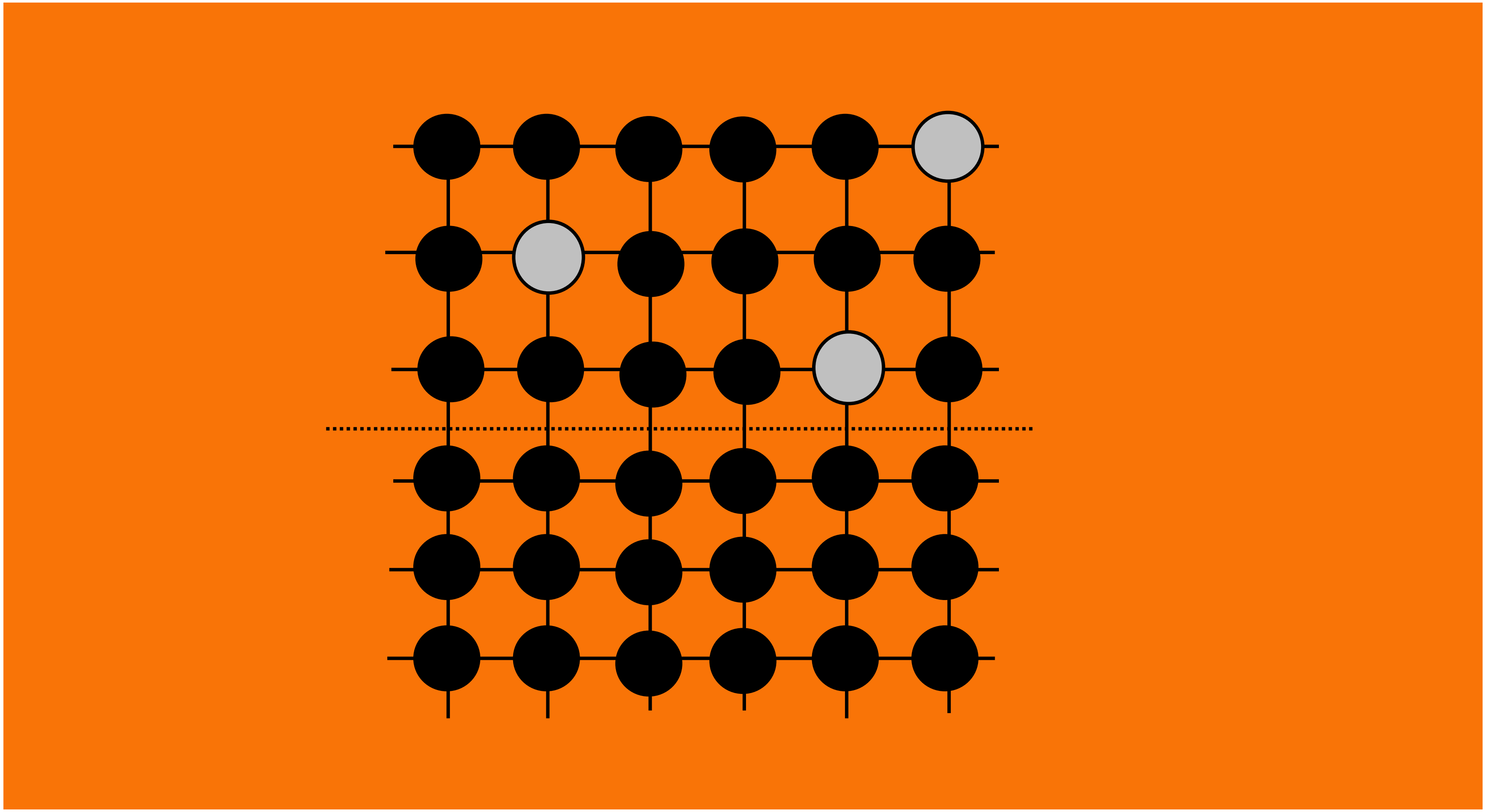
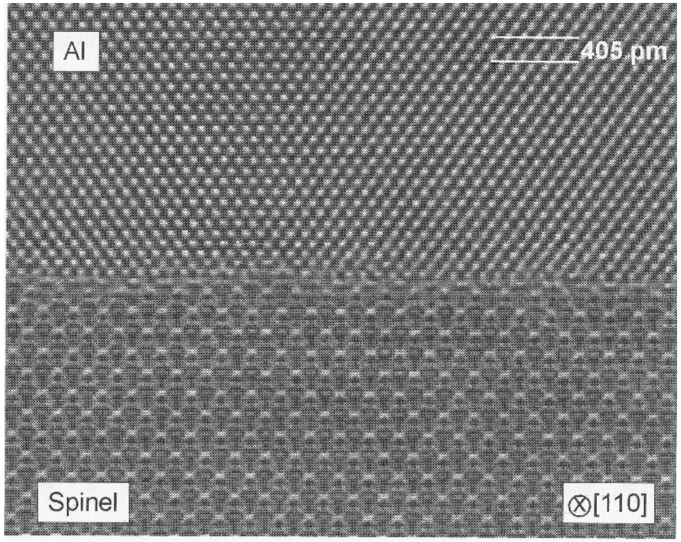
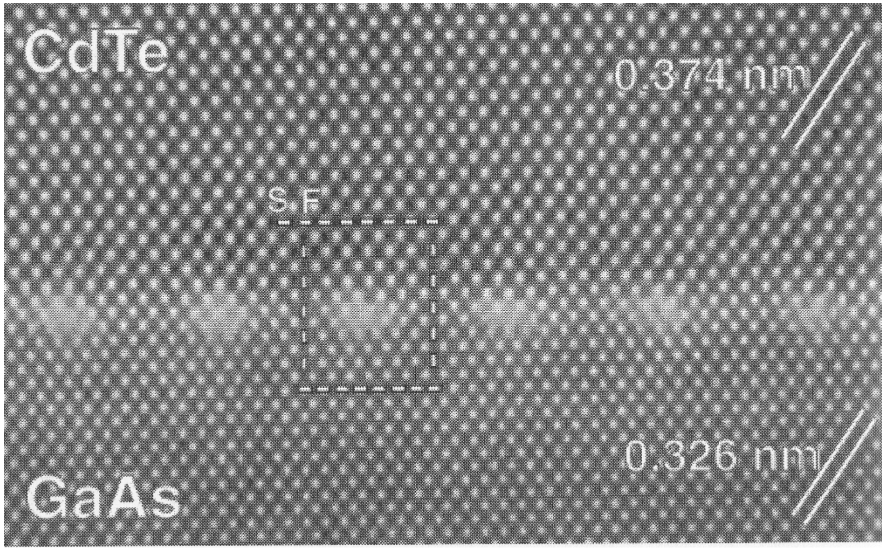
Epitaxy, superlattices, nanolaminates



Epitaxy: single crystalline film on single crystalline substrate

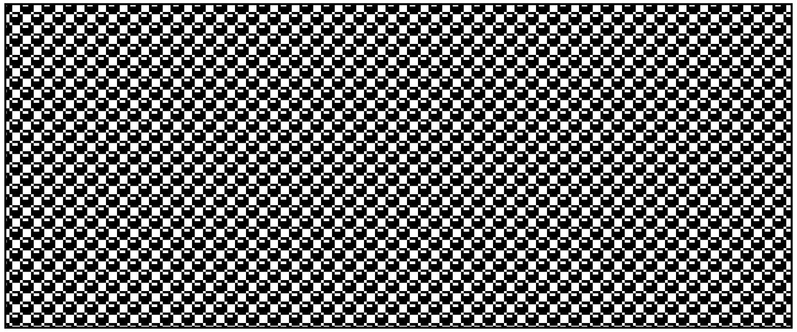




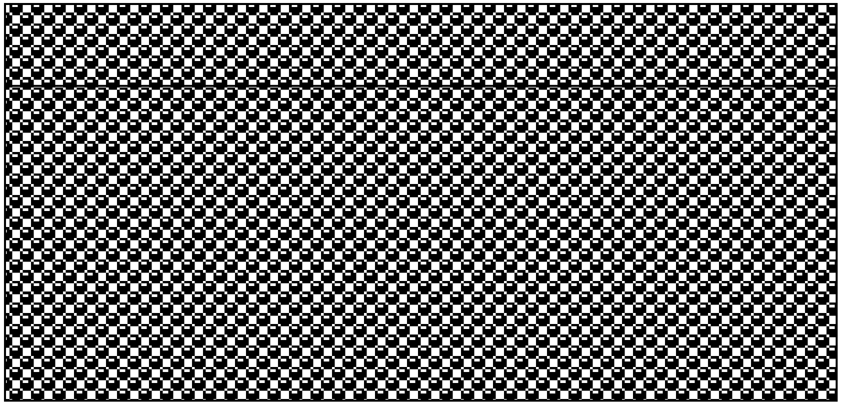
Aluminum on spinel

CdTe on GaAs.
Stacking faults are arranged at regular intervals at the interface and epilayer is perfect

Homoepitaxy: crystalline film A on top a crystalline wafer A



Single crystal wafer



Epitaxial layer of the same material deposited on top

Why indeed ?

Epilayer doping concentration different from starting wafer.

Epilayer dopant type different from substrate (n/p –type)

No radial doping profile (as in CZ-crystal pulling)

No vertical doping variation (as along CZ-crystal)

No oxygen (10-15 ppma in CZ-silicon)

No carbon (which comes from SiC and C in CZ)

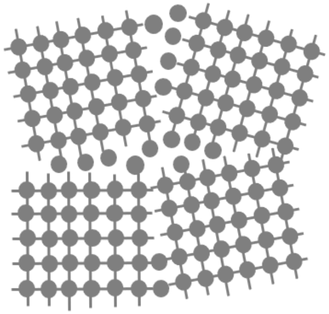
Epi requirements

Clean surface

Matching lattices

Small enough CTE difference

Polycrystalline vs. epitaxial



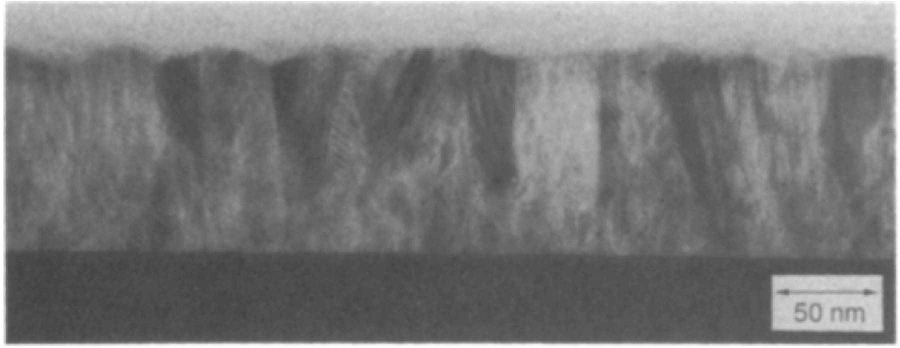
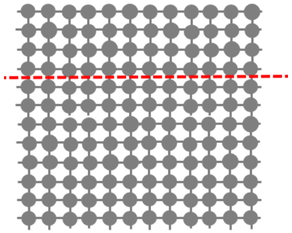


Fig. 5. TEM photograph of deposited Si film after 700°C surface cleaning in hydrogen at 3.3×10^2 Pa.

Crystallites easily seen



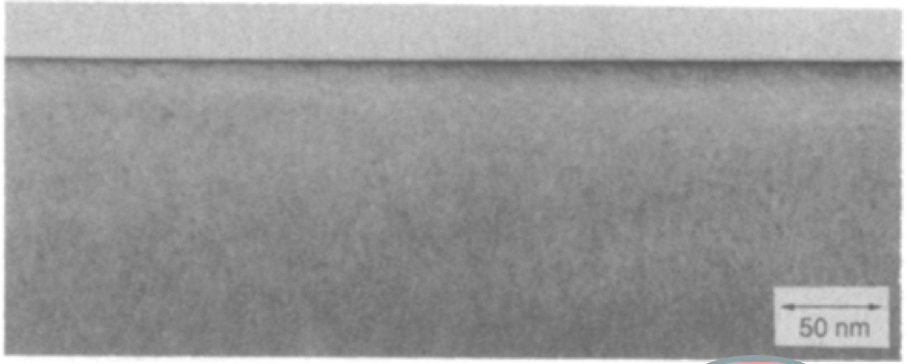
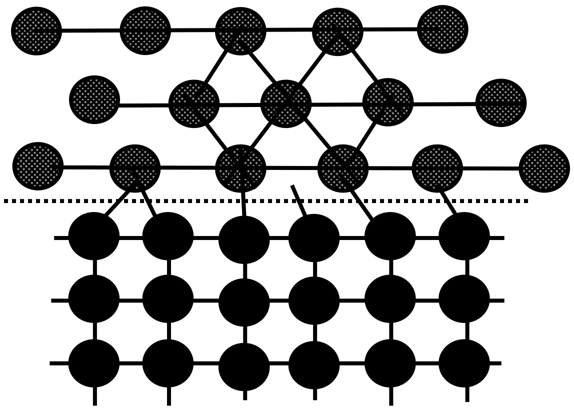


Fig. 7. TEM photograph of deposited Si film after 790°C surface cleaning in hydrogen at 3.3×10^2 Pa.

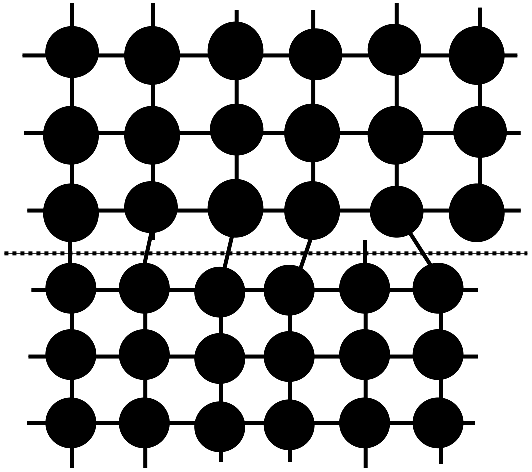
Perfectly crystalline film with no grains visible

Yamazaki et al: J. Electrochem. Soc., Vol. 139, No. 4, April 1992

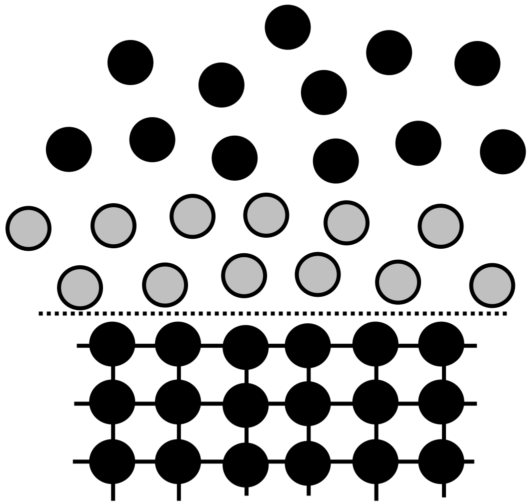
Epitaxy failure



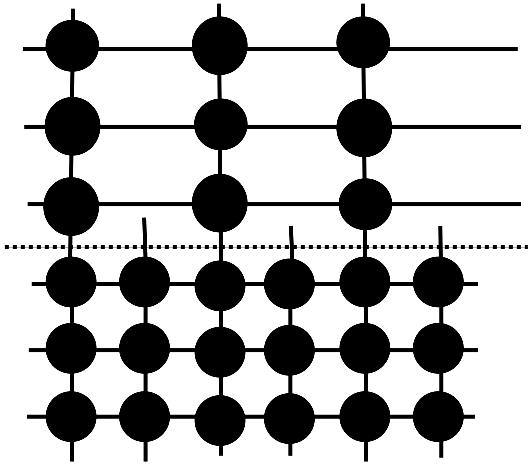
Lattices do not match



Lattice constant difference



Interfacial contamination



May work if lattice constants integer multiples !

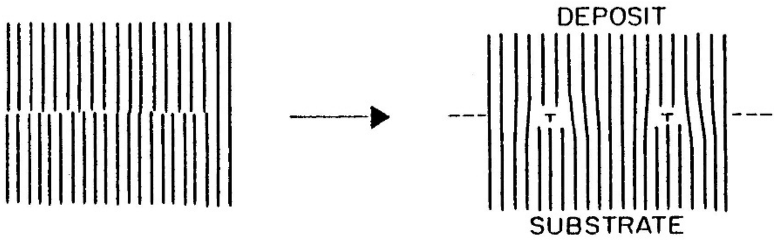
Lattice mismatch

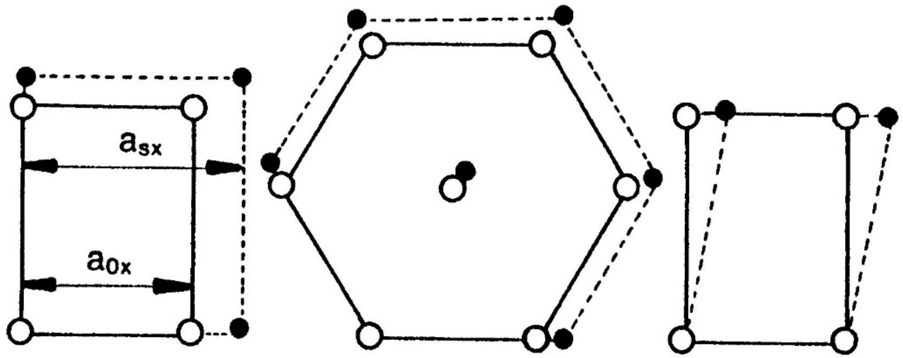
In homoepitaxy film and substrate lattices are almost identical (because dopants change lattice constants slightly)

In heteroepitaxy lattice mismatch has to be small enough:

$\eta = (a_f - a_s)/a_s$ where a is lattice constant

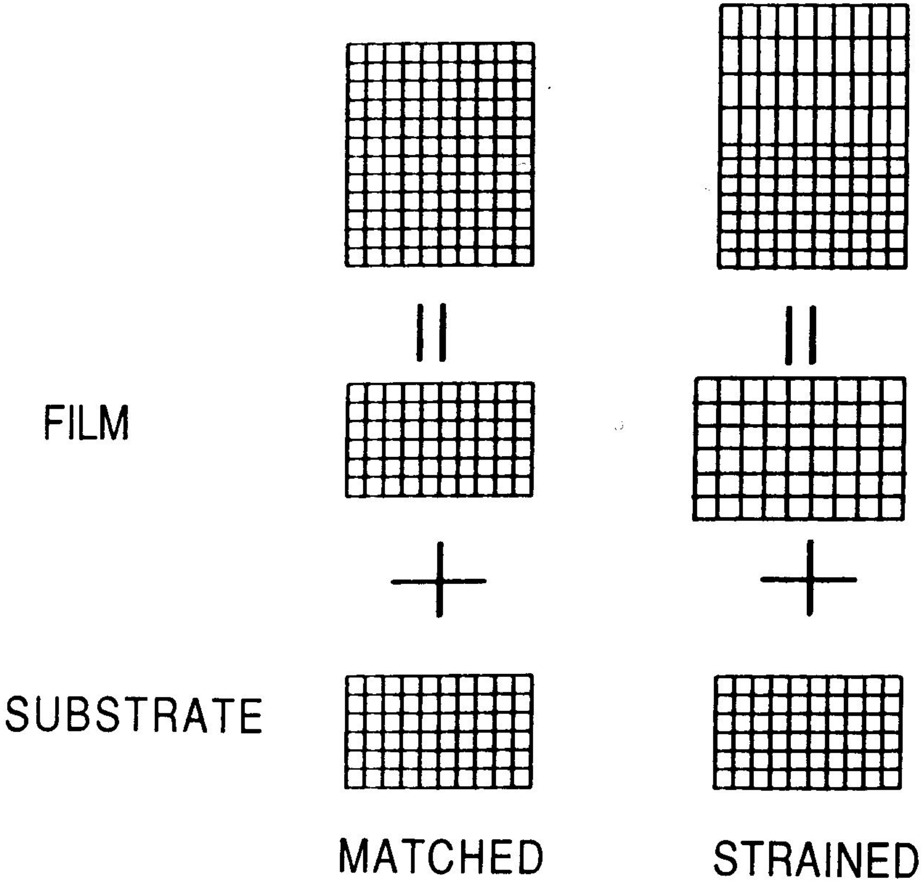
Higher the mismatch η, the larger the film-substrate potential W must be



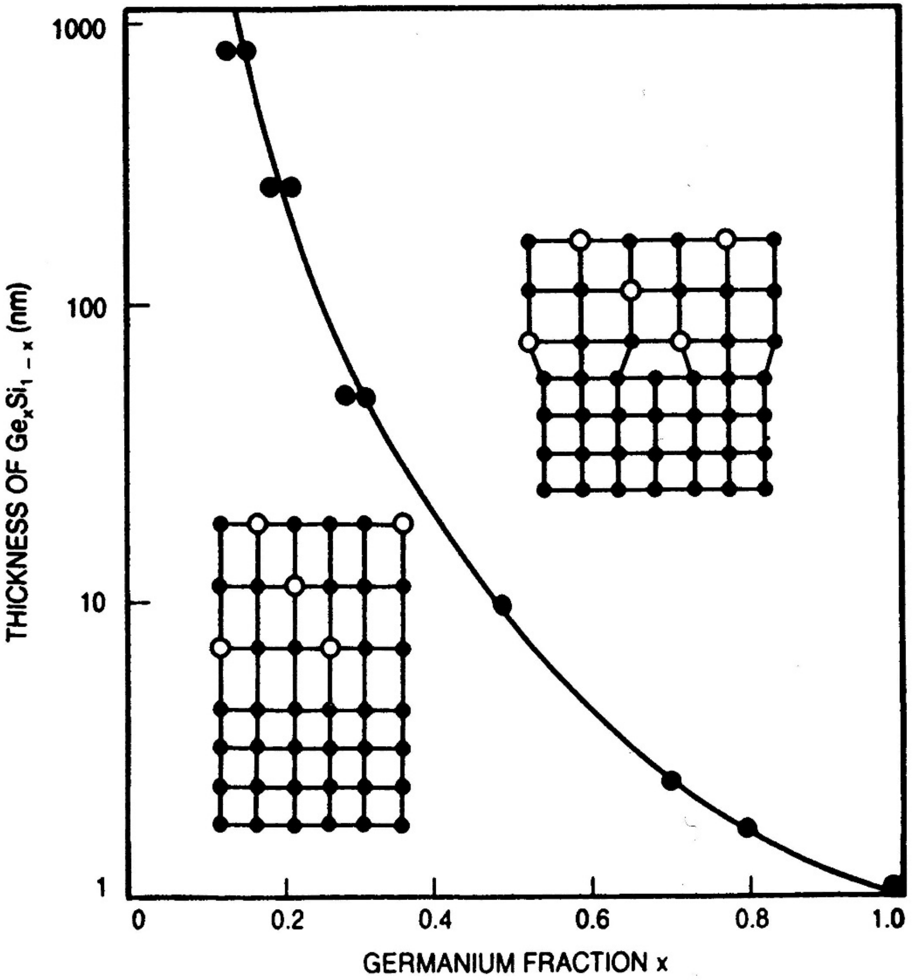


Strained & relaxed

Strained
epi-layer



Strained & relaxed (2)



Relaxed, with defects confined to interface (but it does not always work that way)

Strained, but with limited epi layer thickness

CVD epitaxy of silicon

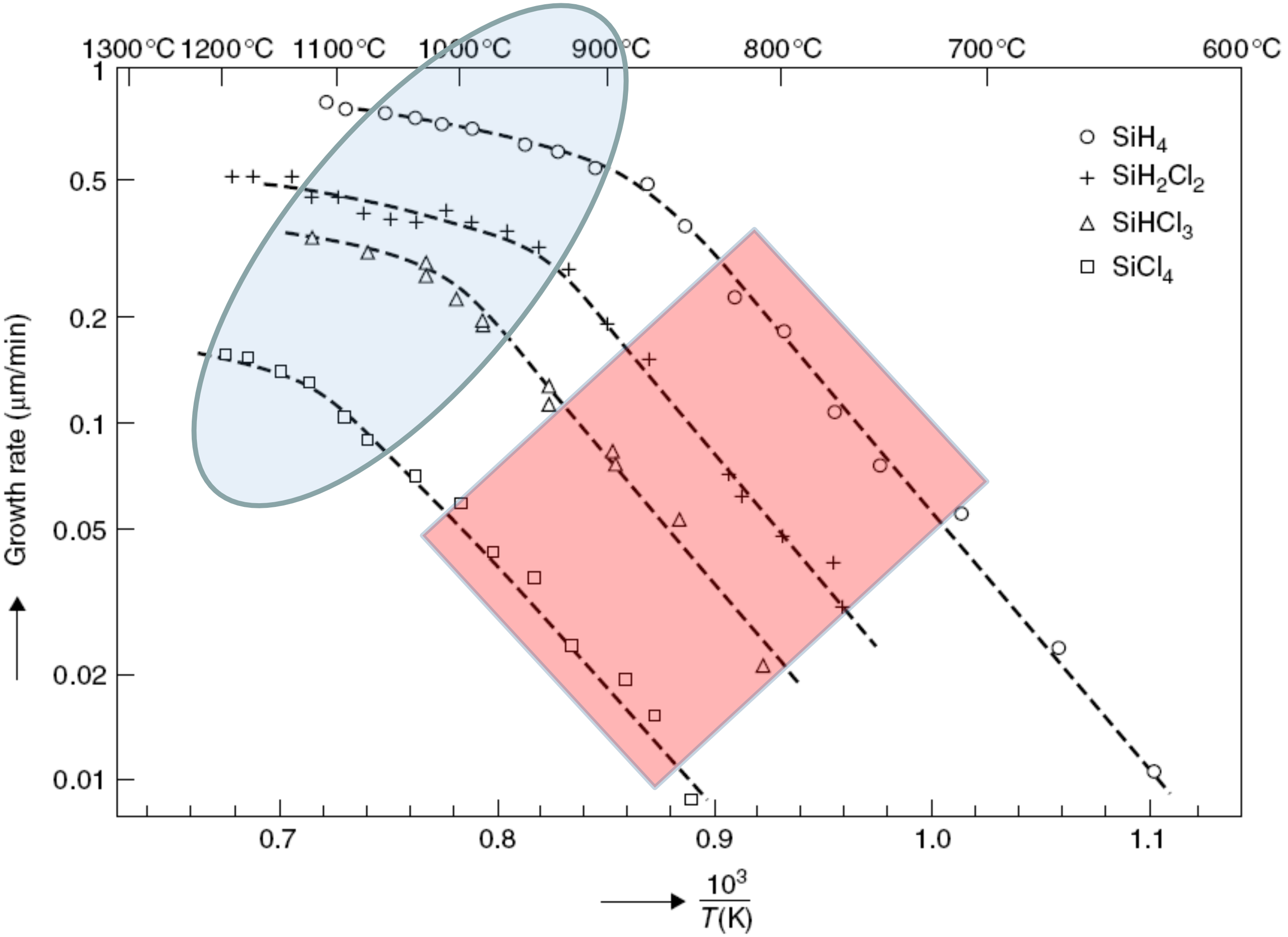
SiH_4 (g) ==> Si (s) + 2 H_2 (g) T = 1100°C

SiH_2Cl_2 (g) ==> Si (s) + 2 HCl (g) T = 1150°C

$SiCl_4$ (g) + 2 H_2 (g) <==> Si (s) + 4 HCl (g) T = 1200°C

Rate

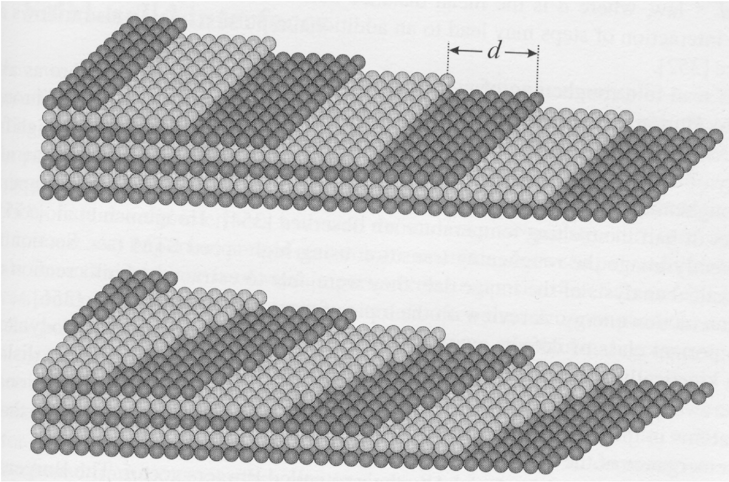
mass
transport
limited



surface
reaction
limited.

Miscut & off-orientation

Miscut relative to wafer surface



Off-orientation relative to wafer flat.

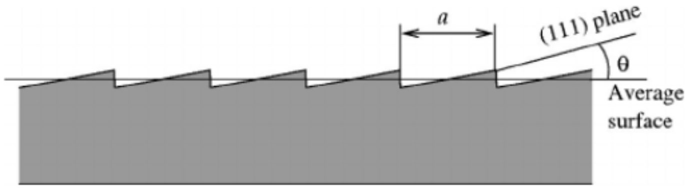
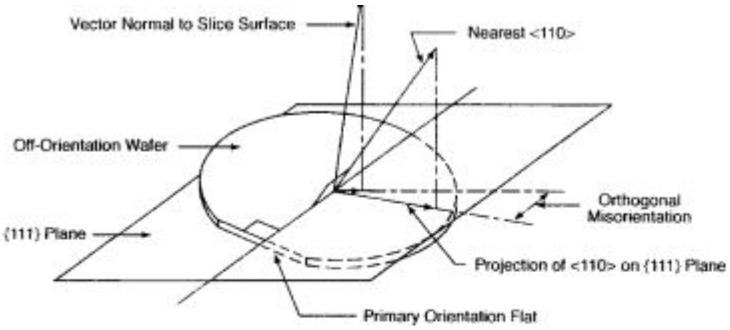


FIG. 7. Schematic representation of a surface with a miscut. For miscut angle θ and step height d, step width is $a = d/\theta$.

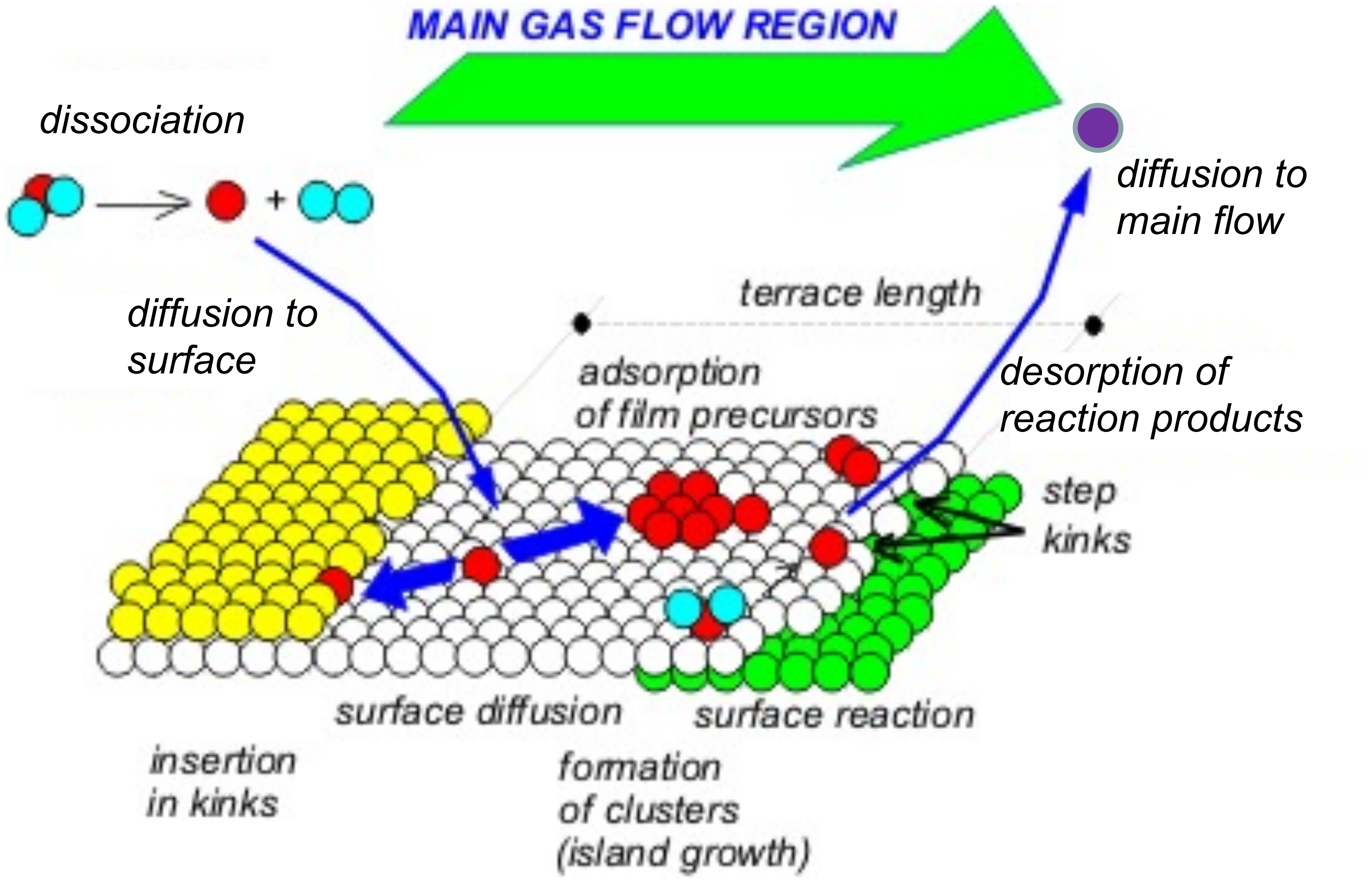
Penanen et al: Phys Rev B DOI: 10.1103/PhysRevB.62.9621



Orthogonal Misorientation

https://www.virginiasemi.com/?cont_uid=49

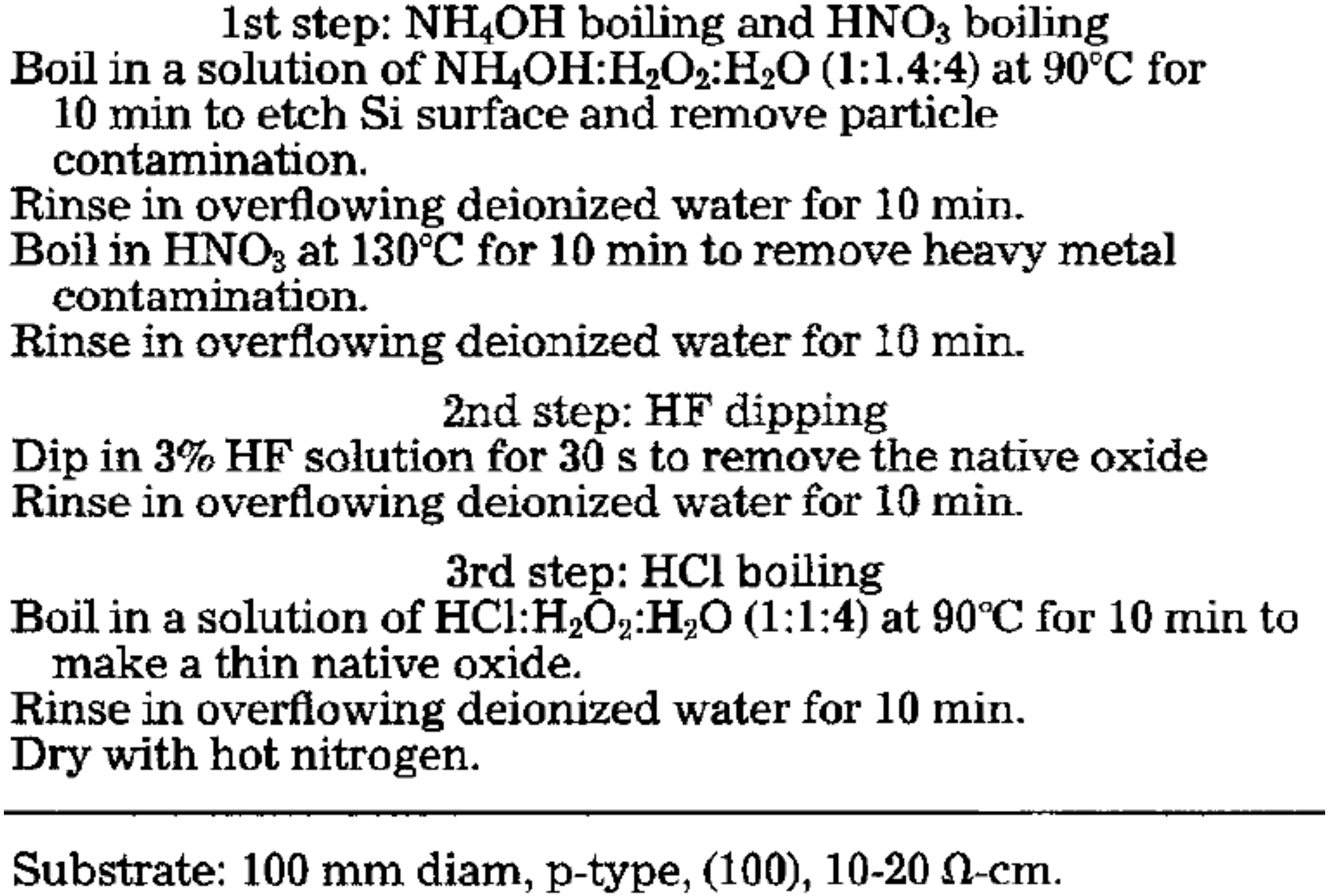
CVD epitaxy


MAIN GAS FLOW REGION
dissociation
diffusion to main flow
diffusion to surface
terrace length
adsorption of film precursors
desorption of reaction products
step
kinks
surface diffusion
surface reaction
insertion in kinks
formation of clusters (island growth)

Major factors affecting film structure

1. Deposition rate
2. Vacuum level
3. Substrate temperature
4. Surface structure and chemistry

Ex-situ wet cleaning before depo



1st step: NH_4OH boiling and HNO_3 boiling

Boil in a solution of $NH_4OH:H_2O_2:H_2O$ (1:1.4:4) at 90°C for 10 min to etch Si surface and remove particle contamination.

Rinse in overflowing deionized water for 10 min.

Boil in HNO_3 at 130°C for 10 min to remove heavy metal contamination.

Rinse in overflowing deionized water for 10 min.

2nd step: HF dipping

Dip in 3% HF solution for 30 s to remove the native oxide

Rinse in overflowing deionized water for 10 min.

3rd step: HCl boiling

Boil in a solution of $HCl:H_2O_2:H_2O$ (1:1:4) at 90°C for 10 min to make a thin native oxide.

Rinse in overflowing deionized water for 10 min.

Dry with hot nitrogen.

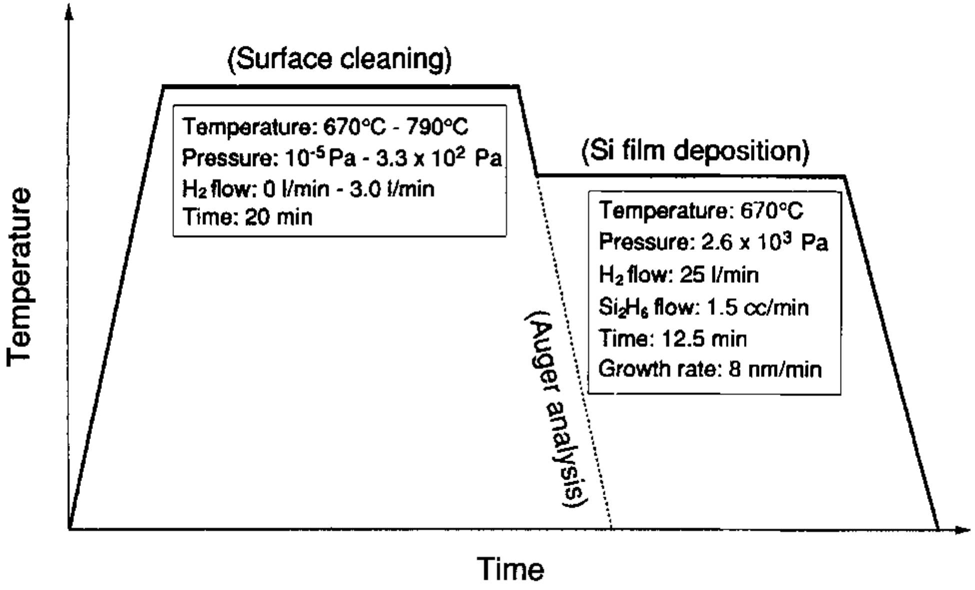
Substrate: 100 mm diam, p-type, (100), 10-20 Ω-cm.

Yamazaki et al: J. Electrochem. Soc., Vol. 139, No. 4, April 1992

In-situ H_2 cleaning in CVD reactor

In-situ cleaning:

SiO_2 (s) + H_2 (g) <==> SiO (g) + H_2O (g)



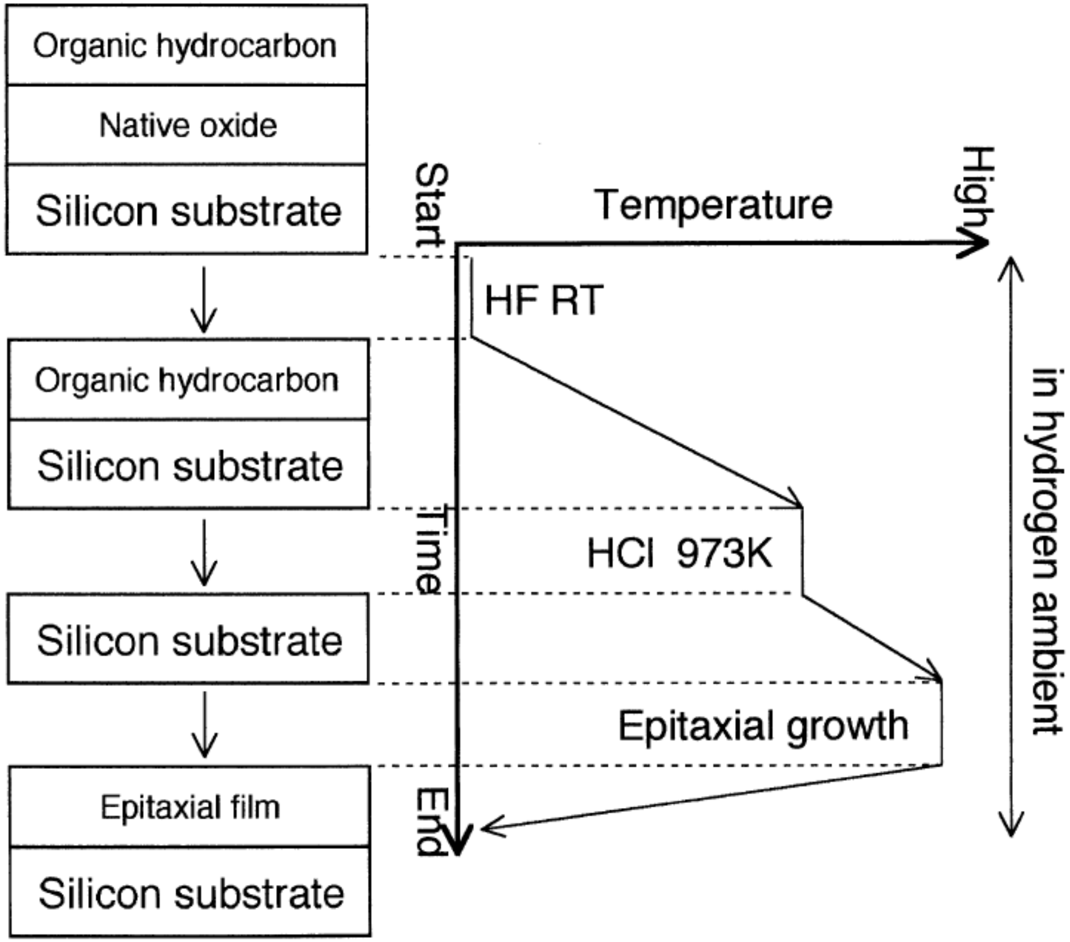
Deposition:

SiH_2Cl_2 (g)

➔ Si (s) + 2 HCl (g)

Yamazaki et al: J. Electrochem. Soc., Vol. 139, No. 4, April 1992

In-situ HCl cleaning



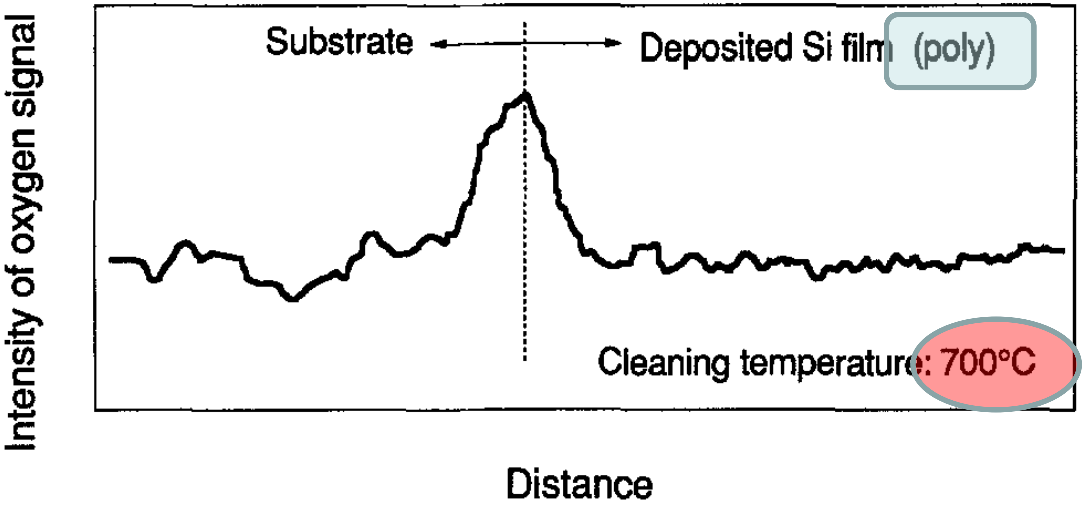
HF wet cleaning removes native oxide, by diffusing thru discontinuous organic film.

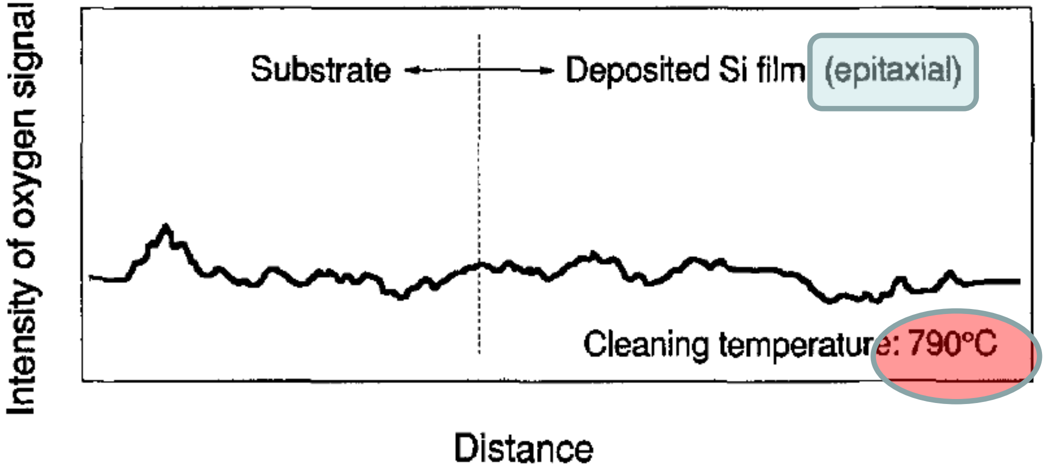
HCl etches organic material away.

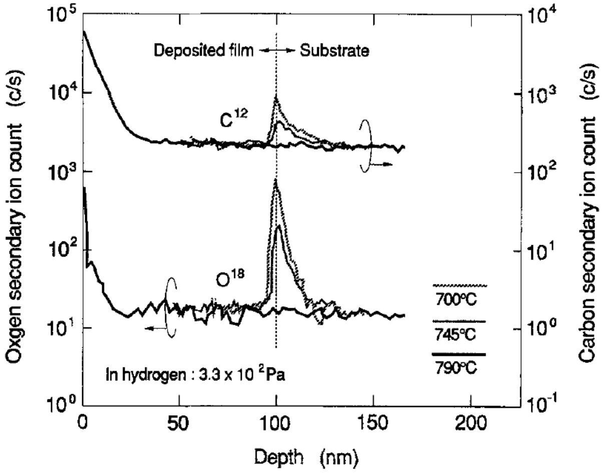
Only then can epitaxial film deposition begin.

Habuka et al: Journal of Crystal Growth 186 (1998) 104Ð112

Interfacial contamination







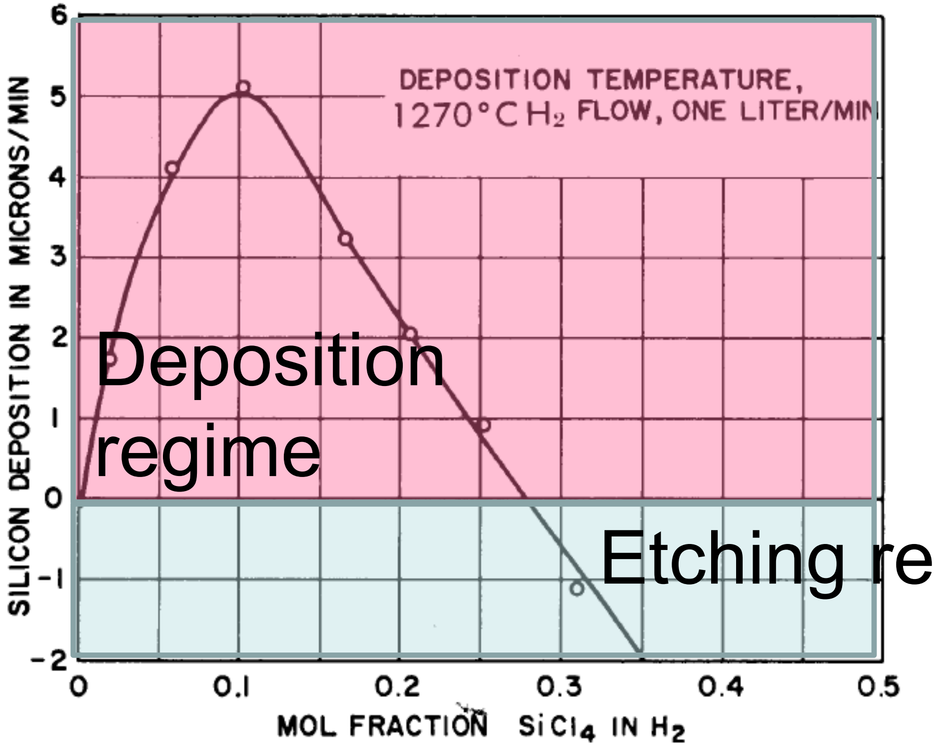
SIMS analysis

Yamazaki et al: J. Electrochem. Soc., Vol. 139, No. 4, April 1992

Growth vs. etching

$SiH_2Cl_2\ (g) \Longleftrightarrow Si\ (s) + 2\ HCl\ (g),$

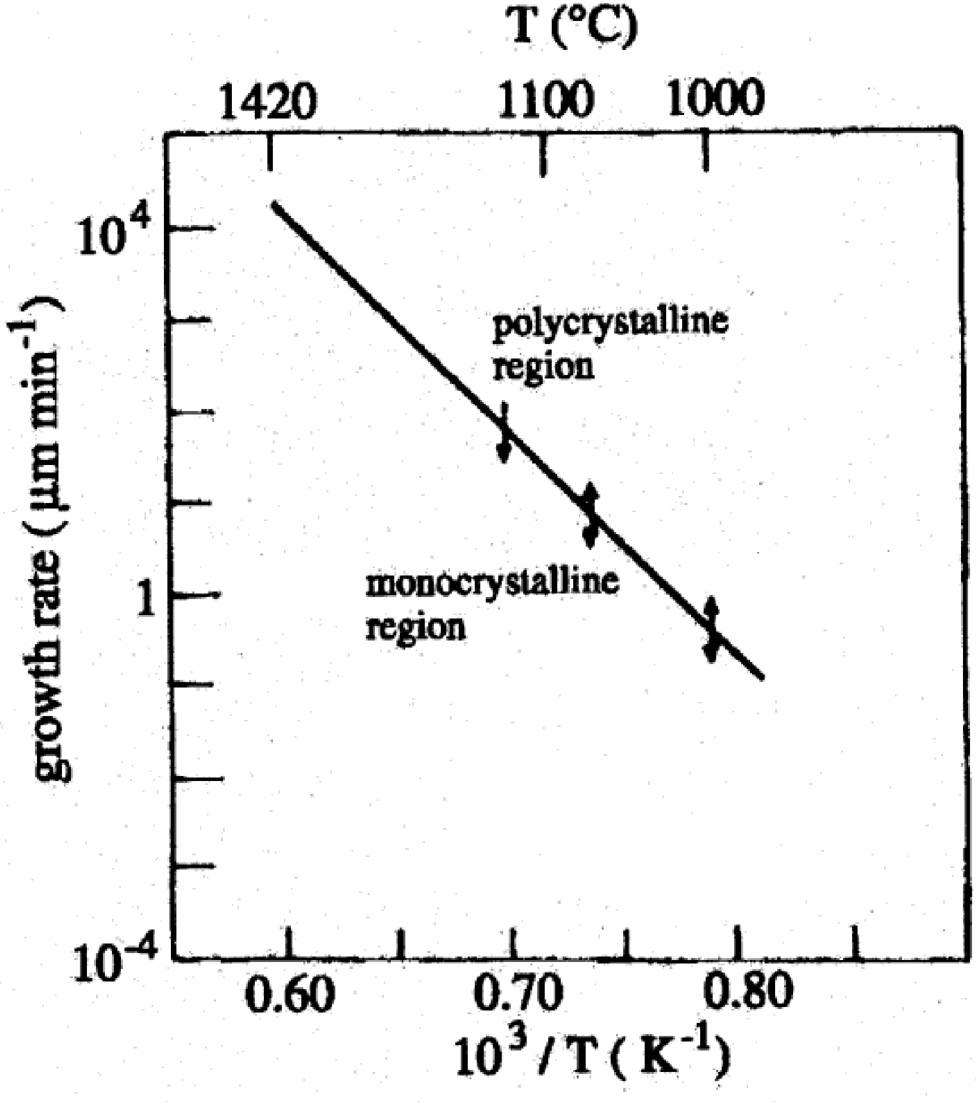
$SiCl_4\ (g) + Si\ (s) \Longleftrightarrow 2\ SiCl_2\ (g)$



Deposition regime

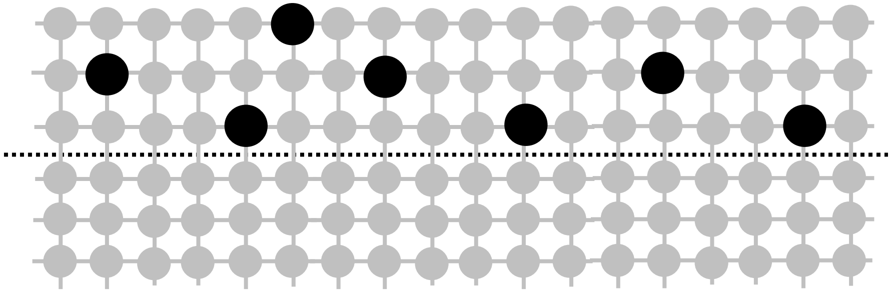
Etching regime

Epi vs. poly



High growth rate results in polycrystalline material: the arriving atoms do not have enough time to find energetically favourable positions before the next layer of atoms arrive.

Doping in epitaxy



SiH_4 (g) ➔ Si (s) + 2 H_2 (g)
2PH_3 (g) ➔ 2P (s) + 3H_2 (g)
B_2H_6 (g) ➔ 2 B (s) + 3 H_2 (g)

Arsenic is a big atom ➔ lattice under compressive stress

Boron is a small atoms ➔ lattice under tensile stress

Too high doping leads to relaxation.

Hig boron concentration ➔ stress & dislocations

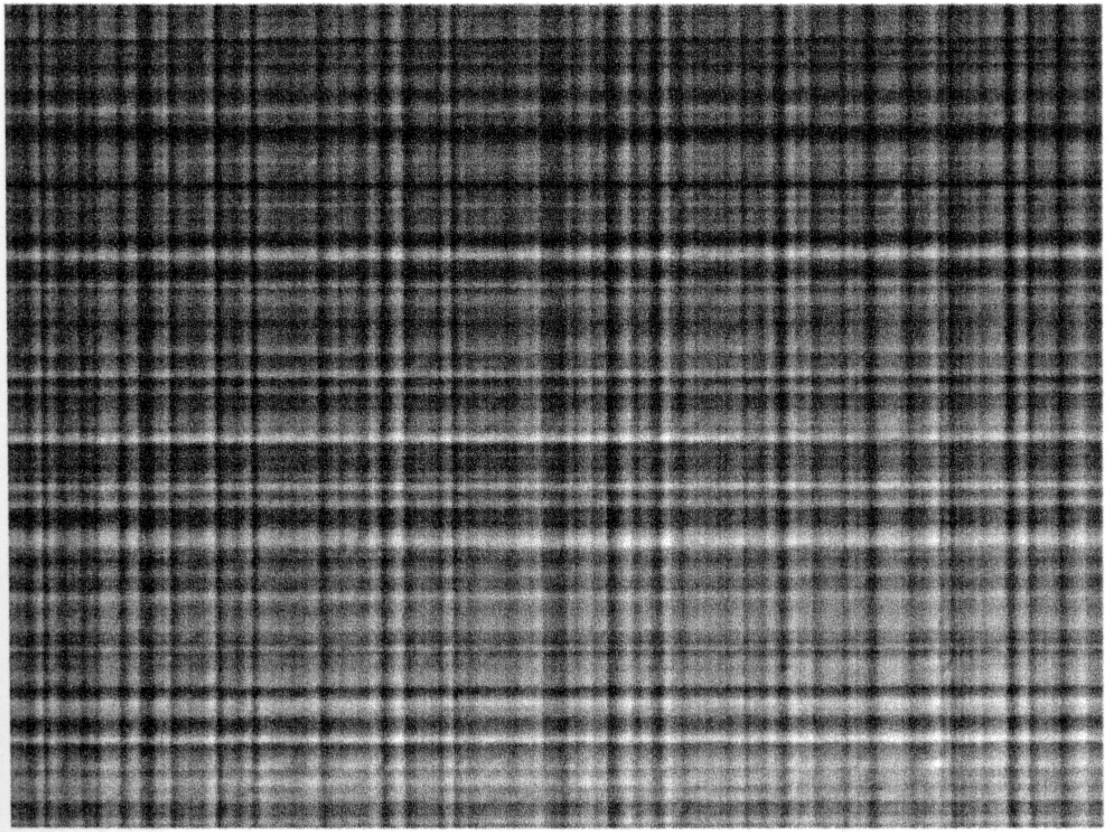
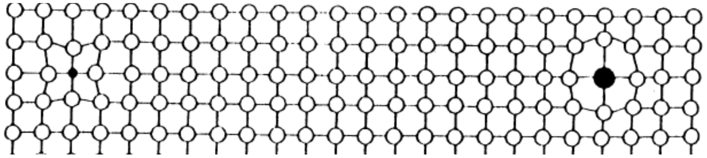


FIGURE 5.11 Misfit dislocation matrix with 10 μm of 1 mΩ cm B doped Si Epi over a p − substrate [13].

1 mΩ-cm resistivity corresponds to $1*10^{20}$ cm^{-3}

Germanium-compensation

Lattice distortion

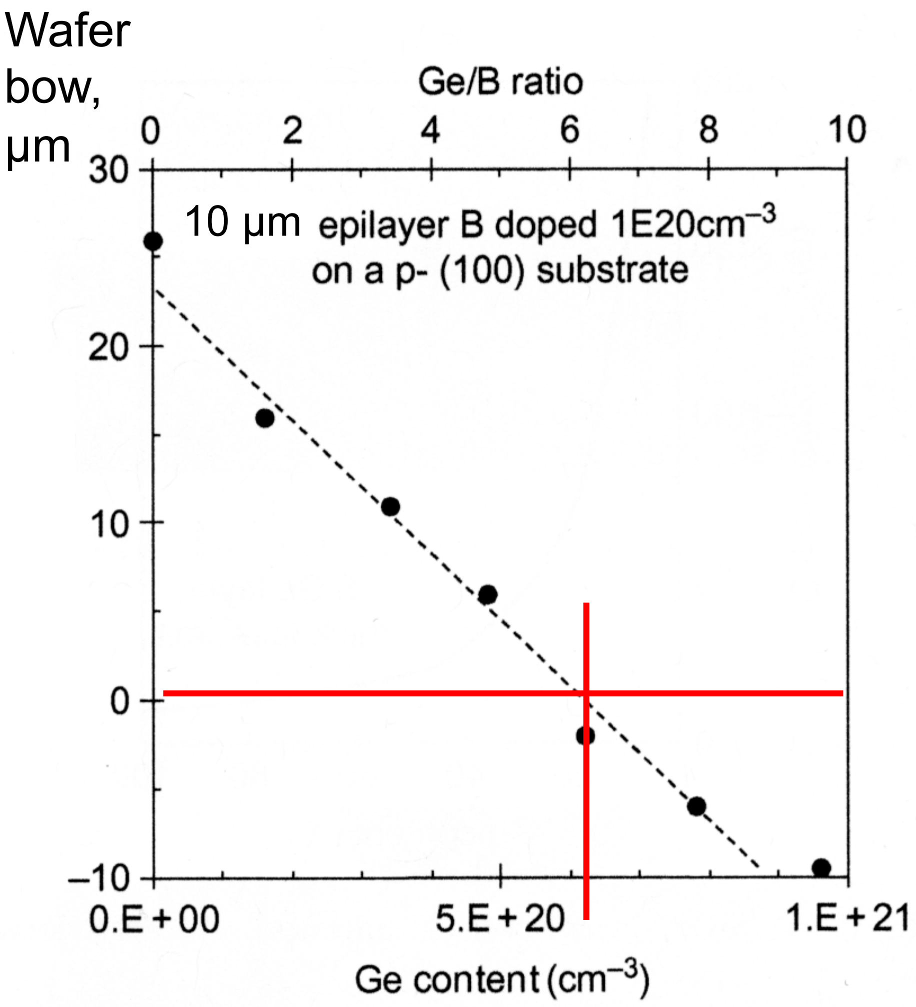


Small boron

Big arsenic and germanium

Germanium compensates for volume changes and stresses due to small boron atoms.

Why Ge and not As?



Germanium atom distance ?

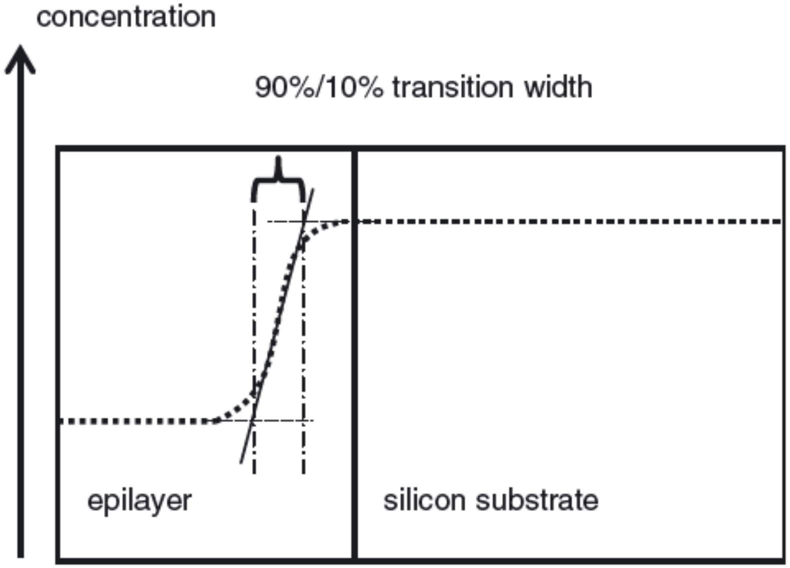
$6*10^{20}$ cm^{-3} Ge
$5*10^{22}$ cm^{-3} Si

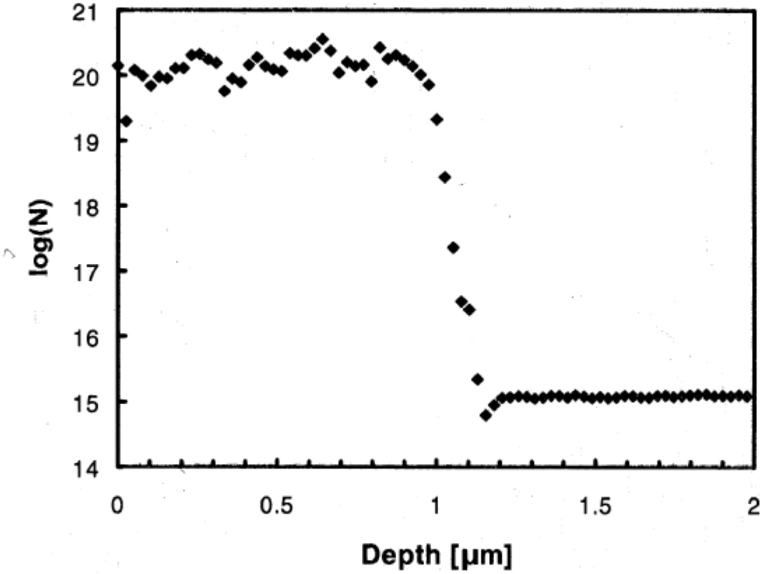
Ca. 1% Ge

$$N = \sqrt[3]{100} \sim 4.5$$

~5*5*5 silicon atoms for each Ge atom.

Transition width



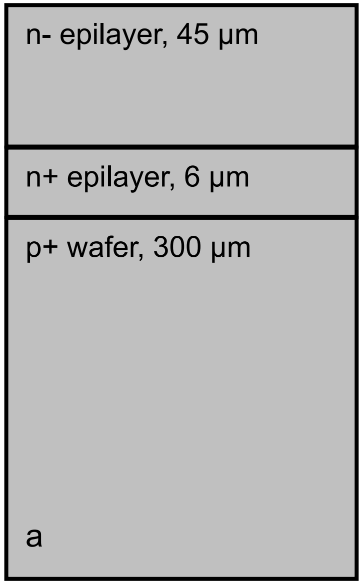


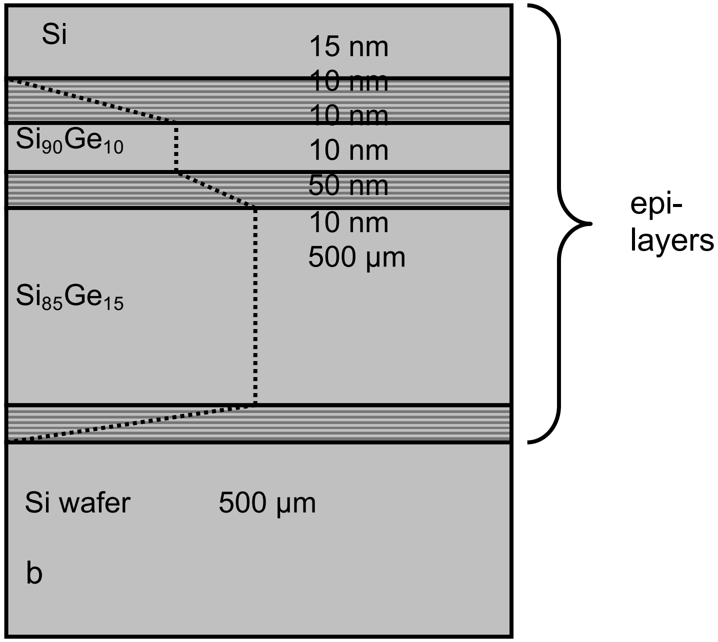
Because epitaxy is a high temperature process, diffusion is bound to happen.

If substrate doping higher ➔ dopants will diffuse into epi-layer

But if epilayer is more highly doped, dopants will diffuse into substrate.

Layer thickness and interface abruptness





Thick homoepitaxial silicon layers for IGBT power transistor;

Thin heteroepitaxial $Si_{1-x}Ge_x$ layers for high speed bipolar transistors. The hatched layers are graded epi layers with constantly changing germanium content.

Characterization

·**Visual** inspection on all wafers.

·**Resistivity** measurement from a test wafer using either a 4-point probe (n/P and p/N -structures) or CV (p/P and n/N). Destructive methods!

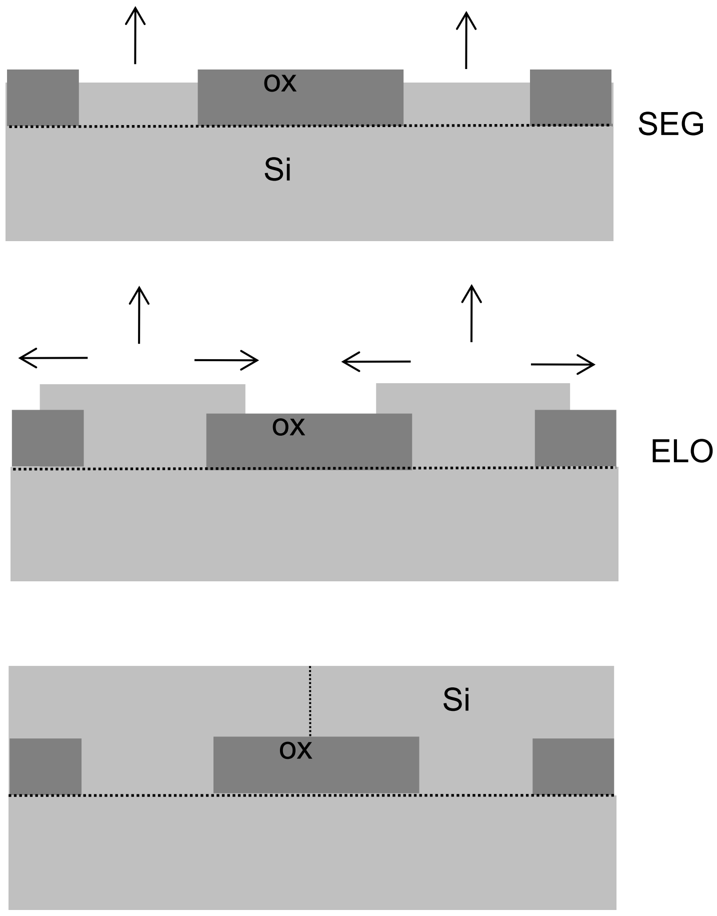
·**Thickness** measurement optically with an FTIR from a p/P^+ or n/N^+ -structure. Nondestructive!

·**Transition width** using SRP.

·Automated inspection for **particles, surface defects** of all
SSP wafers.

·Other measurements as required.

Selective epitaxy

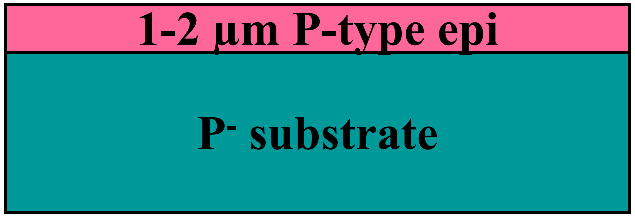


SEG:
Selective Epitaxial Growth

ELO:
Epitaxial Lateral Overgrowth

What happens at the seam ?

Epi applications: electronics

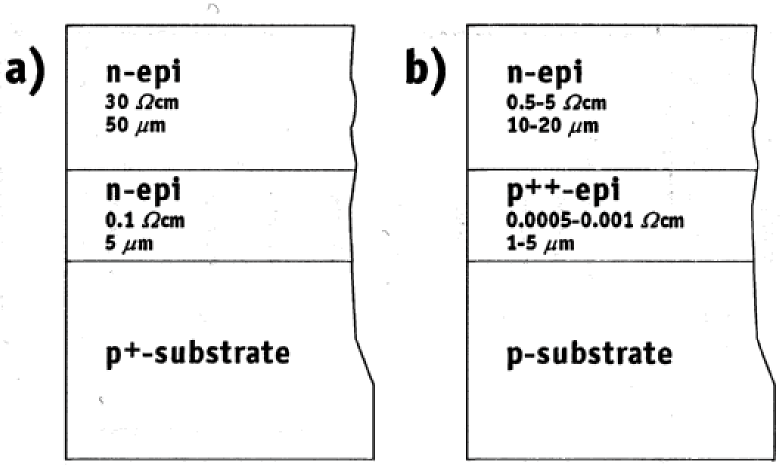


1-2 μm P-type epi

P^- substrate

CMOS:

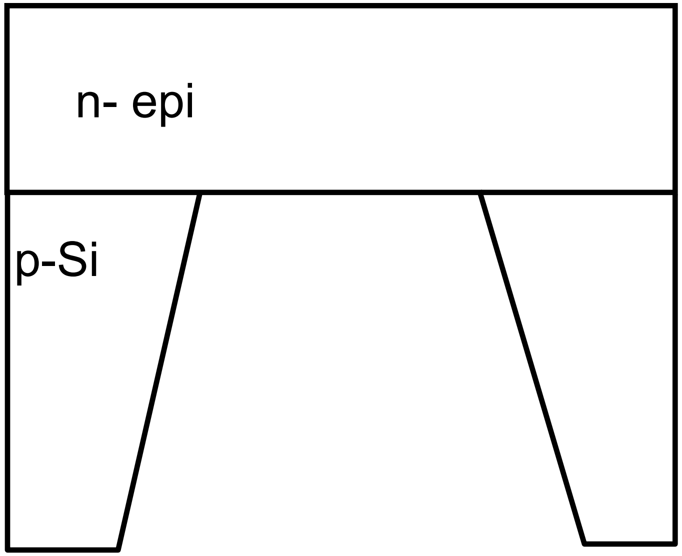
p-type epi on a P-substrate.
Produces COP-free surface.
Thickness and resistivity uniformity specifications not critical.



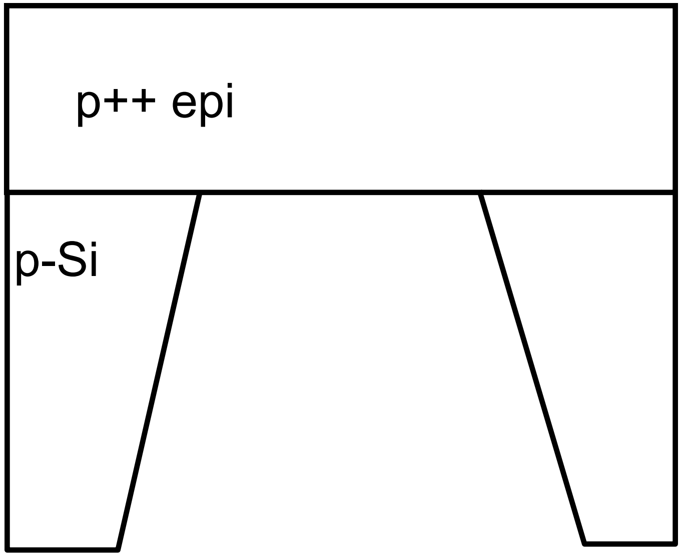
Power devices:

Highly doped substrate reduces resistive losses, but devices need to be made in lightly doped material.

Epi applications: MEMS



Membrane thickness control in MEMS: electrochemical etch stop



P++ etch stop: when boron concentration exceeds $5*10^{19}$ cm^{-3}, KOH etching slows down

Heteroepitaxy:
crystalline film A on top a crystalline wafer B

074501-2 Hu *et al.*

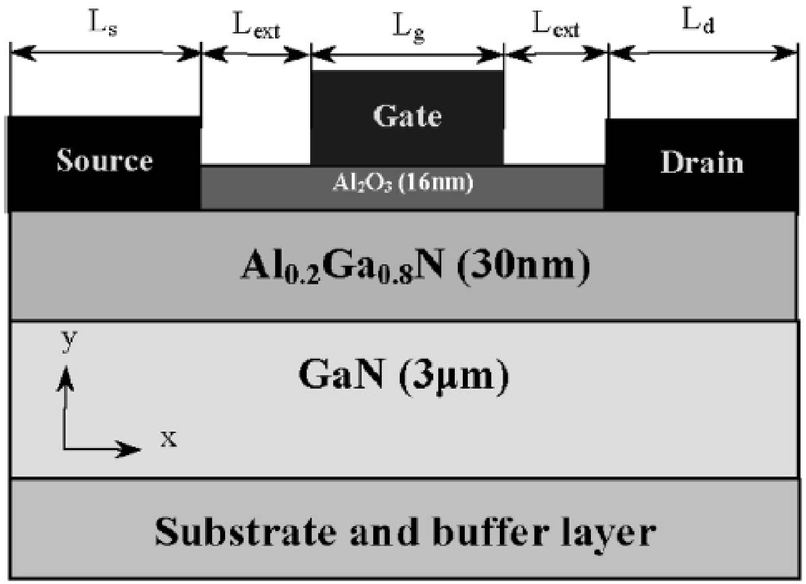
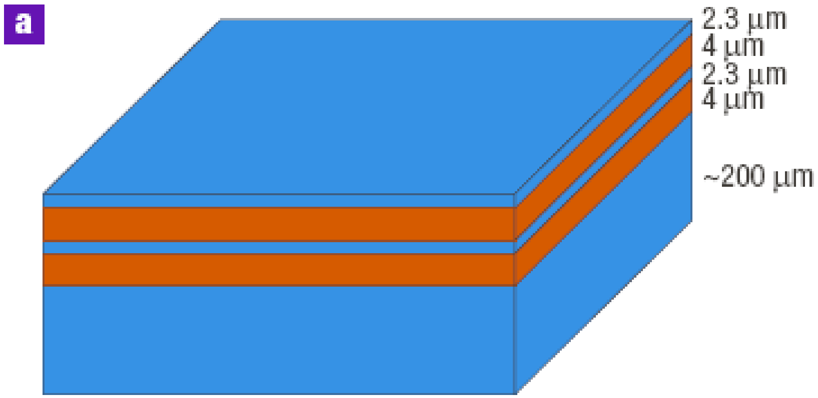


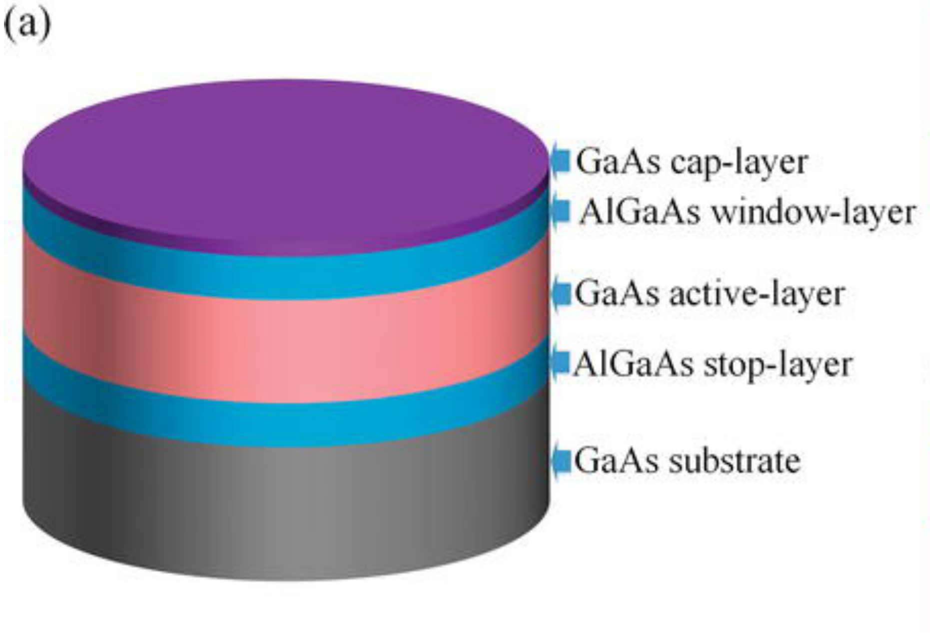
FIG. 1. Schematic structure of GaN-based MOS-HEMT with Al_2O_3 gate dielectric.



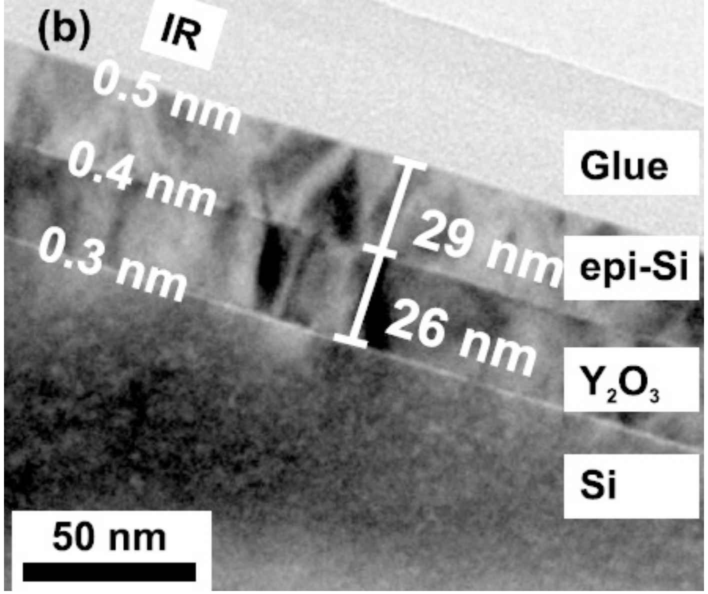
Multiple layers of single crystal AlAs and GaAs grown on top of single crystal GaAs wafer

Multilayer hetero-epitaxy

If we can grow A on B, we can grow B on A.

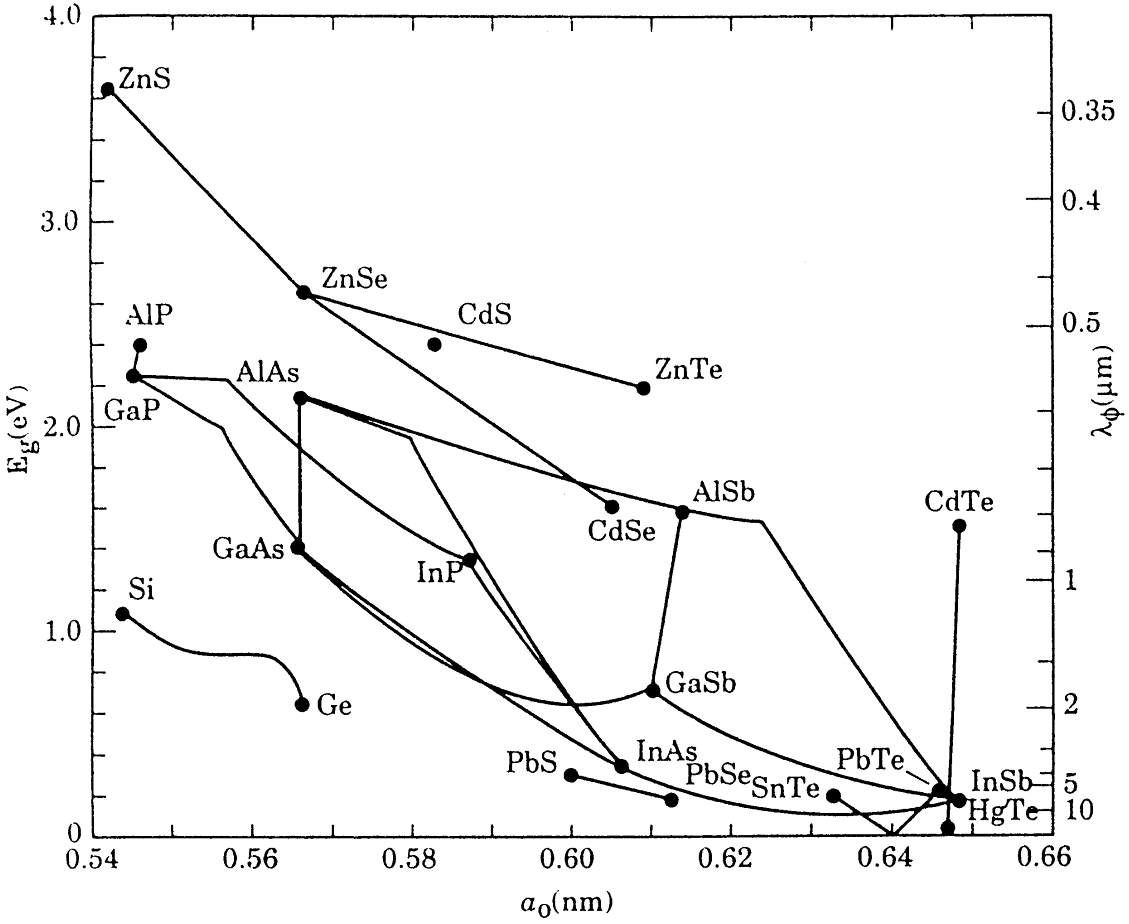


Zhang & Jiao: Energy Bandgap Engineering of Transmission-Mode AlGaAs/GaAs Photocathode 2018



Borschel, C. et al: Structure and defects of epitaxial Si (111) layers on Y_2O_3 (111)/Si(111) support systems, J. Vac. Sci. Technol. B 27 (2009) pp. 305-309

Lattice match requirement



Lattice constant

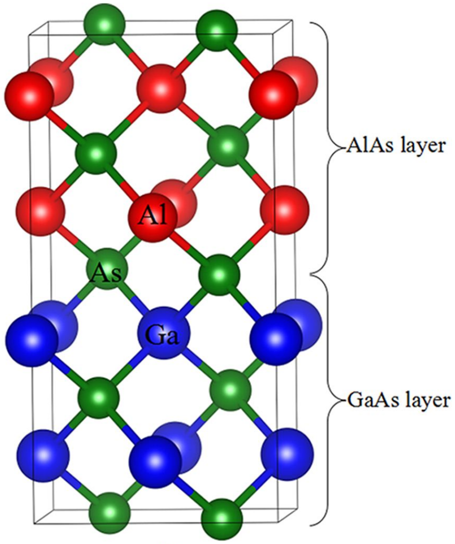
Lattice match difference:

= (a $_{subs}$ – a $_{film}$)/a $_{subs}$

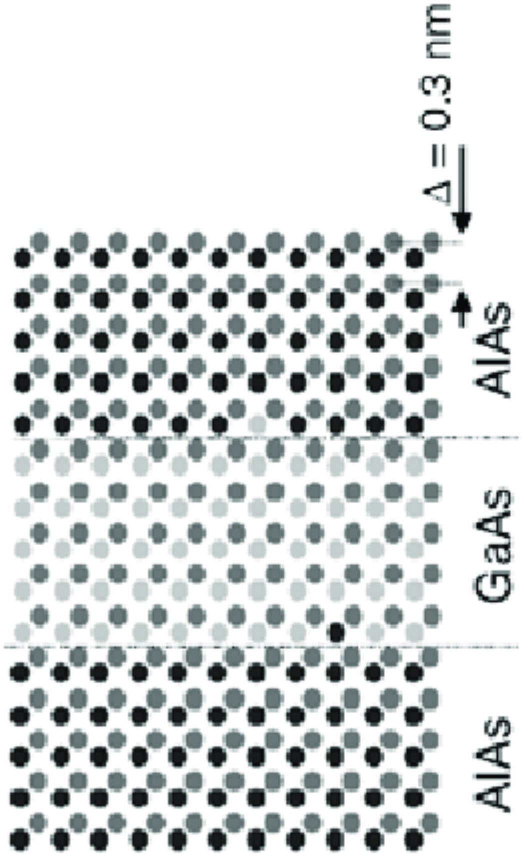
GaAs/AlAs 0.2% ➔ small and easy

Si/Ge, 4.17 % ➔ difficult (but not impossible)

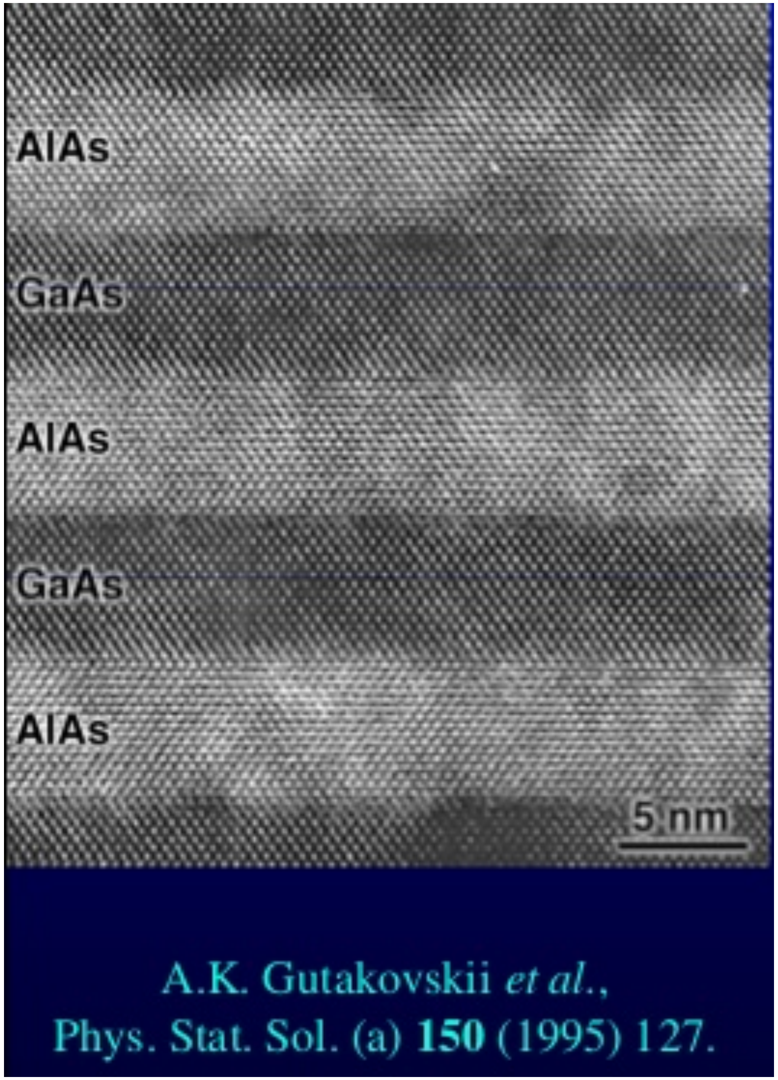
Hetero-epitaxy GaAs/AlAs



$Al_xGa_{1-x}As$ can be grown in any ratio, since lattice matching.



https://www.nature.com/articles/s41598-018-20155-0

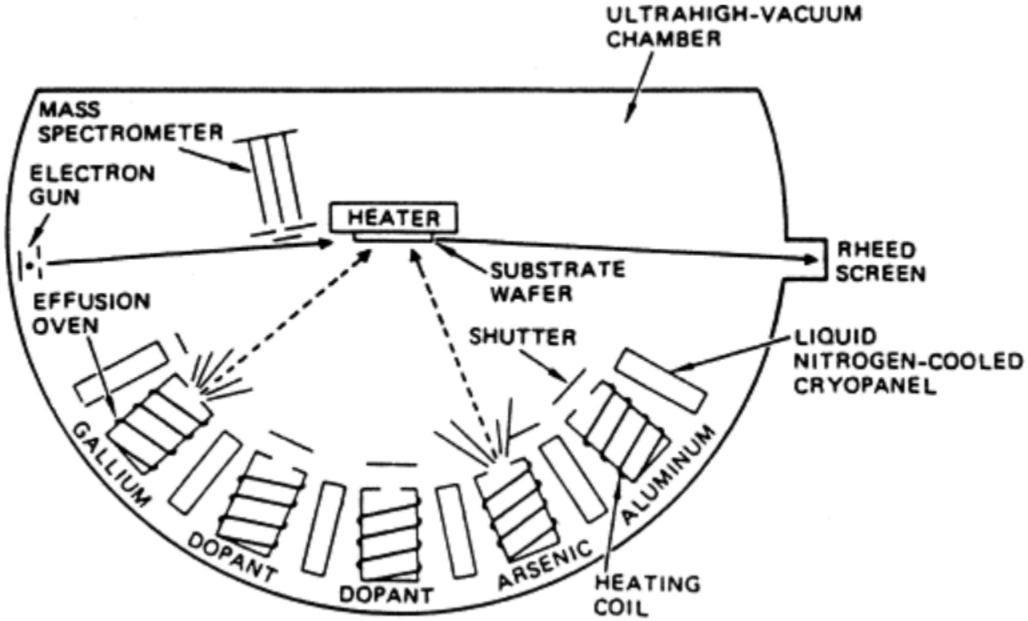


A.K. Gutakovskii *et al.*, Phys. Stat. Sol. (a) **150** (1995) 127.

Thermal expansion

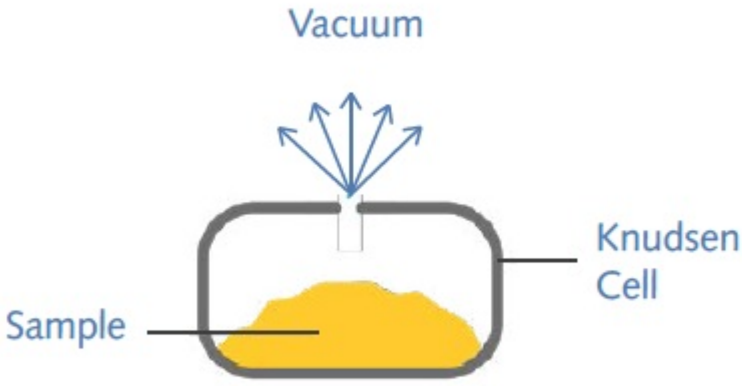
Si	2.6 ppm/^{o}C
Ge	5.9 ppm/°C
GaAs	6.8 ppm/^{o}C
AlAs	5.2 ppm/^{o}C
InP	4.6 ppm/°C

MBE: Molecular Beam Epitaxy



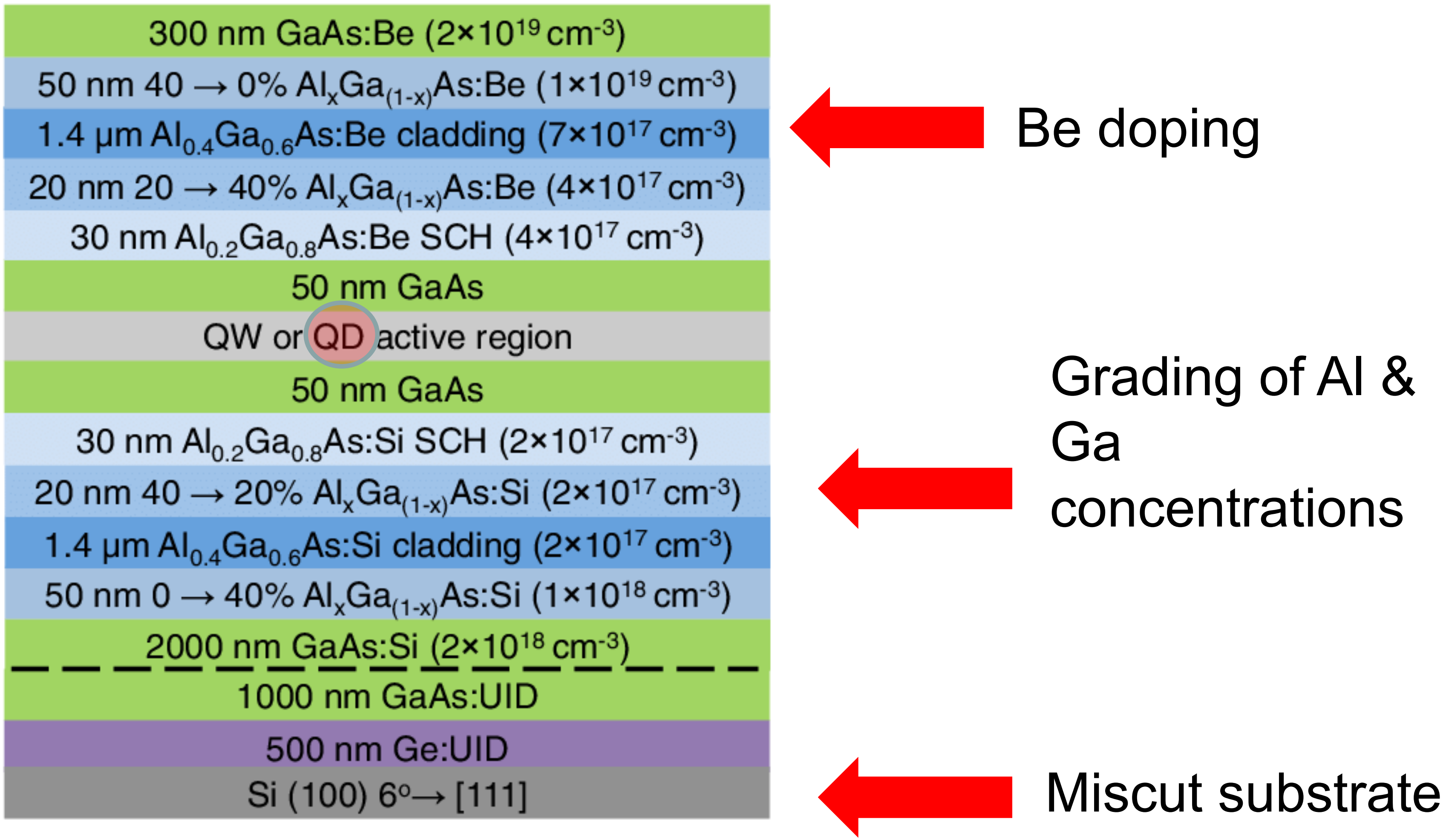
MBE = advanced evaporator

Lynn F. Schneemeyer, in Encyclopedia of Physical Science and Technology (Third Edition), 2003



Effusion cell = Knudsen cell = thermal equilibrium source ➔ stable flux of vapor

GaAs quantum dot (QD) laser



300 nm GaAs:Be (2×10^{19} cm^{-3})

50 nm 40 → 0% $Al_xGa_{(1-x)}As$:Be (1×10^{19} cm^{-3})

1.4 µm $Al_{0.4}Ga_{0.6}As$:Be cladding (7×10^{17} cm^{-3})

20 nm 20 → 40% $Al_xGa_{(1-x)}As$:Be (4×10^{17} cm^{-3})

30 nm $Al_{0.2}Ga_{0.8}As$:Be SCH (4×10^{17} cm^{-3})

50 nm GaAs

QW or QD active region

50 nm GaAs

30 nm $Al_{0.2}Ga_{0.8}As$:Si SCH (2×10^{17} cm^{-3})

20 nm 40 → 20% $Al_xGa_{(1-x)}As$:Si (2×10^{17} cm^{-3})

1.4 µm $Al_{0.4}Ga_{0.6}As$:Si cladding (2×10^{17} cm^{-3})

50 nm 0 → 40% $Al_xGa_{(1-x)}As$:Si (1×10^{18} cm^{-3})

2000 nm GaAs:Si (2×10^{18} cm^{-3})

1000 nm GaAs:UID

500 nm Ge:UID

Si (100) 6° → [111]

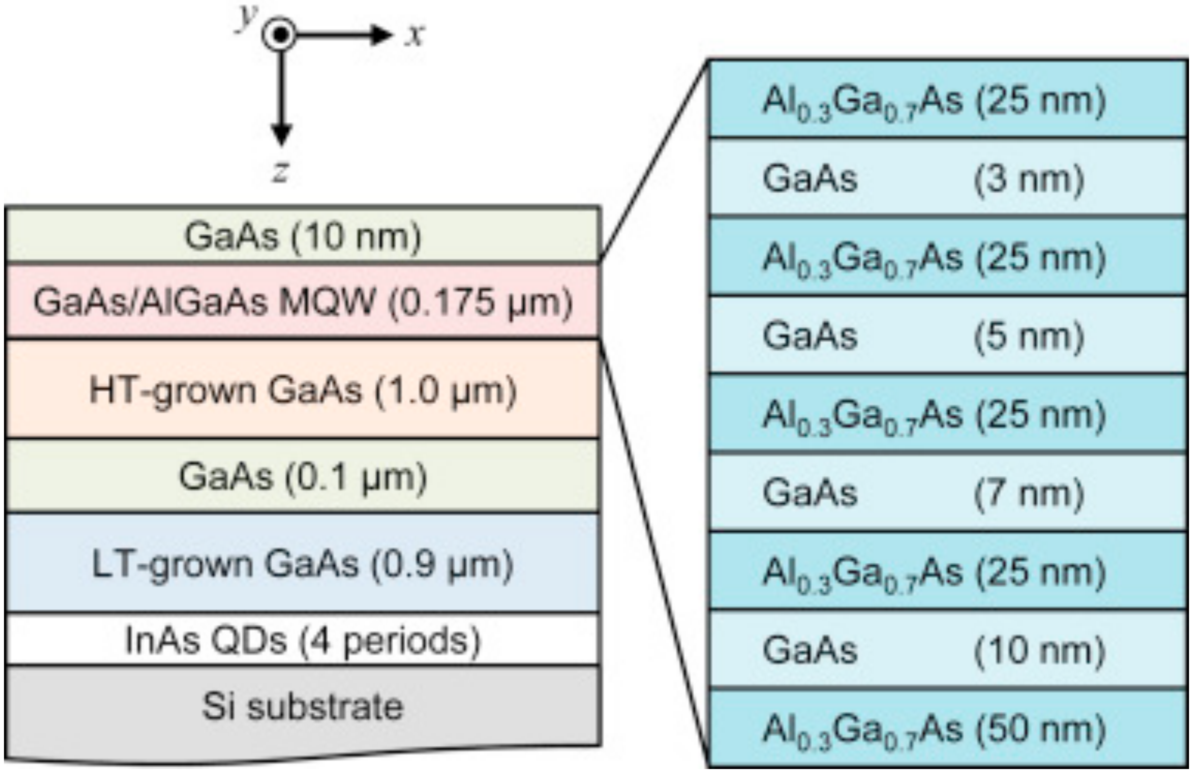
Be doping

Grading of Al & Ga concentrations

Miscut substrate

Liu et al: Quantum dot lasers for silicon photonics, 2015

Superlattice and quantum well (SQW/MQW, single/multiple)



Lee et al: Current Applied Physics Volume 17, Issue 3, March 2017, Pages 398-402

Epitaxy considerations

Thermal mismatch:
CTE differences cause strains

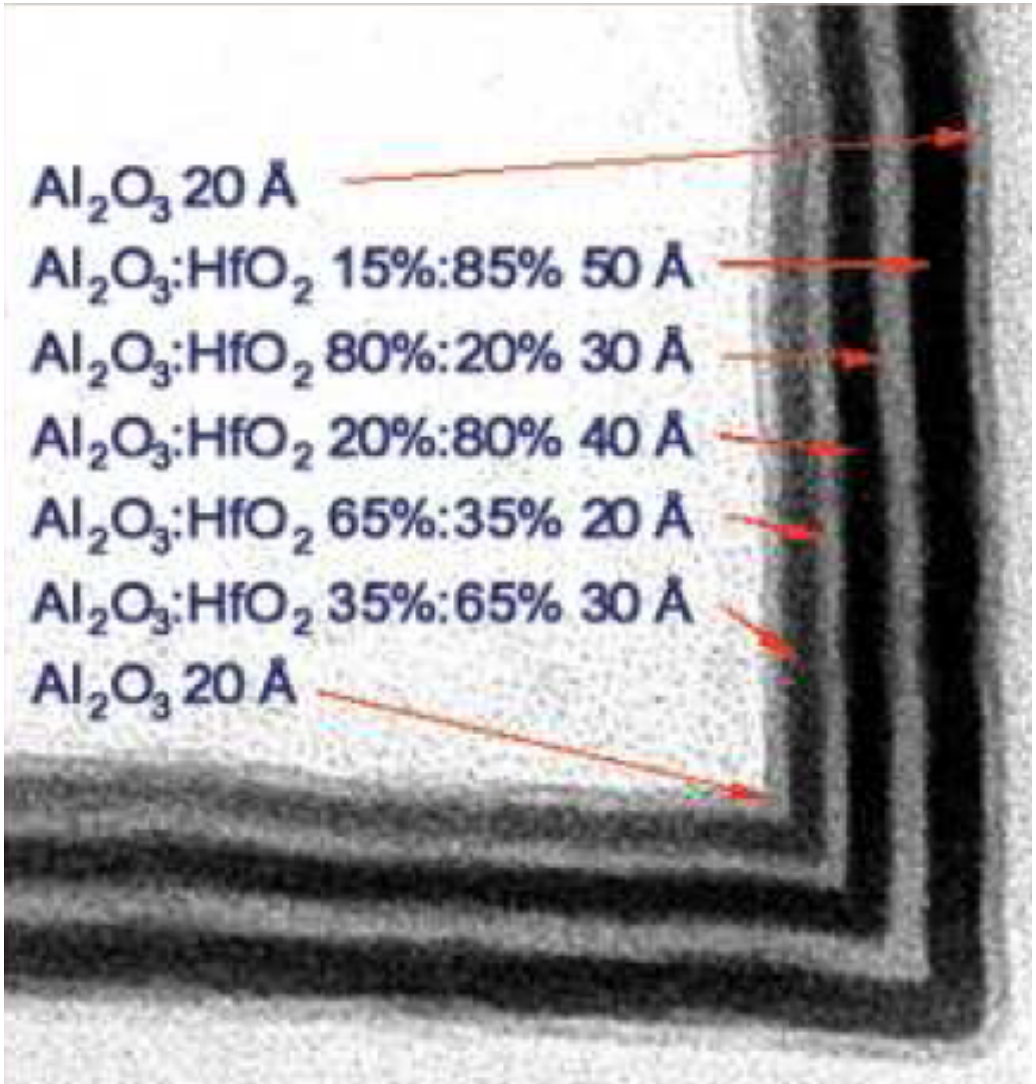
Diffusion:
high T produces surface diffusion which helps epitaxy, but too high T produces diffusion of film atoms into substrate
➔Usable temperature range e.g. 0.35T – 0.4T

Defects in substrate:
Misfit dislocations can propagate into film

Impurities (from the gas phase):
Can act as faux nucleation sites, prevent surface diffusion, generate defects, cause oxidation (oxygen, water vapor)

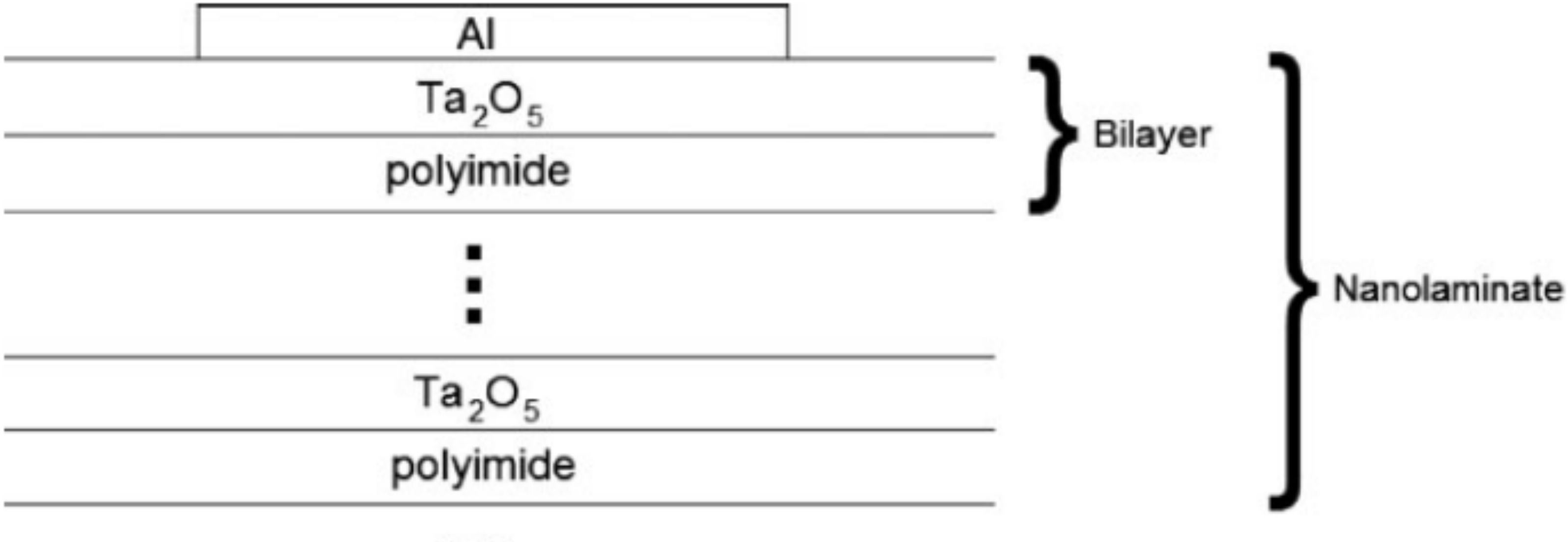
Surface impurites (not removed by cleaning):
Native oxides completely prevent epi, and must be in situ removed

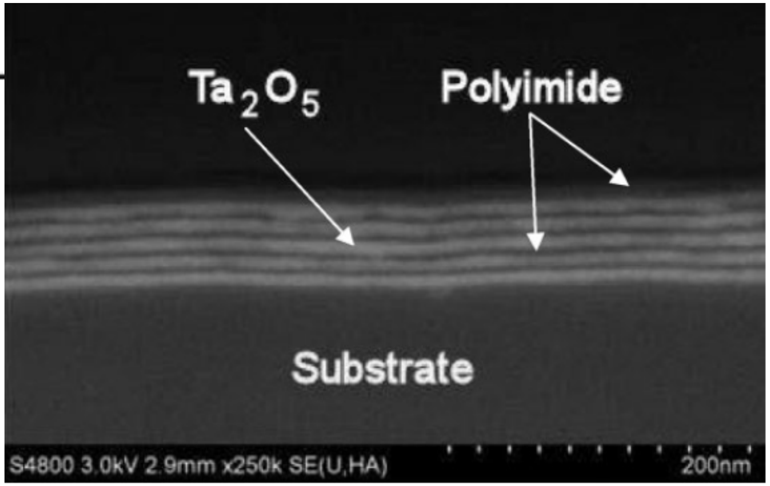
New materials: nanolaminates



Adriana Szeghalmi,Stephan Senz, Mario Bretschneider, Ulrich Gösele, and Mato Knez, APL 2009

Inorganic-organic NL





5x(10 nm PI/10nm Ta_2O_5)/Si.

Salmi, Ritala, DOI: 10.1002/cvde.200906770

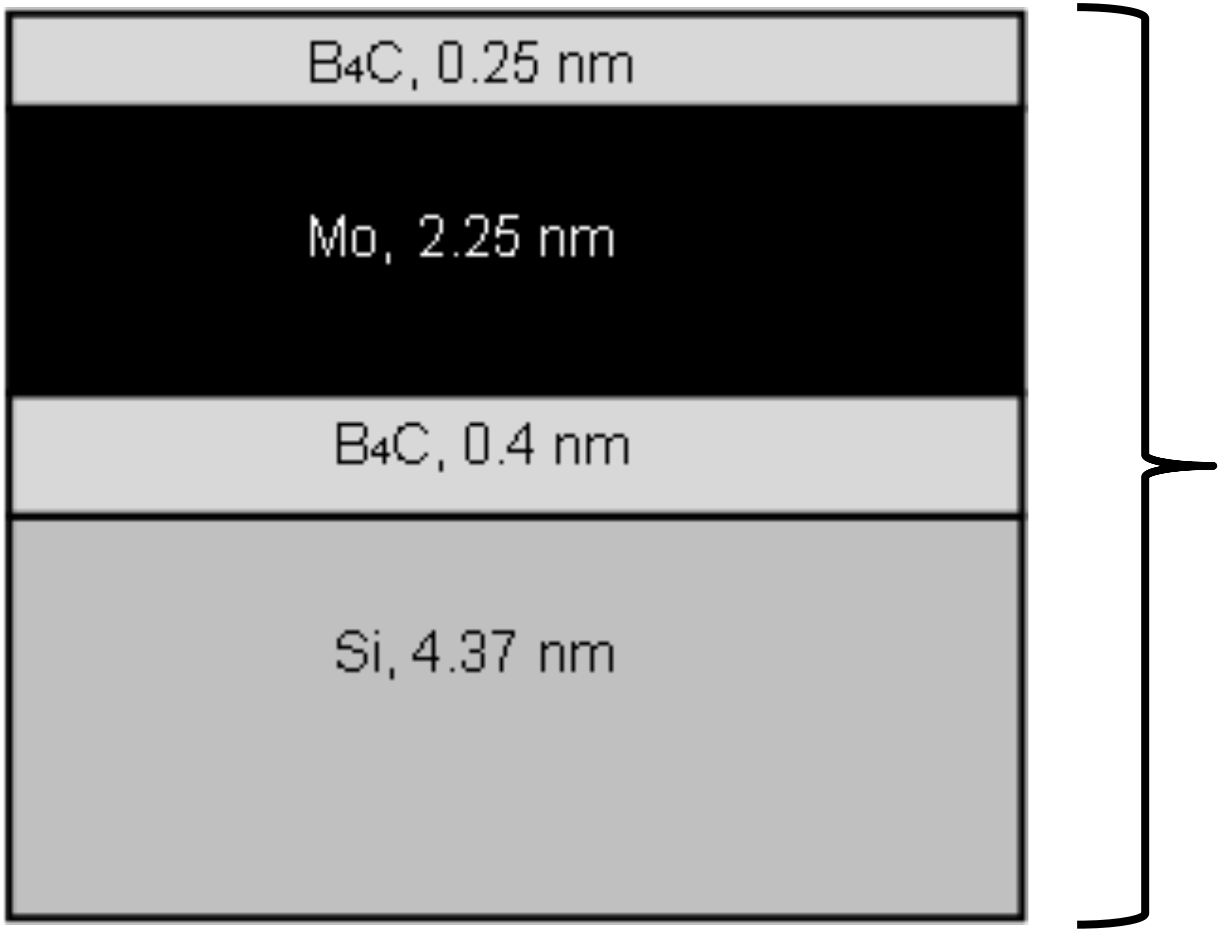
Nanolaminate vs. superlattice

Similar layer thicknesses

Similar deposition equipment

But: amorphous or polycrystalline films

Sputtered NL


B_4C, 0.25 nm

Mo, 2.25 nm

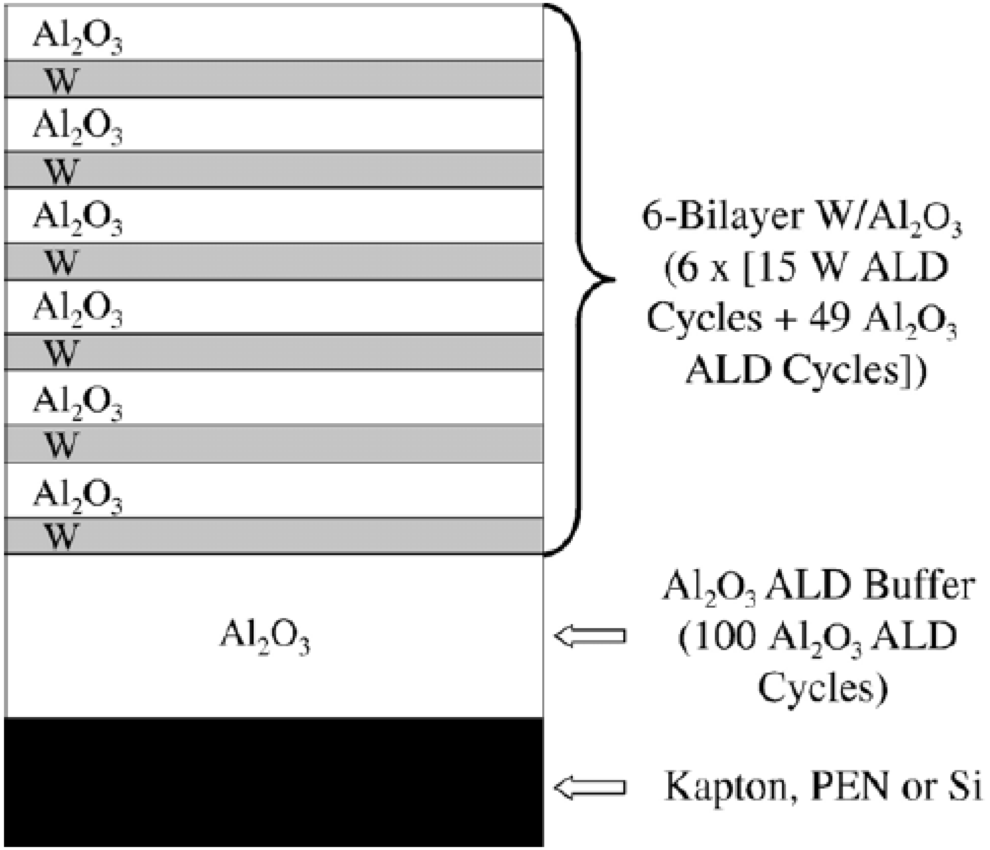
B_4C, 0.4 nm

Si, 4.37 nm

This structure repeated 50 times

Bajt, S.: Improved reflectance and stability of Mo-Si multilayers, Opt. Eng. 41(2002), pp.1797–1804.

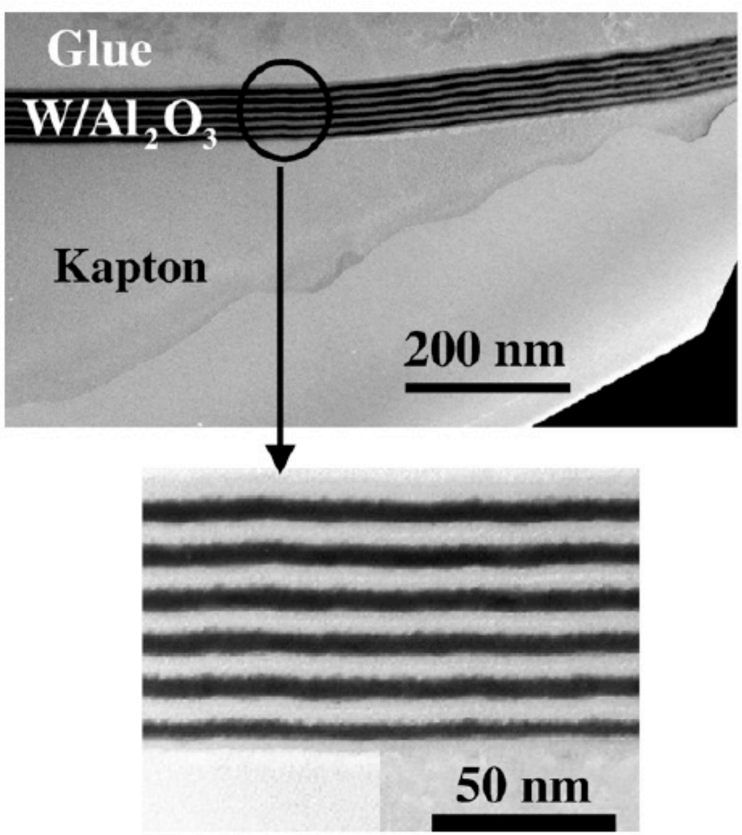
NL by ALD



Flexible polymer substrate ➔ folding space mirror for X-ray telescope

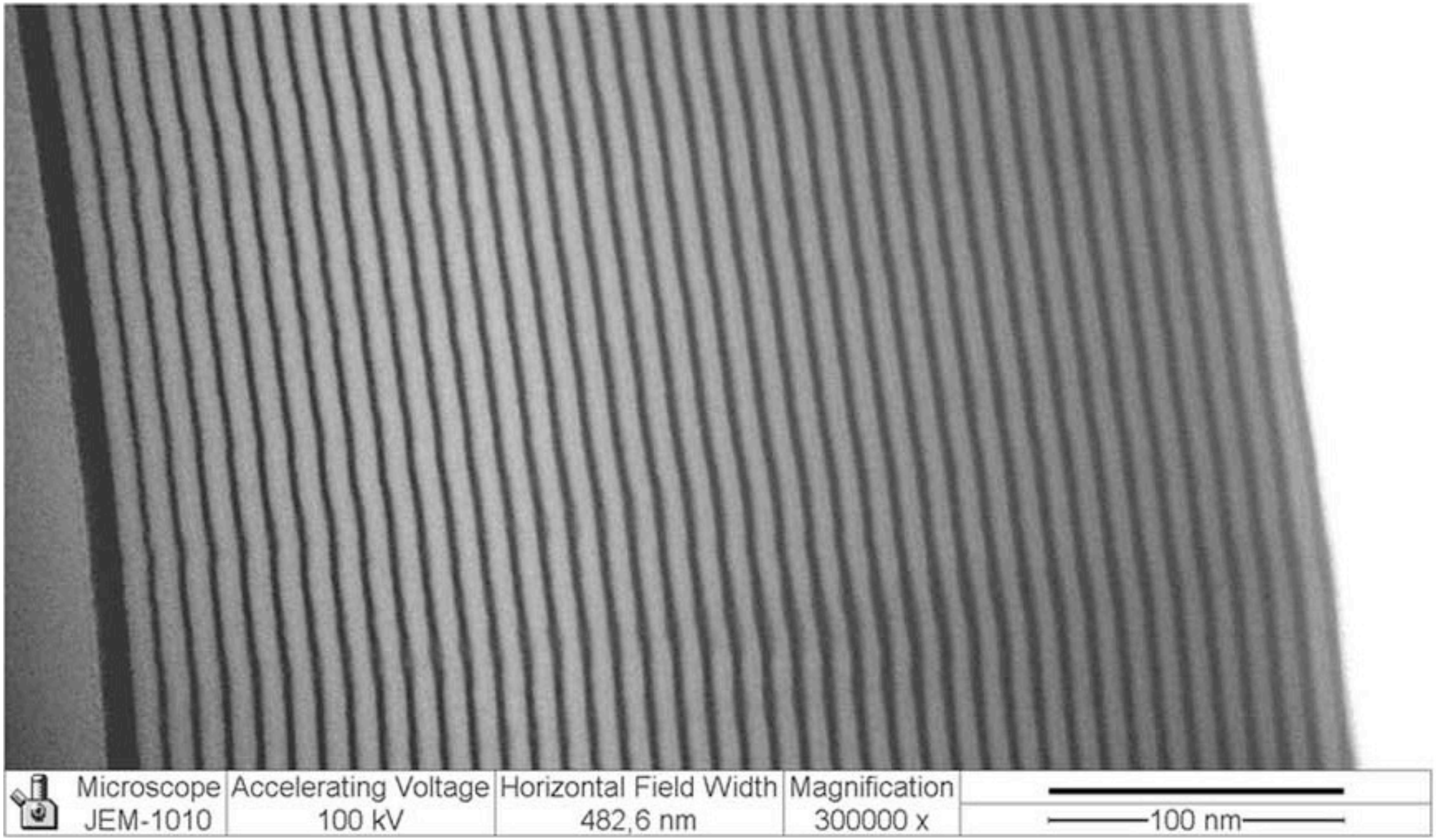
S.M.George et al: Thin Solid Films 515 (2007) 7177–7180

X-ray mirror



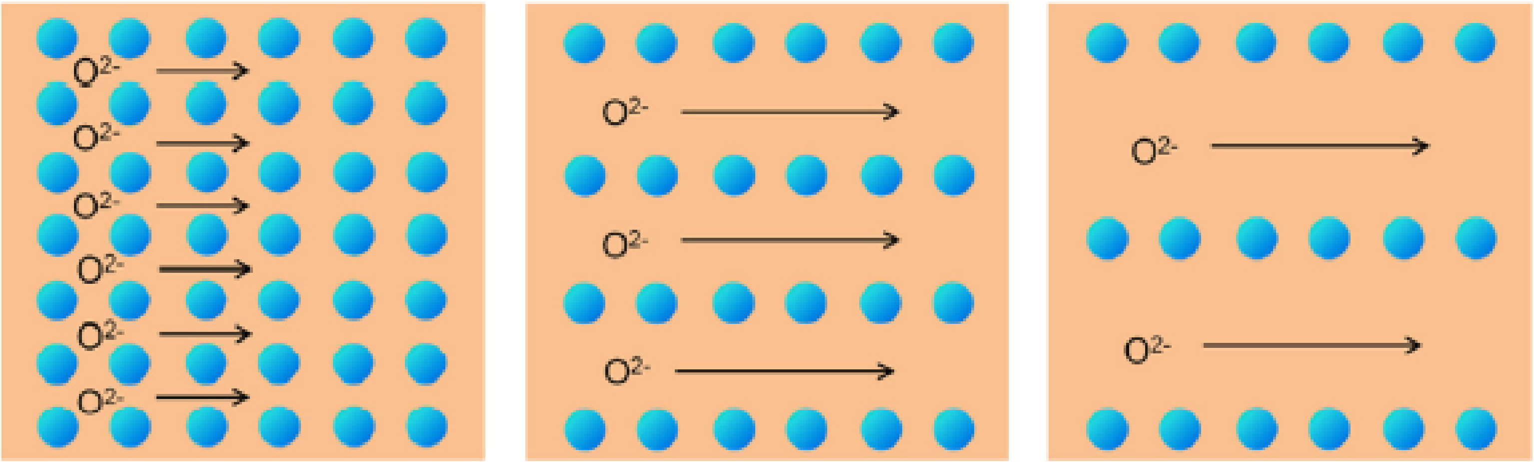
S.M.George et al: Thin Solid Films 515 (2007) 7177–7180

Al_2O_3/Ta_2O_5



Szeghalmi & Knez: APPLIED PHYSICS LETTERS **94**, 133111 2009

Ionic conductivity



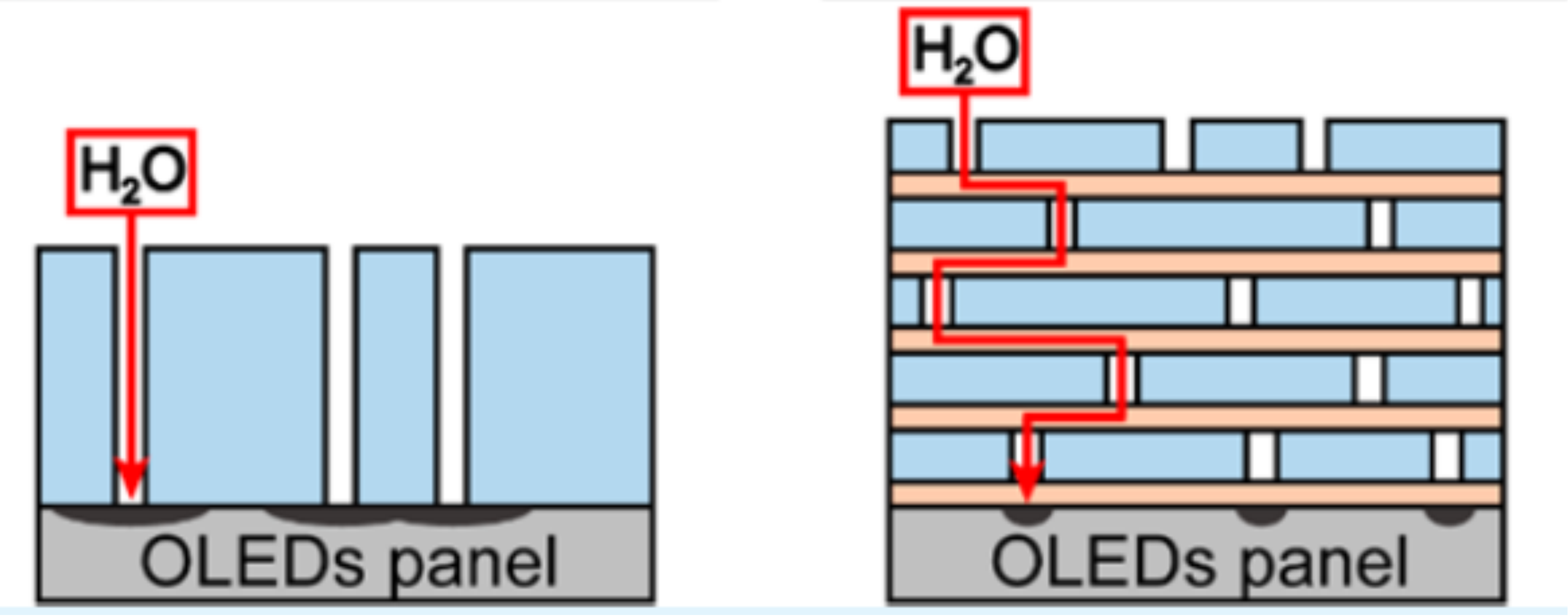
ALD ZrO_2:Y_2O_3 = 1:1 ALD ZrO_2:Y_2O_3 = 4:1 ALD ZrO_2:Y_2O_3 = 6:1

The 4:1 cycle ratio (10.4 mol% Y dopant) resulted in the highest conductivity of all films, which was 2 orders of magnitude greater than bulk YSZ (8 mol% Y dopant).

Johnson et al: Materials Today Volume 17, Number 5 June 2014

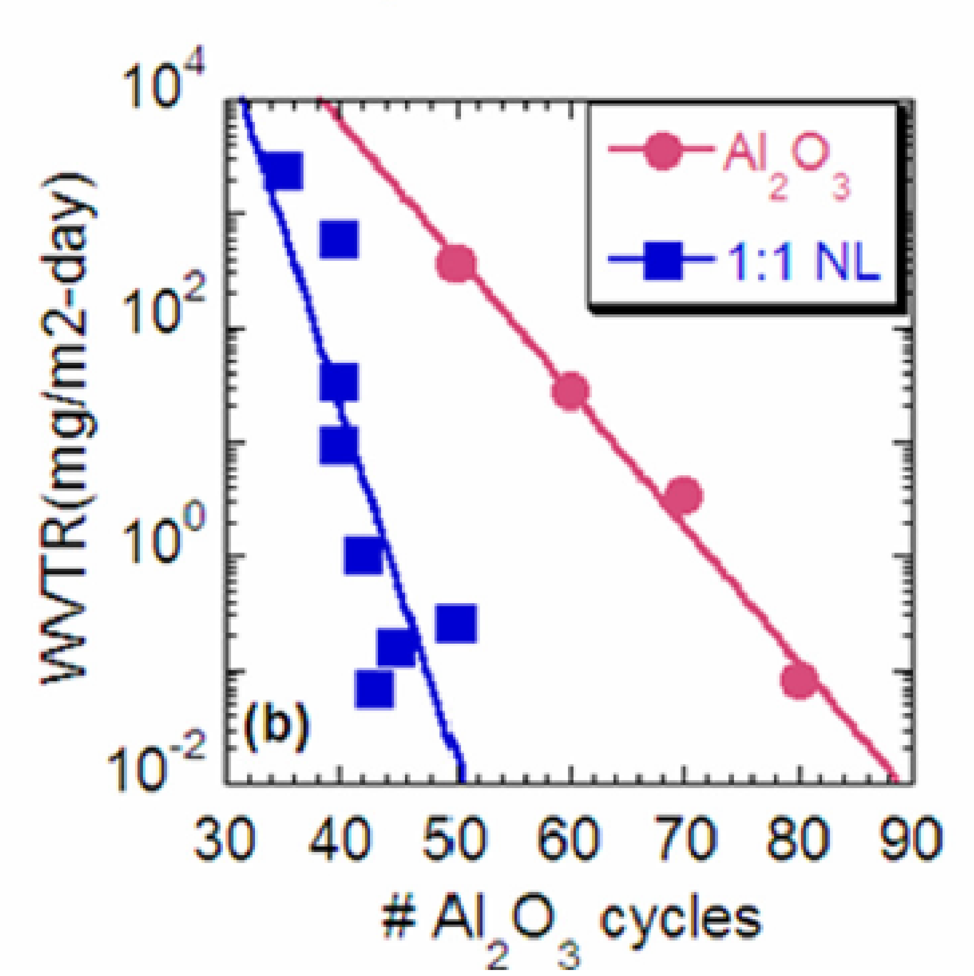
NLs as vapor barriers

Multilayer structures are unlikely to have defect in the same position in every layer ➔ improved leak tightness.



Yoon & Sung: DOI: 10.1021/acsami.6b15404

Barrier properties of NL



Water vapor transmission rate reduced by 4 orders of magnitude for same thickness.

Peter F. Carcia, Robert S. McLean, Zhigang G. Li, Michael H. Reilly, and Will J. Marshall
Citation: Journal of Vacuum Science & Technology A **30**, 041515 (2012); doi: 10.1116/1.4729447