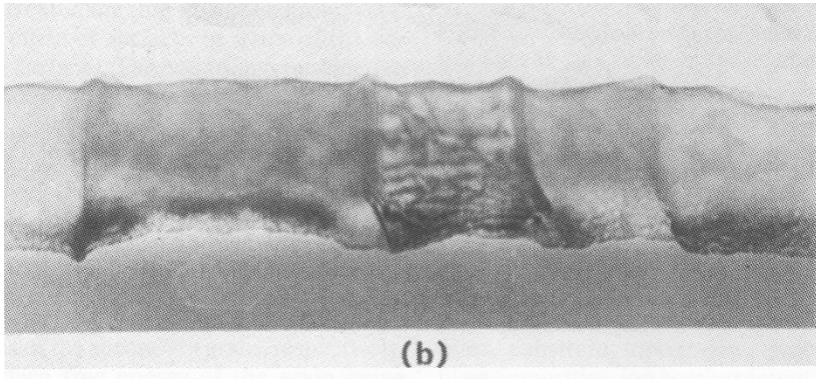
Grain boundary diffusion vs. bulk diffusion

Murarka p. 84

Bamboo structure



3-grain boundaries, active processes during anneal

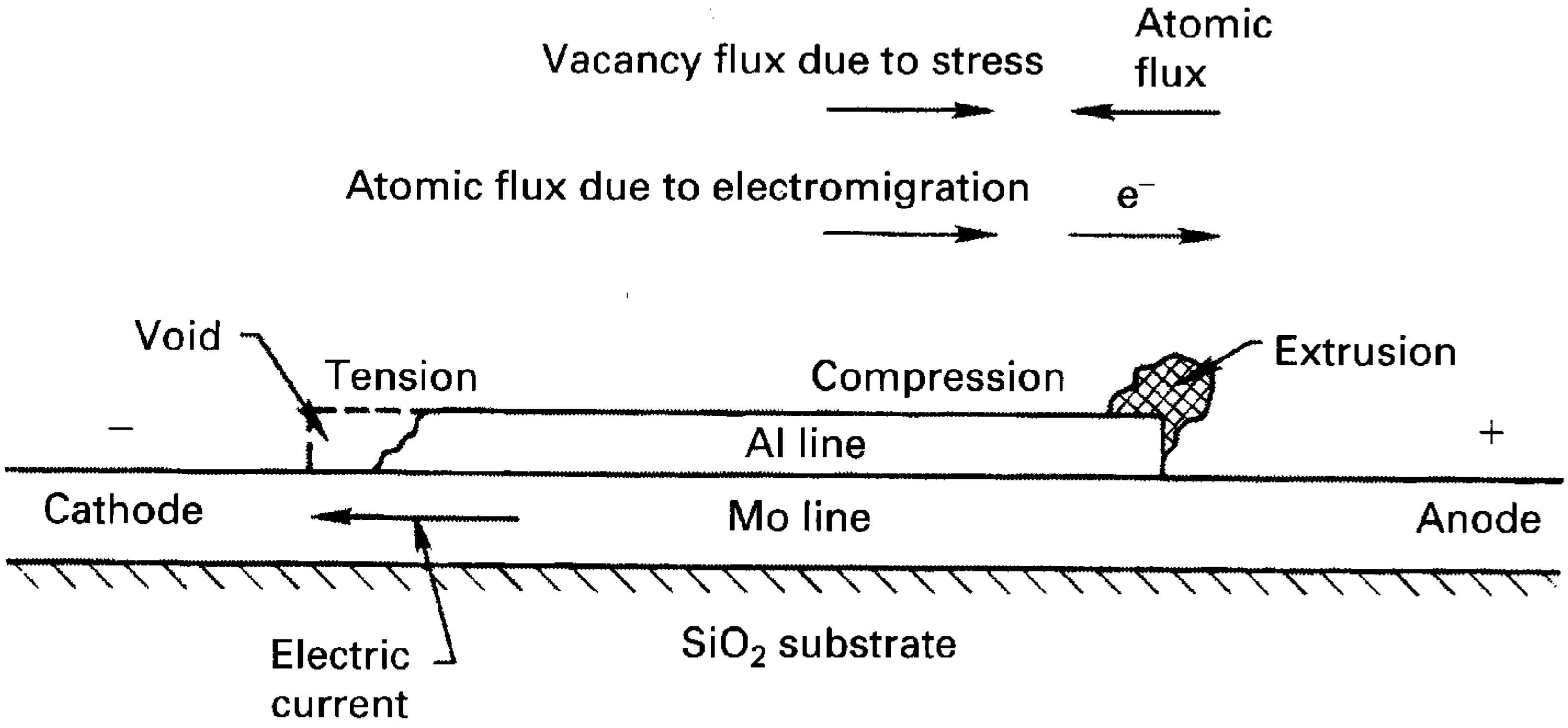


No 3-grain boundaries ➔ fewer processes at GBs

Murarka p. 99

Electromigration

Electron collisions move atoms. Voids formed.
Happens when current density is high.



King Tu, p. 240

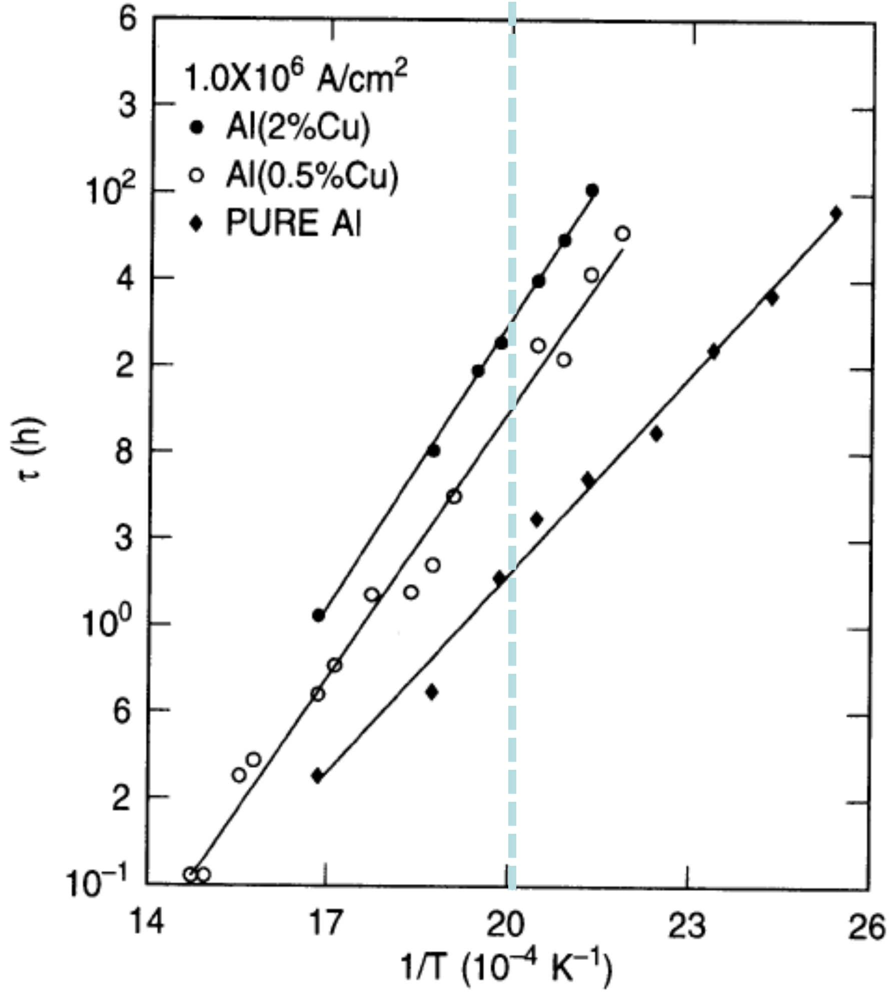
Mean time to failure (MTF) due to electromigration

$$MTF = AJ^{-n} e^{\frac{E_a}{kT}}$$

where A is a constant dependent on wire geometry and metal microstructure, J is the current density and E_a the activation energy. The factor n is not known very accurately, but n=1.7 is used for aluminum. For aluminum thin films E_a is of the order of 0.5-0.8 eV, whereas for bulk aluminum it is 1.4-1.5 eV. As a general trend the higher the activation energy, the better the electromigration resistance

.

Alloying to prevent EM



500 K = 227°C

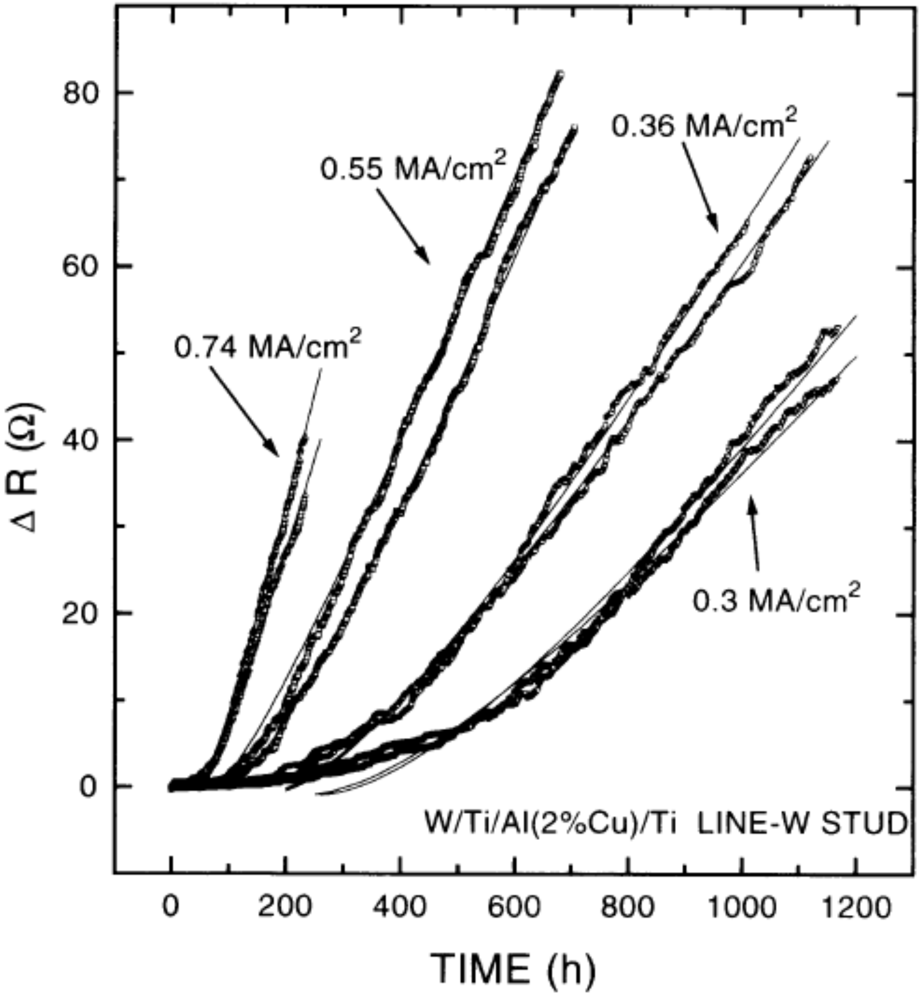
Mean time to failure of 2.5 µm wide lines

- pure Al,
- Al (0.5 wt % Cu)
- Al (2 wt% Cu)

at different temperatures with 1 MA/cm^2 current density

Hu, C.-K. et al: Electromigration of Al(Cu) two-level structures: effect of Cu kinetics of damage formation, J.Appl.Phys. 74 (1993), p. 969

Incubation time



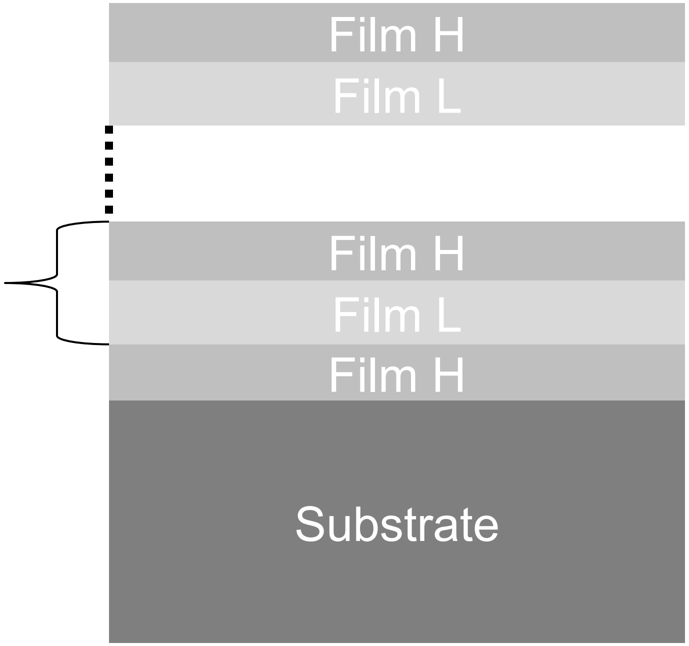
Incubation time before resistance increase sets in (measured at 255°C)

Hu, C.-K. et al: Electromigration and stress-induced voiding in fine Al- and Al-alloy thin- film lines, IBM J.Res.Dev. 39 (1995), p. 465

Dielectric mirrors, enhanced metal mirrors

$SH(LH)^n$ =
substrate, high refractive index film,
low+high film stack of n-layer pairs

$n_H t_H = \lambda/4$ condition for thicknesses



$$R_o = \left[\frac{1-\left(\frac{n_H}{n_L}\right)^{2n}\left(\frac{n_H^2}{n_s}\right)}{1+\left(\frac{n_H}{n_L}\right)^{2n}\left(\frac{n_H^2}{n_s}\right)}\right]^2$$

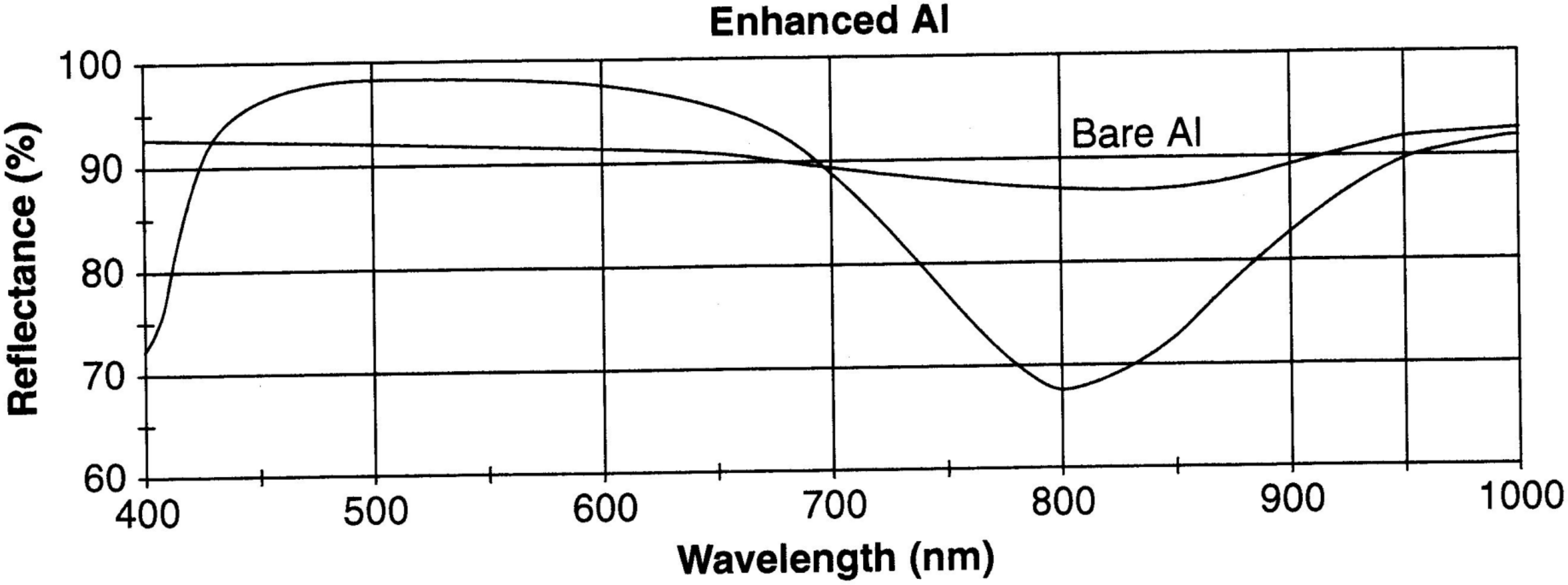
Martin p. 303

Enhanced aluminum mirror

SM(LH)^2 design

Glass/Aluminum/SiO_2/Ta_2O_5/SiO_2/Ta_2O_5

510 nm centre wavelength



Martin p. 301