

Advanced Micro and Nanofabrication Technologies

Engineering Physics – Ingegneria Fisica - Cod. 055559

a.a. 2024/2025

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Lecture 4 Epitaxy

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Outline of the course

➤ **Where** we will grow? **Vacuum** ➡ **Vacuum technology: pressure, gas transport, vacuum systems**

➤ **On what** we will grow? **Surfaces** ➡ **Surface properties, nucleation, film growth modes**

➤ **Which kind** of films we will grow? **Epitaxy** ➡ **Crystals, homo/heteroepitaxy, other modes**

➤ **How** we will grow?

- **Physical techniques**
 - **Evaporation**
 - **Sputtering**
- **Chemical techniques**

➤ **How** we will check the growth? **Characterization**

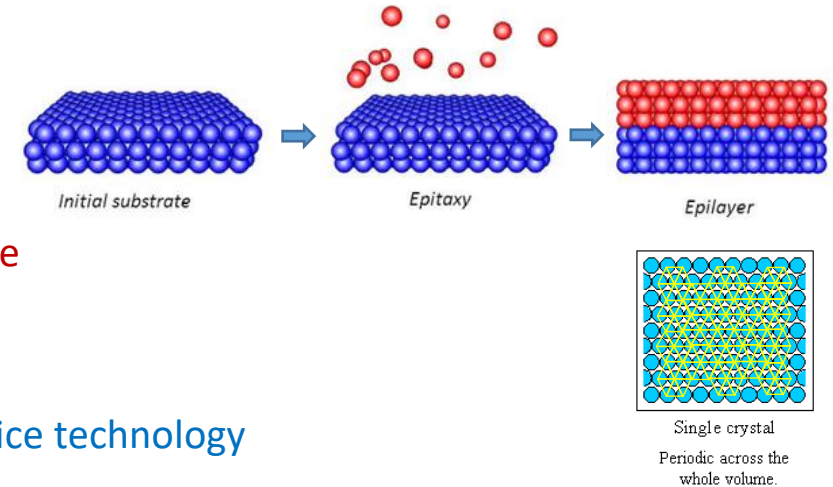
Reference for this lecture: M. Ohring, Materials Science of Thin films, Academic Press, Chapter 8

What is epitaxy?

Epitaxy = *epi* (placed or resting upon) + *taxis* (arrangement)



extended **single-crystal film** formation on top of a **crystalline substrate**



Epitaxy is **fundamental** in **semiconductor thin-films device technology**
(electronics, optoelectronics)...

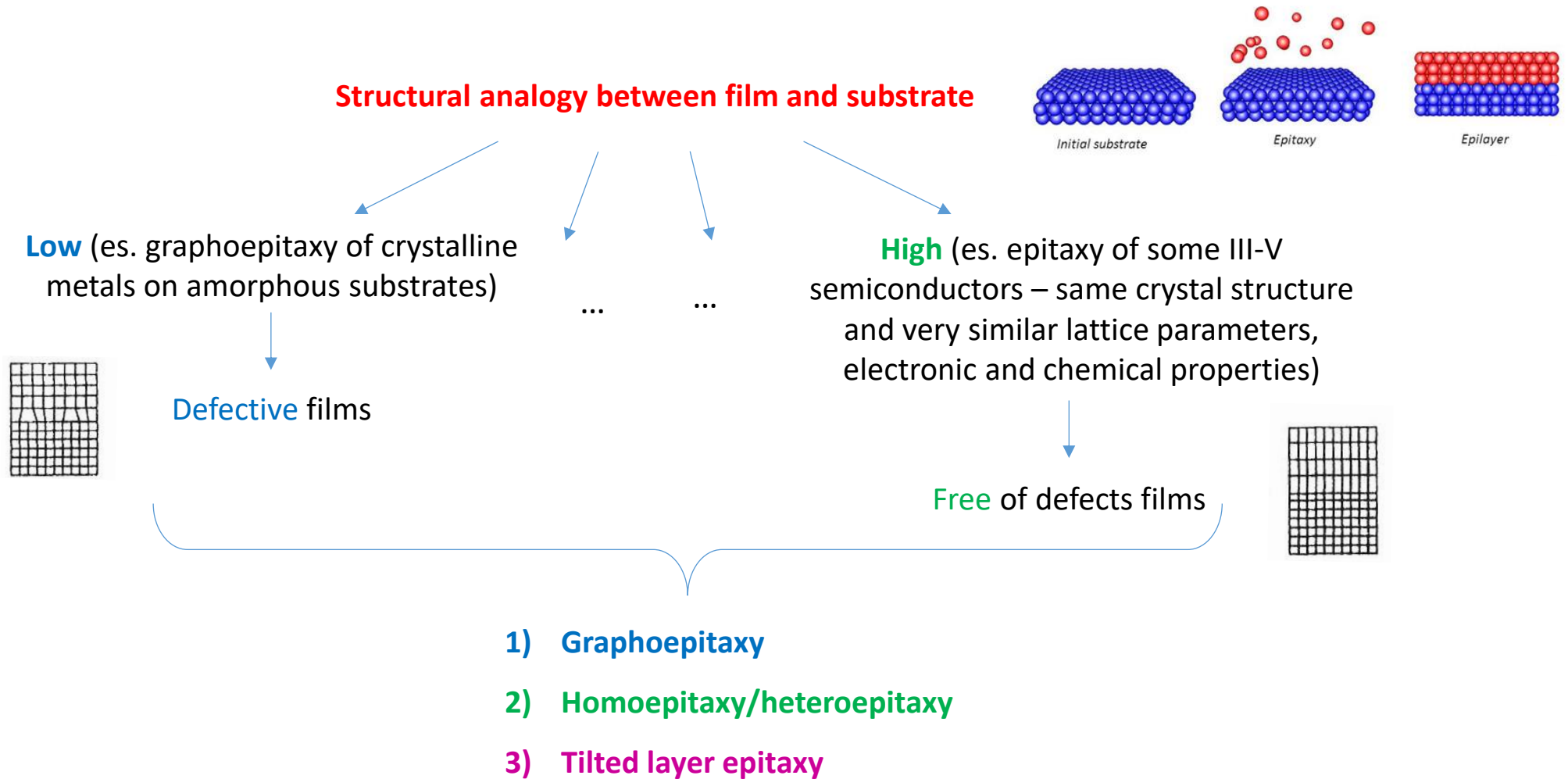
... but **not** in other major applications (**coatings, recording, display, ...**)

Where epitaxy is required?

- MgO-based tunneling magneto-resistance devices (TMR) – see [Appendix 1](#) for more detail
 - Wide-bandgap **optoelectronic** devices (i.e., LEDs and lasers) based on GaInN
- High-speed **microelectronic** high-frequency and wireless communication devices based on $\text{Ge}_x\text{Si}_{1-x}$ and compound semiconductors
 - Three dimensional integrated circuits with high packing density based on Silicon
- Multilayer heterojunctions composites, including **quantum** wells and superlattices, for nanoscale quantum electronic and optical devices
- Electroceramic films and multilayers for HT **superconductors**, magneto-optical devices, ferroelectric films, ...
 - etc.

Manifestations of epitaxy

Epitaxy = *epi* (placed or resting upon) + *taxis* (arrangement) \longleftrightarrow extended **single-crystal** film formation on top of a substrate



Crystal structure

Epitaxial structures are **crystalline**

How to describe them?

We consider, for simplicity, a **simple cubic lattice**.

The lattice (**Bravais lattice**) is obtained by a set of **discrete translation operations** in three dimensional space of a **primitive cubic cell**.

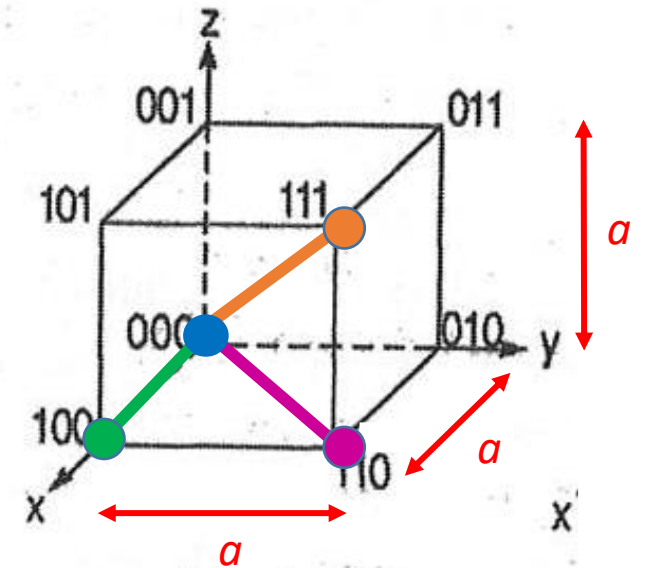
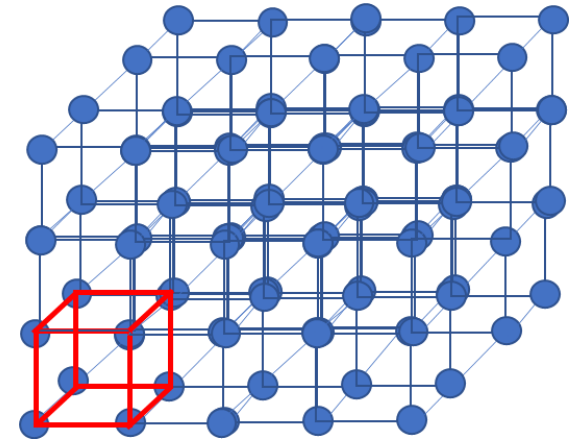
In each cell, the atoms are placed at the 8 vertices of a cube of side a .

How to «label» lattice sites?

- Consider the cell with a vertex in the **origin (000)**.
- The other vertices can be labelled by their (x,y,z) coordinates, in units of the lattice parameter a .
- The distance d of a vertex from the origin is given by the Pitagora's thorem.

E.g:

- $100 \rightarrow (a,0,0)$; $d = a$ (the side of the cube)
- $110 \rightarrow (a,a,0)$; $d = \sqrt{a^2 + a^2} = a\sqrt{2}$ (the diagonal of a face of the cube)
- $111 \rightarrow (a,a,a)$; $d = \sqrt{a^2 + a^2 + a^2} = a\sqrt{3}$ (the diagonal of the cube)

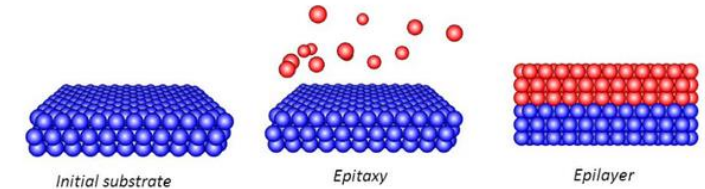


Miller indices

Epitaxial structures are **crystalline**

How to describe them?

- We consider **heteroepitaxial** structures where **film and substrate materials differ structurally, chemically and/or electronically** (e.g., metal-semiconductor, metal-insulator, ...)
- We use the **crystallographic notation** for the **film** and the **substrate**.



Miller indices:

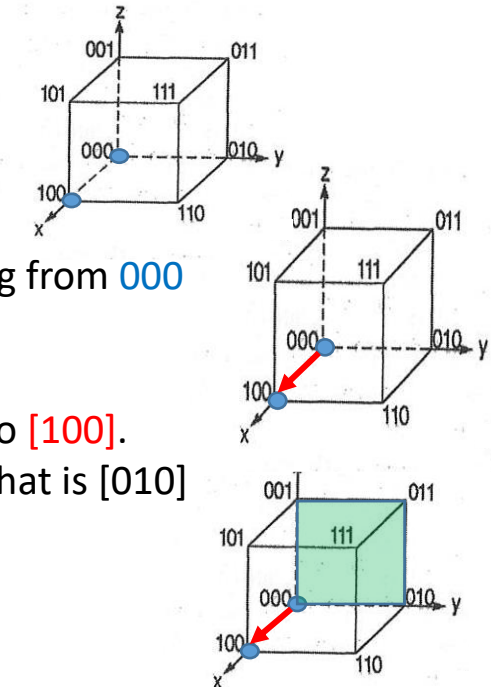
	Overgrown film	Substrate
Plane	(HKL)	(hkl)
Direction	[UVW]	[uvw]

We consider, a **simple cubic lattice** (the atoms are placed at the 8 vertices of a cube)

Lattice sites: xyz, es. **000**, **100** (without brackets)

Direction: [uvw], es. **[100]** is the direction pointing from **000** to **100**

Plane: (hkl), es. **(100)** is the plane perpendicular to **[100]**.
The two direction perpendicular to [100], that is [010] and [001], lie in the (100) plane



Homo/heteroepitaxy (1)

Epitaxy = *epi* (placed or resting upon) + *taxis* (arrangement) ↔ extended **single-crystal** film formation on top of a **crystalline** substrate

Homoepitaxy

The substrate and the film are made by the **same** material.

Es. Si/Si

Why?

Because the epilayer has less defects, is purer than the wafer substrate, and can be doped independently on it

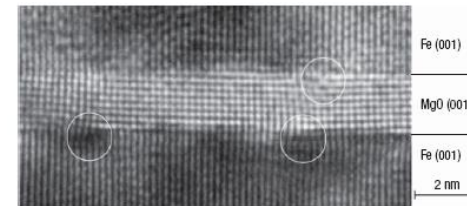
Heteroepitaxy

The substrate and the film are made by **different** materials.

Es. Fe/MgO/Fe, AlAs/GaAs, ...

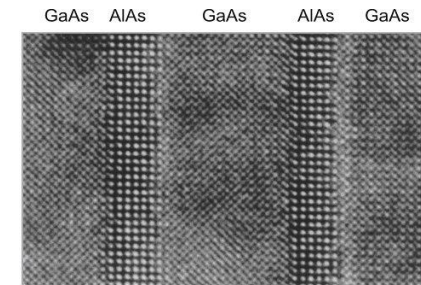
Why?

In order to obtain epitaxial – well ordered – stacked device structures (**multilayers**)



S. Yuasa et al, Nature Materials, 3 868 (2004)

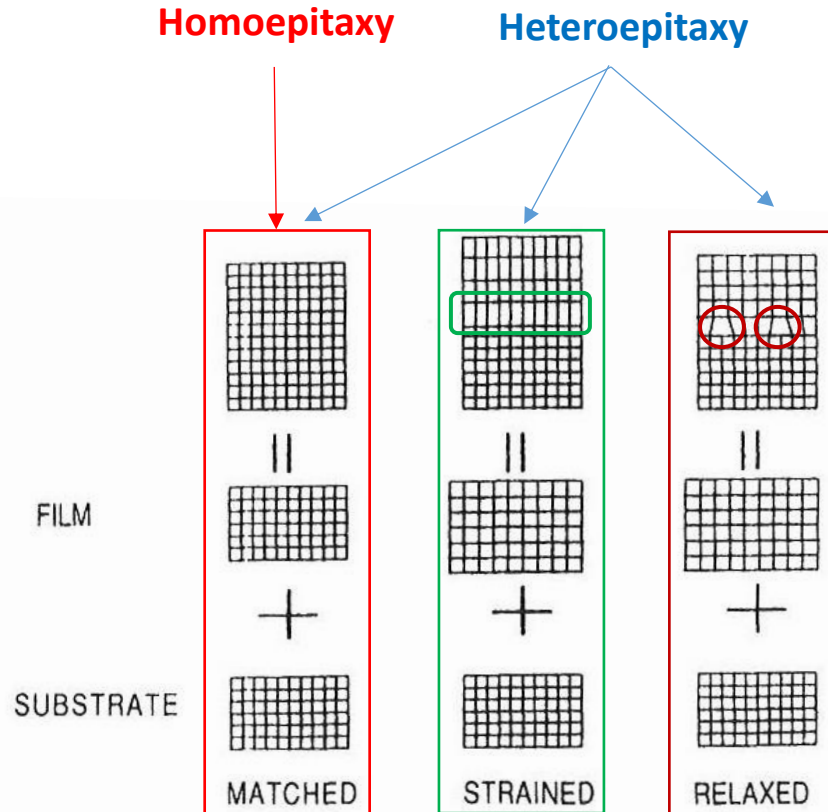
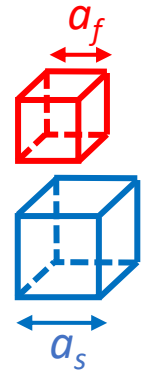
Applications: TMR based MRAMs, magnetic sensors



<https://www.doitpoms.ac.uk/tlplib/epitaxial-growth/intro.php>

Application: THz emission devices, ultrafast all-optical switching, optical Bragg reflectors, ...

Homo/heteroepitaxy (2)



Schematic illustration of lattice-matched, strained and relaxed structures (from M. Ohring, Materials Science of Thin films, Academic Press, Chapter 8)

Which structures can be obtained depending on the lattice mismatch between film (a_f) and substrate (a_s)?

Matched: for homoepitaxy or in presence of small lattice mismatch ($a_f \approx a_s$)

Strained: the lattices strain to accommodate their crystallographic differences. It prevails in the *early film formation stage*, and occurs in presence of materials with different lattice parameter but the same crystal structure.

Near the interface the first few film layers strain to match the substrate crystal structure (*pseudomorphic film growth*)

$$a_f \neq a_s$$

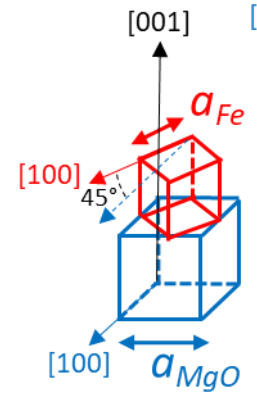
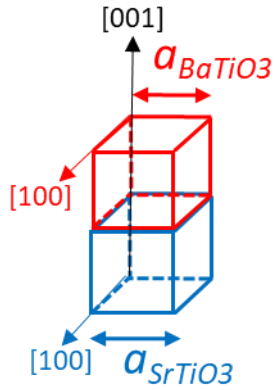
Relaxed: the lattices can not accommodate their differences by strain, so that *dislocation defects* form at the interface

Crystal orientation (1)

We consider an heterostructure made by **film** and **substrate** both with **cubic structure**:

Ex. 1: BaTiO_3 (film) on SrTiO_3 (substrate) \Rightarrow experimentally we find that $\text{BaTiO}_3(001)//\text{SrTiO}_3(001)$, $\text{BaTiO}_3[100]//\text{SrTiO}_3[100]$
(cube-on-cube growth: both planes and directions coincide)

Ex. 2: Fe (film) on MgO (substrate) \Rightarrow experimentally we find that $\text{Fe}(001)//\text{MgO}(001)$, $\text{Fe}[110]//\text{MgO}[100]$
(there is an in-plane rotation of the Fe lattice around the $[001]$ axis, by 45°)



Why?

Because of lattice misfit

How the lattice misfit influences the in-plane orientation?

The lattice mismatch strain (or **misfit**) is defined as $\underline{f} = \frac{a_s - a_f}{a_f}$, where a_f and a_s are the *unstrained* lattice parameters of the film and the substrate, respectively.

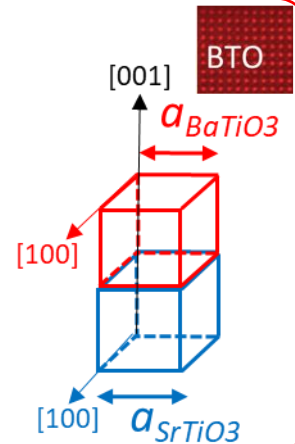
Often (not always) the epitaxial relationships can be predicted on the basis of **lattice fitting** arguments: the plane and direction orientations giving the **better lattice fit** (the *smaller lattice misfit*) determine the **film-substrate orientation**

Crystal orientation (2)

Ex. 1: BaTiO₃ (film) on SrTiO₃ (substrate)

$a_{\text{BaTiO}_3 [100]} = 0.3992 \text{ nm}$, $a_{\text{SrTiO}_3 [100]} = 0.3905 \text{ nm} \Rightarrow \underline{f} = \frac{a_s - a_f}{a_f} = -0.022 \Rightarrow$ **epitaxy is allowed**, with the film compressed (a_{BTO} must decrease to match a_{STO}) close to the surface

\Rightarrow The [100] directions of film and substrate are parallel $\Rightarrow \text{BaTiO}_3[100]//\text{SrTiO}_3[100]$ (cube-on-cube growth)



Ex. 2: Fe (film) on MgO (substrate)

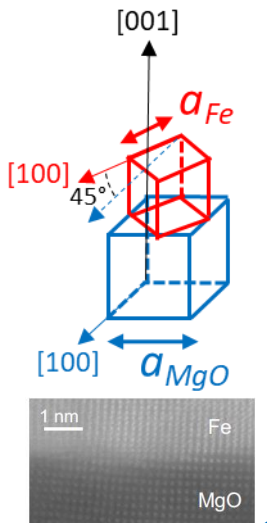
$a_{\text{Fe} [100]} = 0.287 \text{ nm}$, $a_{\text{MgO} [100]} = 0.4212 \text{ nm} \Rightarrow \underline{f} = \frac{a_s - a_f}{a_f} = 0.467 \Rightarrow$ *too large for allowing epitaxy*



$a_{\text{Fe} [110]} = 0.287 \text{ nm} \sqrt{2} = 0.406 \text{ nm}$, $a_{\text{MgO} [100]} = 0.4212 \text{ nm} \Rightarrow \underline{f} = \frac{a_s - a_f}{a_f} = 0.037 \Rightarrow$ **epitaxy is allowed** with the film strained ($a_{\text{Fe}}\sqrt{2}$ must increase to match a_{MgO}) close to the surface



\Rightarrow The [100] directions of film and substrate are rotated by 45° around the [001] axis $\Rightarrow \text{Fe}[110]//\text{MgO}[100]$

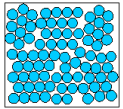


(See Appendix 2 for more examples)

Grapho- and tilted layers epitaxy

Graphoepitaxy

Artificial microstructuration on substrate

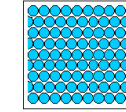


+

Deposition of textured polycrystals

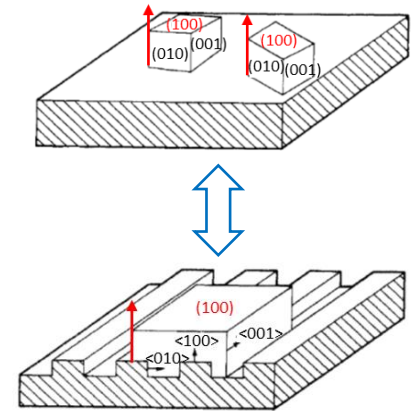


Single-crystal film (uniform orientation)



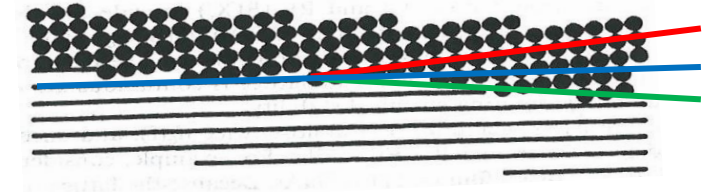
- Substrate can even be **amorphous** because no crystal or bonding constraints are given.
- The process starting from **polycrystalline grains** deposited on the **patterned substrate** will yield to an **uniformly oriented film (single-crystal)**.

([See Appendix 3 for more detail](#))



Tilted layer epitaxy

- This kind of epitaxy occurs on vicinal surfaces of a **miscut** substrate.
- **Planes of the film** are **coherently tilted** ($\sim 2-3^\circ$) with respect to the **substrate plane** (they are **not parallel** as in the previous cases of graphoepitaxy and heteroepitaxy).
- **Mismatch can be partially relieved by this method** – *but not completely*, in general (this is an *alternative* way to achieve strain relaxation with respect to misfit dislocation). The additional misfit will be instead relieved, e.g., by the formation of dislocations and/or **interfacial phases**.



([See Appendix 4 for more details](#))

Summary

Epitaxy = *epi* (placed or resting upon) + *taxis* (arrangement) ↔ extended film formation on top of a substrate

Structural analogy between film and substrate

Graphoepitaxy

- It employs **artificial microstructures** on the substrate to manipulate the nucleation, growth and orientation of film overlayers
- Substrates can be **amorphous**



Micro-nanolithography of self-assembled structures
(**bottom-up approach**)



Homoepitaxy

- The substrate and the film are made by the **same** material.
- The epilayer will be **less defective, purer** than the wafer substrate, and can be **doped** independently on it

Heteroepitaxy

- The substrate and the film are made by **different** materials.
- Epitaxial – **well ordered** – stacked device structures can be obtained
- Lattice **mismatch** must be considered for determining the film **orientation** and **stress** relief mechanisms

Tilted layer epitaxy

- It employs **miscut substrates** to induce growth with planes of the epitaxial film **coherently tilted** with respect to substrate planes
- It allows **relaxation of the epilayer** in presence of a small misfit

Growth modes

Epitaxial growth takes places by layer-by-layer growth or forming islands? (see lecture #3)

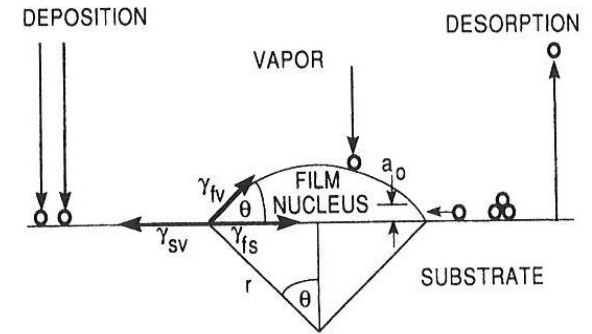
It depends on the three macroscopic **surface/interface tensions**:

- γ_{SV} between substrate (S) and vapor (V)
- γ_{fV} between film (f) and vapor (V)
- γ_{fS} between film (f) and substrate (S)

Thermodynamics – based approach **for epitaxial growth** (Bauer, 1958):

(i) Layer growth - Frank-van der Merwe (FM), 1949: $\gamma_{SV} \geq \gamma_{fS(n)} + \gamma_{fV(n)}$

(ii) Island growth - Volmer-Weber (VW), 1926: $\gamma_{SV} < \gamma_{fS(n)} + \gamma_{fV(n)}$



Schematic of basic nucleation processes on substrate during vapor deposition (from M. Ohring, Materials Science of Thin films, Academic Press, Chapter 7)

What's new with epitaxy?

We introduce the **n-dependence** of γ_{fV} and γ_{fS} , where n is the number of **epitaxial layers** composing the film, that reflects:

- possible changes in **lattice** constant and/or **structure** at the **film surface** (γ_{fV})
- the **interface** energy caused by the difference between **lattice** constants and/or crystallographic **structure** of overlayer and substrate (γ_{fS})
- the **volume strain** accumulated in a **pseudomorphic overlayer** (γ_{fS})

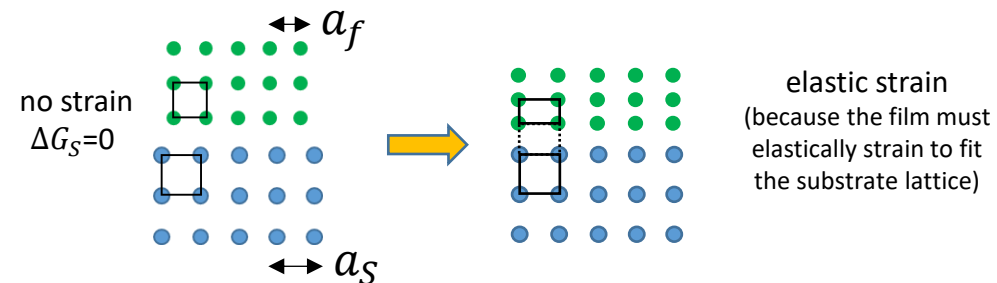
Pseudomorphic overlayer

What is a *pseudomorphic overlayer* ?

- A *pseudomorphic overlayer* corresponds to the first few ML of the films close to the interface, that *strain* to match the substrate crystal structure giving rise to coherent epilayers.

Why strain originates at interfaces between layers?

Because of **bonding mismatch** between **film** and **substrate**



The **lattice mismatch strain** (or misfit) is defined as $\underline{f} = \frac{a_s - a_f}{a_f}$

- Generally, structural mismatch between film and substrate leads to a monotonic **increase of volume strain energy** in the *pseudomorphic layer* with increasing film thickness (n)



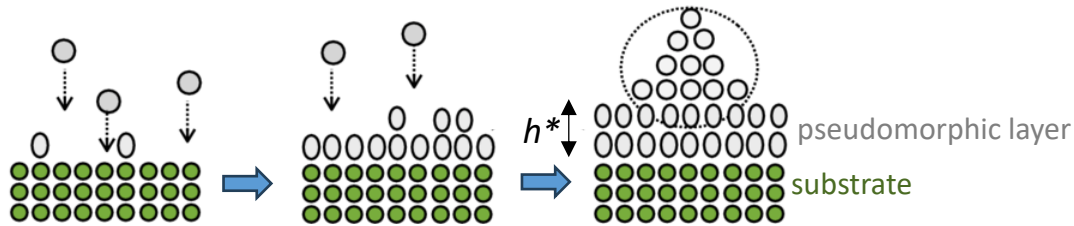
- $\gamma_{fs}(n)$ takes into account this strain energy (being an interface-related term)
- it increases with n up to reaching an unstable situation at a given **critical thickness**

Layer+island growth

What happens if we grow an epitaxial film on a planar substrate with misfit?
How the film recovers stability?

Option 1

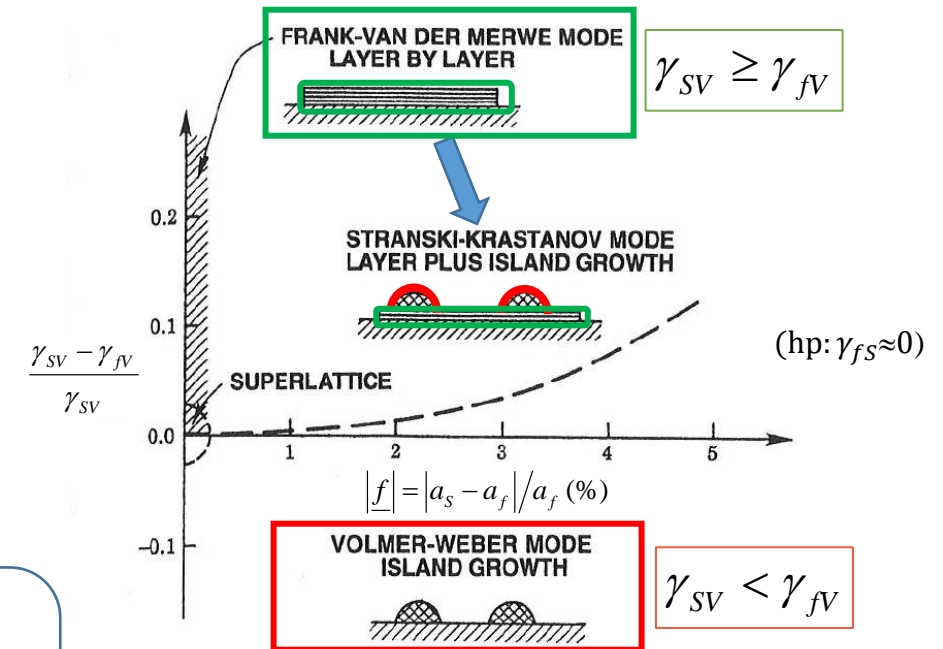
At the **critical thickness** h^* a transition from 2D (FM) to 3D (VW) growth modes can take place \Rightarrow **Stransky-Krastanov (SK) growth mode**



The **lattice mismatch strain** (or misfit) is defined as $\underline{f} = \frac{a_s - a_f}{a_f}$, where a_f refers to the unstrained film \rightarrow in the pseudomorphic layer the film structure is accommodated so that $a_f^* = a_s$ (i.e. $\underline{f} = 0$)

The **critical thickness** h^* is the thickness for which the pseudomorphic layer becomes unstable and island nucleation occurs \Rightarrow **island formation** takes place on top of the pseudomorphic layer

h^* increases as the initial misfit (\underline{f}) decreases \Rightarrow layer by layer growth is favoured by good matching (small \underline{f})



Stability regions of the three film growth modes in coordinates of surface energy difference between film and substrate (y-axis) and lattice misfit (x-axis) (from M. Ohring, Materials Science of Thin films, Academic Press, Chapter 7)

Film-substrate misfit

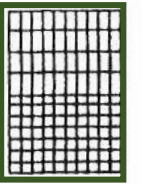
*What happens if we grow an epitaxial film on a planar substrate with misfit?
How the film recovers stability?*

Option 2

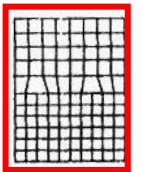
The misfit is accommodated between the two lattices.

Consider a film starting to grow on a substrate with a lattice misfit.

At very small film thicknesses and moderate lattice mismatches (less than ~9%), the film strains elastically and adopts the lattice constant of the substrate (pseudomorphic growth), making the interface coherent with atoms on either side lining up. The film is tetragonally distorted but its surface remains smooth.



With increasing film thickness, the rising total elastic strain energy exceeds the energy associated to a relaxed structure, composed by an array of misfit dislocations separated by wide regions of relatively good fit. Consequently, the initially strained film decomposes to this relaxed structure where part of the misfit is relieved by dislocations.



As the thickness continues to increase, more and more misfit is relieved by dislocations, up to completely remove the elastic strain at infinite thickness.

[F.C.Frank and J.H. van der Merwe, Proc. Roy. Soc. A189, 205, 1949]

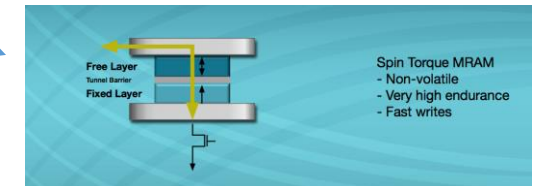
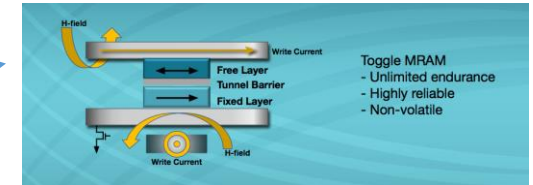
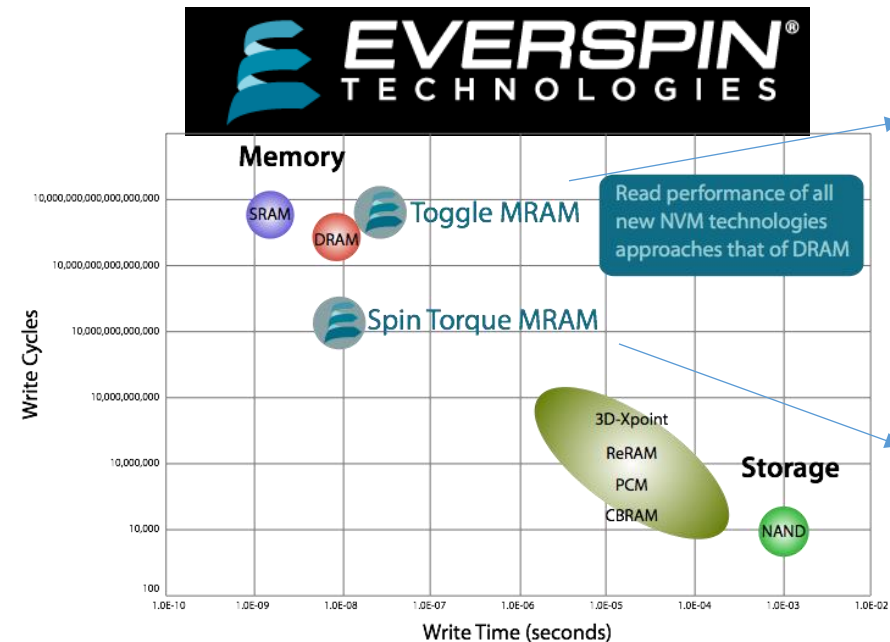
In the case of epitaxial growth without interdiffusion, pseudomorphism exists up to a critical thickness d_c , above which dislocations start to appear.

- i) For $d < d_c$ the film minimizes its total energy with no misfit dislocations \Rightarrow fully coherent epitaxial films are thermodynamically stable
- ii) For $d > d_c$ the equilibrium state includes misfit dislocations. The critical thickness is $d_c \propto 1/\underline{f}$, i.e. d_c increases as the initial misfit (\underline{f}) decreases (as for the SK growth mode – option 1)

Appendix 1: TMR-based MRAMs

Memory	Advantages	Drawbacks	Main fields of application
Hard drive	High density (~1 Tbit/in ²); very low cost per byte stored (~0.004 \$/Gbit)	Moderate read and write speeds (~1 Gbit/s); bulky moving parts	Secondary data storage device in computers
SRAM	Fast read and write speeds (~35 Gbit/s); low power consumption	Large memory cells taking up considerable space; low density (~4.5 Gbit/in ²); volatile	Cache memory in computers
DRAM/SD RAM	High density (>500 Gbit/in ²); low cost (~1 \$/Gbit); superfast read and write speeds (~200 Gbit/s)	Volatile ; constant refreshing of data draining power	Primary memory in computers
Flash	Nonvolatile ; very high density (>1 Tbit/in ²); low cost (<1 \$/Gbit)	Power consuming ; moderate read and write speeds (~6 Gbit/s); limited endurance	Long-term external storage, firmware, SSD drives
MRAM	Nonvolatile ; fast read and write speeds (~1 Tbit/s); high density (~128 Gbit/in ²); low power consumption; unlimited write endurance; radiation hardness	High writing currents	Long-term memory drive in computers, military and space applications

[Adapted from R. Bertacco and M. Cantoni, *New Trends in Magnetic Memories*, chapter book in *Ultrahigh Density Magnetic Recording* by G. Varvaro and F. Casoli, Pan Stanford Publishing (2016)]



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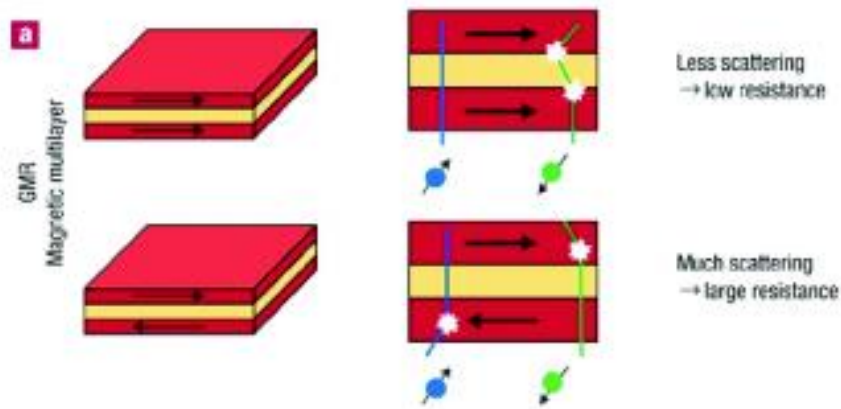
HITACHI
Inspire the Next



Appendix 1: How they work ...

Magnetoresistance (MR) \longleftrightarrow dependence of the electrical resistance on the magnetic configuration $\rightarrow MR = \frac{R_{AP} - R_P}{R_P}$

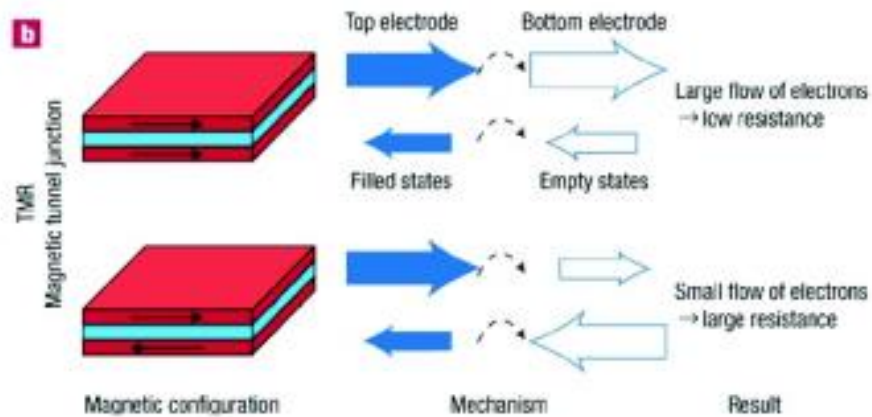
GMR



Giant MR – two magnetic layers separated by a non-magnetic conducting layer (e.g., Co/Cu/Co)

GMR $\sim 55\%$

TMR



Tunneling MR – two magnetic layers separated by a non-magnetic insulating layer acting as tunnel barrier (e.g., Fe/MgO/Fe)

TMR $\rightarrow 640\%$



P (AP) means parallel (antiparallel) configuration of the two magnetic layers. Typically we have $R_{AP} > R_P$.



The Nobel Prize in Physics 2007
Albert Fert, Peter Grünberg

Giant room-temperature magnetoresistance in single-crystal Fe/MgO/Fe magnetic tunnel junctions

SHINJI YUASA^{1,2*}, TARO NAGAHAMA¹, AKIO FUKUSHIMA¹, YOSHISHIGE SUZUKI¹ AND KOJI ANDO¹

¹NanoElectronics Research Institute, National Institute of Advanced Industrial Science and Technology (AIST), Tsukuba, Ibaraki 305-8568, Japan

²PRESTO, Japan Science and Technology Agency, Kawaguchi, Saitama 332-0012, Japan

*e-mail: yuasa-s@aist.go.jp

(2004)

Giant tunnelling magnetoresistance at room temperature with MgO (100) tunnel barriers

STUART S. P. PARKIN^{1*}, CHRISTIAN KAISER¹, ALEX PANCHULA¹, PHILIP M. RICE¹, BRIAN HUGHES², MAHESH SAMANT¹ AND SEE-HUN YANG¹

¹IBM Research Division, ²Infineon Technologies, IBM Almaden Research Center, IBM-Infineon MRAM Development Alliance, 650 Harry Road, San Jose, California 95120, USA

*e-mail: parkin@almaden.ibm.com

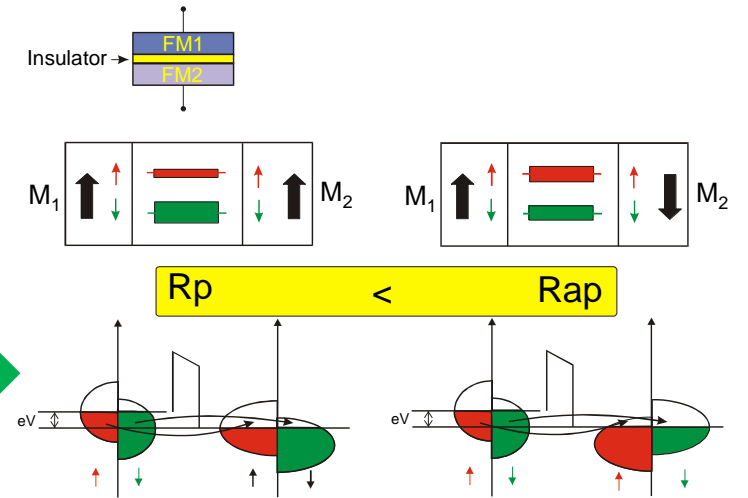
(2004)

Appendix 1: ... and why epitaxy is welcome

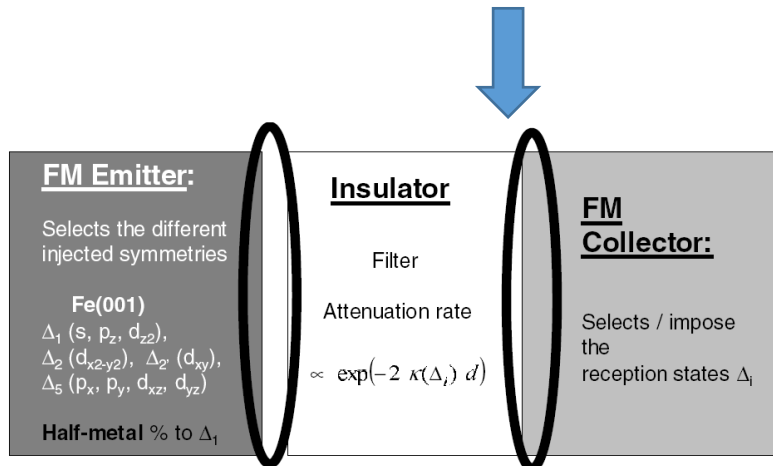
Tunneling Magnetoresistance (TMR): $TMR = \frac{R_{AP} - R_P}{R_P} \rightarrow 640\% \text{ @ RT}$

Why MR can be so high?

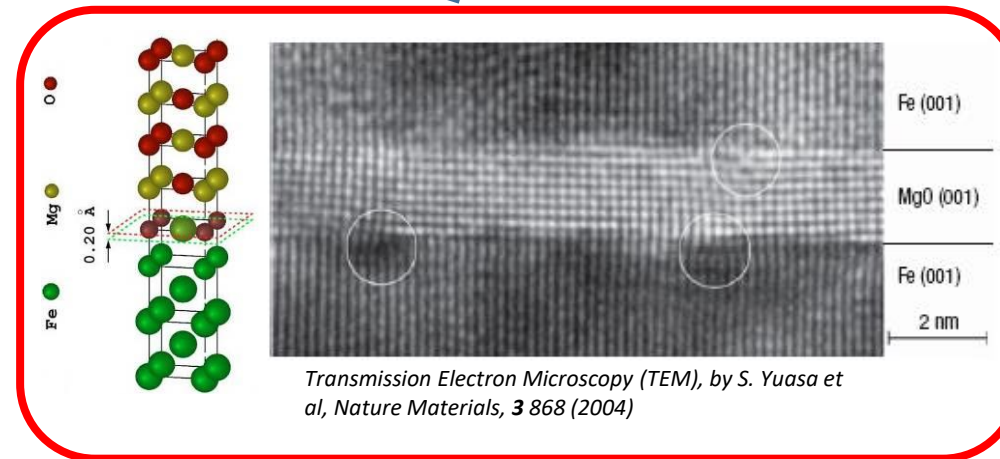
- 1) **tunneling probability across the barrier** (because of the dependence of the DOS on the magnetic configuration) – e.g. Al_2O_3 barrier (**TMR ≈ 70%**)
- 2) **Spin filtering by symmetry constraints of the electronic states** in barrier and electrodes – e.g. MgO barrier (**TMR up to 640%**) \Rightarrow **it needs epitaxy**



$$j = \sum_k \int_{-\infty}^{+\infty} dE D_1(E) D_2(E + eV) |M(E)|^2 (f(E) - f(E + eV))$$



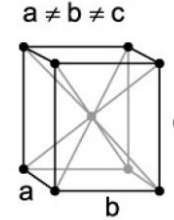
C. Tiusan et al, J.Phys.:Cond. Matter **19** 165201 2007



Appendix 2: Examples of crystal orientation (1)

Ex. 3: β -FeSi₂/Silicon (semiconductor/silicon) for thermoelectric, LED, solar cells...

The structure is **orthorhombic** with $a=0.986$ nm, $b=0.779$ nm, $c=0.788$ nm

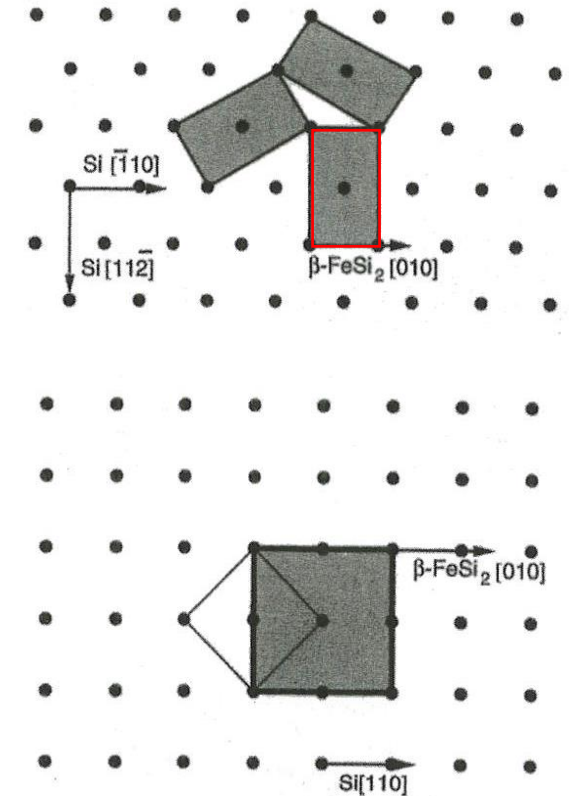


On Si (111) substrates: oriented domains of epitaxial β -FeSi₂ are formed and **rotated** relative to one another.

E.g., the epitaxial relationship for **red** domain are β -FeSi₂(101)//Si(111) and β -FeSi₂[010]//Si[$\bar{1}10$] [Note: Si [$\bar{1}10$] and [$11\bar{2}$] directions define the plane (111)]

On Si (100) substrates: assuming the tetragonal structure approximates the orthorhombic lattice, the epitaxial relationship is β -FeSi₂(100)//Si(100), β -FeSi₂[010]//Si(110)

The lattice misfit is quite small:
$$\underline{f} = \frac{a_{Si}\sqrt{2} - a_{Fe2Si(b)}}{a_{Fe2Si(b)}} = \frac{0.543\sqrt{2} - 0.779}{0.779} = -0.014$$

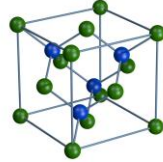


Epitaxial relationship between β -FeSi₂ and Silicon with (111) and (100) orientations (from M. Ohring, Materials Science of Thin films, Academic Press, Chapter 8)

Appendix 2: Examples of crystal orientation (2)

Ex. 4: **metal/GaAs** for contact applications in solid-state devices (epitaxy is not strictly needed in some cases, but it becomes essential as far as dimensions are shrinking and to fabricate 3D structures)

- GaAs is **cubic (zinc blende)**, with $a_s = 0.5653$ nm
- Based on simple **geometrical matching**, *three different epitaxial arrangements* can be considered for (i) metal films with cubic structure and *different lattice parameters* on (ii) *different GaAs crystal planes* :

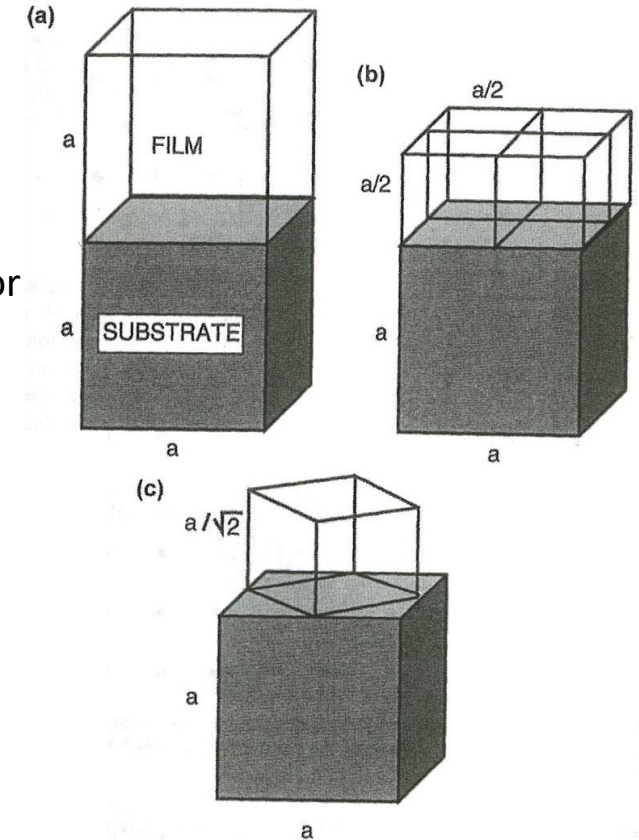


(a) $a_s \approx a_f$ (cube-on-cube), e.g. Ca (FCC), Rb (BCC), ErAs and YbAs (NaCl structure) on GaAs (100)

(b) $a_s \approx 2a_f$, e.g. Fe (110) on GaAs (110) : $a_f = 0.2866$ nm (bcc) $\Rightarrow \underline{f} = \frac{a_s - 2a_f}{2a_f} = -0.0138$

(c) $a_s \approx \sqrt{2}a_f$ (45° rotation), e.g. Al on GaAs (100): $a_f = 0.405$ nm $\Rightarrow \underline{f} = \frac{a_s - 2a_f}{2a_f} = -0.0138$

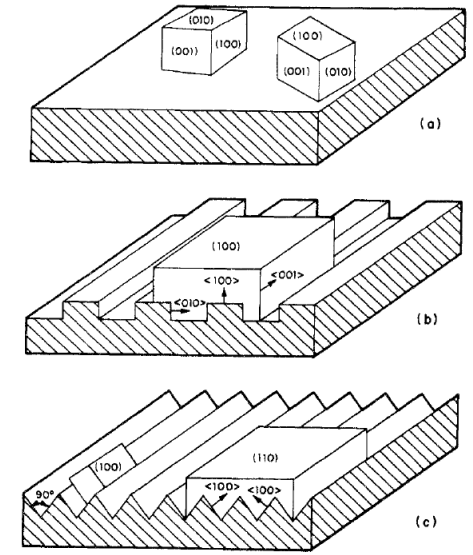
Note: in all these cases, we assume the epitaxial films grow with their planes *parallel* to those of the substrate.



Epitaxial alignments of cubic films on cubic substrates (from M. Ohring, Materials Science of Thin films, Academic Press, Chapter 8)

Appendix 3: Graphoepitaxy

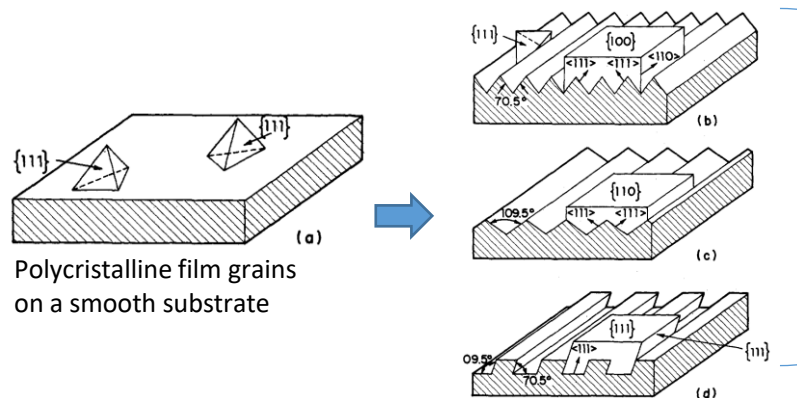
- It employs **artificial microstructures**, fabricated on the substrate surface, to *manipulate* the **nucleation, growth, and orientation** of a **film overlayer**.
- It requires that films deposit in forms of **polycrystals with a given texture**, e.g. **(100)** orientation \Rightarrow (100) planes are parallel to the substrate surface, but their orientation is random and can rotate around the [100] axis (a).
- If the grains encounter a **substrate pattern with surface relief structures**, e.g. a grating with period smaller than the grain size, **the grain will be forced to follow the pattern orientation** (b,c).
- Substrate can even be **amorphous** because no crystal or bonding constraints are given.
- The process starting from **polycrystalline grains** (that individually behave as a single crystal but their orientation in the plane is random) deposited on the **patterned substrate** will yield to an **uniformly oriented film (single-crystal)**.



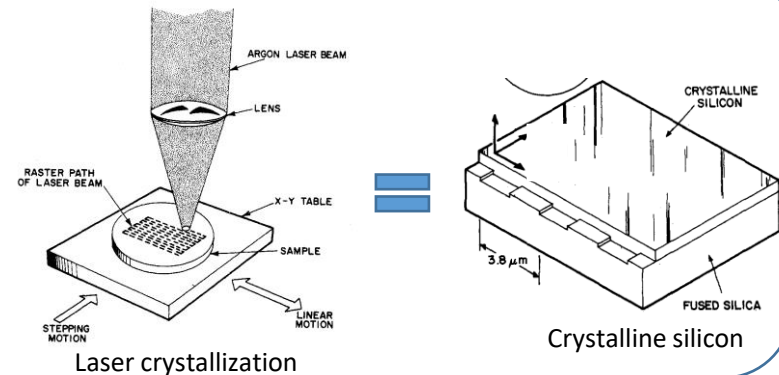
Examples of graphoepitaxy (from M. Ohring, Materials Science of Thin films, Academic Press, Chapter 8)

Example: growth of **crystalline Silicon** on insulators

[M.W.Geis et al., conference proceeding, doi: [10.1109/IEDM.1979.189581](https://doi.org/10.1109/IEDM.1979.189581)



Silicon orientation depends on the substrate texturation

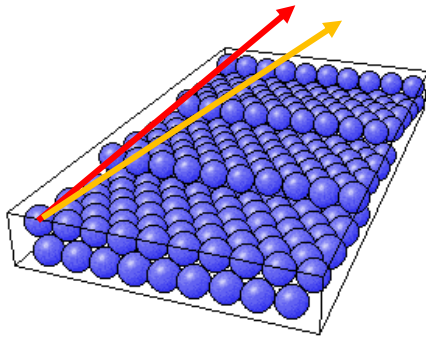


Laser crystallization

Crystalline silicon

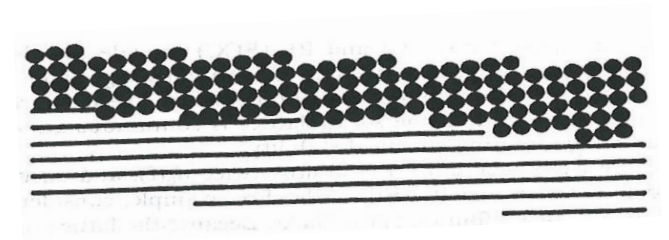
Appendix 4: Tilted layer epitaxy (1)

- Planes of the film are **coherently tilted** ($\sim 2-3^\circ$) with respect to the substrate plane (they are *not parallel* as in the previous cases of graphoepitaxy and heteroepitaxy).
- This kind of epitaxy occurs on **vicinal surfaces of a miscut substrate**.
- The exposed vicinal planes are slightly misoriented from some low-index major plane, resulting in a surface breaking up into an array of low-index terraces of variable length and steps with variable height.



High index planes, e.g. $\text{fcc}(775)$, are those for which one or more of the Miller indices are relatively large numbers. Vicinal surfaces are high index planes which are cut at a relatively small angle to one of the low index surfaces, e.g. $\text{fcc}(111)$. The ideal surfaces can then be considered to consist of terraces which have an atomic arrangement identical with the corresponding low index surface, separated by monatomic steps (steps which are a single atom high).

- When deposition takes places at high T and/or low rate, adatoms are **mobile** enough for moving on the substrate and incorporating at step edges \Rightarrow growth takes place by **incorporating adatoms at step edges**
- In this regime, film growth occurs by **step advancement along terraces** (*step-flow* process)



Appendix 4: Tilted layer epitaxy (2)

- We consider, e.g., a **substrate with (100) planes** misoriented from the exposed growth plane by α .

→ With a tilt of $\Delta\alpha$ of the **film (100) surface**, both film and substrate will **periodically match when they intersect at the interface** (parallel to the growth plane):

$$a_{GP} = \frac{a_f}{\cos(\alpha - \Delta\alpha)} = \frac{a_s}{\cos \alpha} \Rightarrow \frac{a_f}{a_s} \cos \alpha = \cos(\alpha - \Delta\alpha) \Rightarrow \left(\frac{a_f}{a_s} + 1\right)^{-1} \cos \alpha = \cos(\alpha - \Delta\alpha)$$

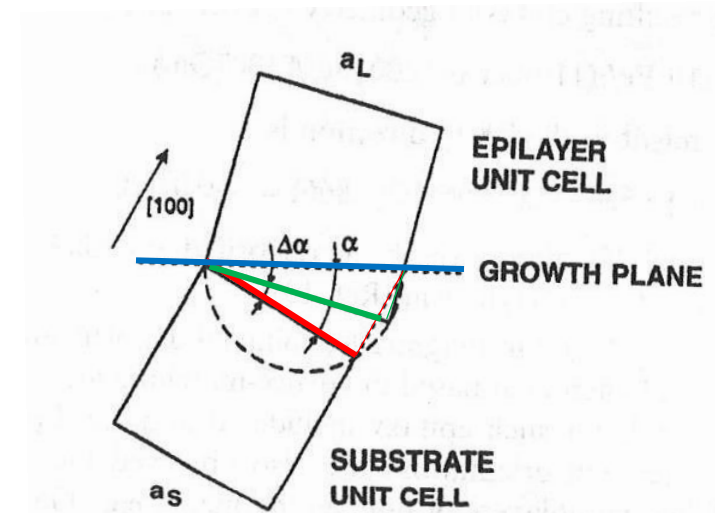
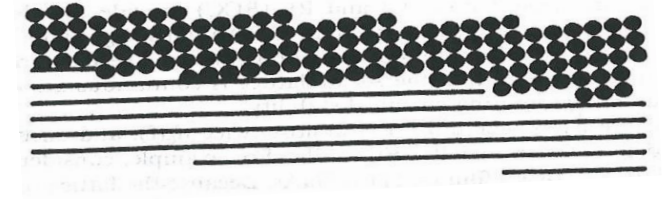
[F. Riesz, Vacuum 46, 1021 (1995)]

(The projection of the lattice parameter of the **substrate** (a_s) and of **the film** (a_f) on the **growth plane** (a_{GP}) is the same)

Note: mismatch can be partially relieved by this method – but not completely, in general (this is an alternative way to achieve strain relaxation with respect to misfit dislocation).

E.g., GaAs ($a_f=0.5653$ nm) on Si ($a_s=0.5431$ nm) has a misfit $\frac{a_f}{a_s} - 1 = -0.0393$, but the maximum misfit (corresponding to $\frac{a_f}{a_s} \cos \alpha = 1$) that can be relieved by substrates with 2° or 4° miscut (α) is -0.000609 or -0.002436, respectively.

The additional misfit will be instead relieved, e.g., by the formation of interfacial phases.

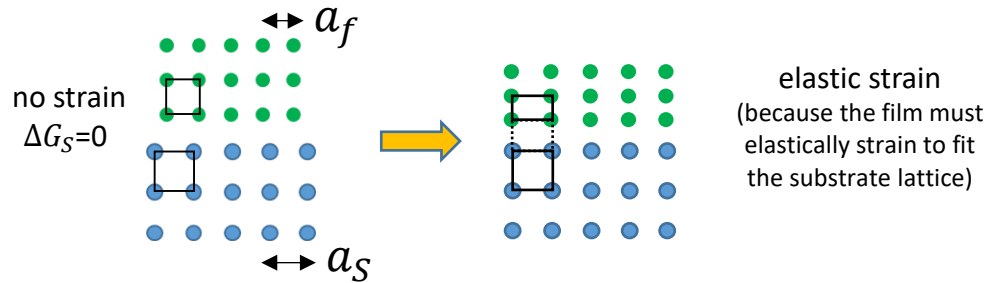


(Top) tilted-layer epitaxy between film (atoms) and vicinal planes of substrate; (Bottom) Strain relief by tilting lattice-mismatched vicinal heterosystems (from M. Ohring, Materials Science of Thin films, Academic Press, Chapter 8)

Appendix 5: Strain contribution to interfaces (1)

Why strain originates at interfaces between layers?

Typically, because of **bonding mismatch** between **film** and **substrate**



How to address quantitatively strain at the interface?

- From **elasticity theory** the **strain free energy** per unit volume (E_s) can be expressed as

$$E_s = \frac{1}{2} Y \varepsilon^2$$

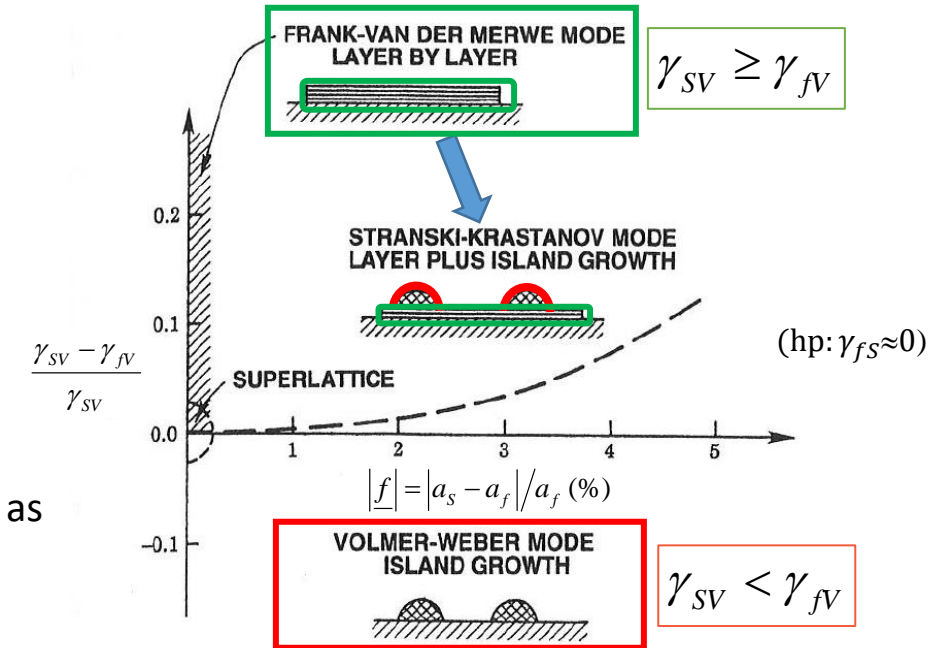
where Y is the elastic modulus of the film and ε is the strain.

- The strain ε at the interface can be measured as the **lattice mismatch strain** (or misfit) defined as

$$\underline{f} = \frac{a_s - a_f}{a_f}$$

where a_s and a_f are the lattice parameters of the lower layer (e.g., the *substrate*) and the upper layer (e.g., the *film*), respectively.

Which is a possible consequence of strain?



Stability regions of the three film growth modes in coordinates of surface energy difference between film and substrate (y-axis) and lattice misfit (x-axis) (from M. Ohring, Materials Science of Thin films, Academic Press, Chapter 7)

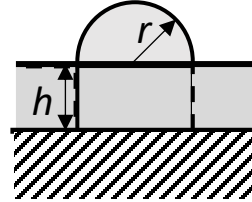
Appendix 5: Strain contribution to interfaces (2)

- Consider a lattice relaxed **hemispherical island of radius r** , nucleating from the vapor phase, on top a growing, strained **epitaxial layer of thickness h** of the same material

$$\Delta G = a_3 r^3 \Delta G_V + a_1 r^2 \gamma_{fV} + a_2 r^2 \gamma_{fS} - a_2 r^2 \gamma_{SV}$$

$a_1 = 2\pi(1 - \cos\theta)$, $a_2 = \pi \sin^2\theta$, $a_3 = \pi/3 (2 - 3\cos\theta + \cos^3\theta)$, with $\theta = \pi/2$ for the hemispherical cap

$$\Rightarrow \Delta G = \frac{2}{3} \pi r^3 \Delta G_V + 2\pi r^2 \gamma_{fV} + \pi r^2 \gamma_{fS} - \pi r^2 \gamma_{SV}$$



- Consider the **strain free energy change ΔG_S** :

$$\Delta G = \frac{2}{3} \pi r^3 \Delta G_V + 2\pi r^2 \gamma_{fV} + \pi r^2 \gamma_{fS} - \pi r^2 \gamma_{SV} + \Delta G_S$$

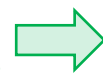
- Assuming $\gamma_{fV} = \gamma_{SV} = \gamma_f$ and $\gamma_{fS} = 0$ because *film and substrate are of the same material*, we have:

$$\Delta G = \frac{2}{3} \pi r^3 \Delta G_V + \pi r^2 \gamma_f + \Delta G_S$$

Net free energy change

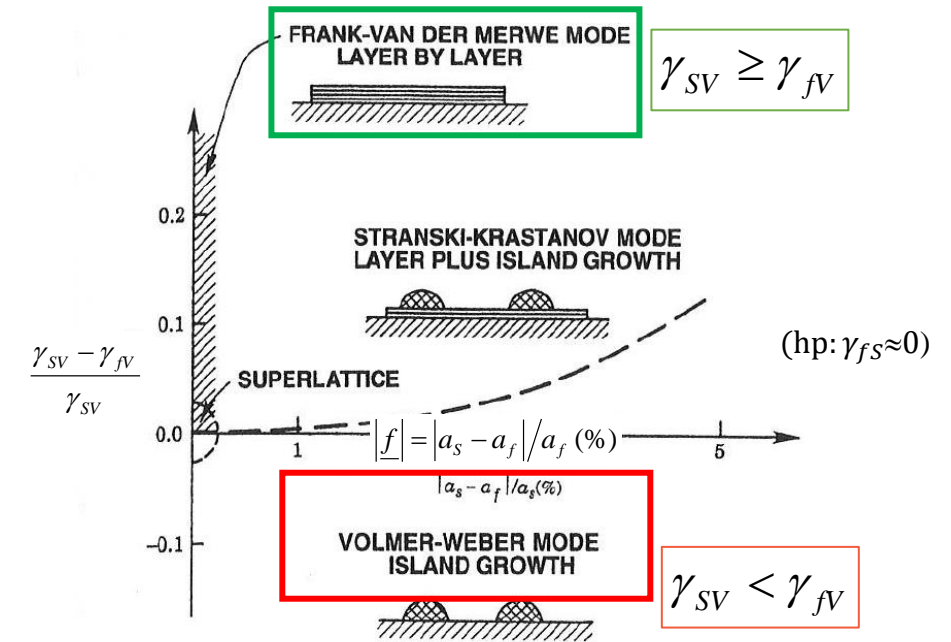
Free energy change per unit volume

Interfacial tension (or energy) between film (f) or substrate (S) and vapor (V) per unit area



Energy of the additional free surface exposed when the island is formed

Energy resulting from the interaction between the **lattice relaxed island** and the **strained layer** through **elastic deformation**



Stability regions of the three film growth modes in coordinates of surface energy difference between film and substrate (y-axis) and lattice misfit (x-axis) (from M. Ohring, Materials Science of Thin films, Academic Press, Chapter 7)

[B. W. Wessels, J. Vac. Sci. Technol. B 15 (4), 1056 (1997)]

Appendix 5: Strain contribution to interfaces (3)

Which is the critical film thickness **beyond which** a **strained planar film** roughens due to the growth of **islands**?

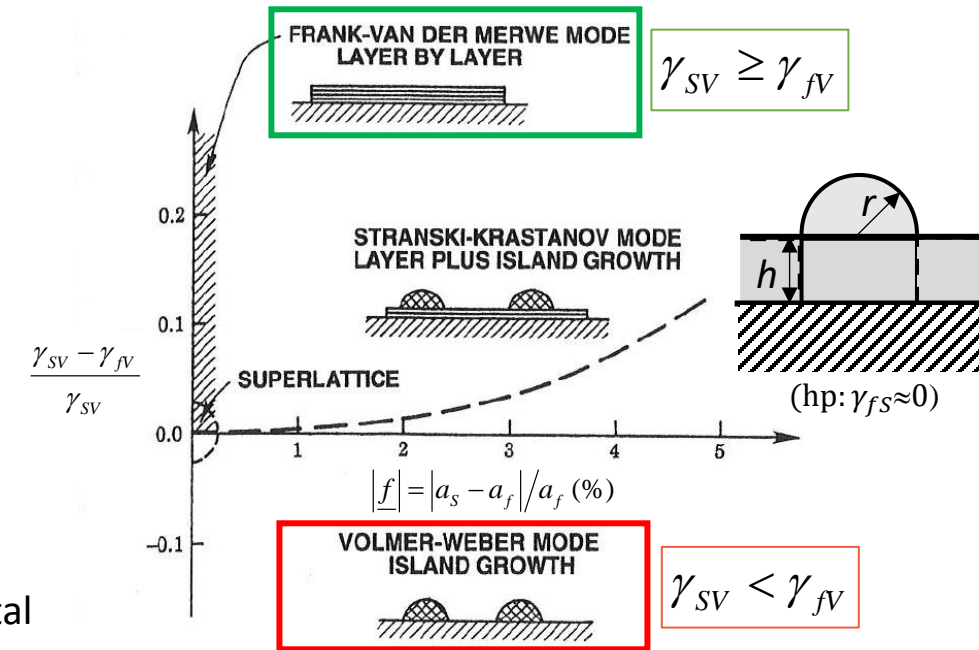
- In the nucleation process the **island is assumed to be fully relaxed**, while the **epilayer partially relaxes** after nucleation.
- The **strain free energy** ΔG_S is interpreted as the difference in epilayer strain energy **after** the island nucleation, relative to that in the epilayer **prior** to island nucleation:

$$\Delta G_S = E_{S,after}V - E_{S,before}V = \frac{1}{2}Y\varepsilon^2 hA - \frac{1}{2}Y\underline{f}^2 hA = \frac{1}{2}Y(\varepsilon^2 - \underline{f}^2) h\pi r^2$$

where:

- ε is the mean misfit in the **strained epilayer after** nucleation, that **minimizes** the total energy by **partially relaxing**
- \underline{f} is the misfit of the **epilayer prior** to nucleation, due to the initial **misfit** with the substrate
- h is the epilayer thickness
- $V=hA=h\pi r^2$ is the volume affected by strain (πr^2 is the area below the hemispherical island)

- Note that $\Delta G_S = -\frac{1}{2}Y\underline{f}^2 h\pi r^2 \left(1 - \frac{\varepsilon^2}{\underline{f}^2}\right) = -\frac{1}{2}Y\underline{f}^2 h\pi r^2 \lambda < 0$, with $\lambda = 1 - \frac{\varepsilon^2}{\underline{f}^2} > 0$ because $\varepsilon^2 < \underline{f}^2$ (the epilayer partially relaxes after nucleation, leading to **strain energy relieving**)



Stability regions of the three film growth modes in coordinates of surface energy difference between film and substrate (y-axis) and lattice misfit (x-axis) (from M. Ohring, Materials Science of Thin films, Academic Press, Chapter 7)

Appendix 5: Strain contribution to interfaces (4)

$$\Delta G = \frac{2}{3}\pi r^3 \Delta G_V + \pi r^2 \gamma_f - \frac{1}{2} Y \underline{f}^2 h \pi r^2 \lambda$$

Strain free energy

- The critical radius r^* is the radius above which nucleation occurs and island formation takes place (see slide 18) and is given by:

$$\frac{d\Delta G}{dr} = 2\pi r^2 \Delta G_V + 2\pi r \gamma_f - \lambda Y \underline{f}^2 h \pi r = 0$$

$$\rightarrow r^* = -\frac{\gamma_f - \frac{1}{2} Y \underline{f}^2 h \lambda}{\Delta G_V}$$

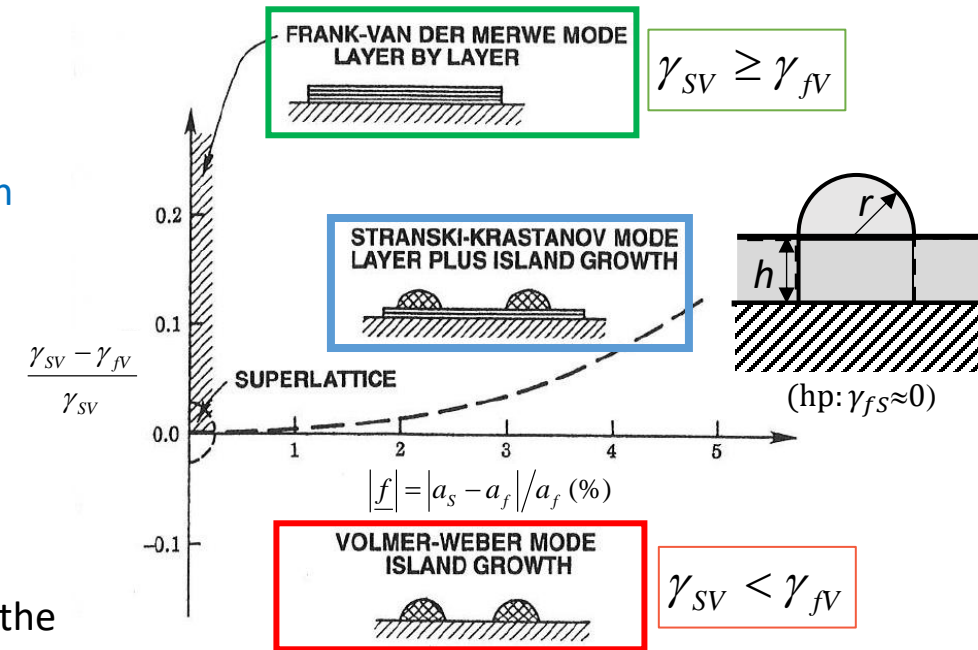
- In the limit $r^*=0$ (island nucleation on continuous films – no prior nuclei are needed) the **critical thickness h^*** of the epilayer film is

$$h^* = \frac{2\gamma_f}{Y \underline{f}^2 \lambda} = \frac{2\gamma_f}{Y (\underline{f}^2 - \varepsilon^2)}$$

This corresponds to the onset of the rough island morphology (S-K growth mode)

- Note that h^* varies roughly as \underline{f}^{-2} , that is **the critical thickness h^* decreases as the initial misfit (\underline{f}) increases**

→ Layer by layer growth is favoured by good matching (small \underline{f})

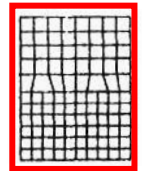
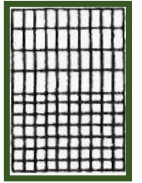


Stability regions of the three film growth modes in coordinates of surface energy difference between film and substrate (y-axis) and lattice misfit (x-axis) (from M. Ohring, Materials Science of Thin films, Academic Press, Chapter 7)

Appendix 5: equilibrium theory of lattice misfit (1)

What happens if we grow an epitaxial film on a planar substrate with misfit?

- The **Frank-van der Merwe** theory for elastic/plastic changes in the bilayer accounts for the **accomodation of misfit** between two lattices.
 - Consider a **film** starting to grow on a **substrate** with a lattice **misfit**.
 - The theory predicts:
 - At **very small** film thicknesses and moderate lattice mismatches (**less than ~9%**), the film **strains elastically** and adopts the lattice constant of the **substrate (pseudomorphic growth)**, making the interface coherent with atoms on either side lining up. The film is **tetragonally distorted** but its surface remains smooth.
- ↓
- With **increasing** film thickness, the rising total elastic strain energy exceeds the energy associated to a **relaxed structure**, composed by an array of **misfit dislocations** separated by wide regions of relatively **good fit**. Consequently, the initially strained film decomposes to this relaxed structure where **part of the misfit is relieved by dislocations**.
- ↓
- As the thickness continues to **increase**, more and more misfit is relieved by dislocations, up to completely **remove the elastic strain** at infinite thickness.



Note: In the case of epitaxial growth without interdiffusion, **pseudomorphism** exists up to a **critical thickness d_c** , above which **dislocations** start to appear.

[F.C.Frank and J.H. van der Merwe, Proc. Roy. Soc. A189, 205, 1949]

How to calculate the critical thickness d_c ?

Appendix 5: equilibrium theory of lattice misfit (2)

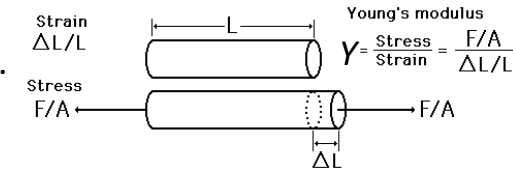
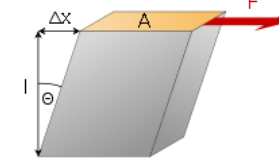
How to calculate the critical thickness d_c ? Model by Nix (1989) (but there are many different models...)

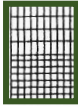
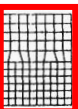
- We assume the same Young modulus (Y) and shear modulus (μ) for film and substrate.

The **Young modulus** Y is the ratio between stress (F/A) and strain ($\Delta L/L$) in the linear elasticity regime of an uniaxial deformation.

The **Shear modulus** μ is the ratio between the shear stress (F/A) and shear strain ($\Delta x/l = \tan(\theta)$)

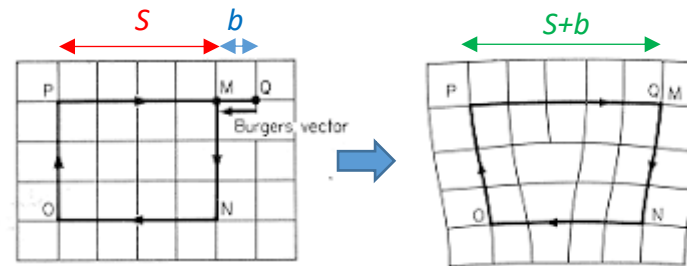
The **Poisson ratio** ν is related to Y and μ , in isotropic homogeneous materials, by the relation $Y = 2\mu(1-2\nu)$



1. For $d < d_c$ the elastic strain energy per unit area is $E_e = \frac{Y d \varepsilon^2}{1-\nu}$, where ε is the **biaxial elastic strain**. No dislocations are present in the film. 
2. At $d > d_c$ the **misfit dislocations** start to appear at the film-substrate interface, to **relieve** the elastic strain that will develop during further film growth. 

We assume the dislocations to be arrayed in a **square grid of side S** \Rightarrow the elastic strain is reduced from its initial misfit value (\underline{f}) to $\varepsilon = \underline{f} - b/S$, where b is the **Burger vector magnitude**.

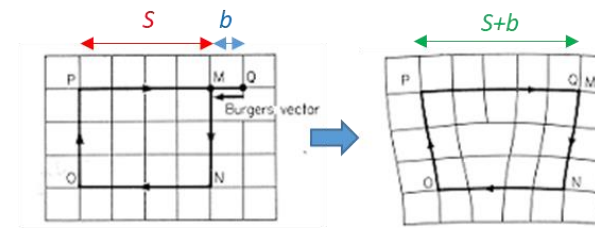
The **Burger vector** represents the magnitude and direction of the lattice distortion resulting from dislocations in a crystal lattice.



[W.D.Nix, Metall. Trans. 20A, 2224, 1989]

Appendix 5: equilibrium theory of lattice misfit (3)

1. $d < d_c$: **elastic strain energy** per unit area = $E_e = \frac{\gamma d \varepsilon^2}{1-\nu}$, no dislocation.
2. $d > d_c$: **misfit dislocations** to **relieve** the elastic strain from \underline{f} to $\varepsilon = \underline{f} - b/S$



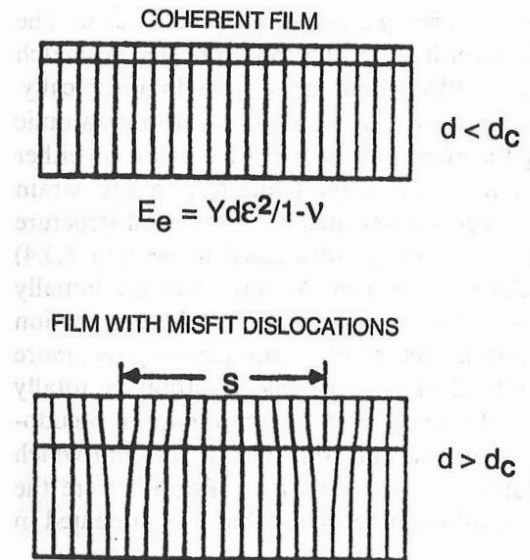
b/S is proportional to the number of misfit dislocations at the film/substrate interface. **When $b/S = \underline{f}$ the strain vanishes ($\varepsilon = 0$).**

The **total strain energy** per unit area E_T is now the sum of the **elastic energy** E_e and the **dislocation energy** E_d :

$$E_T = \frac{\gamma d}{1-\nu} \left(\underline{f} - \frac{b}{S} \right)^2 + \frac{\mu b^2}{4\pi(1-\nu)} \frac{2}{S} \ln \left(\frac{\beta d}{b} \right)$$

Notes:

- β is a constant of the order of 1.
- Whereas the **elastic energy** associated to the homogeneous strain decreases when dislocations are introduced ($b \neq 0$), the **energy associated to dislocations** increases.
- **Strain energy** increases linearly with d , while **dislocation energy** is nearly constant having a weak logarithmic dependence.



Coherent film and film with misfit dislocations (from M. Ohring, Materials Science of Thin films, Academic Press, Chapter 8)

[W.d.Nix, Metall. Trans. 20A, 2224, 1989]

Appendix 5: equilibrium theory of lattice misfit (4)

$$E_T = \frac{Yd}{1-\nu} \left(f - \frac{b}{S} \right)^2 + \frac{\mu b^2}{4\pi(1-\nu)} \frac{2}{S} \ln \left(\frac{\beta d}{b} \right)$$

How to calculate the critical thickness d_c ?

The equilibrium state of the system can be determined by finding the **minimum** of the **total energy** per unit area *with respect to the number of misfit dislocations per unit length* ($1/S$)

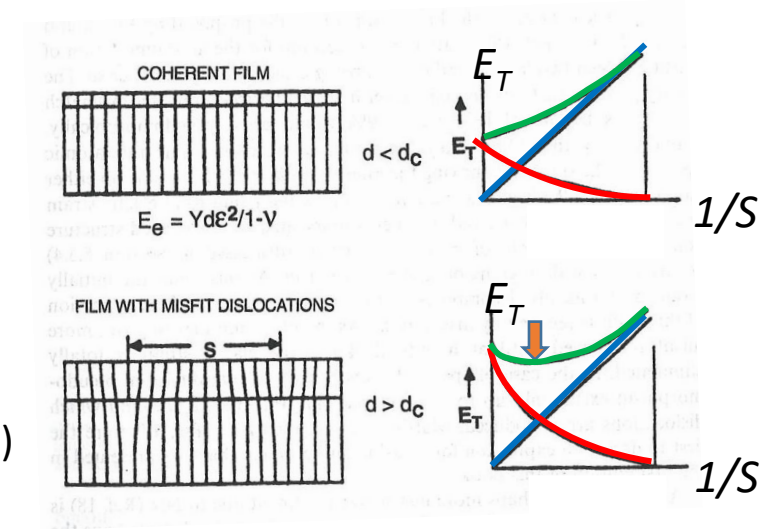
$$\frac{\partial E_T}{\partial (1/S)} = -2b \frac{Yd}{1-\nu} \left(f - \frac{b}{S} \right) + \frac{\mu b^2}{2\pi(1-\nu)} \ln \left(\frac{\beta d}{b} \right) = 0$$

The **critical film thickness** is found by solving this equation for the special case $b/S=0$ (i.e. $S \rightarrow \infty$)

$$-2b \frac{Yd_c}{1-\nu} f + \frac{\mu b^2}{2\pi(1-\nu)} \ln \left(\frac{\beta d_c}{b} \right) = 0 \Rightarrow d_c = \frac{\mu b}{4\pi Y f} \ln \left(\frac{\beta d_c}{b} \right)$$

- i) For $d < d_c$ the minimum of the total energy E_T is achieved at $1/S \rightarrow 0$, that is **no misfit dislocations** are formed. Fully coherent **epitaxial** films are **thermodynamically stable**.
- ii) For $d > d_c$ there is a minimum of the total energy E_T at **finite $1/S$** , meaning that the equilibrium state **includes misfit dislocations**

Note: when d_c is approximately few hundreds nm, the following relation holds: $d_c \approx \frac{b}{2f} \Rightarrow$ The film will be pseudomorphic until the accumulated misfit in the vertical direction $d_c f$ will exceed half the Burger vector ($b/2$), corresponding to half the unit cell dimension ($a/2$)



Coherent film and film with misfit dislocations
(from M. Ohring, Materials Science of Thin films, Academic Press, Chapter 8)