Vékonyrétegek előállítása és alkalmazásai

2010. szeptember 27.

Dr. Geretovszky Zsolt

The "real" epitaxy

Epitaxy: extended single-crystal film formation on top of a crystalline substrate.
(L. Royer 1928)

Greek: *epi* (placed or resting upon) + *taxis* (arrangement)

Homoepitaxy

- when the film and the substrate are the same material
- (e.g. Si on Si; rationale: higher purity; more defect free; independent control of doping)

Heteroepitaxy

- when the film and the substrate are composed of different materials
  - film and substrate differ *structurally*, *electronically* and *chemically*, e.g. metal-semiconductor systems
  - film and substrate share *common crystallography* and *electronic structure*, but has dissimilar chemistry, e.g. AlAs on GaAs
- more common than homoepitaxy; foster due to interest in optoelectronics

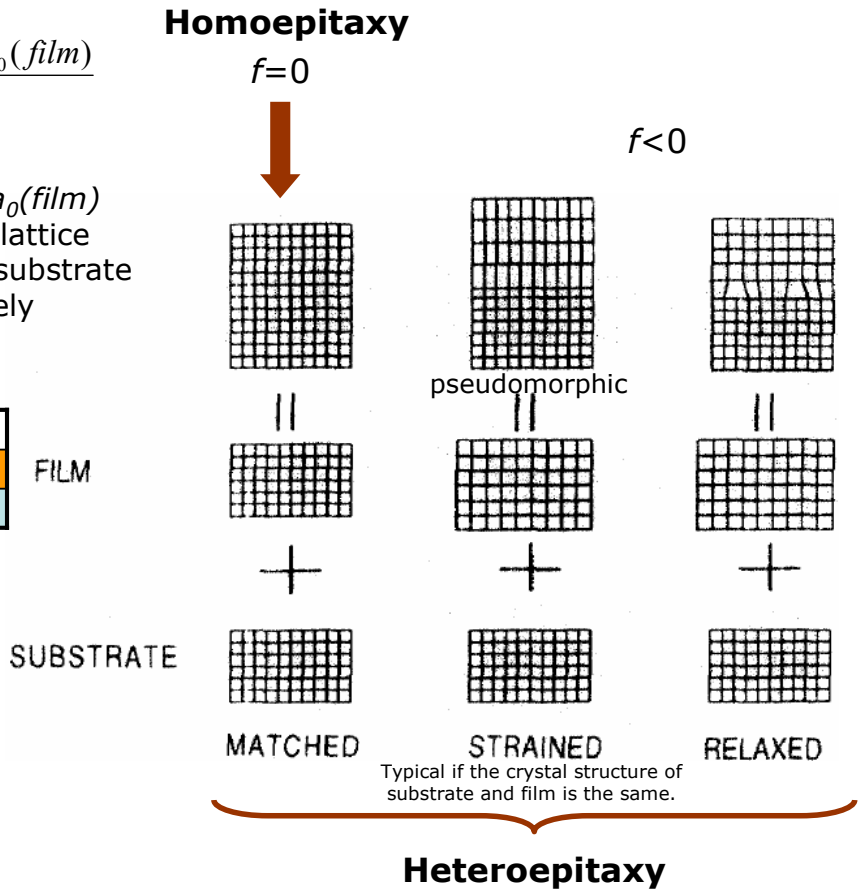
Lattice misfit:

$$f = \frac{a_0(substrate) - a_0(film)}{a_0(film)}$$

$a_0(substrate)$ and $a_0(film)$ are the unstrained lattice parameters of the substrate and film, respectively

	f>0	f<0
Film	Stretched	Compressed
Substrate	Compressed	Stretched

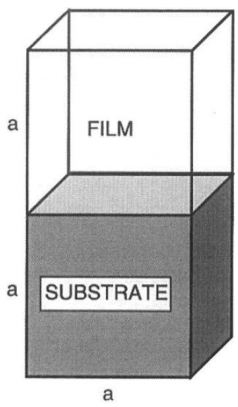
Pseudomorphic growth proceeds if f<9%.



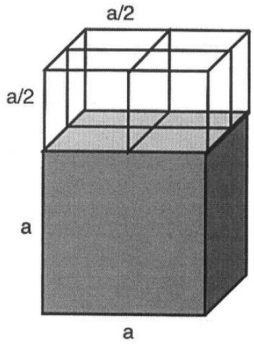
Some potential alignments

In heteroepitaxial systems where film and substrate differ chemically and electronically, and may also differ structurally.

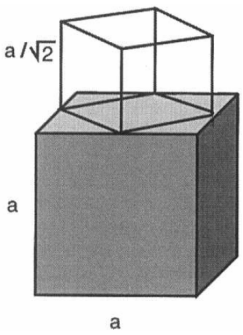
e.g. cubic film on a cubic substrate



Ca or Rb on (100) GaAs



(110) Fe on (110) GaAs



Al or Ag on GaAs

Crystallographic notation

When no surface reconstruction is present a tetrad of indices is necessary to unambigously define the aligned (epitaxial) geometry

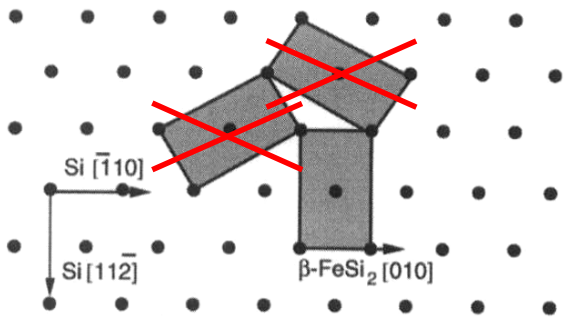
meaning parallel

(HKL)//(hkl):[UVW]//[uvw]

planes directions

where CAPITAL letters refer to FILM and small cap letters refer to substrate

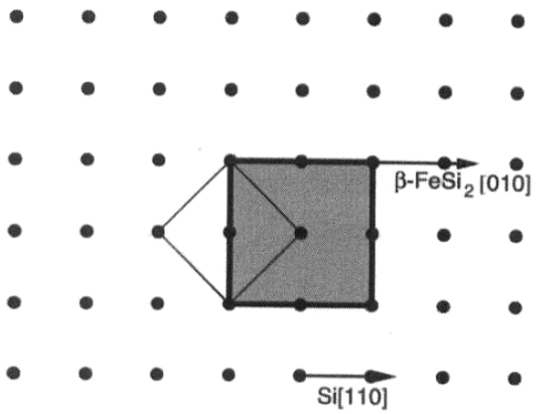
Two examples: $FeSi_2$ on Si



(101)β-$FeSi_2$//($\bar{1}$11)Si:[010]β-$FeSi_2$//[$\bar{1}$10]Si

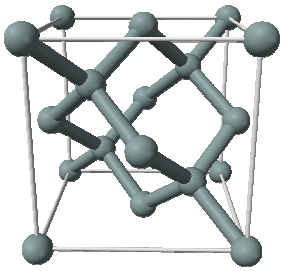
on (111) Si

on (100) Si



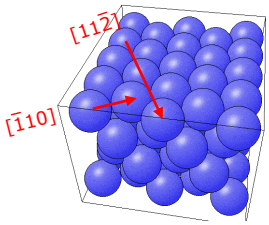
(100)β-$FeSi_2$//(100)Si:[010]β-$FeSi_2$//[110]Si

The crystal structure of Si

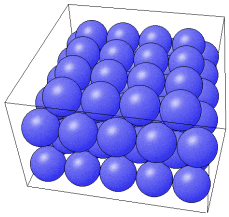


Silicon forms face-centered (diamond) cubic crystal structure.

(111) Si



(100) Si



Rotate the unit cell at http://cst-www.nrl.navy.mil/lattice/struk.jmol/a4.html and check how the (111) and (100) planes look or visualize the planes with Surface Explorer (http://surfexp.fhi-berlin.mpg.de/)

Calculate the misfit!

Si is cubic: a=5.431Å

β-$FeSi_2$ is orthorombic: a=9.86Å, b=7.79Å, c=7.88Å

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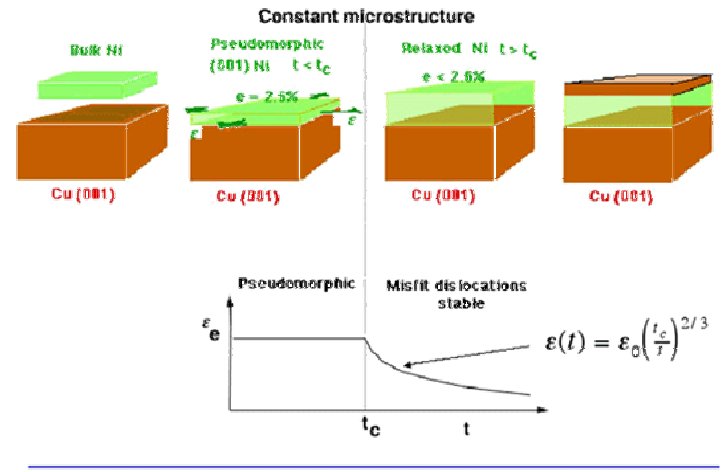
2010. szeptember 28.

Dr. Geretovszky Zsolt

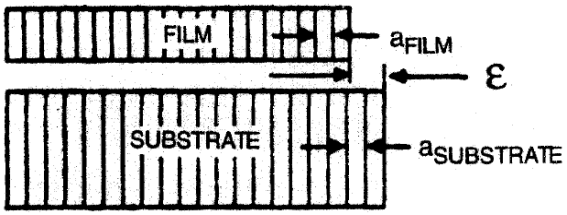
Defects in heteroepitaxy

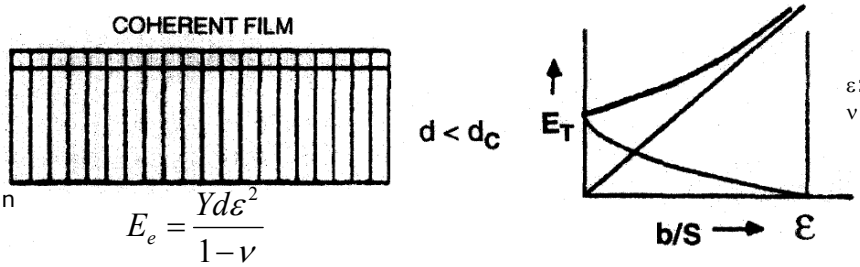


Heteroepitaxy proceeds along this route if no inter-diffusion takes place between film and substrate.

W.D. Nix, Metall. Trans. **20A** (1989) 2224

It is assumed that film and substrate have the same Young modulus, Y and shear modulus, μ.

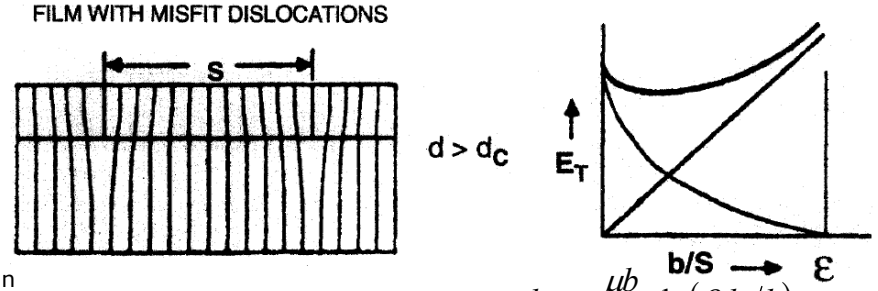




ε: biaxial elastic strain
ν: Poisson's ratio

The *elastic* strain energy per unit area, E_e

$$E_e = \frac{Yd\varepsilon^2}{1-\nu}$$



b: magnitude of Burgers vector
S: distance of arrayed dislocations

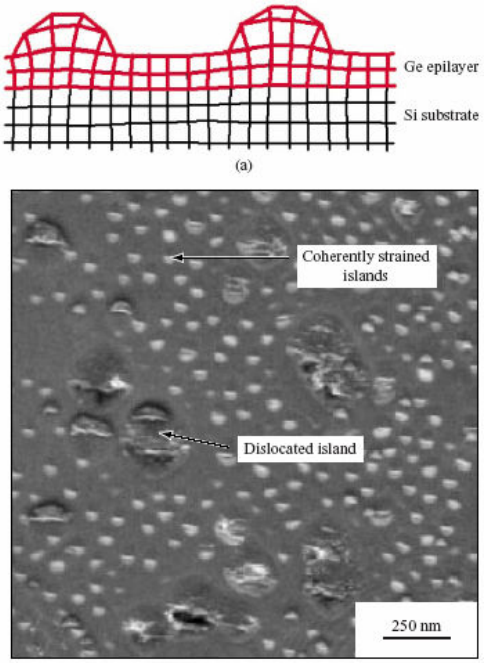
The *total* strain energy per unit area, E_T

$$E_T = \underbrace{\frac{Yd(f-b/S)^2}{(1-\nu)}}_{\text{elastic}} + \underbrace{\frac{\mu b^2 2\ln(\beta d/b)}{4\pi(1-\nu)S}}_{\text{dislocation}}$$

$$d_c = \frac{\mu b}{4\pi Yf}\ln(\beta d_c/b)$$

$$\mu = \frac{Y}{2(1+\nu)}$$

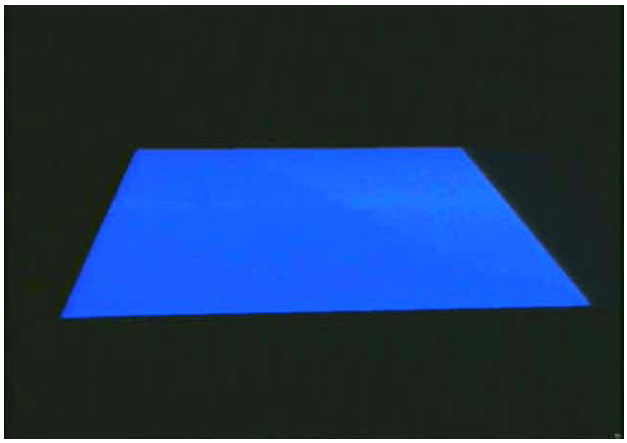
$$d_c = \frac{b}{8\pi(1+\nu)f}\ln(\beta d_c/b)$$



spontaneous island formation after 10ML coverage of Ge on Si (100)
(in-situ TEM, by Francis ROSS at IBM)

ijrd00489.pdf

SK growth of Ge on Si



The atomic distances in a Germanium crystal are larger than in Si(111). The resulting mechanical stress leads to the formation of three dimensional Germanium islands. The shape of the Germanium islands is a flat toped tetrahedron. Typical dimensions of the islands are 700Å base length and 80Å height. Further analysis shows that the aspect ratio of the islands indicates a transition from strained coherent islands (high aspect ratio at low coverage) to relaxed islands with dislocations (lower aspect ratio at higher coverage).

www.fz-juelich.de/ibn/IBN3_STM_Video/

Applied Physics Letters **63** (1993) 3055

Epitaxy of compound semiconductors

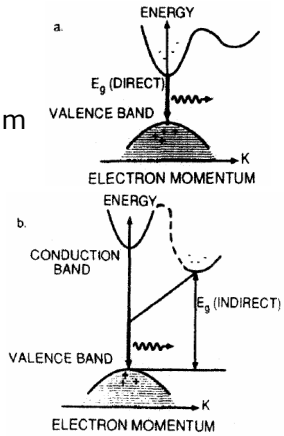
The term **heterojunction** refers to the interface between two single-crystal semiconductors of different composition and bandgap energy brought into contact, not differing doping levels of the same semiconductor.

The possibility and quality of epitaxy is influenced by the following properties:

- Semiconductor nature (direct or indirect)
- **Bandgap energy**
- **Lattice constant**
- Thermal expansion coefficient

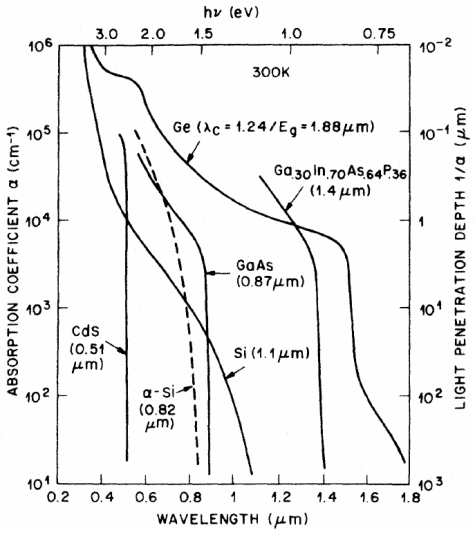
Direct-bandgap semiconductor (e.g. GaAs, InP):
during carrier transition energy is conserved + no change in momentum
hole-electron recombination with photon emission is more probable

Indirect-bandgap semiconductor (e.g. Ge, Si):
during carrier transition energy is conserved accompanied with a change in momentum, → a third party, i.e. the lattice must be involved in the hole-electron recombination ⟶ emission is less probable



Material	Lattice parameter (Å)	Melting point (K)	P_{dis} (atm)	CTE (10^{-6}°C^{-1})	Energy gap (eV at 25°C)	Electron mobility (cm²/V-s)	Hole mobility (cm²/V-s)
Diamond	3.560	~4300		1.0	5.4	1800	
Si	5.431	1685		2.33	1.12I	1350	480
Ge	5.657	1231		5.75	0.68I	3600	1800
ZnS	5.409	3200		7.3	3.68D	120	
ZnSe	5.669	1790		7.0	2.58D	530	
ZnTe	6.101	1568		8.2	2.26D	530	130
CdTe	6.477	1365		5.0	1.56D	700	
HgTe	6.460	943		1.9	~0.15		
CdS				4.0	2.42D	340	
AlAs	5.661	1870	1.4	5.2	2.16I	280	
AlSb	6.136	1330	$<10^{-3}$	3.7	1.58I	900	400
GaP	5.451	1750	35	5.3	2.26I	300	150
GaAs	5.653	1510	1	5.8	1.43D	6500	300
GaSb	6.095	980	$<10^{-3}$	6.9	0.72D	5000	1000
InP	5.869	1338	25	4.5	1.35D	4500	100
InAs	6.068	1215	0.3	4.5	0.36D	30000	450
InSb	6.479	796	$<10^{-3}$	4.9	0.165D	80000	450
GaN	(a) 3.189 (c) 5.185	>1970			3.4D	1000	
AlN	(a) 3.112 (c) 4.982	>3000			6.2D		14
InN	(a) 3.54 (c) 5.705	~1400			1.89D		

D = direct; I = indirect. (a) and (c) refer to the lattice constants of the hexagonal α phases.
From Refs. 11, 12, and M. S. Shur and M. A. Khan, *MRS Bull.* **22**(2), 44 (1997).

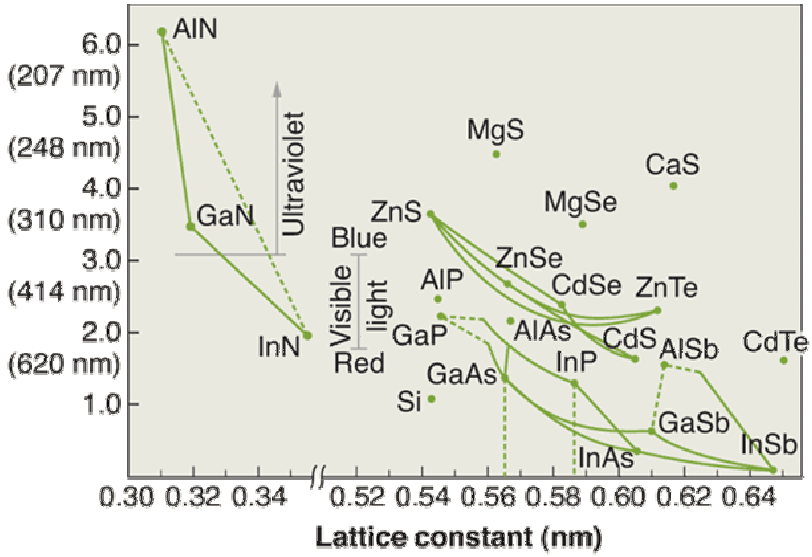


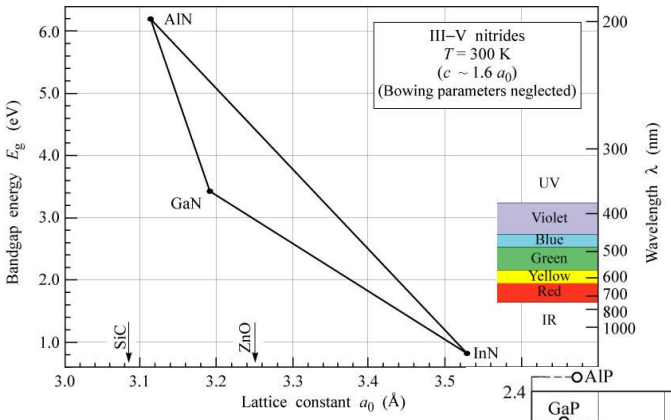
$$\lambda_c(\mu m) = \frac{1.24}{E_g(eV)}$$

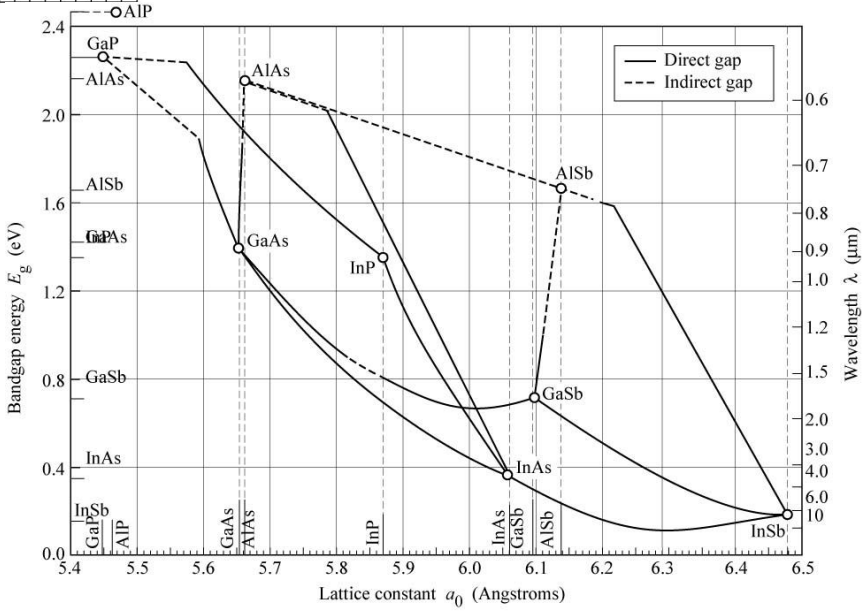
direct → steeper
indirect → shallower

Lattice constant

To ensure defect-free interfaces in semiconductor film/substrate heterostructures, it is essential that the lattice parameters (a_0) of both be closely matched. For optical devices, lattice mismatches of less than 0.1% are sought.





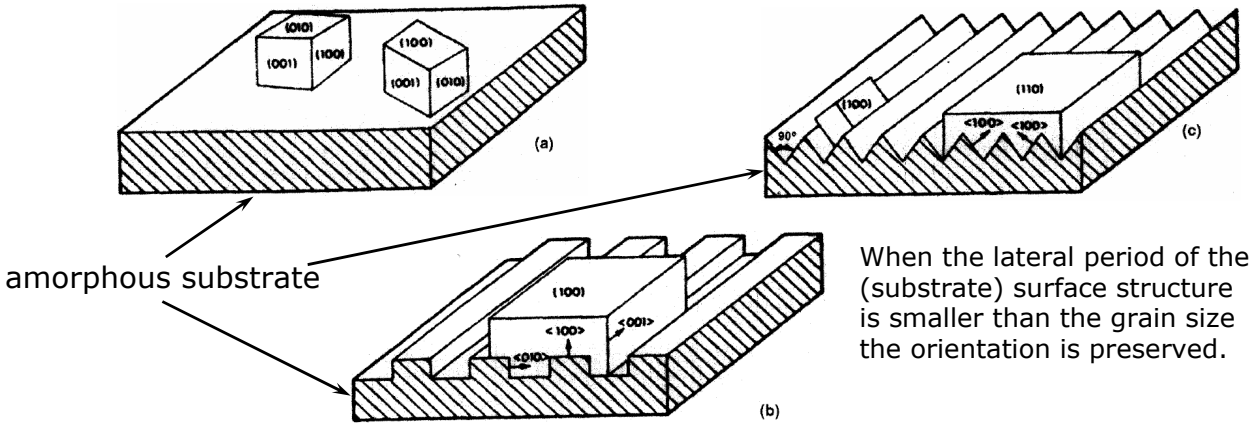


An exotic example

Graphoepitaxy:

Occurs when films deposit with a certain texture, e.g. (100).

On a flat surface this would result in randomly oriented grains.



When the lateral period of the (substrate) surface structure is smaller than the grain size the orientation is preserved.

Films can be aligned even in the presence of a large misfit. e.g. Al interconnect metallization of SiO_2.

Film structure

Structure is the most influential property of both as-deposited and processed films. In particular, controlling grain size, morphology and crystallinity are primary concerns.

Interestingly, similar structural morphologies cut across all material classes and the different processing methods used to produce them.

Analogy between bulk phase transformation and film growth:

	Bulk	**Film**
Driving force	supercooling below m.p.	supersaturation of vapor
Key parameter	T_{mold}	$T_{substrate}$

The influence of deposition variables on the structural features that develop in physically deposited films has been universally depicted in terms of structure-zone diagrams/models (SZDs or SZMs).

Film condensation processes

Condensation: incident atoms, bonded adatoms, surface diffusion, trapping/desorption, bulk diffusion.

Basic processes:

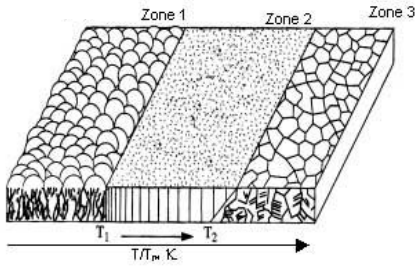
shadowing (geometric constraint)

surface diffusion
bulk diffusion
desorption

} The activation energies of these processes scale directly with the melting point of the condensate, T_M.

The dominance of one or more of these processes, as a function of substrate temperature, T_S, is manifested by different structural morphologies.

SZM for evaporated films



300μm-2mm thick films of metals and oxides dep. rate 1.2-1.8μm/min

Zone 1 ($T_S/T_M < 0.3$)

columnar, inverted cone like units capped by domes and separated by several nm wide (voided) boundaries (arise from ***shadowing*** effects and very limited adatom motion). Sometimes the structure looks like a cauliflower.

Zone 2 ($0.3 < T_S/T_M < 0.45$)

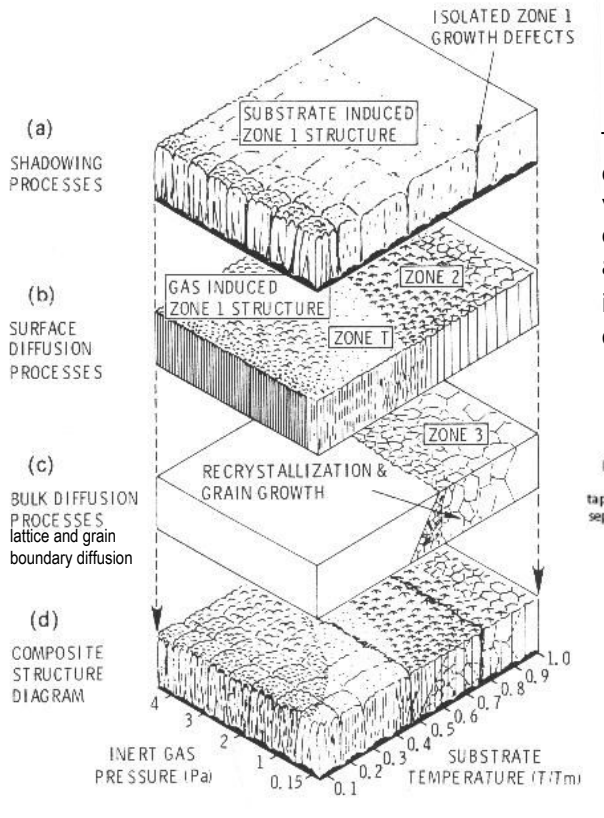
also columnar, but with tighter grain boundaries (~0.5nm) (***surface and grain boundary diffusion*** plays a role in the evolution of this structure, as the columnar grain size increases with T_S/T_M in accord with the activation energies for the relevant mass transport mechanisms)

Zone 3 ($0.5 < T_S/T_M$)

equiaxed grains (***bulk diffusion***)

B.A. Movchan and A.V. Demchishin, "*Study of the Structure and Properties of Thick Vacuum Condensates of Nickel, Titanium, Tungsten, Aluminium Oxide and Zirconium Dioxide*", *Phys. Met. Metallogr.* **28** (1969), pp. 83-90

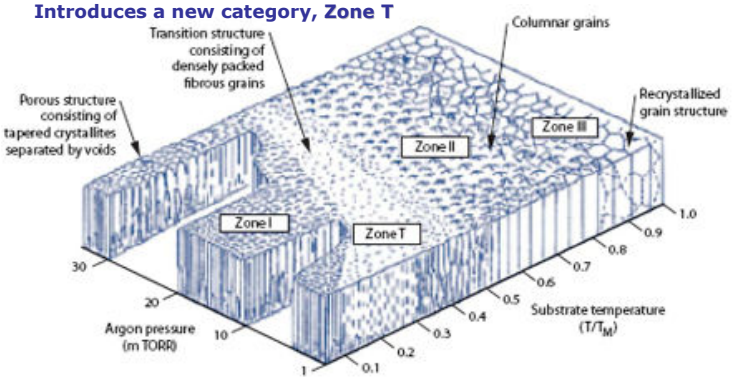
SZM for sputtered films



20μm-250μm thick metal films
dep. rate 0.005-2μm/min

Thornton introduced a new variable, the **pressure** of the inert sputtering gas. It effects the structure via indirect mechanisms (if P increases the oblique component of the flux is increasing + slows down adatom mobility → Zone 1 structure; lower P increase energetic particle bombardment ⟶ film densification)

Introduces a new category, Zone T



J.A. Thornton, Ann. Rev. Mater. Sci. **7** (1977) 239

Evaporated *vs*. sputtered

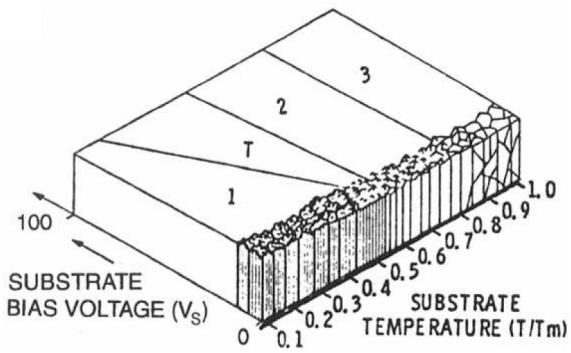
Zone	T_S/T_M	Structural characteristics	Film properties
1(E)	<0.3	Tapered crystals, dome tops, voided boundaries.	High dislocation density, hard.
1(S)	<0.1 at 0.15 Pa to <0.5 at 4 Pa	Voided boundaries, fibrous grains. Zone 1 is promoted by substrate roughness and oblique deposition.	Hard.
T(S)	0.1–0.4 at 0.15 Pa, 0.4–0.5 at 4 Pa	Fibrous grains, dense grain boundary arrays.	High dislocation density, hard. High strength, low ductility.
2(E)	0.3–0.5	Columnar grains, dense grain boundaries.	Hard, low ductility.
2(S)	0.4–0.7		
3(E)	0.5–1.0	Large equiaxed grains, bright surface.	Low dislocation density, soft recrystallized grains.
3(S)	0.6–1.0		

Note: (E) refers to evaporated, (S) refers to sputtered.

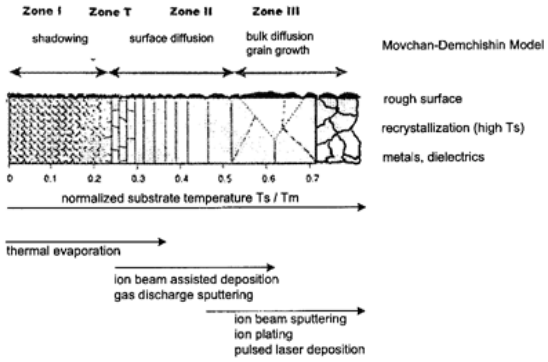
In general, analogous structures evolve at somewhat lower temperatures in evaporated films than in sputtered ones.

The effect of particle energy

V_s replaces P (not a surprise since V_s varies inversely with P)



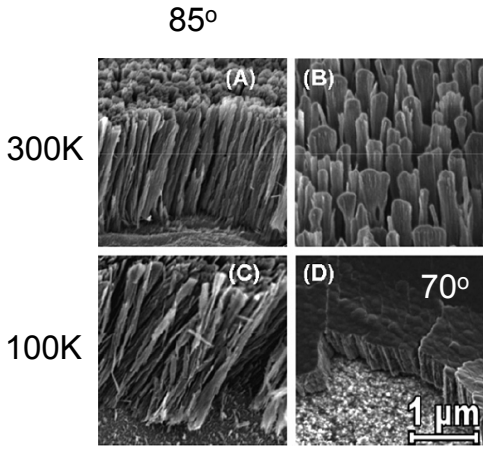
and many more minor variable was studied



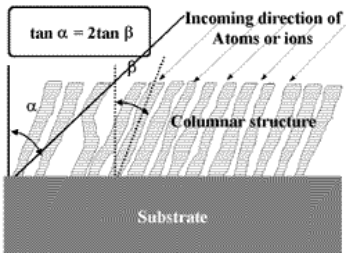
R. Messier, A.P. Giri, and R. Roy, J. Vac. Sci. Technol. **A2** (1984) 500

Columnar grain structure: the tangent rule

Columnar structure is the most ubiquitous morphology. Moreover, magnetic, optical, electrical, mechanical and surface properties of films are very much affected by columnar structures. The structural similarities among varied materials, deposited in different ways suggests common nucleation and growth mechanism for the columnar structure.



www.emsl.pnl.gov/new/highlights/200704/



The columns are oriented towards the vapor source. β is always smaller than α.

With ion impact normal to the surface, adatoms receive additional randomized momentum in the film plane. This may minimize or even eliminate column tilting!