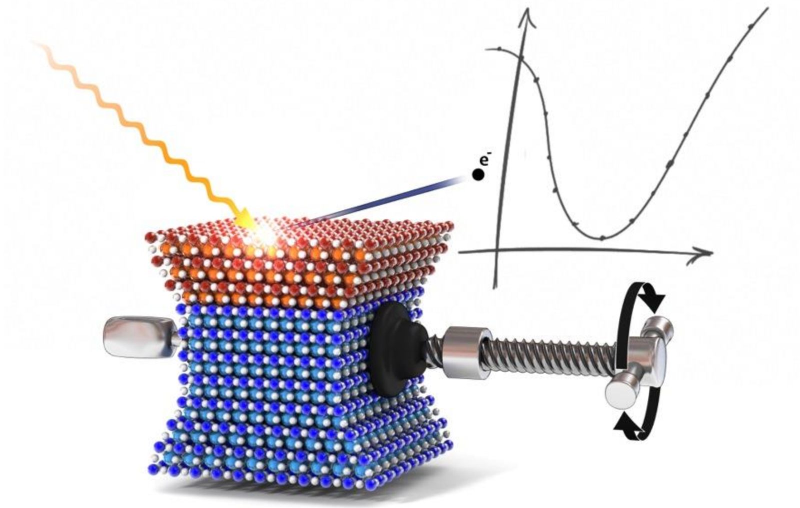
THIN FILMS PHYSICS



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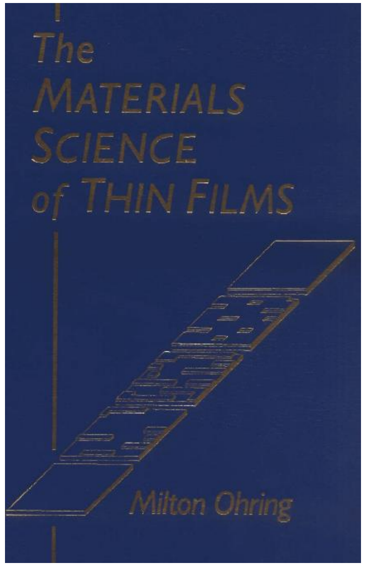
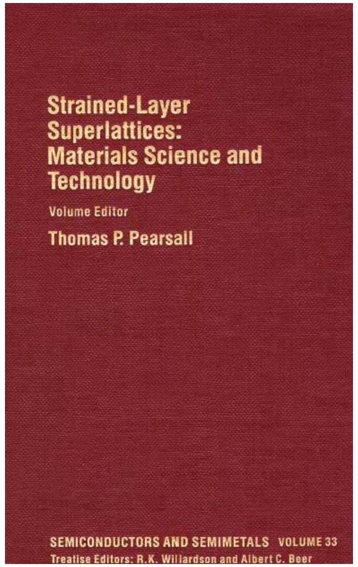
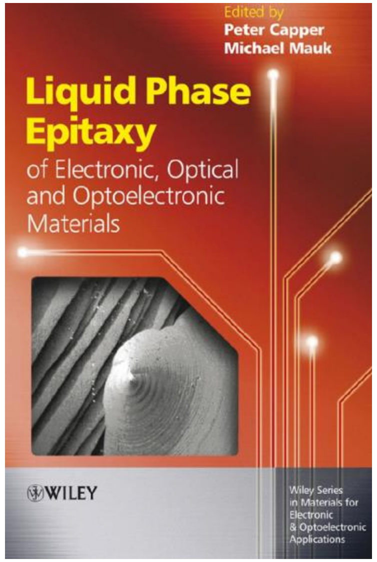

The MATERIALS SCIENCE of THIN FILMS
Milton Ohring


Strained-Layer Superlattices: Materials Science and Technology
Volume Editor
Thomas P. Pearsall
SEMICONDUCTORS AND SEMIMETALS VOLUME 33
Treatise Editors: R.K. Willardson and Albert C. Beer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Crystal Growth Technology

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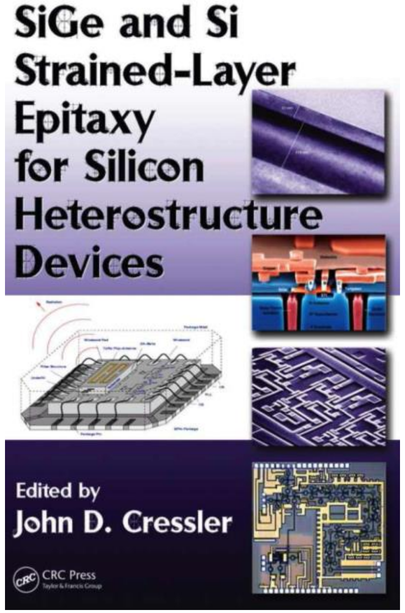

SiGe and Si Strained-Layer Epitaxy for Silicon Heterostructure Devices
Edited by
John D. Cressler
CRC Press
Taylor & Francis Group

03.06.2015, Ionela Vrejoiu

Thin films: motivation and basic definitions

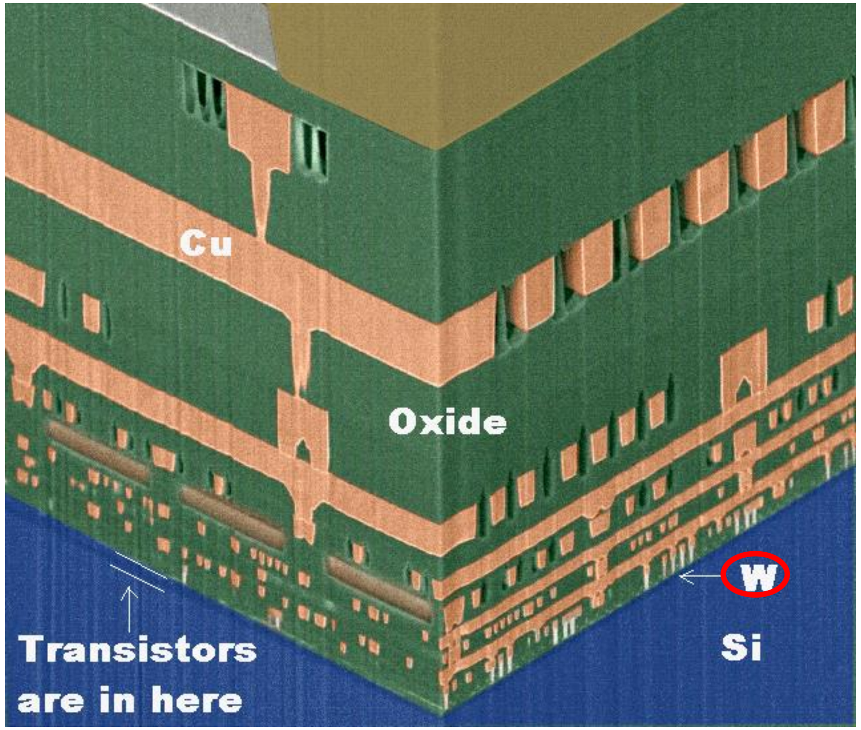
Thin film technology involves deposition of individual molecules or *atoms.*
Thick film technology involves deposition of *particles.*

Semiconductor technology is almost synonymous with thin film technology.

A thin film is adhering to a substrate and is (at least orginally) continous. Thin films may still be found in the product or may have been "sacrificed" during the making of the product.
An integrated circuit **IC** is a study of thin films in and on the **Si** substrate.

Thin always means "thin" relative to some intrinsic (internal) length scale. Examples are:

- Structural length scales
- Wavelength and interaction length scales
- Transport parameter length scales
- Electrical scales



Cross-section of modern chip; colors are artificial.
Picture courtesy IBM

Scale bar: letter W is 1 micron!

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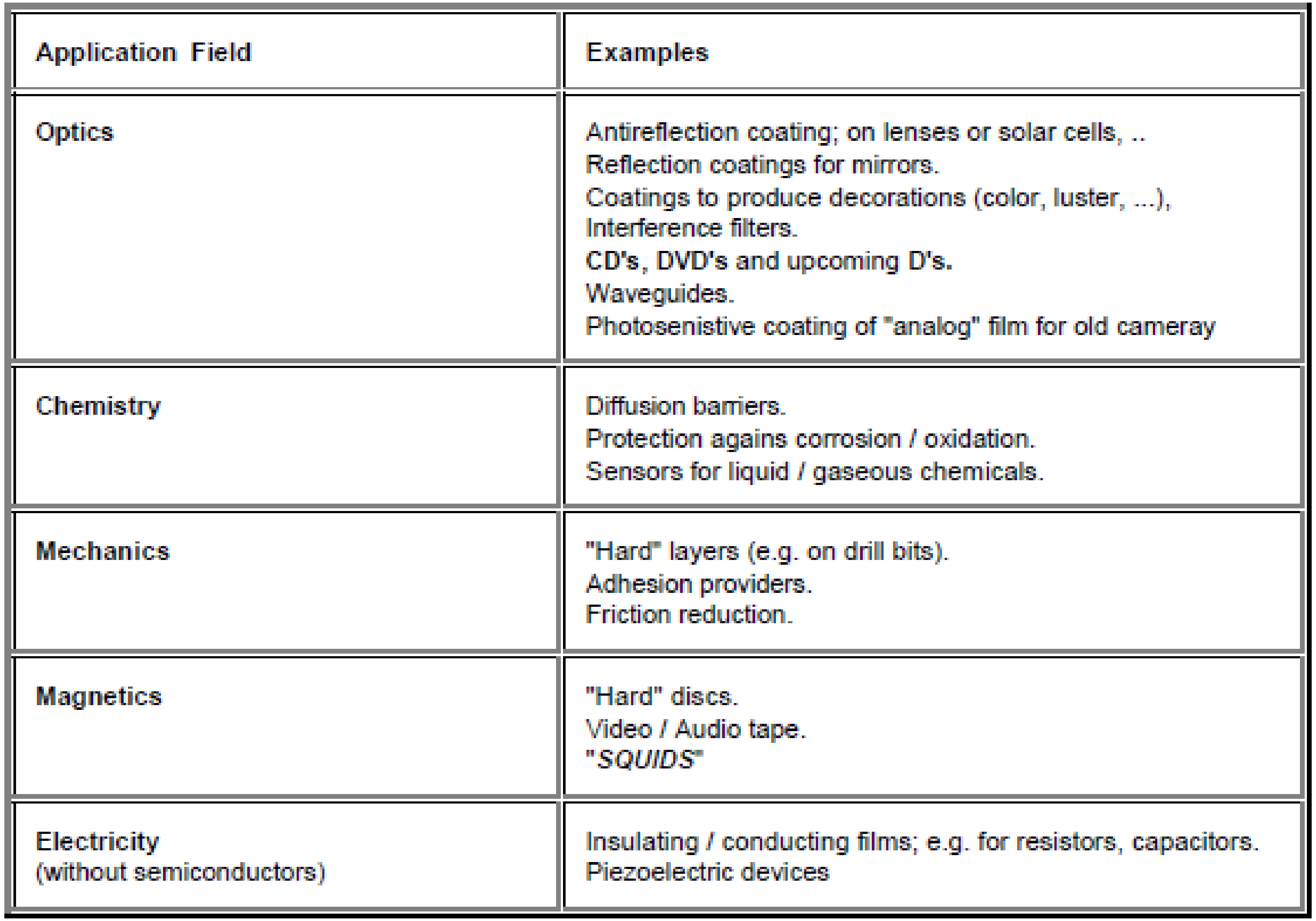
There are many thin film applications outside of semiconductor technolgy:
Optical, electrical, chemical, mechanical, magnetical technologies use thin films



Application Field	**Examples**
Optics	Antireflection coating; on lenses or solar cells, .. Reflection coatings for mirrors. Coatings to produce decorations (color, luster, ...), Interference filters. CD's, DVD's and upcoming D's. Waveguides. Photosenistive coating of "analog" film for old cameray
Chemistry	Diffusion barriers. Protection agains corrosion / oxidation. Sensors for liquid / gaseous chemicals.
Mechanics	"Hard" layers (e.g. on drill bits). Adhesion providers. Friction reduction.
Magnetics	"Hard" discs. Video / Audio tape. "*SQUIDS*"
Electricity (without semiconductors)	Insulating / conducting films; e.g. for resistors, capacitors. Piezoelectric devices

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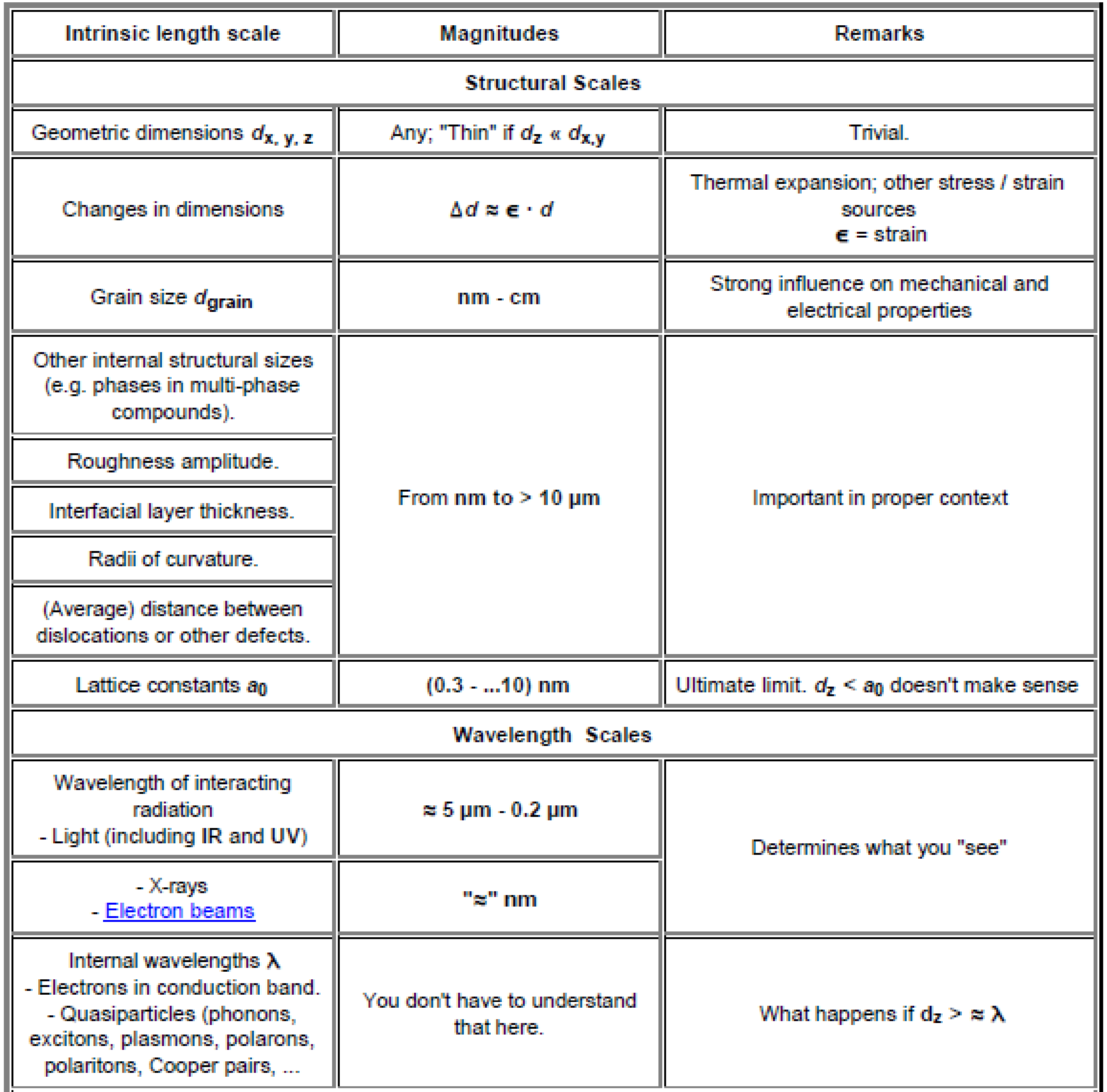

Intrinsic length scale	Magnitudes	Remarks
Structural Scales		
Geometric dimensions $d_{x, y, z}$	Any; "Thin" if $d_z \ll d_{x,y}$	Trivial.
Changes in dimensions	$\Delta d \approx \epsilon \cdot d$	Thermal expansion; other stress / strain sources ϵ = strain
Grain size d_{grain}	nm - cm	Strong influence on mechanical and electrical properties
Other internal structural sizes (e.g. phases in multi-phase compounds).	From nm to > 10 µm	Important in proper context
Roughness amplitude.		
Interfacial layer thickness.		
Radii of curvature.		
(Average) distance between dislocations or other defects.		
Lattice constants a_0	(0.3 - ...10) nm	Ultimate limit. $d_z < a_0$ doesn't make sense
Wavelength Scales		
Wavelength of interacting radiation - Light (including IR and UV)	≈ 5 µm - 0.2 µm	Determines what you "see"
- X-rays - Electron beams	"≈" nm	
Internal wavelengths λ - Electrons in conduction band. - Quasiparticles (phonons, excitons, plasmons, polarons, polaritons, Cooper pairs, ...	You don't have to understand that here.	What happens if $d_z > \approx \lambda$

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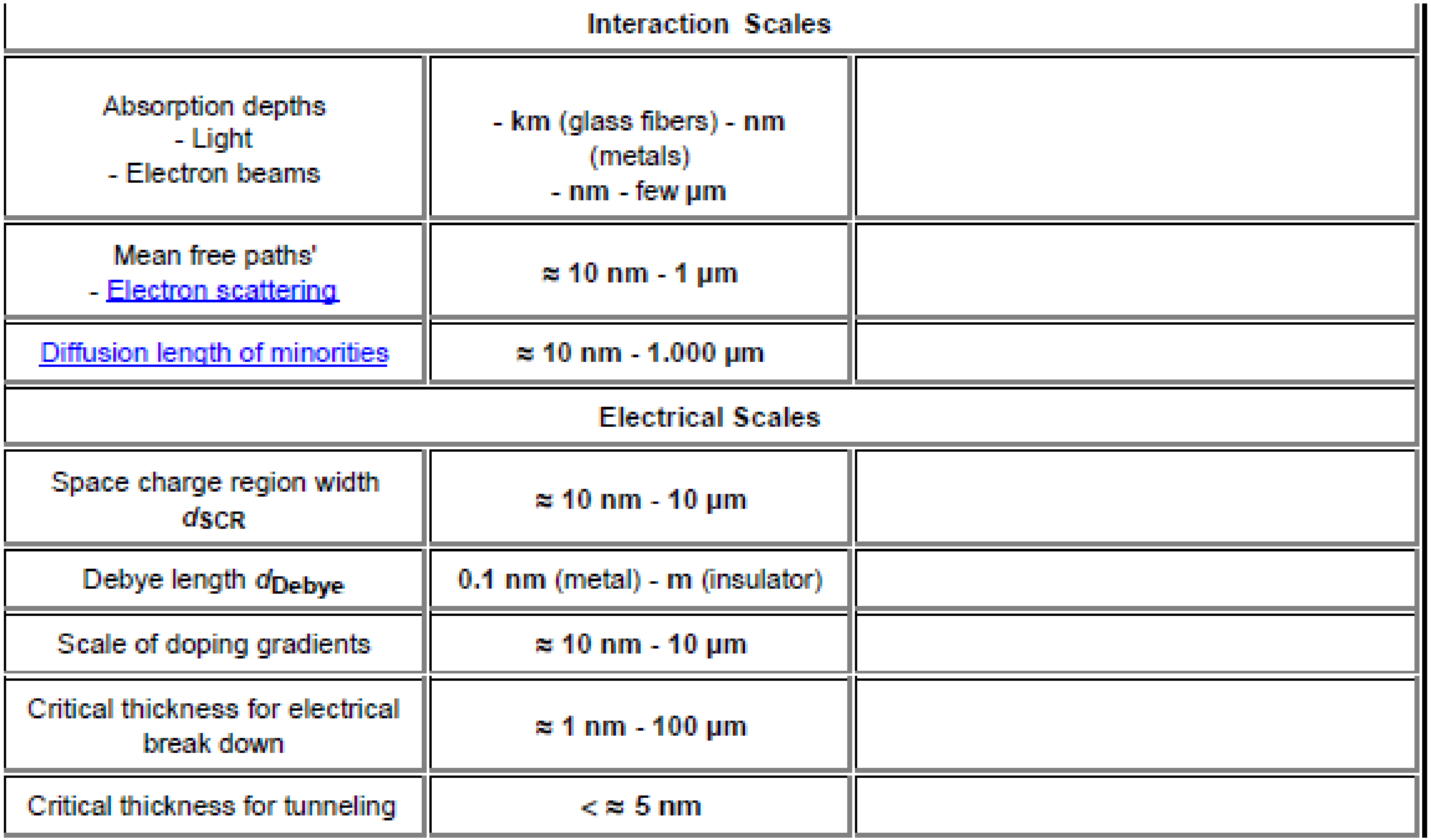

Interaction Scales		
Absorption depths - Light - Electron beams	- km (glass fibers) - nm (metals) - nm - few µm	
Mean free paths' - Electron scattering	≈ 10 nm - 1 µm	
Diffusion length of minorities	≈ 10 nm - 1.000 µm	
Electrical Scales		
Space charge region width d_{SCR}	≈ 10 nm - 10 µm	
Debye length d_{Debye}	0.1 nm (metal) - m (insulator)	
Scale of doping gradients	≈ 10 nm - 10 µm	
Critical thickness for electrical break down	≈ 1 nm - 100 µm	
Critical thickness for tunneling	< ≈ 5 nm	

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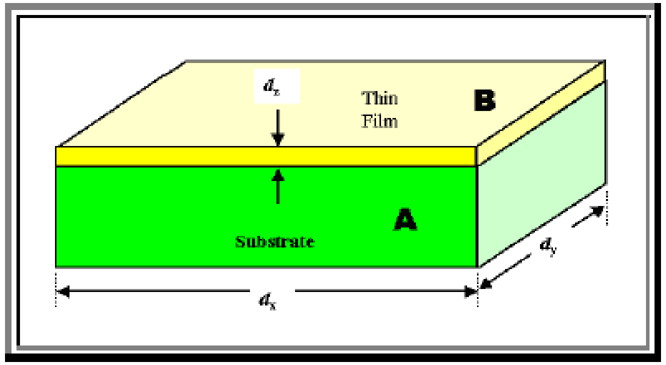
Thin films: motivation and basic definitions

"*Thin*" is indeed a relative measure.
Properties of thin films might be quite different from that of the bulk material if that property depends on an internal length scale.

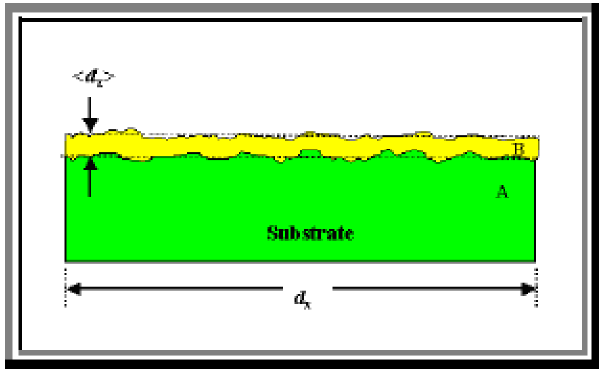
The meaning of "*film*"

We have defined the meaning of "*thin*", we will now define the meaning of "*film*":
Solid films: single crystalline, polycrystalline, amorphous.
Adhesive films: there is some *bonding at the interface*, i.e. the thin film does not easily detach from its substrate.
We might demand that the thin film has about the same thickness everywhere, and that it should be homogenous (same properties everywhere), that it should not contain holes or cracks…

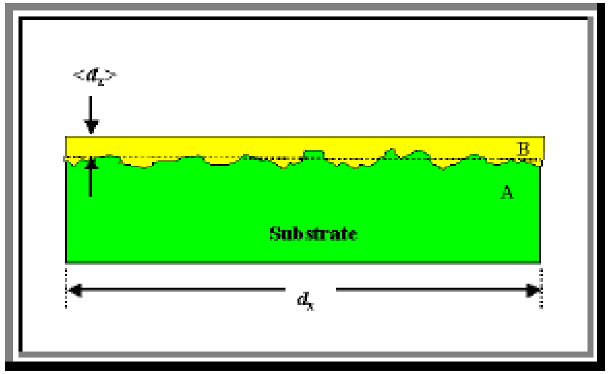
Ideal case



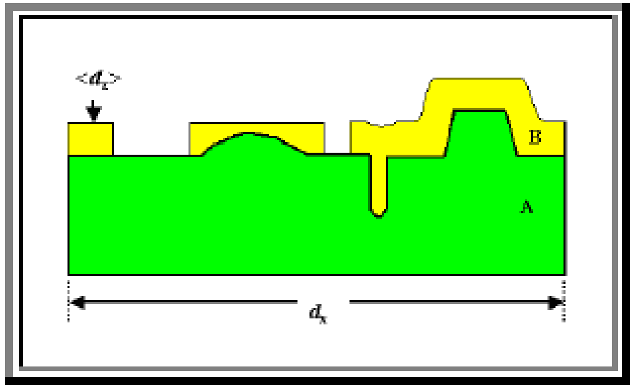
Realistic case



Realistic + surface treated case



Conformal coating of patterned substrates



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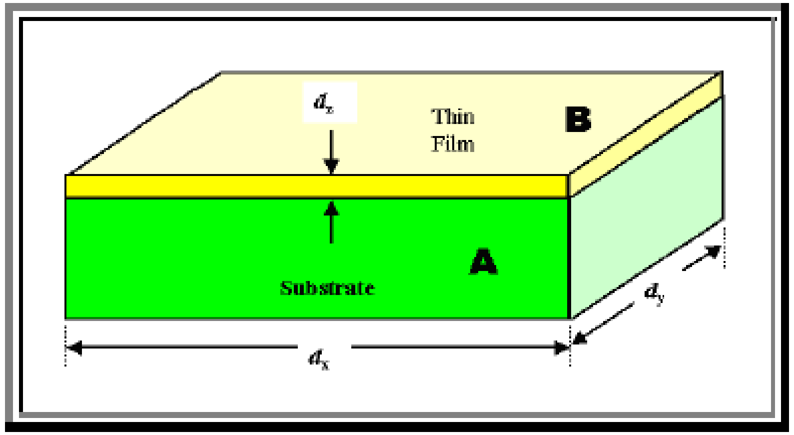
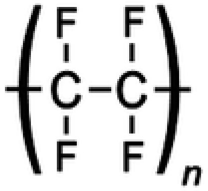
Thin films: adhesion



A thin film of a material **B** on top of material **A**:
the interface (and thus the surface of material **A**) cannot be perfectly flat but can be somewhat rough or even extremely rough.
Thin films **B** that do not *adhere* to their substrate **A** will not be of much use, since they will come off with little force.

Example: Let's say we want a thin film of **Teflon** on top of a semiconductor. *Unfort*unately, nothing *sticks* to Teflon. The **sticking coefficient** of Teflon molecules to any substrate is close to zero. There is indeed such a thing as a well-defined sticking coefficient of **B** on **A**.



$\left(\mathrm{CF_2{-}CF_2}\right)_n$

A direct measure of the amount of adhesion that we have for some interface is the work or energy we need to employ per **cm^2** to remove **B** from **A**. This is the concept of surface and interface energies, applied to thin films, i.e. interfaces between two different materials.

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*Can we calculate the interfacial energy between **A** and **B**?*

The interfacial properties, as far as adhesion is concerned, come just as much from the bonds and their binding potentials in the interface between **A** and **B**, as most of the mechanical properties of pure **A** or pure **B**. Essenti

A few examples for this:
If you deposit a metal **B** on top of a metal **A** and you know from the phase diagram that these metals are completely ***miscible***, you know that you will have no adhesion problem. Complete miscibility, after all, necessitates that the bond strength between **A-A**, **B-B**, and **A-B** is not too different, so your **A-B** bonds in the interface should be just about as strong as those in **A** and **B**.
The same kind of thinking will tell us that **Si** on **Ge**, for example, or any **III-V** semiconductor on top of any other covalently bonded group **IV**, or **III-V** semiconductor should give good adhesion.

The same kind of thinking, however, will also teach us that if there is just *one* molecular layer of "dirt" in between **A** and **B**, you might be in trouble, because you don't know how **A** and **B** bond to "dirt".
If there is not a continuous layer of dirt in between **A** and **B**, but just some
dirt particles (called e.g. dust), you simply will not get **A-B** bonding either. And now you even realize that just a few particles of less then **1 nm** in diameter or some roughness of the two layers before they make contact will already be enough to prevent bonding between **A** and **B** on an atomic scale. After all, if you put a macroscopic piece of metal **A** on top of a metal **B** the adhesion will always be zero.

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Thin films: adhesion

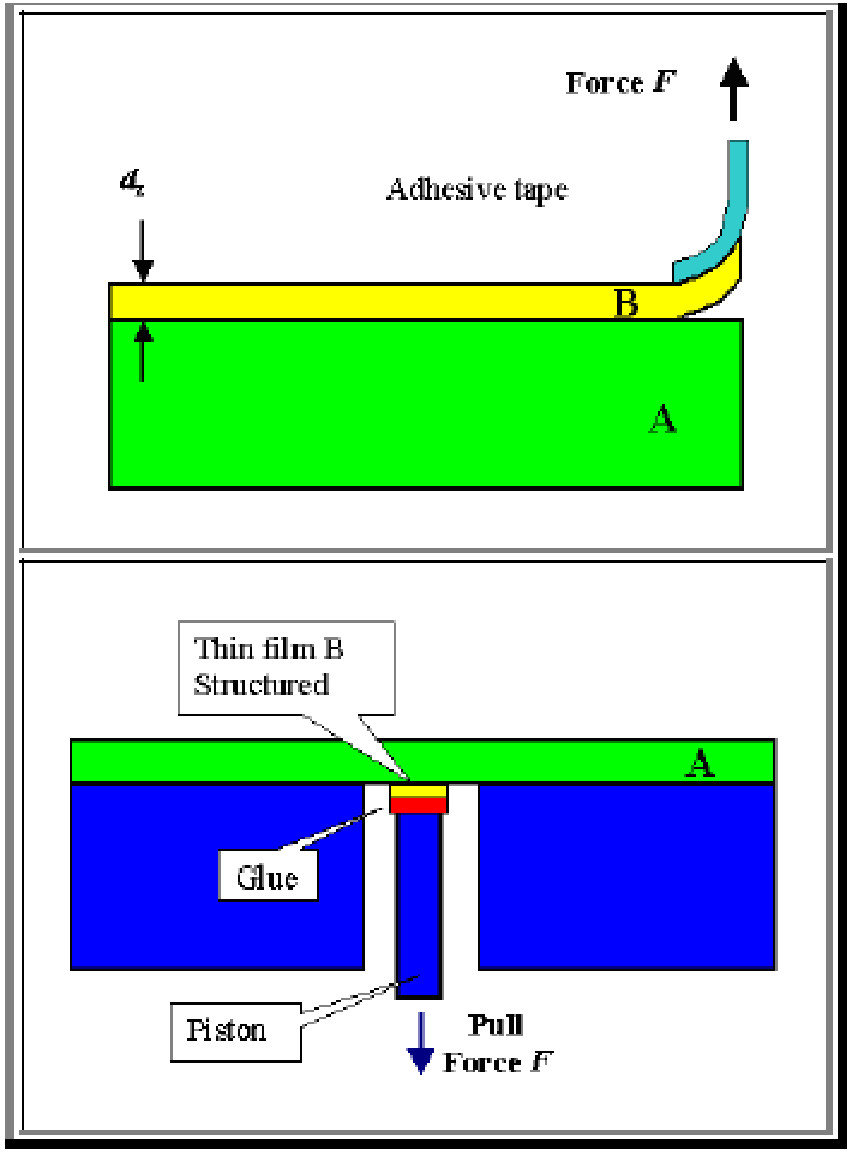
Not counting some exotic techniques ("Wafer bonding"), we *never* produce a thin film by "putting" the film **B** on **A**:

Thin films are always *grown* on their substrate!

*Can we measure the interfacial energy between **A** and **B**?*
"standard" techniques: Essentially you try to delaminate your layer by "pulling" or "pushing". Measuring the force needed to do that gives you a quantitative number that you may be able to convert into the interfacial energy.

The simplest technique is to attach an adhesive tape ("Tesa") to your layer. If there is better adhesion at the interface tape-layer than at the interface layer-substrate, you might be able to pull off your layer as shown.

Or you make a hole in the substrate and push up with a small piston, or you pull down the piston after gluing it to the thin film.



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Thermal stress and strain

Upon cooling from the deposition temperature to RT, substrate and thin film will shrink by some factor given by their **thermal expansioncoefficient** α, a property we have encountered before and seen that it comes straight from the bonding potential.
The thermal expansion coefficient α was defined as

$$\alpha = \frac{l(T) - l_0}{l_0 \cdot T} = \frac{\epsilon_{\text{therm}}}{T}$$

l_0 is the length at the reference temperature, usually room temperature. Of course, α might be a function of the temperature; more generally we would define it as $\alpha(T) = d\varepsilon_{\text{therm}}/dT$.
It follows that two different materials with an α_A and an α_B having the same length l_0 at some T_0 will differ in length at the temperature T by some $\Delta l(T)$ or $\varepsilon_{\text{therm}}$ directly proportional to the **mismatch in the thermal expansion and given by**

$$\Delta l(T) = l_0 \cdot \Delta T \cdot (\alpha_A - \alpha_B)$$

$$\epsilon_{TF} = \Delta T \cdot \Delta\alpha$$

We can generalize to all thin films: A difference of the thermal expansion coefficients of substrate and thin film material of Δα and a temperature difference ΔT relative to a stress few state produces a strain $\varepsilon \cdot \Delta\alpha\, \Delta T$ in the thin film.

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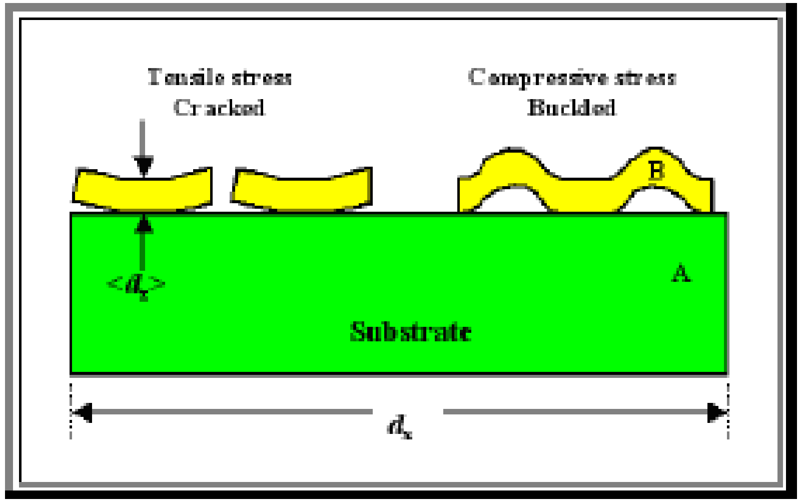
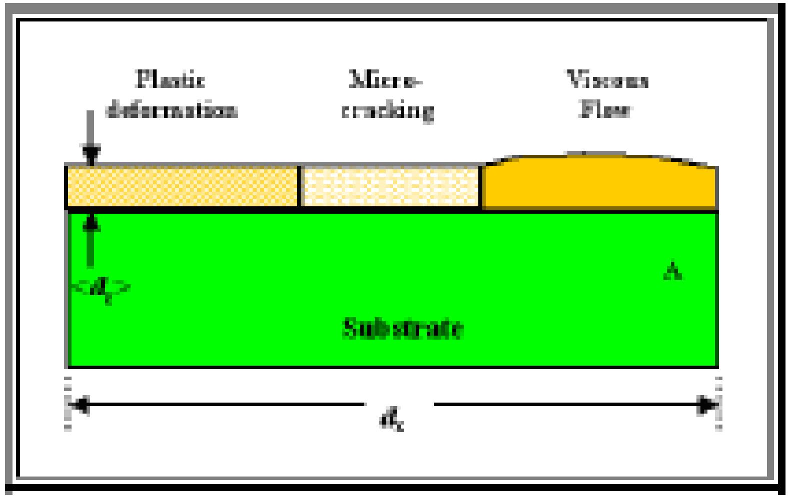
Thermal stress and strain

If the strain is purely elastic it leads to stress in the film given by
$\sigma_{TF} = Y\, \varepsilon_{TF} = Y\, \Delta\alpha\, \Delta T$
where Y is Young's modulus





No material will be able to sustain arbitrarily large amounts of stress. There are mechanisms of *stress relaxation.*

1. The adhesion is not very good.
The film may simply come "loose" - in total or in parts. Wherever it does not adhere to the substrate anymore, the stress can be completely relieved.
The criterion, as always, is that if the energy gained by stress relieve (**=** ½ σ · ϵ per volume = **cm2** times thickness) is larger than the interface energy, it "pays" to rip off.
Obviously, this scales with the film thickness.
The problem is that the energy balance of a mix of partially coming off, partially still sticking, is not that easy to calculate.
First you have to consider if you have tensile or compressive stress, and then what additional energy terms come into play
Fracture or cracking in the tensile stress case, or "**buckling**" in the compressive stress case, also takes some energy.

2. The adhesion is very good - This means that you will find a fully adherent thin film *and* still a lot of stress. But not necessarily the full stress you would calculate!

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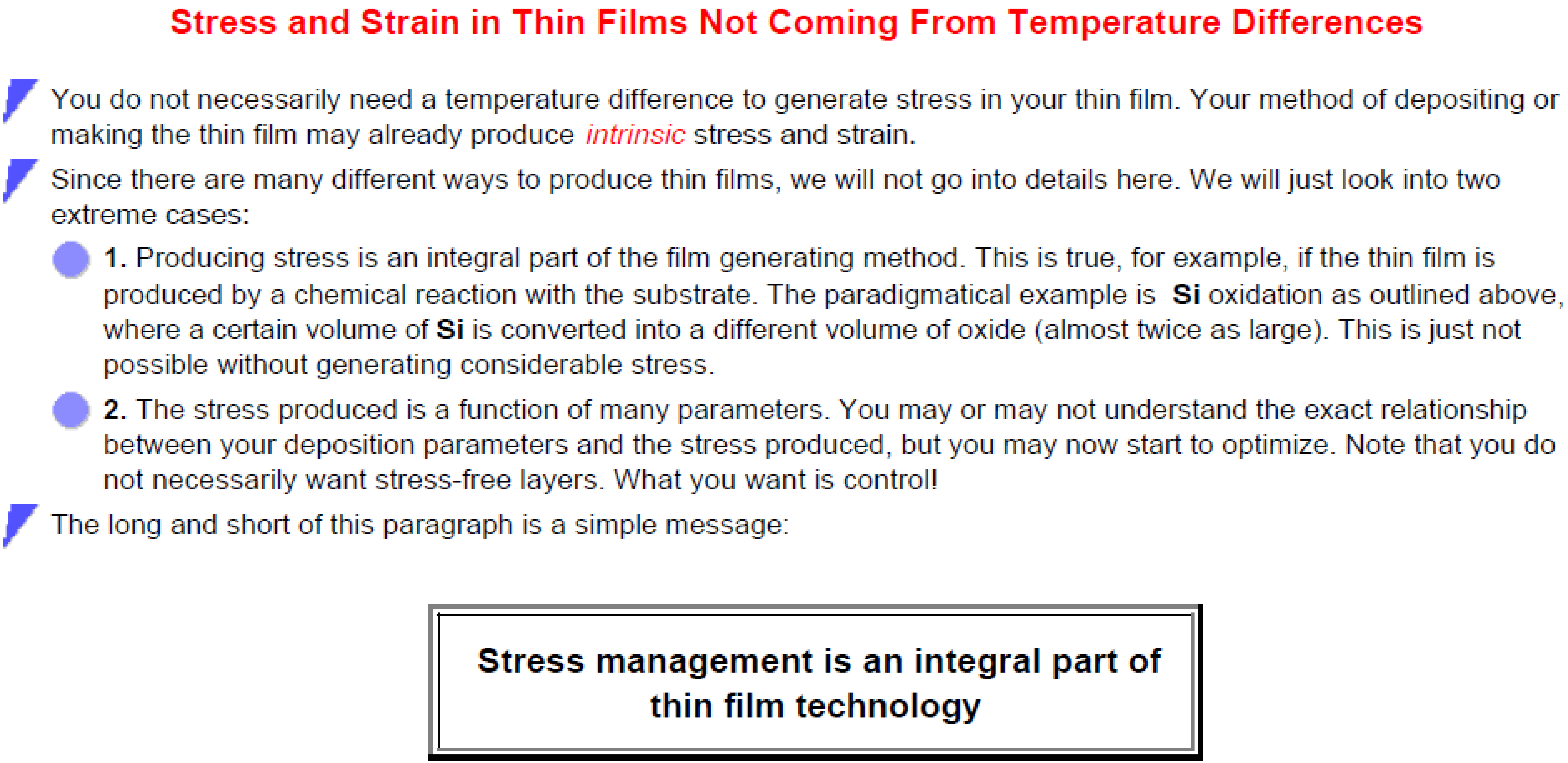

Stress and Strain in Thin Films Not Coming From Temperature Differences

- You do not necessarily need a temperature difference to generate stress in your thin film. Your method of depositing or making the thin film may already produce *intrinsic* stress and strain.
- Since there are many different ways to produce thin films, we will not go into details here. We will just look into two extreme cases:
  - **1.** Producing stress is an integral part of the film generating method. This is true, for example, if the thin film is produced by a chemical reaction with the substrate. The paradigmatical example is **Si** oxidation as outlined above, where a certain volume of **Si** is converted into a different volume of oxide (almost twice as large). This is just not possible without generating considerable stress.
  - **2.** The stress produced is a function of many parameters. You may or may not understand the exact relationship between your deposition parameters and the stress produced, but you may now start to optimize. Note that you do not necessarily want stress-free layers. What you want is control!
- The long and short of this paragraph is a simple message:

Stress management is an integral part of thin film technology

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Strain relief in lattice-mismatched epitaxy

WIKIPEDIA: **Epitaxy** refers to the deposition of a crystalline overlayer on a crystalline substrate. The overlayer is called an epitaxial film or epitaxial layer. The term *epitaxy* comes from the Greek roots *epi* (ἐπί), meaning "above", and *taxis* (τάξις), meaning "an ordered manner". It can be translated as "arranging upon". For most technological applications, it is desired that the deposited material form a crystalline overlayer that has one well-defined orientation with respect to the substrate crystal structure (single-domain epitaxy).

It is possible to grow coherent lattice-mismatched epitaxial structures, where the lattice parameter of the deposit is different from that of the substrate.

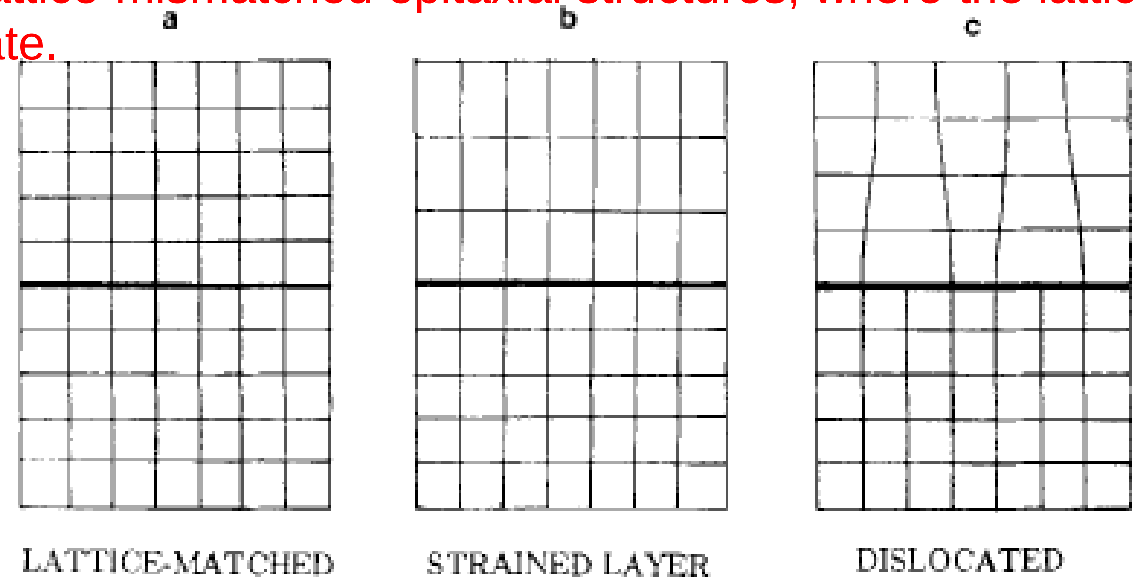


FIG. 16. Schematic illustration of (a) lattice-matched heteroepitaxy; (b) coherently strained lattice-mismatched heteroepitaxy; (c) relaxed lattice-mismatched heteroepitaxy. (Reprinted with permission from Plenum Pub. Corp., from Hull *et al.*, 1989d.)

In lattice-matched heteroepitaxy (Fig. 16a), the deposit and the substrate have the same lattice parameter, and deposition of the epilayer atoms onto the substrate surface allows them to easily locate the potential minima corresponding to the substrate lattice sites, assuming they have sufficient thermal energy (i.e., if the growth temperature is high enough) to move to the nearest minimum. In strained-layer epitaxy (Fig. 16b), despite the difference in substrate and deposit lattice parameters, deposit atoms are constrained to the substrate interatomic spacings in the plane of the interface. We designate such structures commensurate or coherent.

Strain relief in lattice-mismatched epitaxy: misfit dislocations

Significant elastic strain energy is stored in the structure (accommodation of a lattice mismatch of just 1% in this fashion produces a stress field equivalent of 2GPa, assuming a shear modulus of 5 x 10^{10} Pa and ν Poisson's ratio of 0.33). **A** tetragonal distortion of the unit cell of the deposit is also produced, since elasticity theory shows that the planar stress parallel to the interface, σ_i**,** will produce a normal strain ε_n, given by:

$$\varepsilon_n = \frac{1+\nu}{1-\nu}\varepsilon_i$$

Here ν is Poisson's ratio, and ε_i is the interfacial strain produced by accommodation of the lattice mismatch, equal to $\sim(a_e-a_s)/a_s$, where a_s and a_e, are the substrate and epilayer bulk (relaxed) lattice parameters, respectively.

These relationships assume effectively that the substrate is of infinite thickness, such that all the elastic strain energy is stored in the deposit. In practice, the thickness of the substrate (typically 0.5 mm) is very much greater than the epilayer thickness (Å to microns), so this approximation is reasonably valid.

For a given lattice mismatch, the elastic strain energy in the coherent deposit will increase approximately linearly with the substrate thickness. When the strain energy is sufficiently large, it will start to be relieved by deformation of the hitherto coherent structure. This process occurs via the introduction of slipped regions into the crystal, bounded by line defects known as MISFIT DISLOCATIONS.

Strain relief in lattice-mismatched epitaxy: misfit dislocations

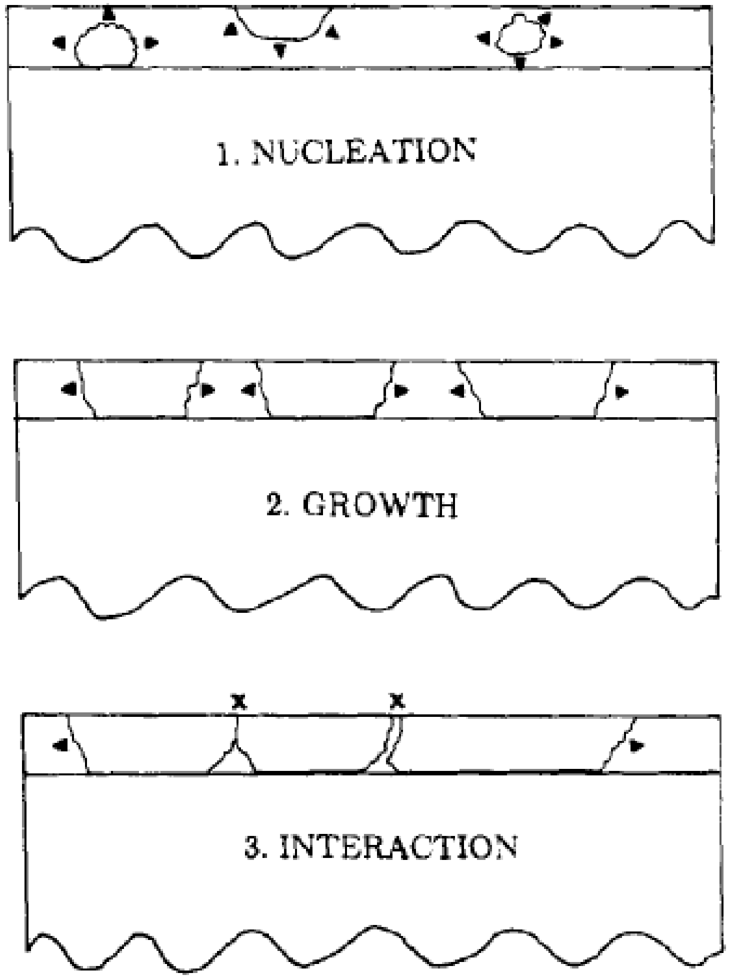
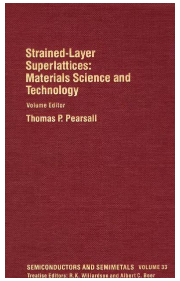


FIG. 21. Schematic illustration of (1) nucleation, (2) growth, and (3) interaction of misfit dislocations. (Reprinted with permission from Plenum Pub. Corp., from Hull *et al.*, 1989d.)


Strained-Layer Superlattices: Materials Science and Technology
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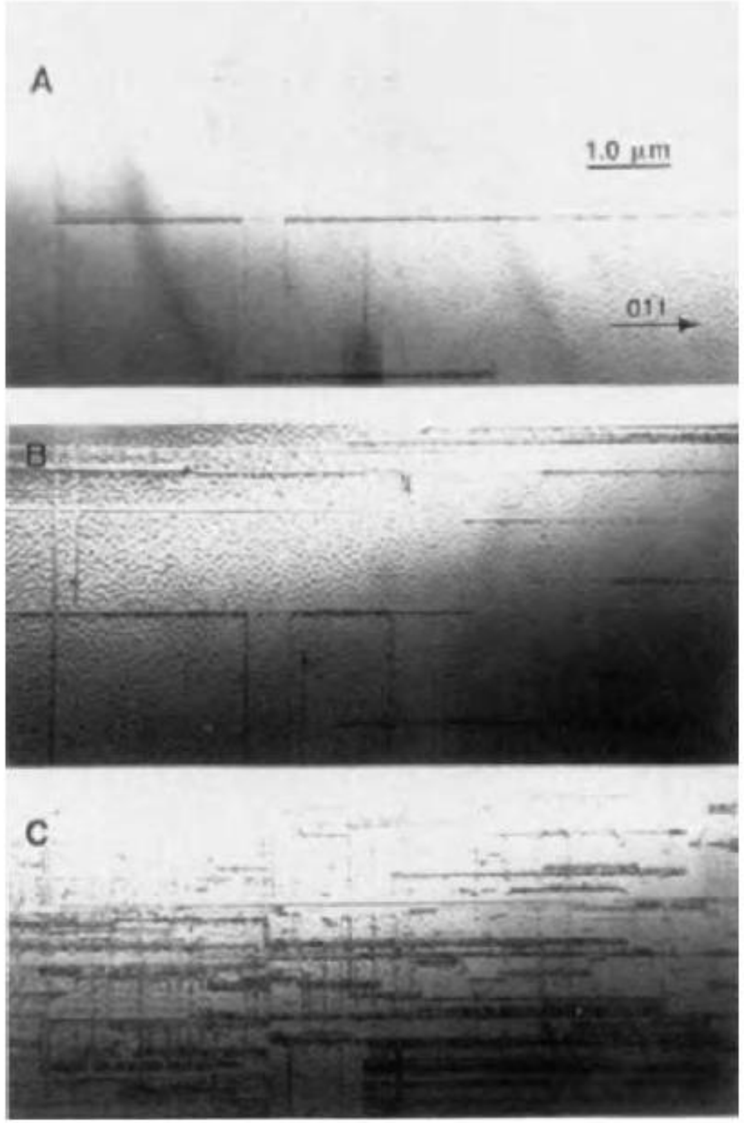


FIG. 24. Plan-view TEM images of a 350 Å $Ge_{0.25}Si_{0.75}/Si(100)$ structure (a) as-grown at 550°C; (b) annealed to 700°C; and (c) annealed to 900°C (from Hull *et al.*, 1988b).

Misfit dislocations (edge and screw dislocations): Burgers vector

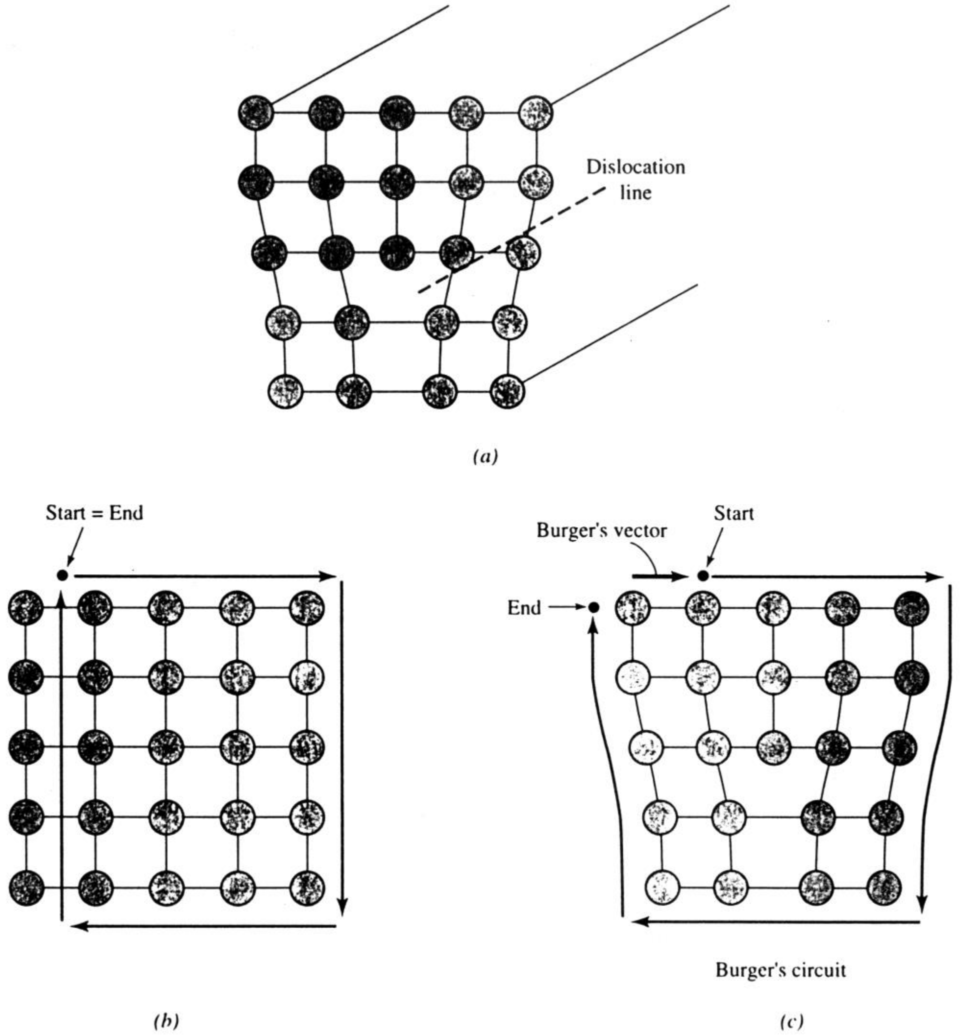
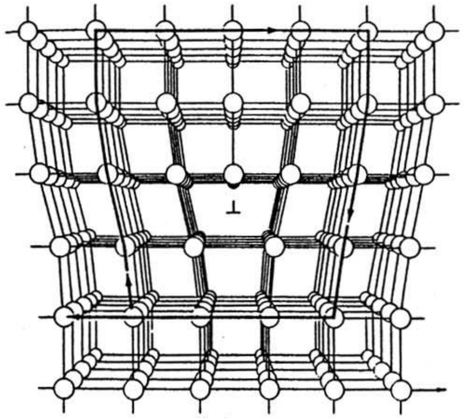
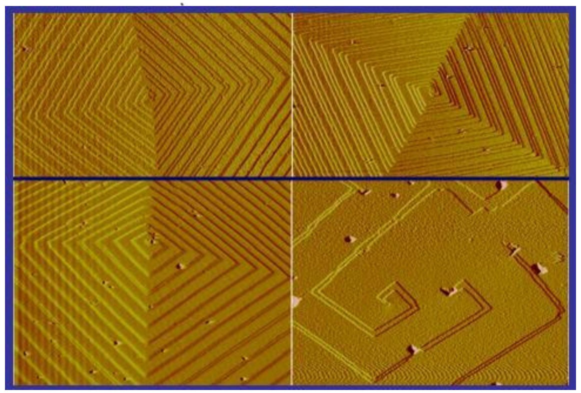


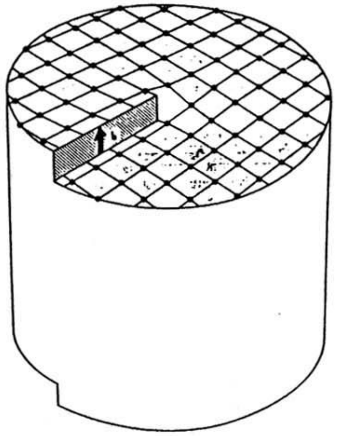
Figure 5.2–6 Illustration of Burger's circuit and Burger's vector for an edge dislocation: *(a)* a 3-D view of an edge dislocation; *(b)* a Burger's circuit closes upon itself when it surrounds a dislocation-free region of a crystal; *(c)* when the Burger's circuit surrounds a dislocation, the start and stop points

Edge Dislocation:



Screw Dislocation





Mixed dislocations show characteristics of both edge and screw.

H. Henry Teng,
Washington University

http://www.mrl.ucsb.edu/~edkramer/LectureVGsMat100B/99Lecture11VGs/EdgeScrewDislocationsVG.html

Strain relief in lattice-mismatched epitaxy: critical thickness for misfit dislocations

Hirsch et al, 1977

Critical thickness for misfit dislocations formation h_c:

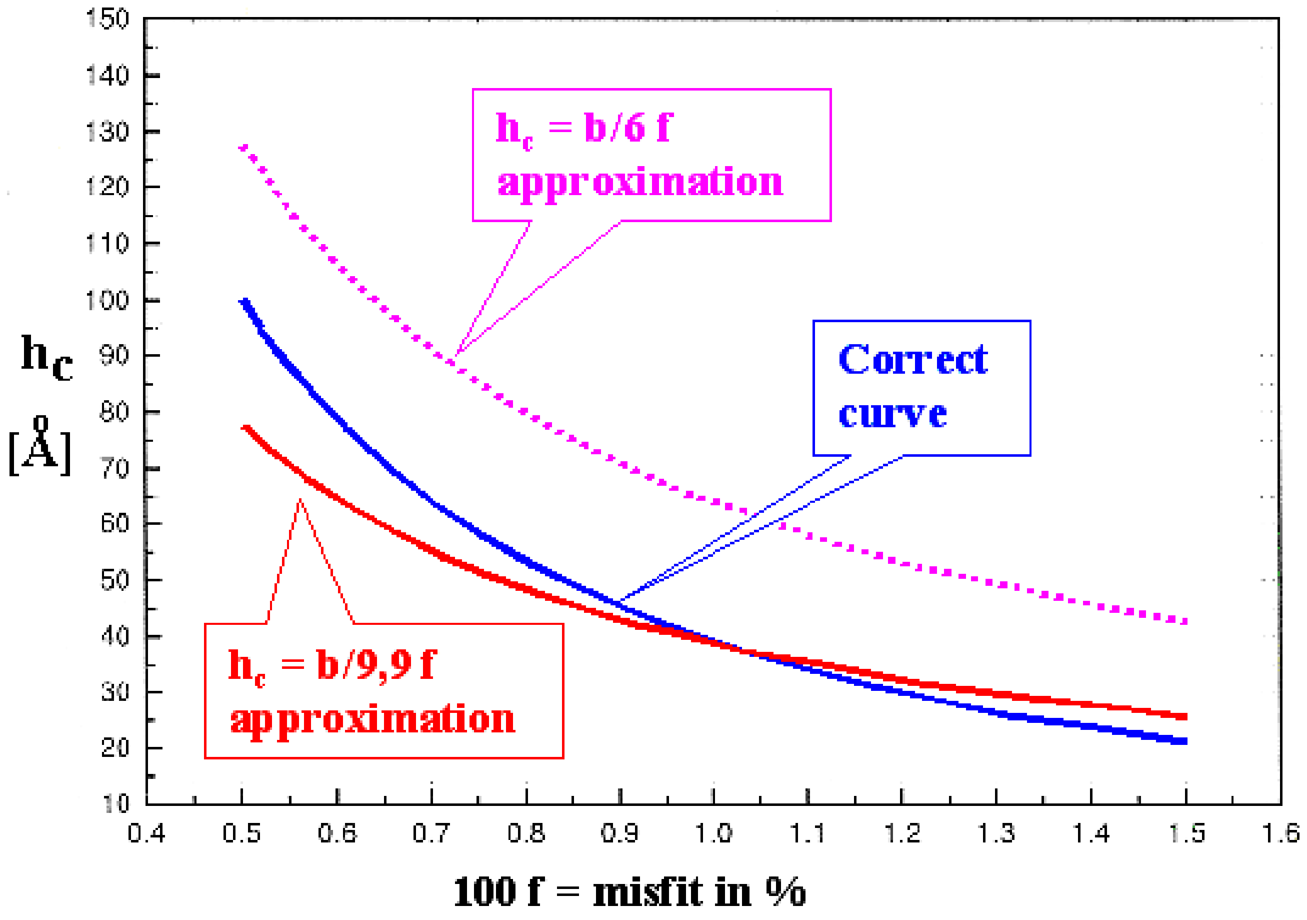
$$h_c = \frac{b}{8\pi \cdot f \cdot (1 + \nu)} \cdot \ln \frac{e \cdot h_c}{r_0}$$

b- Burgers vector (actually only the edge component in the plane of the interface)

f- misfit

ν- Poisson ratio

r_0- core radius of the dislocation



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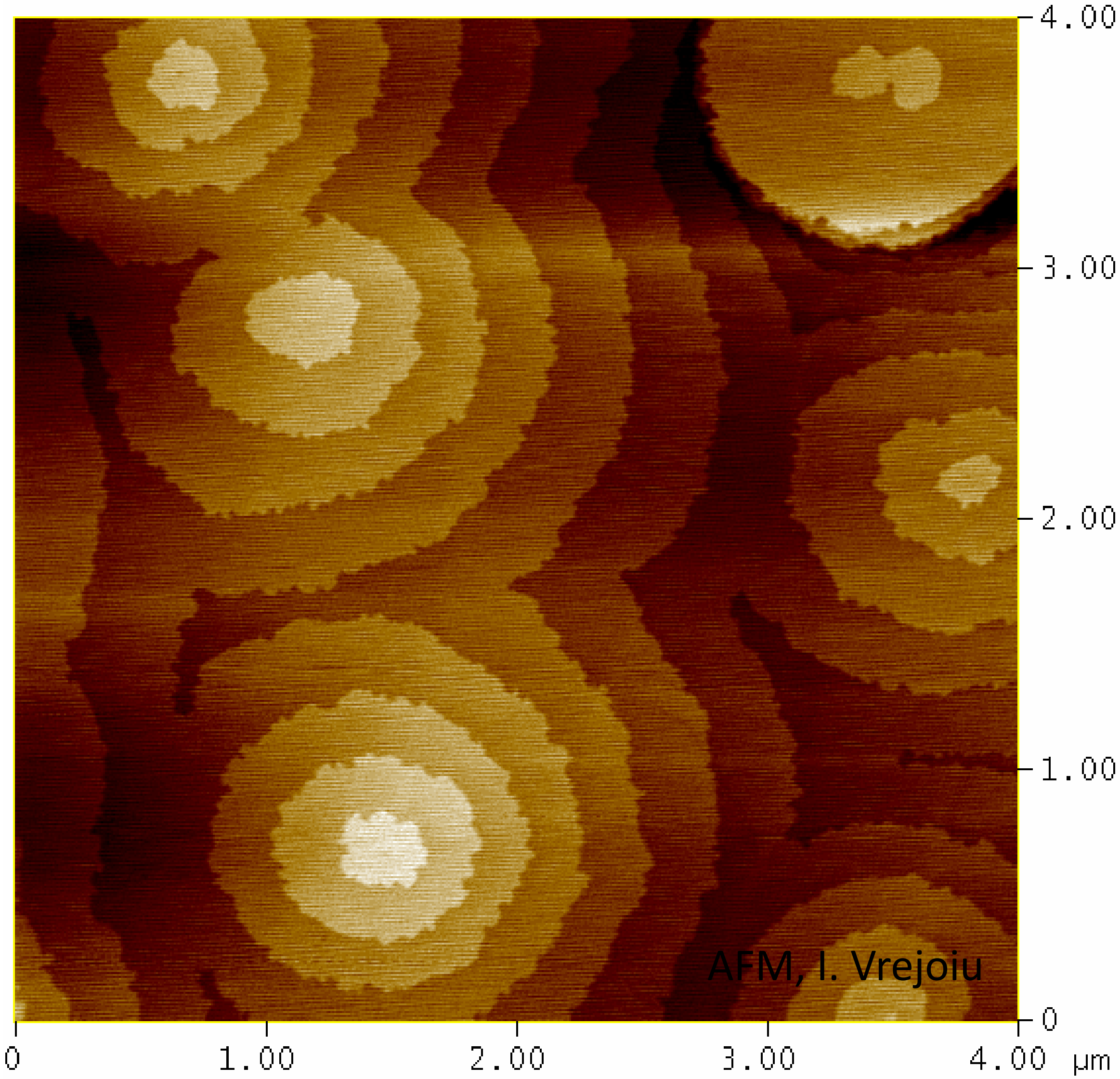
Edge and screw dislocations: Can we “see” their fingerprints on the top surface?

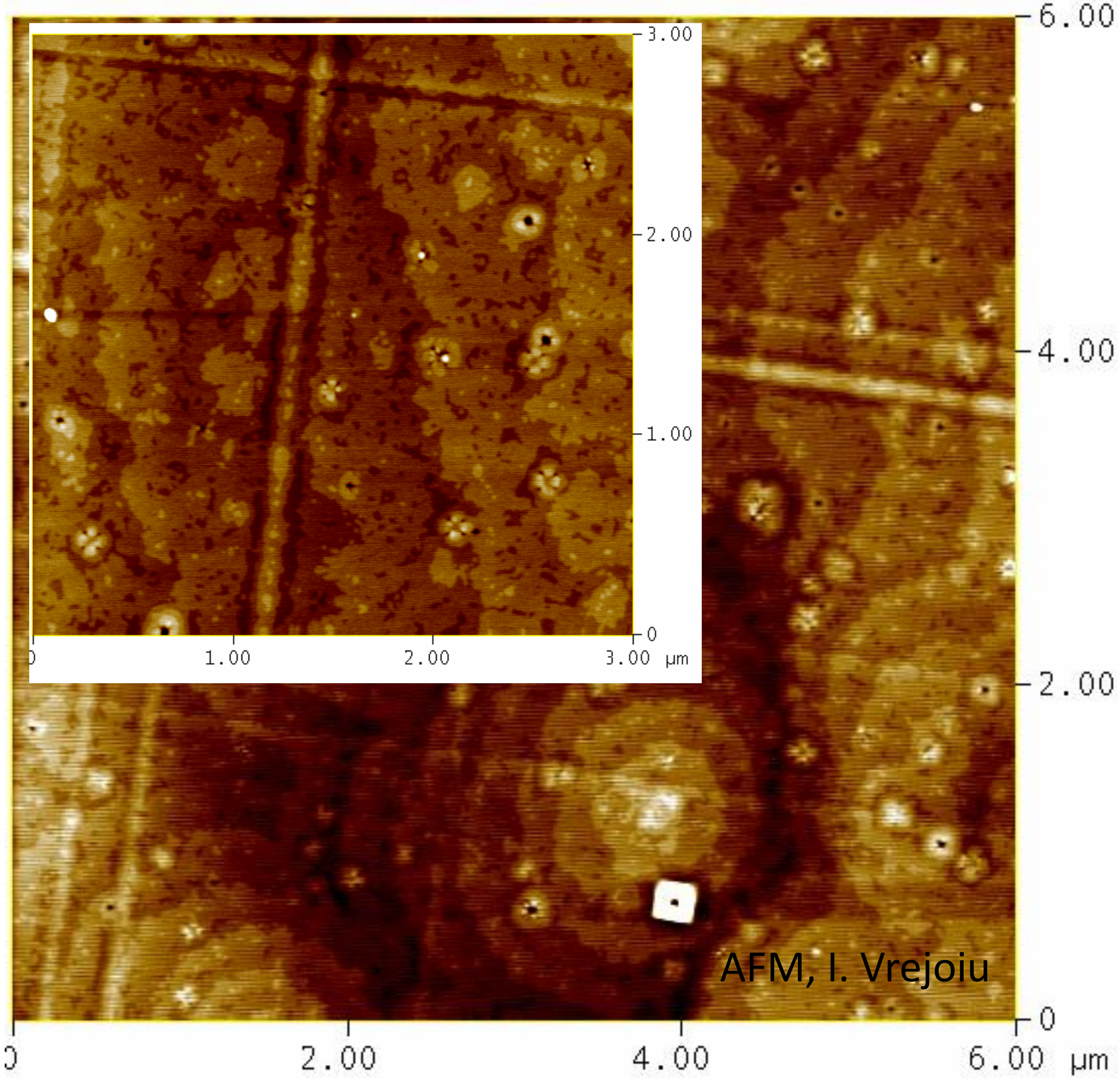
ATOMIC FORCE MICROSCOPY

Epitaxial growth of $SrRuO_3$ on TiO_2-terminated $SrTiO_3$ (100)



AFM, I. Vrejoiu

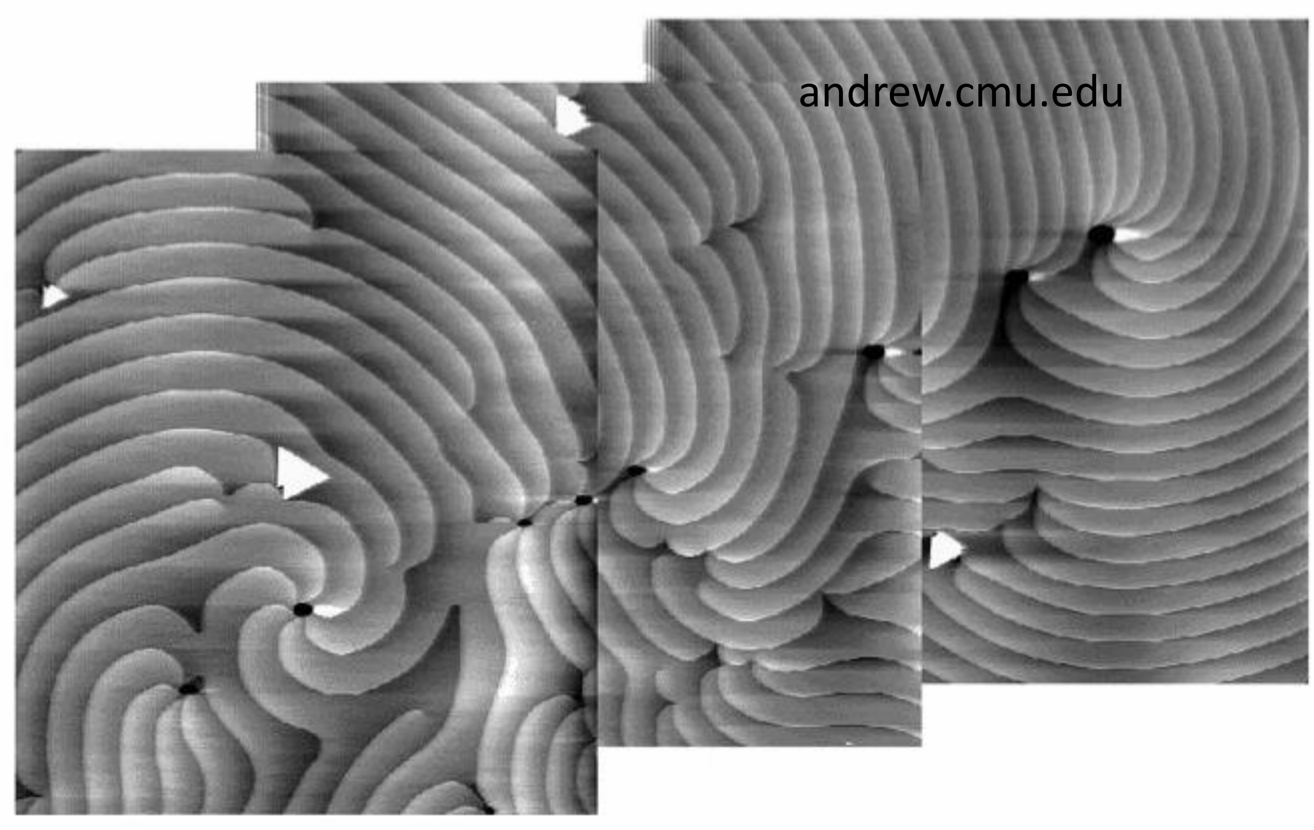
Growth of $PbZr_{0.2}Ti_{0.8}O_3$ on the $SrRuO_3$ with misfit dislocations



AFM, I. Vrejoiu

Edge and screw dislocations: Can we "see" their fingerprints on the top surface?

ATOMIC FORCE MICROSCOPY



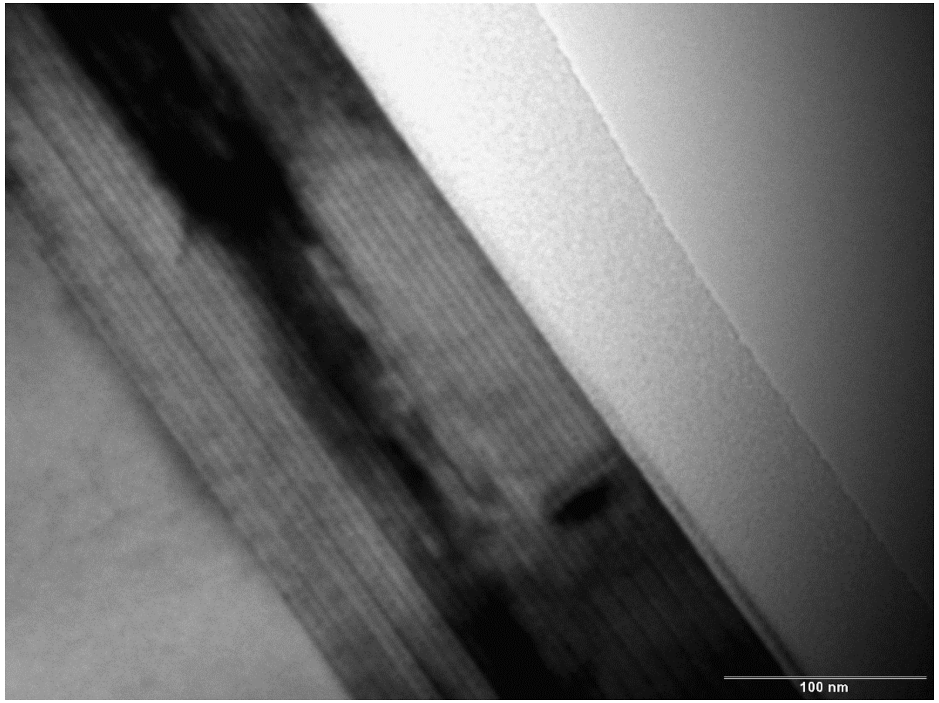
andrew.cmu.edu

Atomic Force Microscopy image of 6H-SiC growth surface showing an array of empty core super-screw dislocations.

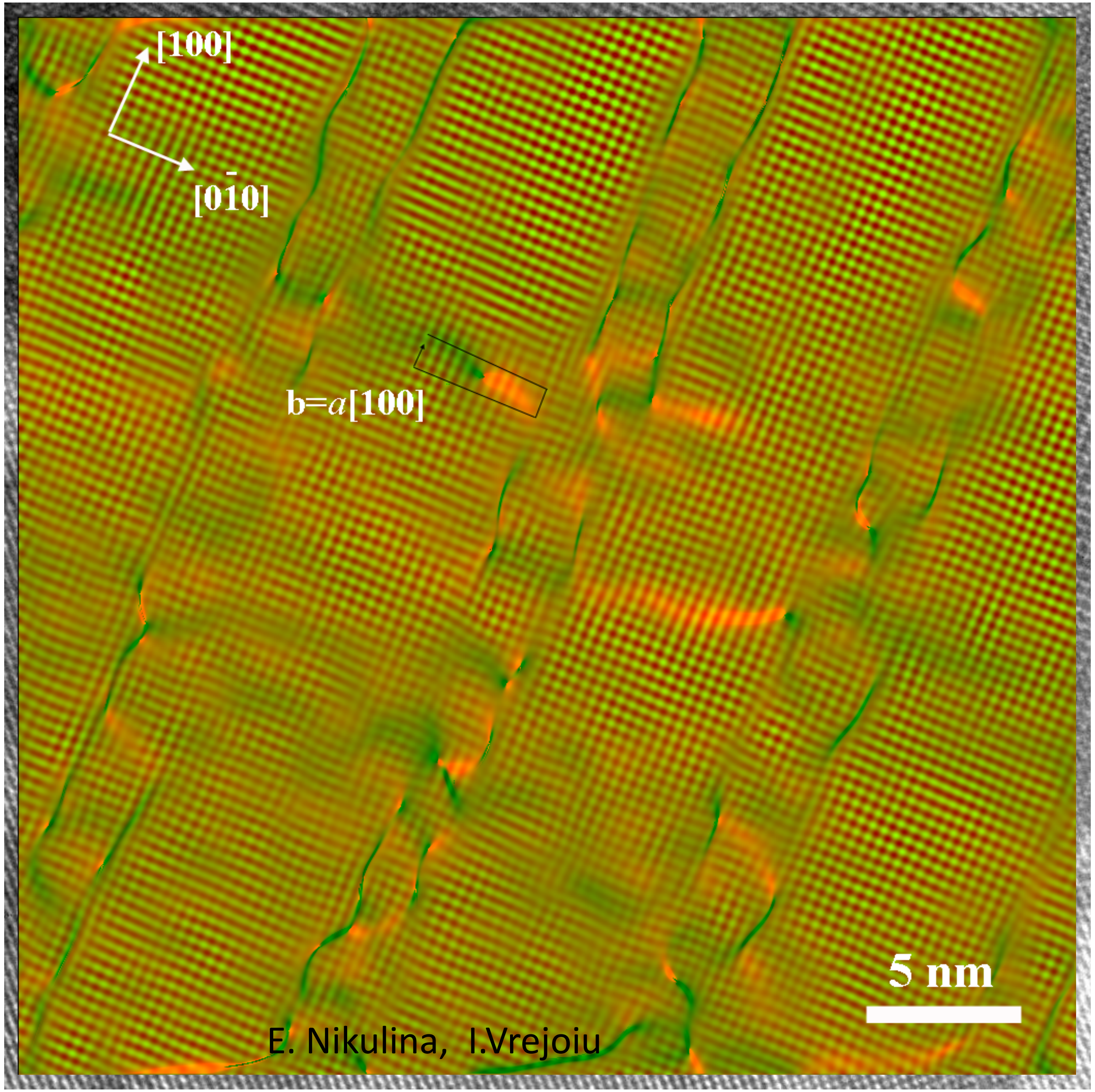
Edge and screw dislocations: Can we “see” them?

High resolution transmission electron microscopy

Multilayer of $BaTiO_3/SrRuO_3/La_{0.7}Sr_{0.3}MnO_3$ on $SrTiO_3$ (100)



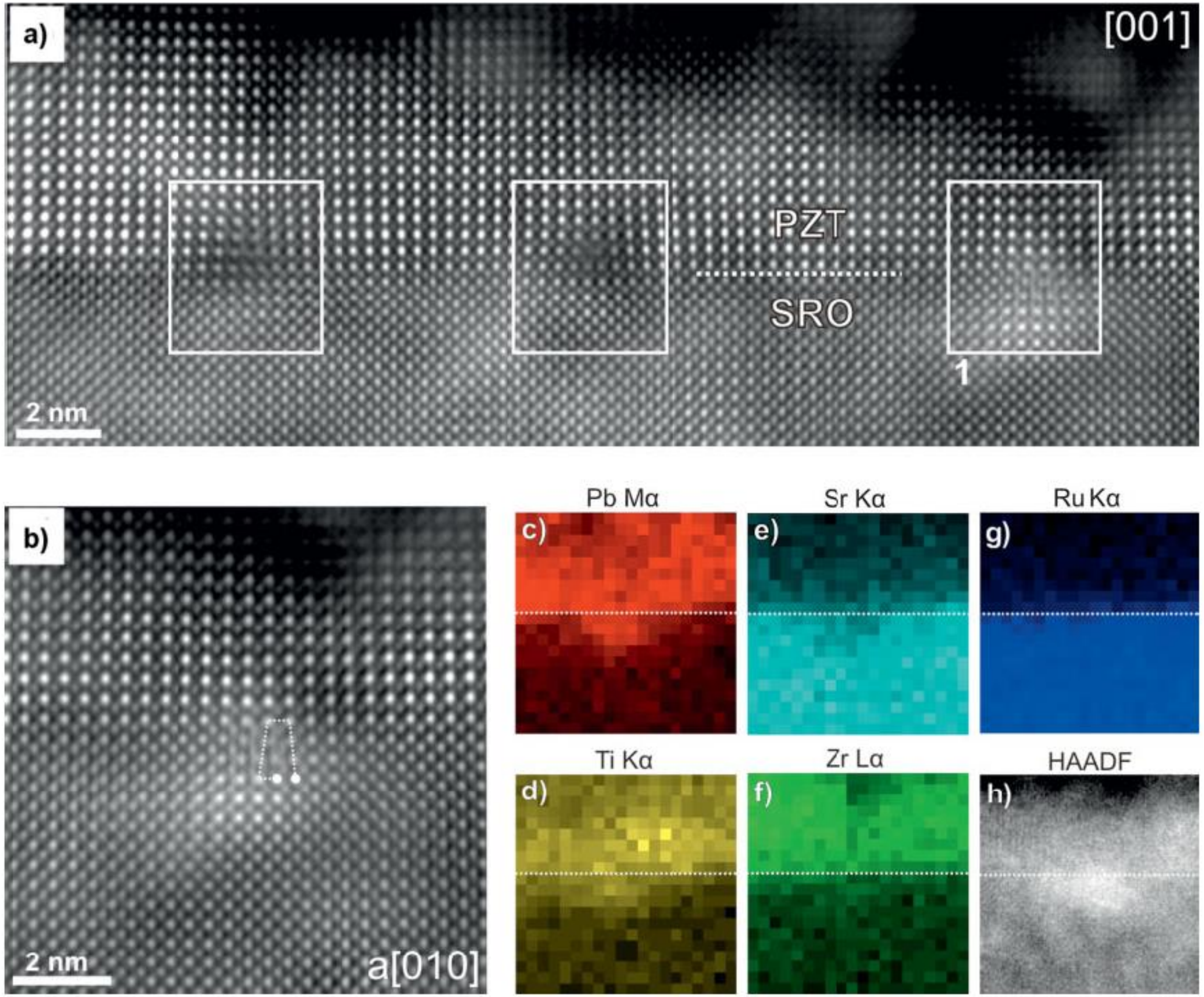
E. Nikulina, I.Vrejoiu



E. Nikulina, I.Vrejoiu

Edge and screw dislocations: Can we “see” them?

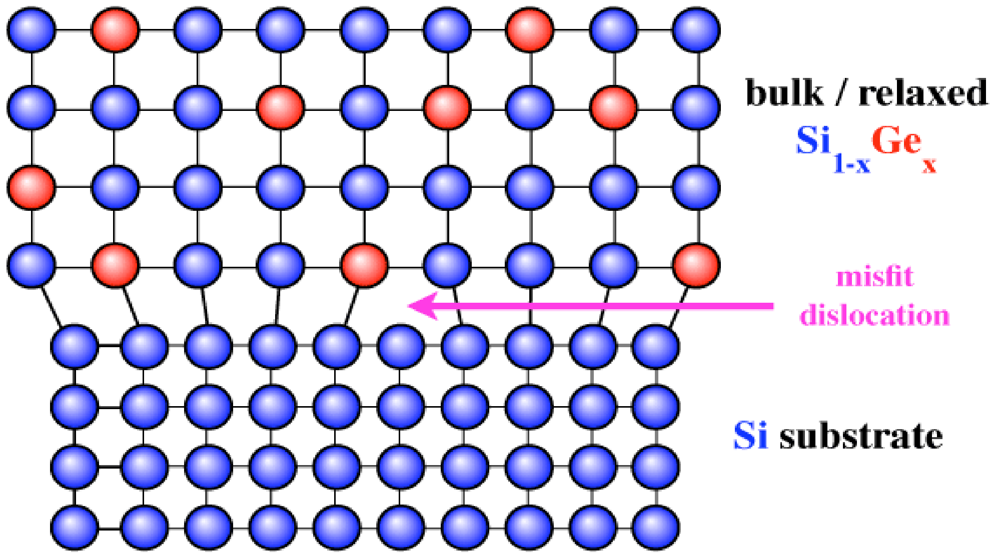
Scanning transmission electron microscopy with EDX mapping



Growth of $PbZr_{0.52}Ti_{0.48}O_3$ on $SrRuO_3$
with edge dislocations

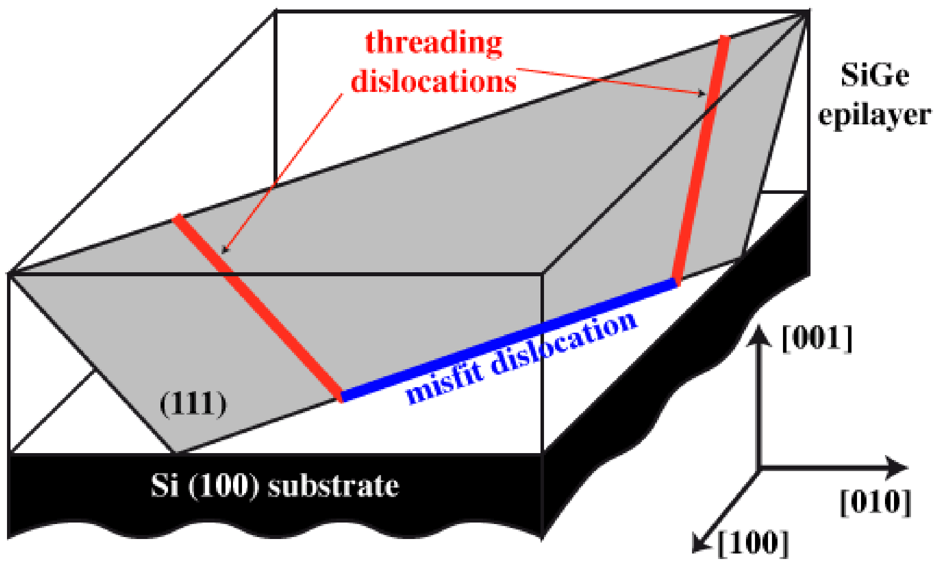
Adv. Mater. **2010**, *22*, 2430–2434

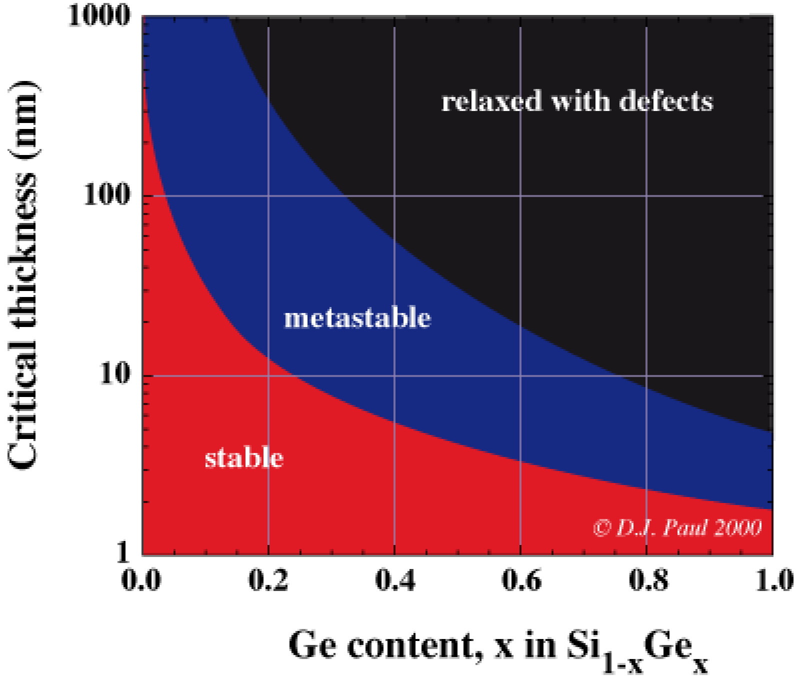
Strain relief in lattice-mismatched epitaxy: example of depositing SiGe on Silicon



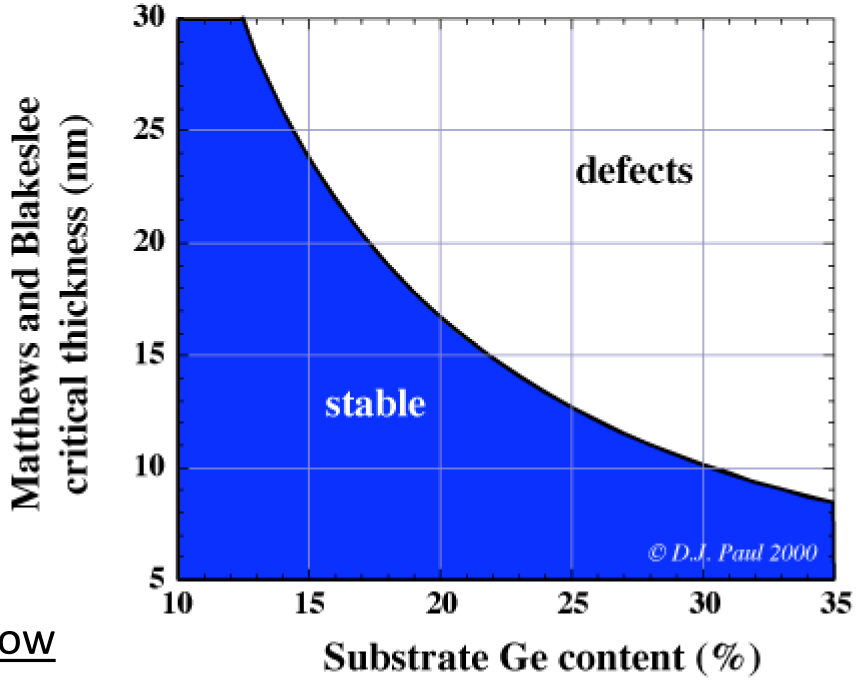
Ge has a 4.2% larger lattice constant than Si and therefore only a certain number of heterolayers can be grown coherently on top of Si before the energy is so large that defects and misfit dislocations form to relieve the strain.

In Si/SiGe heterostructures, when SiGe is grown on Si above the critical thickness 60 degree misfit dislocations result due to the silicon lattice.





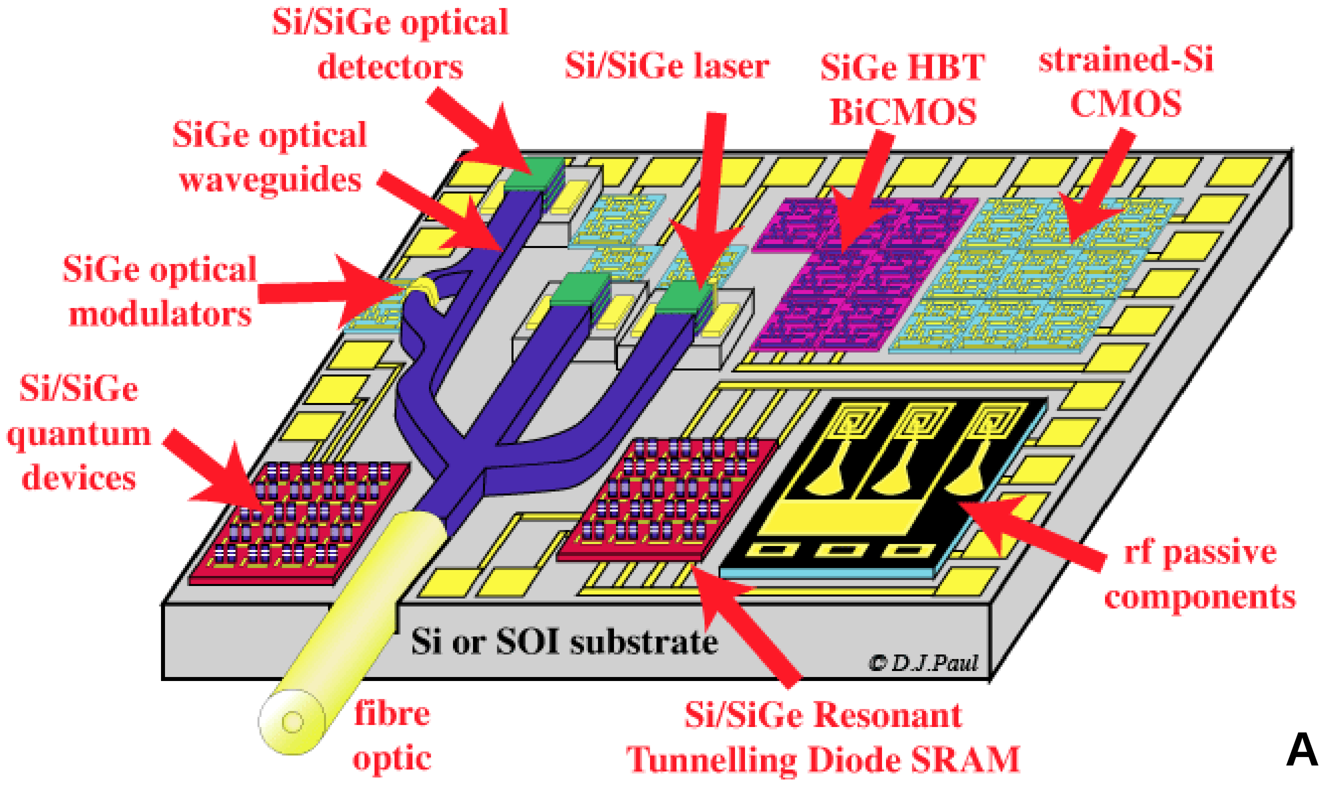
Prof Douglas J. Paul, University of Glasgow



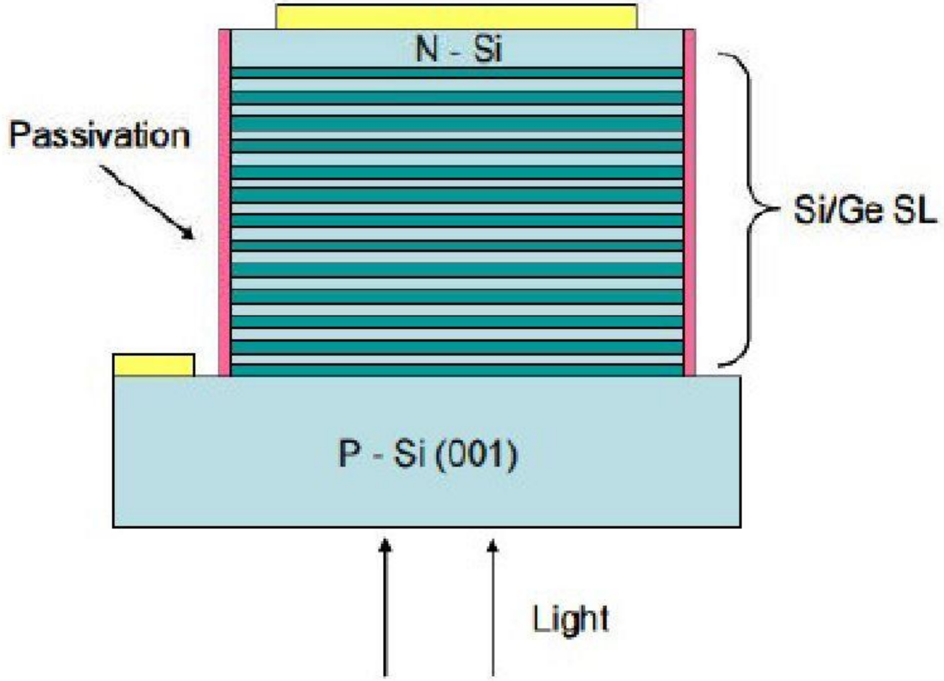
Controlling defects in epitaxial semiconductor heterostructures

Performance and lifetime of microelectronic, photonic and magnetic devices are limited by the purity, structural perfection and homogeneity of the epitaxial layers and by the flatness and abruptness of the layer surfaces and interfaces.

For example, the detrimental effects of dislocations for transistors (variations of threshold voltages across the wafer) has been proven by Miyazawa *et al*. (IEEE Trans. Electron Devices **ED-33**, 227(1986)), and the dependence of the efficiency of light-emitting diodes on dislocation densities has been reviewed by Lester *et al*. (Appl. Phys. Lett. **66**, 1249 (1995)).



Prof Douglas J. Paul (University of Glasgow)

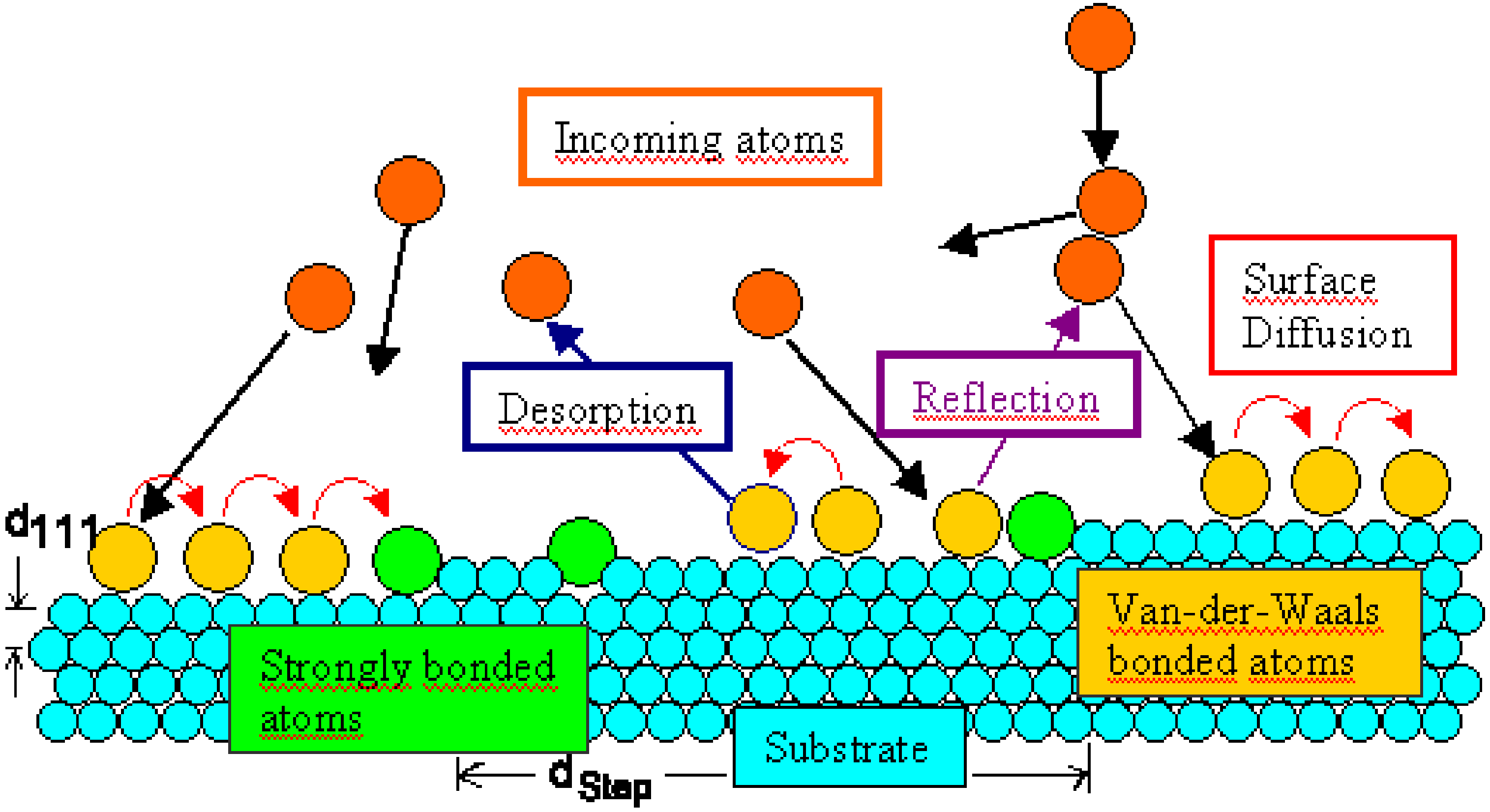


Advances in Infrared Detector Array Technology

By Nibir K. Dhar, Ravi Dat and Ashok K. Sood

Atoms sticking, nucleation and growth of thin films

In the beginning of a thin layer we have a substrate with a "receptive" surface (being clean at least) and a source of atoms or molecules (we are ignorant at the moment of the particularities of the source, which do matter) that are supposed to build up a continuous layer on the substrate.



http://www.tf.uni-kiel.de/matwis/amat/semitech_en/kap_3

1. Atoms impinging, diffusing and sticking on a substrate

- Impinging atom may just be reflected like at solid wall and then runs away to infinity.
- Incoming atom may just be reflected like at solid wall but then hits an incoming atom and is redirected to the substrate.
- The atom may loosely bond to one or two of the substrate atoms (by one or the other of the secondary bonding mechanisms, like "**van der Waals**"), or, to use surface science terminology, it will become **"physisorbed"**.
- At finite temperatures, it may now jump to equivalent positions in its neighborhood, i.e. it diffuses in a **2**-dimensional random walk manner on the surface.
- On occasion, while running around at random, the foreign atom may just get **desorbed** again and flies off
- Landing atom may also find a cozy place where it can *seriously* bond to more than just one (or two) substrate atoms, it will get **chemisorbed**; i.e. bonded by one of the strong bonding mechanisms.
- This *chemisorption* will happen with higher probability if our so far loosely bonded or physisorbed atom is seriously cornered by the substrate atoms - at a **step** or a surface vacancy.

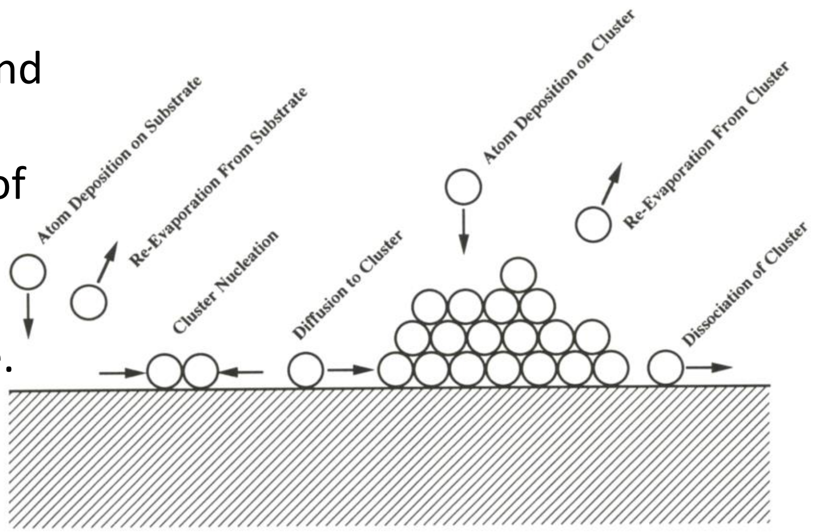


Figure 8.1. Schematic diagram of atomic processes in the nucleation of three-dimensional clusters of deposited film atoms on a substrate surface. Each process depicted (deposition from the vapor on substrate and cluster, evaporation from substrate and cluster, nucleation from mobile atoms, addition of mobile atoms to existing clusters, and dissociation of clusters) can, in principle, involve a different free energy change.

From "Pulsed laser deposition of thin films" by D. B Chrisey & G. K. Huber

1. Not all atoms reaching the substrate "get stuck". The percentage of "**B**" atoms (or molecules) remaining on the substrate **A** (the **sticking coefficient**") depends on many things, but the probably most important parameter is the binding energy between **A** and **B**.
2. In the initial phase of layer growth - the **nucleation** phase - first clusters of **B** atoms (or molecules) most likely form at irregularities of the substrate, in particular at (atomic) steps.

SCIENCE • VOL. 276 • 18 APRIL 1997

Atomistic Processes in the Early Stages of Thin-Film Growth

Zhenyu Zhang and Max G. Lagally

Growth of thin films from atoms deposited from the gas phase is intrinsically a nonequilibrium phenomenon governed by a competition between kinetics and thermodynamics.
Precise control of the growth and thus of the properties of deposited films becomes possible only after an understanding of this competition is achieved.

The diffusion of an adatom on a flat surface, or terrace, is by far the most important kinetic process in film growth. Smooth,uniform films could not be formed without sufficient surface mobility. In the extremecase of zero mobility parallel to the surface, an adatom stays where it has landed, and the resulting growth front is always very rough. Nevertheless, higher surface mobility does not necessarily lead to smoother films.

The surface diffusion coefficient D is related to the site-to-site hopping rate of anadatom, ks, by $D = a^2 ks$, where a is the effective hopping distance between sites, and $ks \sim exp\{Vs/kBT\}$, where Vs is the potential-energy barrier from site to site, T is the substrate temperature, and kB is the Boltzmann constant. In the initial stage of growth on a flat surface, if the depositionrate F is fixed, the value of D determines the average distance an adatom will have to travel before (i) finding and joining an existing island or (ii) meeting another adatom to create the possibility of nucleating a new island. As nucleation continues, this distance decreases and eventually becomes constant. In this steady-state regime, newly deposited atoms will predominantly join existing islands and effectively prevent nucleation of new islands. Intuitively, the island density N should increase with F and decrease with D and has the qualitative form $N \sim F^p/D^q$

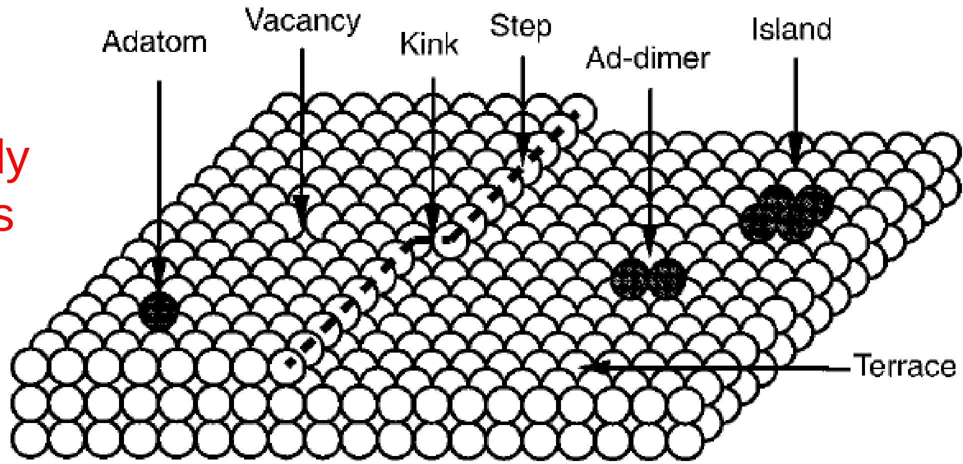
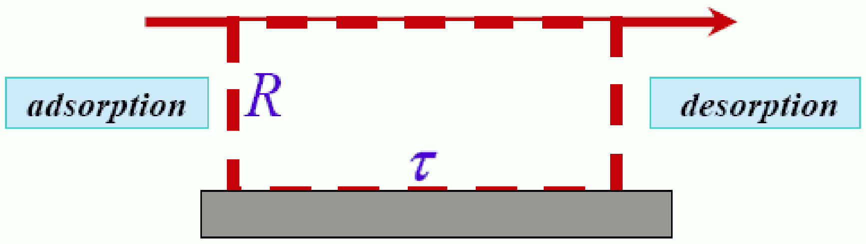
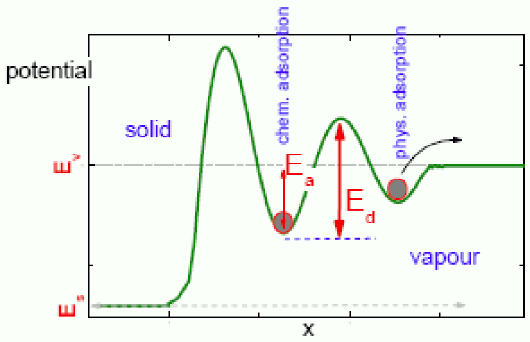


Fig. 1. The TSK model of a surface defined for a simple cubic crystal. The white circles represent atoms of the substrate. The dashed line indicates the location of a step separating the upper and the lower terraces, with a kink along the step. The step-down direction is from left to right. The black circles are atoms adsorbed on the terraces.

Adsorption vs. Desorption



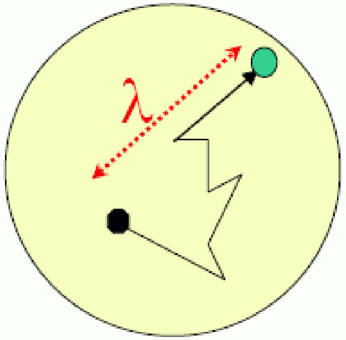


<u>Adsorption</u>: $R = dn/dt$ [adatom/(area x time)]

<u>Migration</u>: $D = D_o \exp(-E_d/kT_s)$ (diffusion const.)

$\tau = (1/\nu) \exp(E_a/kT_s)$ (average resident time)

with $\nu \approx 10^{12} - 10^{14}$ Hz (attempt frequency = 'thermal vibration')



$\tau < 1$ps for oxides

=>

$$\lambda = \sqrt{2D\tau} = \sqrt{2}a_o \exp\left(\frac{E_a - E_d}{2kT_s}\right)$$

(migration length)

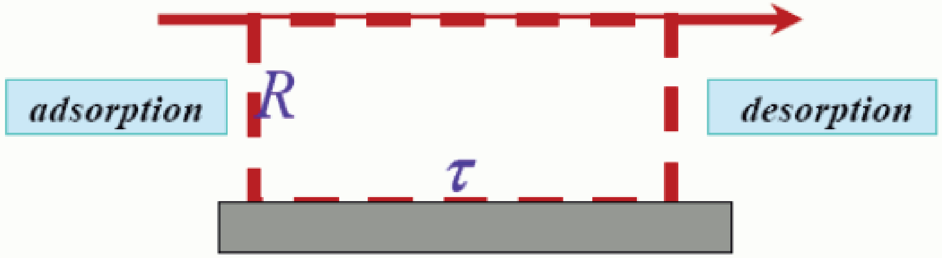
hopping range
$a_o = (D_o/\nu)^{1/2}$

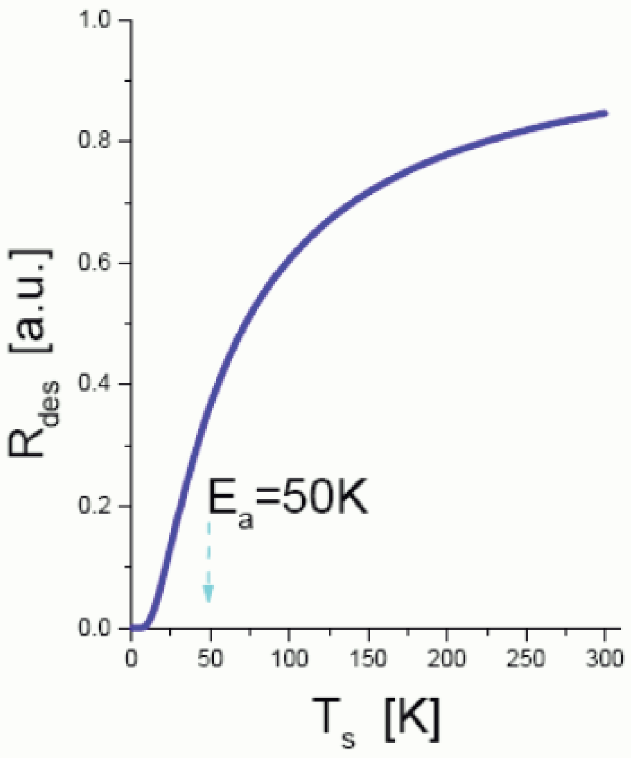
chem. adsorption potential

desorpt. potential

Guus Rijnders, ESMF 2009, Groningen

Adsorption vs. Desorption

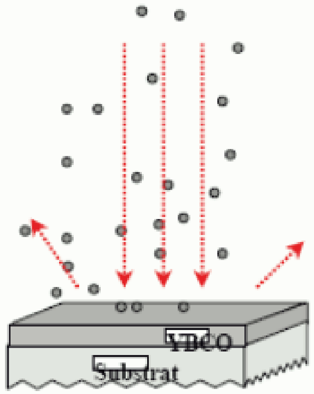




Adsorption: $R = particles / time = \frac{dn}{dt}$

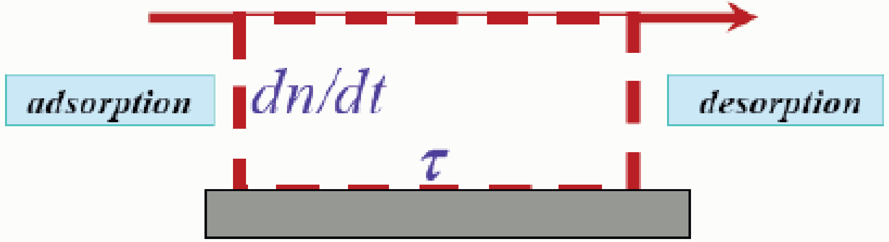
Desorption: $R_{des} = \frac{n(t)}{\tau} = n(t) \cdot \nu \cdot \exp\left(\frac{-E_a}{kT_s}\right)$

Sticking coeff.: $\alpha(t) = \frac{R - R_{des}}{R} = 1 - \frac{n(t) \cdot \nu}{R} \cdot \exp\left(\frac{-E_a}{kT_s}\right)$



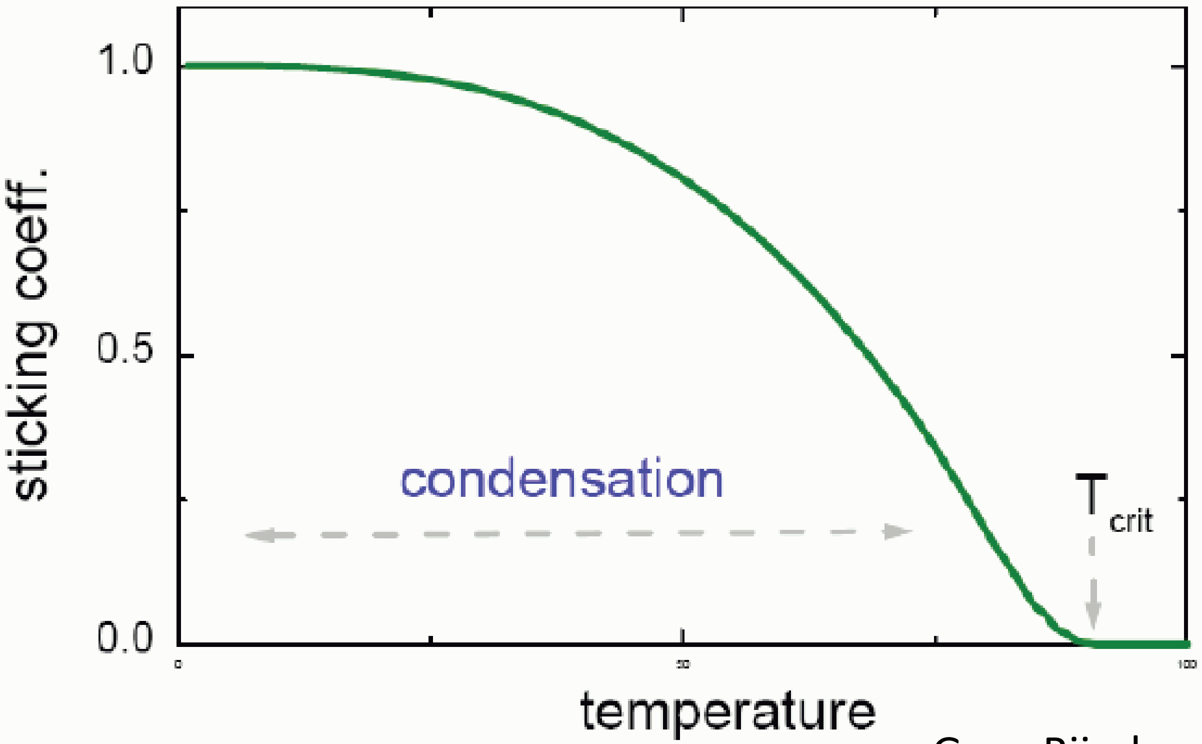
Guus Rijnders, ESMF 2009, Groningen

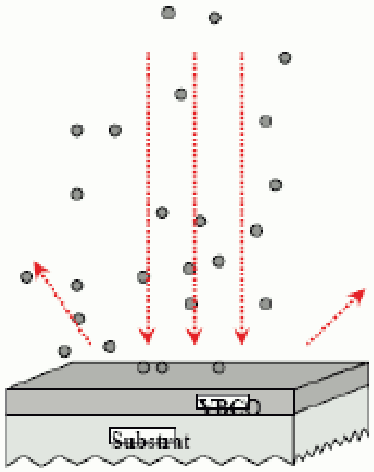
Adsorption vs. Desorption



sticking coefficient α:

$$\alpha(t) = \frac{R - R_{des}}{R} = 1 - \frac{n(t)\cdot \nu}{R}\cdot \exp\left(\frac{-E_a}{kT_s}\right)$$





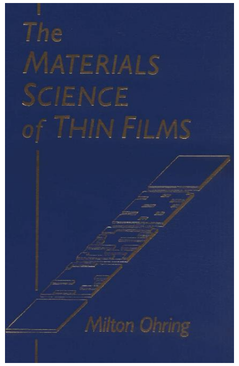
Guus Rijnders, ESMF 2009, Groningen

2. Nucleation

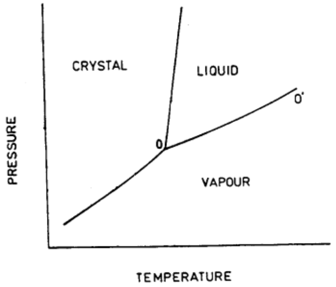
Simple models of nucleation are first of all concerned with thermodynamic questions of the energetics of the process of forming a single stable nucleus.

Once nucleation is possible, we try to specify how many such stable nuclei will form within the system per unit volume and per unit time-i.e., nucleation rate.

As an example, consider the homogeneous nucleation of a spherical solid phase of radius **r** from a prior supersaturated vapor. Pure homogeneous nucleation is rare but easy to model since it occurs without benefit of complex heterogeneous sites such as exist on an accommodating substrate surface. In such a process the gas-to-solid transformation results in a reduction of the chemical free energy of the system given by **$(4/3)\pi r^3\Delta G_V$**, where **ΔG_V**, corresponds to the change in chemical free energy per unit volume.



For the condensation reaction vapor (v) →solid (s) to occur the free energy change is negative and given by



$$\Delta G_V = \frac{kT}{\Omega}\ln\frac{P_s}{P_v} = -\frac{kT}{\Omega}\ln\frac{P_v}{P_s}$$

where ***P_S***, is the vapor pressure above the solid, ***P_V***, is the pressure of the supersaturated vapor, and **Ω** is the atomic volume

$$\Delta G_V = -(kT/\Omega)\ln(1+S)$$

where S is the supersaturation, ***$S = (P_V - P_S)/P_S$. Without supersaturation*** **$\Delta G_V = 0$ and *nucleation is impossible.***

2. Nucleation

New surfaces and interfaces form during nucleation. Total free energy change in forming the nucleus is thus given by

$$\Delta G = (4/3)\pi r^3 \Delta G_V + 4\pi r^2 \gamma$$

Where γ is the surface energy per unit area and r is the size of the nucleus.
And minimization of ΔG with respect to r yields the equilibrium size of the nucleus, $r = r^*$:

$d(\Delta G)/dr = 0 \rightarrow r^* = -2\gamma / \Delta G_V$

And $\Delta G^* = 16\pi\gamma^3/3(\Delta G_V)^2$

It is thus evident that represents an energy barrier to the nucleation process.

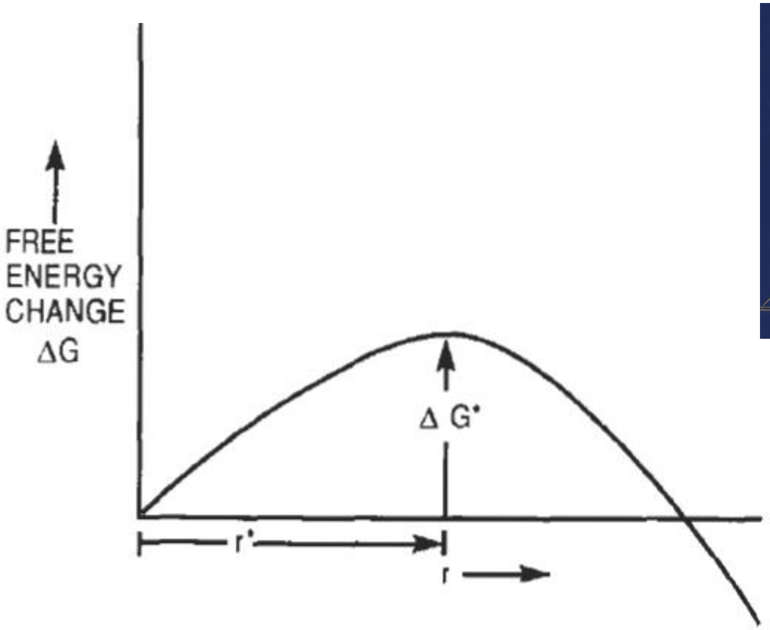
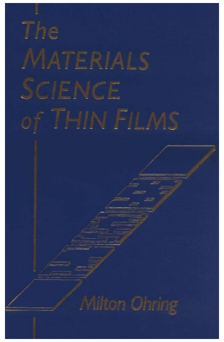


Figure 1-19. Free-energy change (ΔG) as a function of cluster ($r^* > r$) or stable nucleus ($r > r^*$) size. r^* is critical nucleus size, and ΔG^* is critical free-energy barrier for nucleation.



The nucleation rate N is essentially proportional to the product of three terms

$N = N^* A^* \omega$ (nuclei/cm^2-sec)

N^* is the equilibrium concentration of stable nuclei and ω is the rate at which the atoms impinge onto the nuclei of the critical area A^*.

2. Nucleation

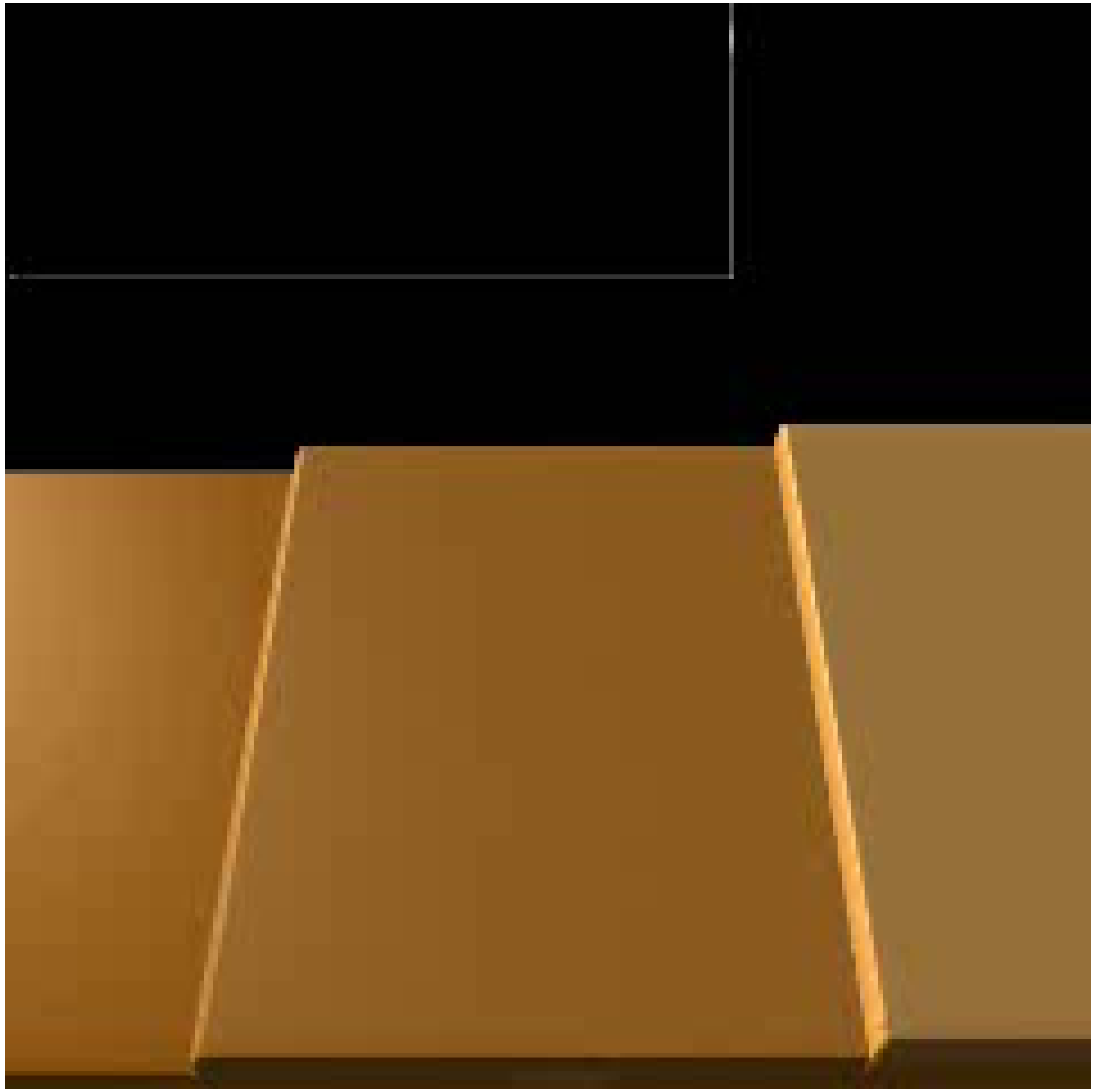
It is appropriate to take $N^* = n_S\, e^{-\Delta G^*/kT}$, here n_S is the density of all possible nucleation sites.
The atom impingement flux ω is equal to the product of the concentration of vapor atoms and the velocity with which they strike the nucleus.
This flux is given by $\alpha(P_V - P_S)N_A/(2\pi MRT)$, where α the sticking coefficient, N_A is the Avogadro's number, M - the atomic weight, R- the gas constant, and T- temperature. We obtain:

$$N = ns\ e^{-\frac{\Delta G*}{kT}} 4\pi r^2 \frac{\alpha(P_v - PS)N_A}{\sqrt{2\pi MRT}}$$

The most influential term in this expression is the exponential factor. It contains **ΔG*,** which is, in turn, ultimately a function of **S.** When the vapor supersaturation is sufficiently large, homogeneous nucleation in the gas is possible. This phenomenon causes one of the more troublesome problems associated with chemical vapor deposition processes since the solid particles that nucleate settle on and are incorporated into growing films destroying their integrity.
Heterogeneous nucleation of films is a more complicated subject in view of the added interactions between deposit and substrate. The nucleation sites in this case are kinks, ledges, dislocations, etc., which serve to stabilize nuclei of differing size.

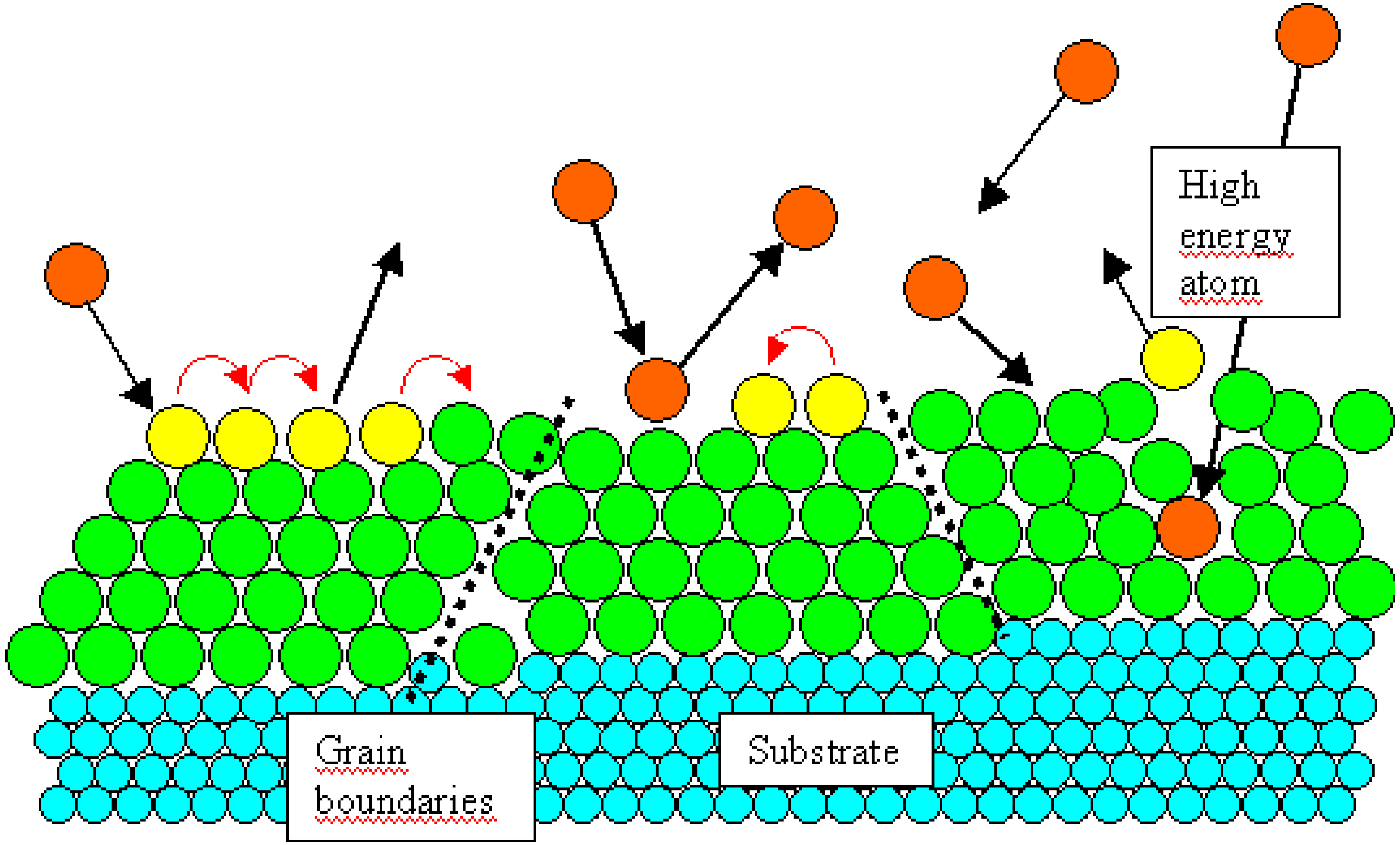
Cartoon with simulation of “interval” dreposition for materials with unstable nucleation

Take advantage of a “pulsed” method of deposition (such as pulsed-laser deposition) and of instability of small clusters of particular deposits, to grow smooth metastable epitaxial films



http://www.utwente.nl/tnw/ims/

3. Crystalline film growth on a single crystalline substrate. Epitaxy



Initial phase of epitaxial growth

In heteroepitaxy the mode of nucleation and initial growth is strongly dependent on the bonding between the substrate and deposited film.
The surface and interfacial free energies can be used to discuss the initial phase of film formation.
If the deposit is in the form of a droplet as shown in Figure 28.1, then the equilibrium condition is defined by the Young equation

$$\gamma_{SV} = \gamma_{FS} + \gamma_{FV} \cos\theta$$

where γ_{SV}, γ_{FS} and γ_{FV} are the free interfacial energies of substrate–vapour, film–substrate and film–vapour, respectively, with θ the contact or wetting angle.

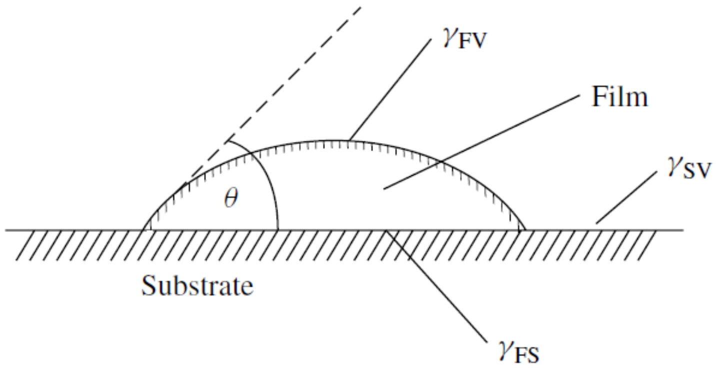


Figure 28.1 Surface and interface energies and contact angle Θ of a substrate with deposited film for the case of significant wetting ($0 < \Theta < 90°$).


Crystal Growth
Technology

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Significant wetting is defined by a small contact angle: at $\theta \rightarrow 0$ with $\gamma_{SV} = \gamma_{FS} + \gamma_{FV}$, we expect layer-by-layer growth (Frank and Van der Merwe 1949; abbreviation F–VM).
Medium or little wetting, corresponding to a large contact angle and the relation $\gamma_{FS} + \gamma_{FV} > \gamma_{SV}$:
the deposit forms discrete nuclei that successively grow three-dimensionally and coalesce to a compact continuous film; this is the Volmer–Weber (V–W) growth mechanism.
Intermediate case, when the substrate–film interactions are stronger than the binding within the film with $\gamma_{FS} + \gamma_{FV} < \gamma_{SV}$, then first a continuous film of one or two monolayers is deposited onto which in the second phase discrete islands are formed that eventually coalesce. This epitaxial mechanism was named the Stranski–Krastanov mode (S–K, 1938).

3. Epitaxial growth modes

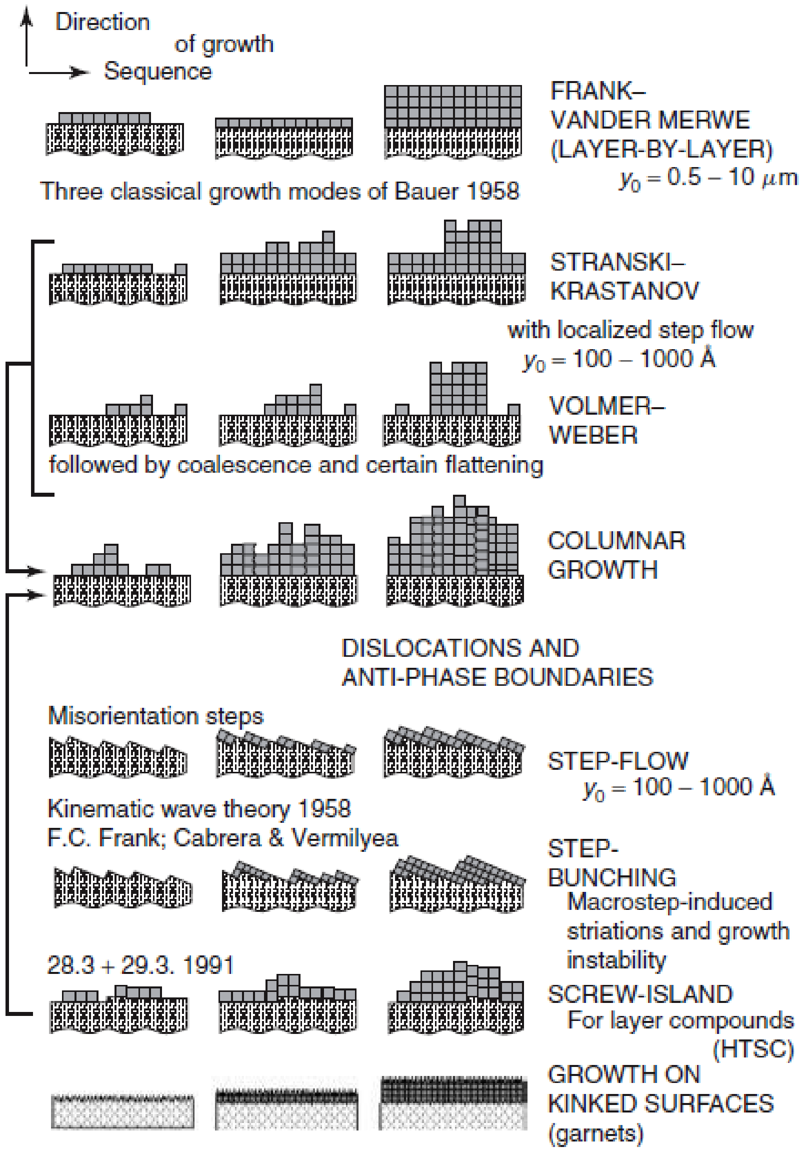


Figure 1.1 Eight epitaxial growth modes. Reprinted from H.J. Scheel, Chapter 28 *Crystal Growth Technology*, editors H.J. Scheel and T. Fukuda, Copyright (2003), with permission from John Wiley & Sons, Ltd

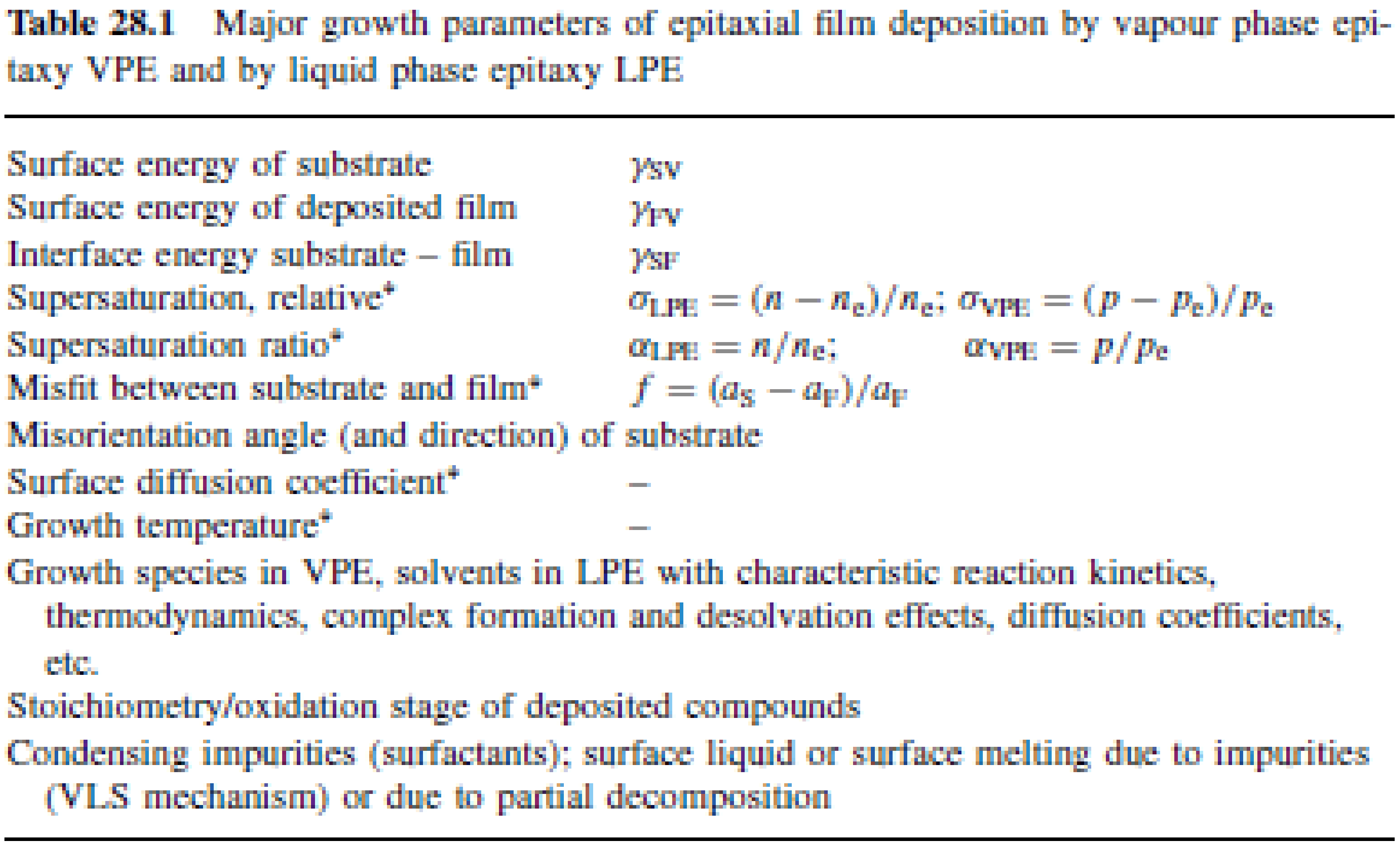
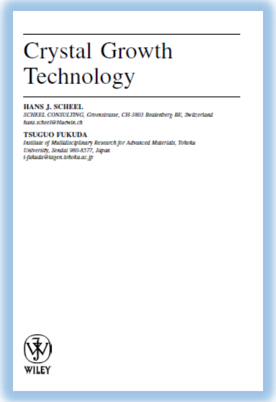


Table 28.1 Major growth parameters of epitaxial film deposition by vapour phase epitaxy VPE and by liquid phase epitaxy LPE

Surface energy of substrate	γ_{SV}
Surface energy of deposited film	γ_{FV}
Interface energy substrate – film	γ_{SF}
Supersaturation, relative*	$\sigma_{LPE} = (n - n_e)/n_e$; $\sigma_{VPE} = (p - p_e)/p_e$
Supersaturation ratio*	$\alpha_{LPE} = n/n_e$; $\alpha_{VPE} = p/p_e$
Misfit between substrate and film*	$f = (a_S - a_F)/a_F$
Misorientation angle (and direction) of substrate	
Surface diffusion coefficient*	–
Growth temperature*	–
Growth species in VPE, solvents in LPE with characteristic reaction kinetics, thermodynamics, complex formation and desolvation effects, diffusion coefficients, etc.	
Stoichiometry/oxidation stage of deposited compounds	
Condensing impurities (surfactants); surface liquid or surface melting due to impurities (VLS mechanism) or due to partial decomposition	



Crystal Growth
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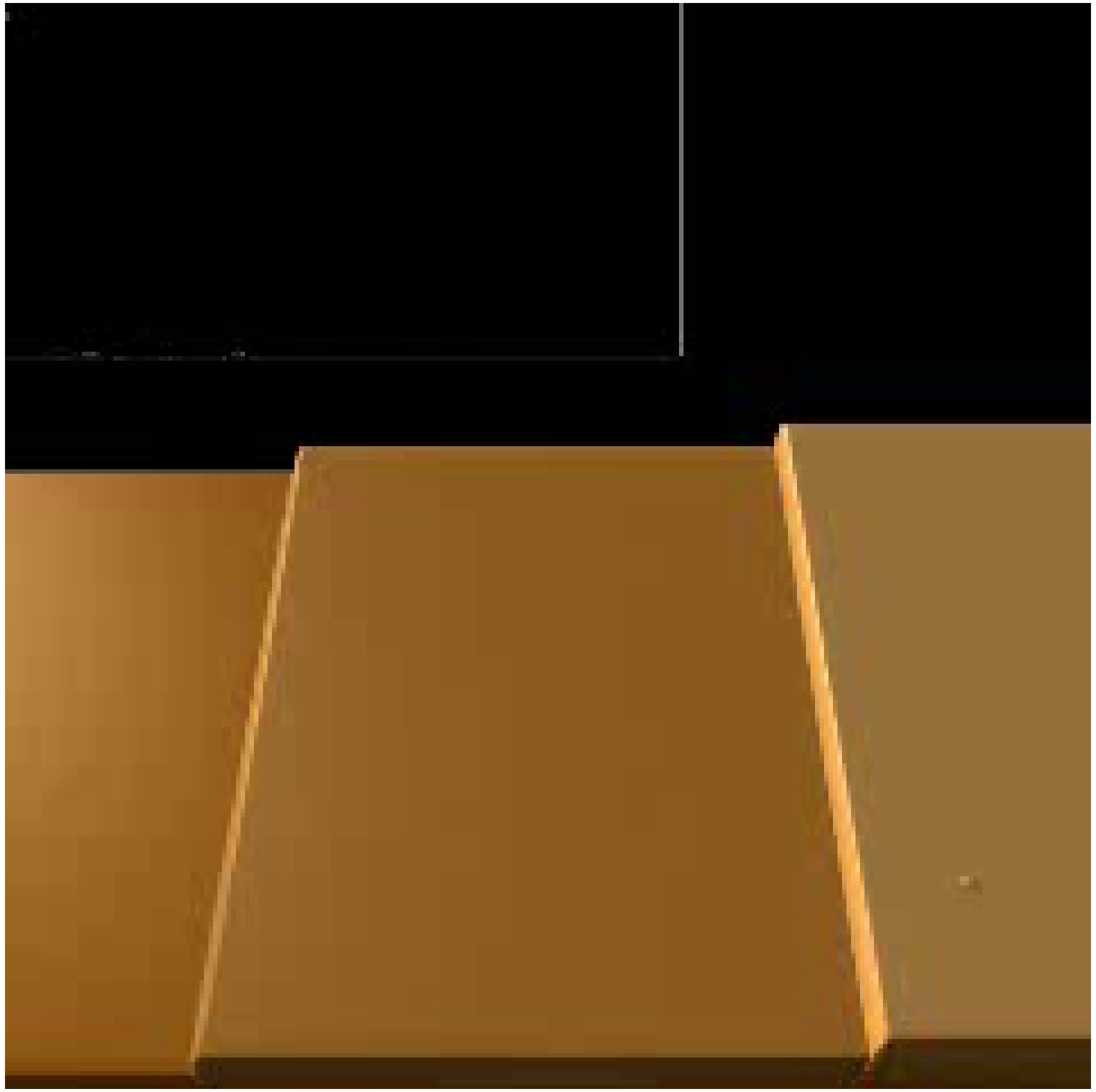
*The relative supersaturation, the equilibrium values of concentration n_e and pressure p_e, the supersaturation ratio, the misfit, and transport phenomena like surface diffusion and bulk diffusion are determined by the growth temperature.

n and p are the actual values of concentration and pressure, and a_s and a_f are the lattice constants of substrate and film, respectively.

Cartoons with simulations of epitaxial growth of thin films

Layer-by-layer growth (Frank and Van der Merwe)

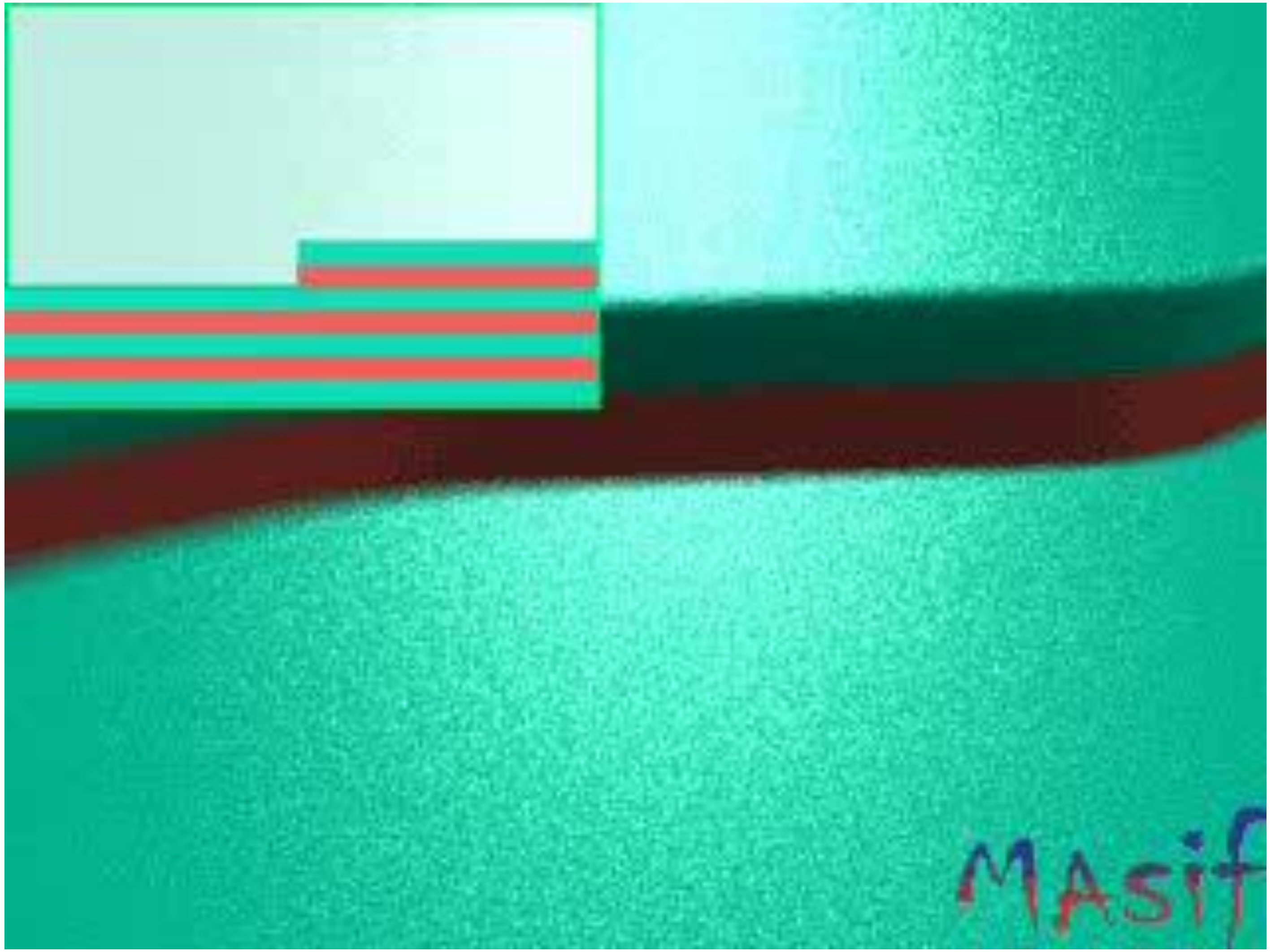


Intermediate 2D to 3D Stranski–Krastanov mode

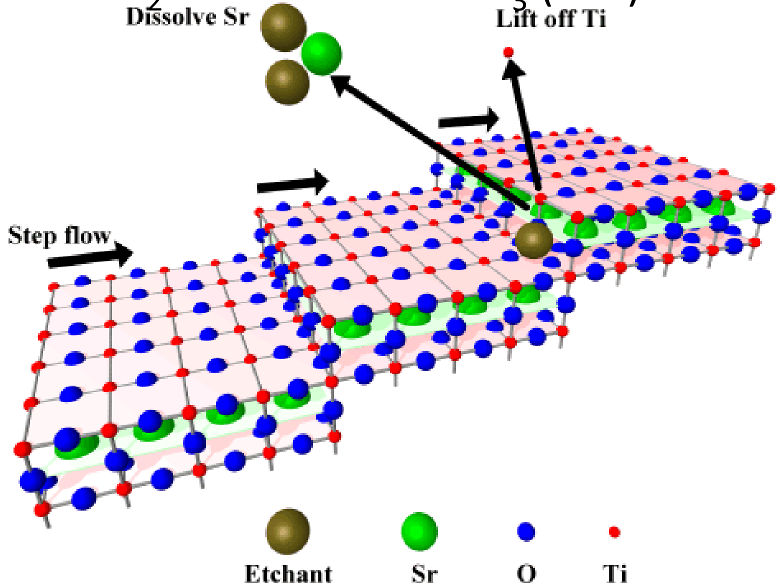
http://www.utwente.nl/tnw/ims/

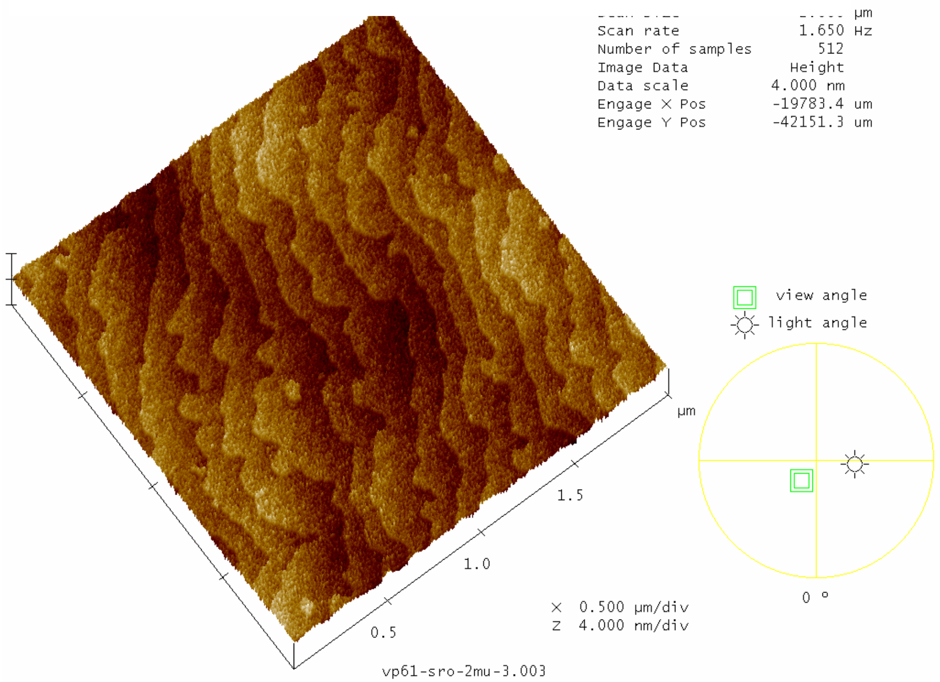
Cartoon with simulation of step-flow growth

Step- flow growth of $SrRuO_3$ on TiO_3-terminated $SrTiO_3$ (100) surface



TiO_2-terminated $SrTiO_3$ (100) surface




Scan rate 1.650 Hz
Number of samples 512
Image Data Height
Data scale 4.000 nm
Engage X Pos -19783.4 um
Engage Y Pos -42151.3 um

X 0.500 µm/div
Z 4.000 nm/div

vp61-sro-2mu-3.003

http://www.utwente.nl/tnw/ims/

Importance of lattice mismatch to the growth mode in heteroepitaxy

In heteroepitaxy the lattice mismatch between substrate and film, the so-called misfit as defined in Table 28.1, has a significant effect on nucleation and growth modes. Grabow and Gilmer (1988) have shown by atomistic simulations using the Lennard–Jones potential that the pure layer-by-layer F–VM growth mode requires quasi-zero misfit at growth temperature as demonstrated in Figure 28.4.
Misfit normally induces the Volmer–Weber mode except for large interface energies between substrate and deposited film, which will cause the Stranski–Krastanov mode. If structurally perfect layers or quasi-atomically flat surfaces are required, either homoepitaxy or substrates with zero misfit at growth temperature have to be applied.
It is experimentally found that the supersaturations in epitaxy from the vapor phase are so high that epitaxial deposition can be achieved even at very high misfit.

The misorientation of the substrate is providing misorientation steps depending on the angle and the direction of misorientation. For a given supersaturation, even for the large supersaturation in epitaxy from the vapor phase, the density of the misorientation steps can be made so high and the interstep distance so small, that 2D-nucleation and the V–W and S–K modes can be suppressed. The layers grow then in the step-flow mode and have a relatively high structural perfection because defects due to coalescence are prevented. Surfaces can, on average, be quite flat but of course show high density steps.

Crystal Growth
Technology

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Importance of lattice mismatch to the growth mode in heteroepitaxy

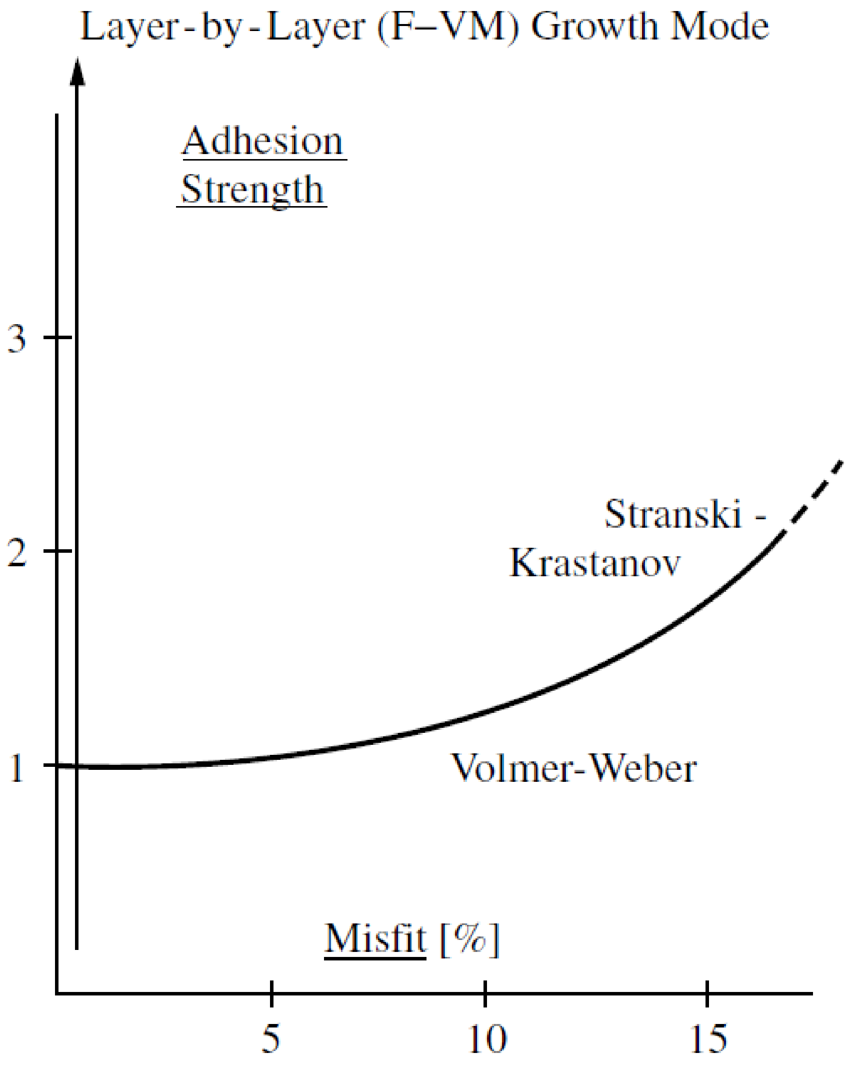

Figure 28.4 The effect of misfit on occurrence of the three classical growth modes, after Grabow and Gilmer 1988.


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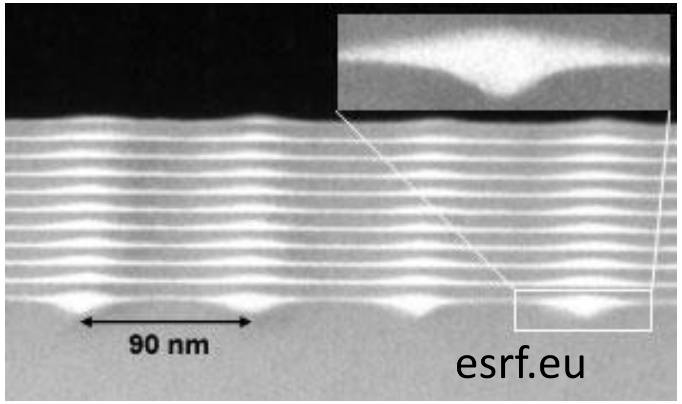
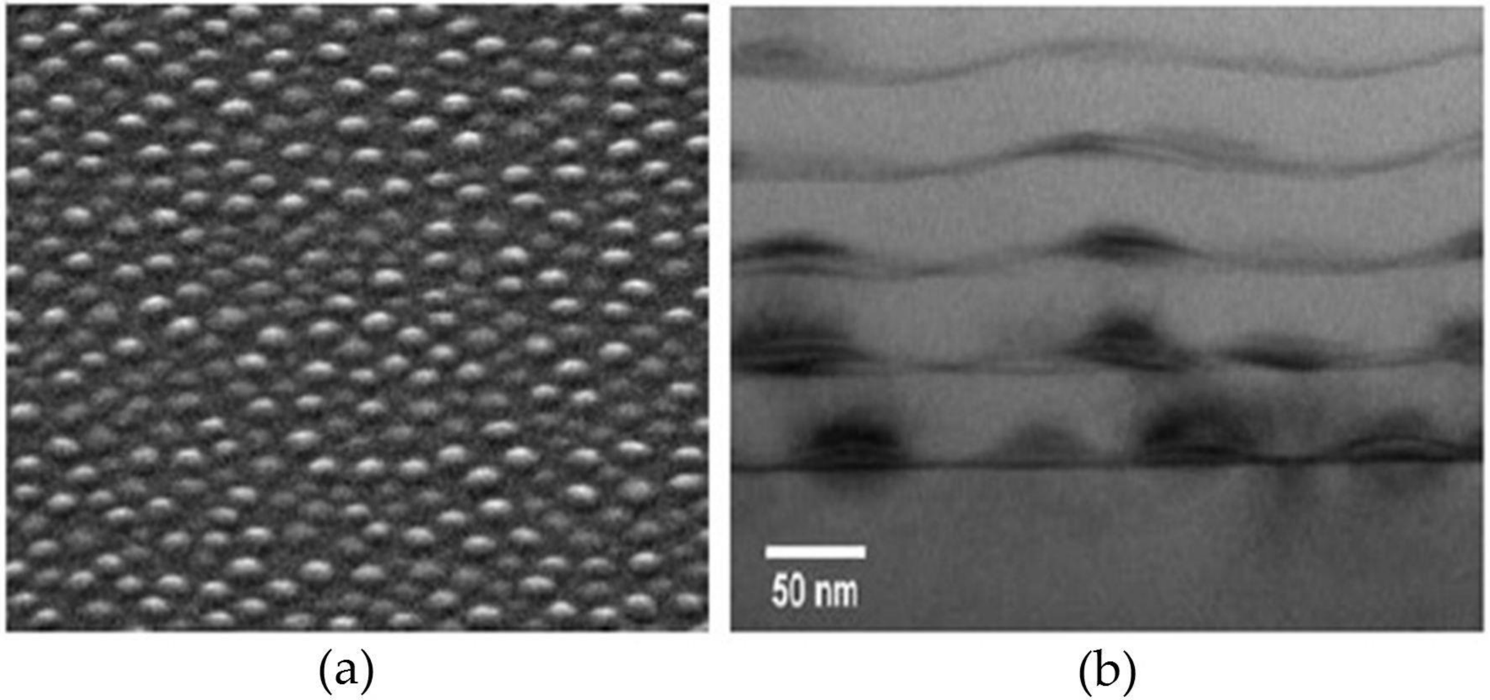
Taking advantage of influence of lattice mismatch on the growth mode in heteroepitaxy



Transmission electron microscopy (TEM) image of 10 period stacks of Ge islands and Si spacer layers (10 nm) deposited on a pre-patterned area, demonstrating the vertical and the lateral ordering, which is maintained after 10 periods.

Three-dimensional Si/Ge quantum dot crystals

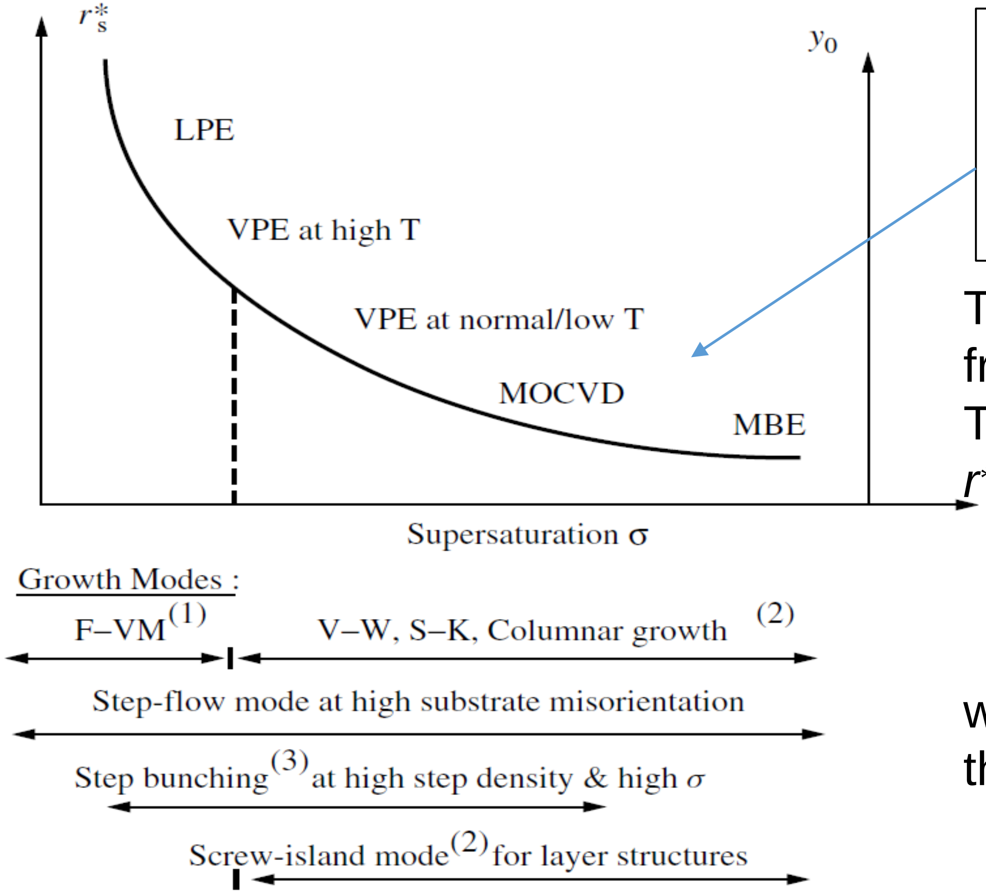


Advances in Infrared Detector Array Technology

Nibir K. Dhar, Ravi Dat and Ashok K. Sood

The strained-layer superlattice and quantum dot superlattice (QDSL) in the SiGe material system have the potential of developing Vis-NIR detector arrays with longer cutoff wavelength and potentially lower dark current. The advantage of quantum dots is the potential to exploit the optical properties of Ge while avoiding dislocation formation. Ge QDs grown on Si in Stranski-Krastanov mode can be deposited well beyond the critical thickness without dislocation nucleation. Semiconductor quantum dots are already being used for optoelectronic applications, exploiting the increased density of states and tuneable energy levels due to quantum confinement.

Importance of supersaturation to the growth mode in heteroepitaxy



LPE-liquid phase epitaxy
VPE-vapor phase epitaxy
MOCVD- metalorganic chemical vapor deposition
MBE-molecular beam epitaxy

The effective supersaturation during the growth process can be derived from the morphology of as-grown surfaces.

The distances y_0 between steps are related to the size of the 2D nucleus r^*_s by

$$y_0 = 19\, r^*_s = 19\, \gamma_m V_m / a^2 R T \sigma$$

with γ_m the energy per growth unit, V_m the molar volume, and a the size of the growth unit.

Step annihilation and coalescence effects (defects) :

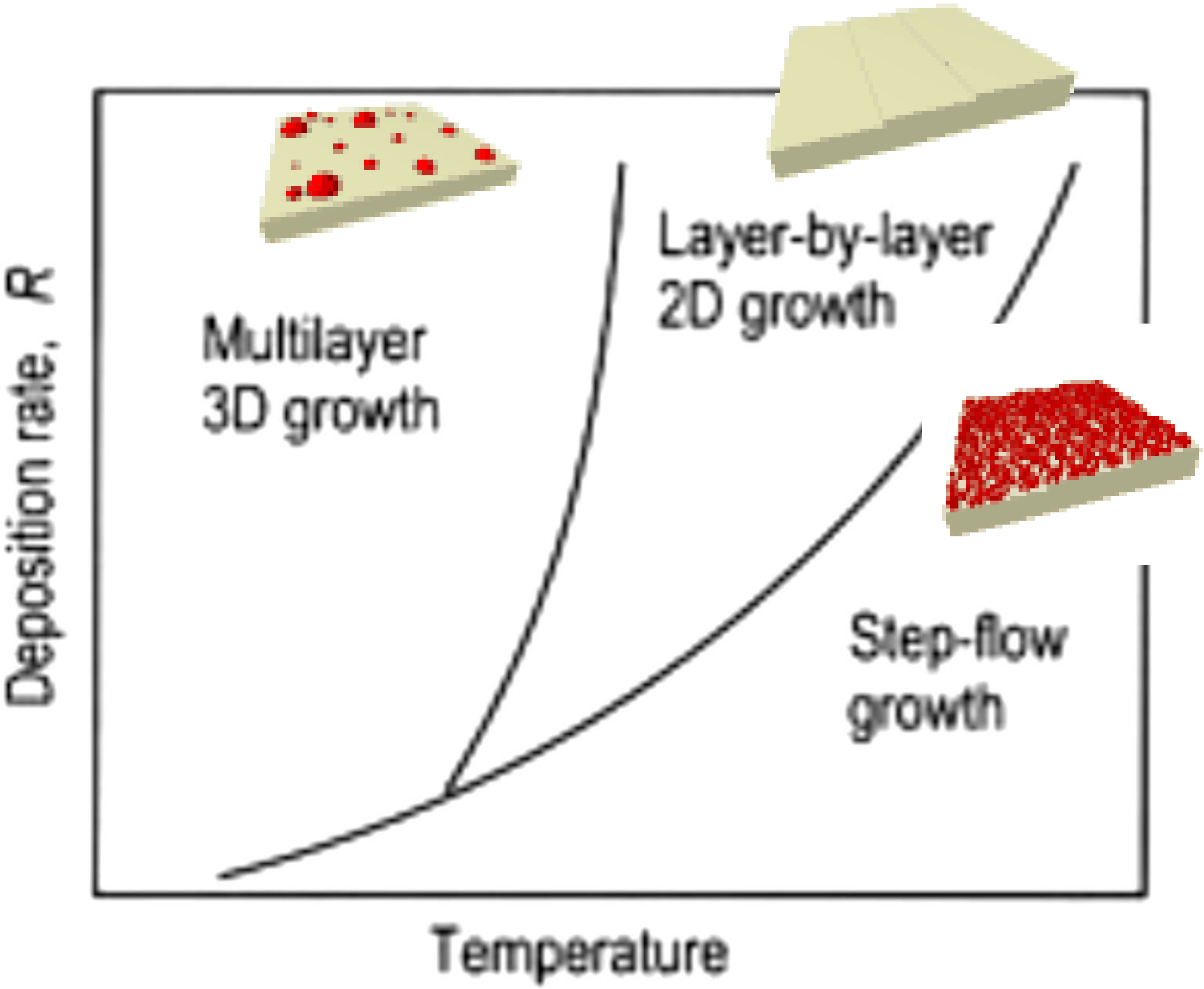
(1) Annihilation of steps from growth hillocks may cause isolated defects at hillock boundaries.

(2) Coalescence of growth islands and columnar growth cause high density of defects (grain boundaries, dislocations, voids, antiphase boundaries, etc.).

(3) Step bunching causes striations-like regions with differing dopant/impurity concentrations.

Figure 28.5 The supersaturation effects on the critical size of surface nuclei r_s^*, on the interstep distance y_0, and on the growth modes for the major epitaxial growth methods. Also, the defects caused by the different growth regimes are listed (Scheel 1997).


Crystal Growth Technology



Enhancement of surface diffusion by increasing T_S is problematic because of concomitant increase in surface-to-bulk diffusion and bulk interdiffusion!

Substrate temperatures between 0.3 and 0.5 of the melting temperature T_m *of the film* were proposed as best to enhance surface diffusion (for films grown in high vacuum), while still avoiding bulk diffusion.

http://lippmaa.issp.u-tokyo.ac.jp/

Guus Rijnders, ESMF 2009, Groningen

4. Multilayers and Superlattices

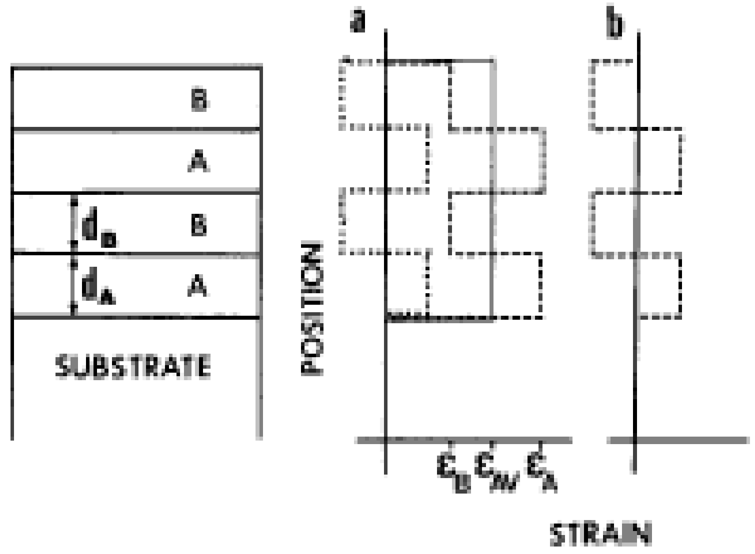


FIG. 30. Schematic illustration of criteria for structural stability of a strained-layer superlattice. (a) shows the unrelaxed superlattice and (b) its energy ground state (from Hull *et al.*, 1986a). In (a) the total strain field is shown by the dashed line and may be regarded as the supposition of a uniform strain (solid line) and an oscillating strain (dotted line).

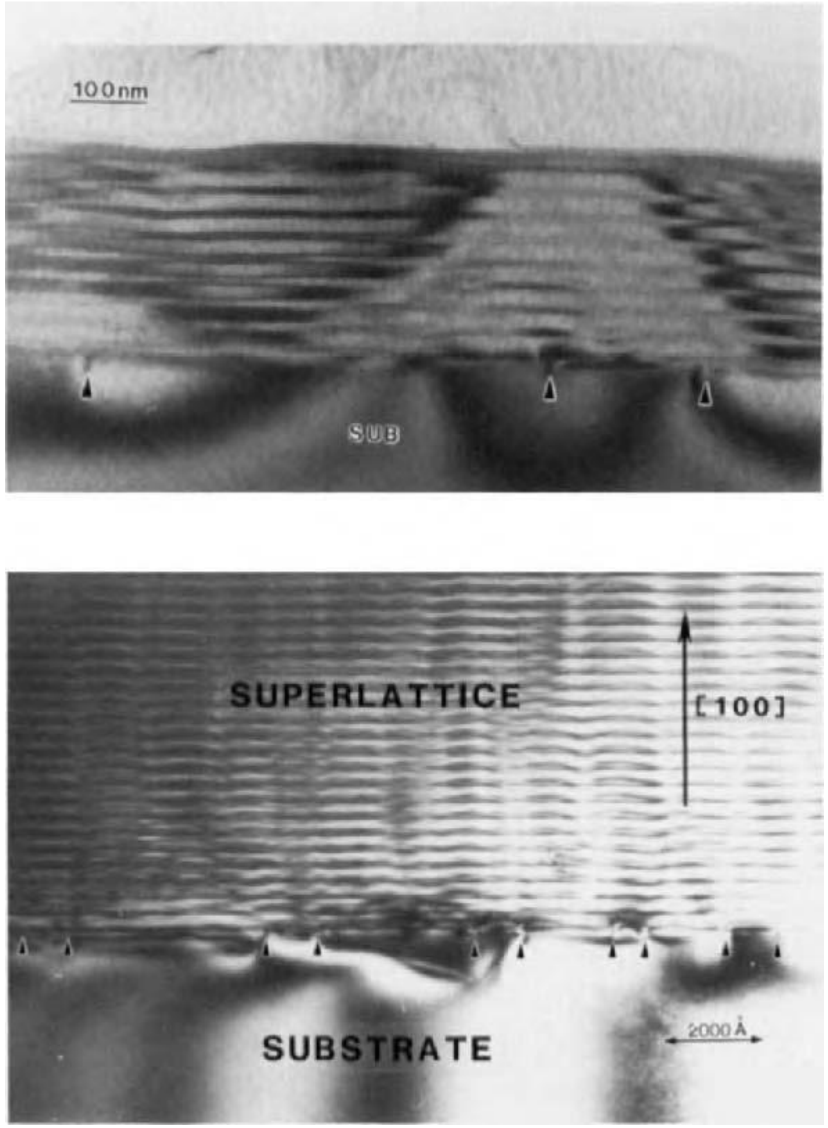
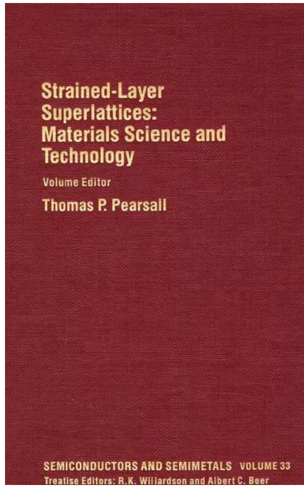


FIG. 31. Cross-sectional TEM images of (a) partially relaxed InGaAs/GaAs on GaAs (from Hull *et al.*, 1987e) and (b) GeSi/Si on **Si** multilayer structures (from Hull et *al.*, 1986a). Note that, as indicated by arrows, the vast majority of misfit dislocations are at the substrate-superlattice interface.



Strained-Layer Superlattices: Materials Science and Technology

Volume Editor

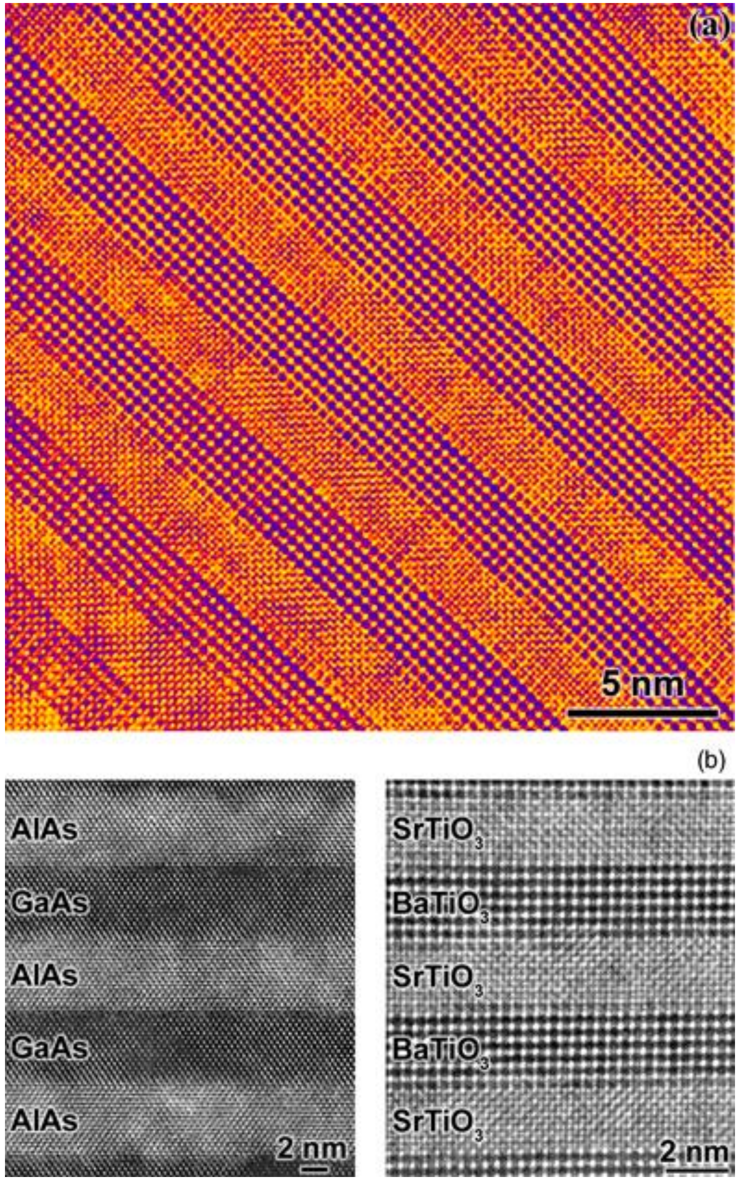
Thomas P. Pearsall

SEMICONDUCTORS AND SEMIMETALS VOLUME 33

Treatise Editors: R.K. Willardson and Albert C. Beer

4. Multilayers and Superlattices

A Thin Film Approach to Engineering Functionality into Oxides



(a) High-resolution TEM image of a $BaTiO_3/SrTiO_3$ superlattice grown by molecular-beam epitaxy (MBE). (b) A comparison between this same functional oxide superlattice is made with a GaAs/AlAs superlattice (reprinted from Gutakovskii *et al.*,[452] with permission; ©1995 Wiley-VCH). Both superlattices are grown by MBE.

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