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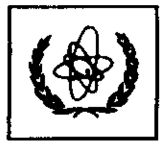

SMR/917 - 27

SECOND WORKSHOP ON
SCIENCE AND TECHNOLOGY OF THIN FILMS

(11 - 29 March 1996)

" The structure and geometry of the interfaces of thin films "

presented by:

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These are preliminary lecture notes, intended only for distribution to participants.

LECTURE 3-4

The Structure and Geometry of the Interfaces of Thin Films

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3. Semibulk and Thin film interfaces

Formation of grain boundaries in thin films:

(See also the lectures given by P. B. Barna and J. E. Greene at this workshop)

Nucleation of single crystalline grains

Coalescence: *liquid phase*, no grain boundaries are formed

solid phase, GB form, can stay in and can migrate out.

Driving force for GB migration: surface and interface as well as GB energies.

Retarding forces: grooving, impurities, second phases, segregates, shape barriers

Kinetics of GB movement: equiblirrium or metastable GB structure.

Film growth: number of grains per unit area decreases with the growth of film thickness.

Development of textures: orientation selection processes influences GB misorientations and GB morphology:

nucleation (surface and interface energy)
coalescence (surface of substrate and film, interface and GB energies, kinetic factors)

grain growth: surface, interface and GB energies, kinetic factors)

GB morphologies in thin films:

vertical GB, and columnar structure (NiCr, Al, Ag/Cu multilayers)

Node formation (NiCr, amorphous Si/Ge, amorphous Si) due to surface irregularities of the substarte: smoothens with increasing layer thickness unless shadowing effects are strong.

competing grain growth GB morphology (e.g. diamond)

faceting of GB (Al, Au)

internal and external dislocations (Al)

special GB in thin films (Al)

GB surface interactions (Al):
- grooves
- surface layers
- growth steps, growth hills
- contaminants and second phases

The role of GB in solid phase reactions (Ag+Se$\rightarrow$ $AgSe_2$, oxidation of Al)

Interaction of GB with dislocations (Al)

captured dislocations (Al)

slip traces on surfaces and in film substrate interface (Al/mica)

The substrate/film interface, epitaxy

Epitaxy can be defined as a process of oriented overgrowth of one crystal on another, or as a unic crystallographic relationship between to crystals formed during growth. When epitaxy is meant, single crystalline films are considered on single crystalline substrate, but a domain structure can be allowed for because of equivalent crystallographic orientations.

The epitaxy can be classified to homoepitaxy and heteroepitaxy.

Homoepitaxy is the growth of a material on itself. It is often used in semiconductor growth, when sharp doping profiles are fabricated in epitaxial device structures.

For crystallographic characterisation of an epitaxial relationship usualy the interface plane scheme (lecture 2) is used: DOF=($\mathbf{n_1}$,$\mathbf{n_2}$,θ), (fig.1).

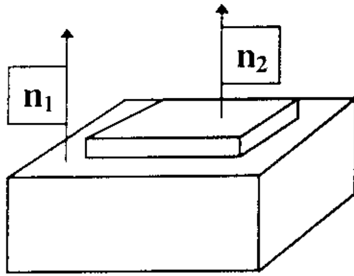


Fig.1. Epitaxial crystals, schematic drowing

For example in the case of epitaxial growth of V(BCC) on MgO (NaCl type) the orientation relationship is given in the form:

1.) $\mathbf{n_1}$ | | $\mathbf{n_2}$, [001] MgO | | [001] V

for plane normals gives the indices of the normals of planes parallel to the interface. It is also accepted if the themselves the crystallographic planes parallel to the interface are given:

(001) MgO | | (001) V

2.) The twist angle θ is usually given by specifying two parallel directions in the plane of the interface. In the above case:

[100] MgO | | [110] V,

or what is equivalnent,

[100] MgO | | [1,-1,0] V

This means, that θ is 45° in this case, when θ=0 is chosen for parallel orientation of the unit cells.

In this case also crystallographic planes standing perpendicular to the interface can be specified:

(100) MgO | | (1,-1,0) or (110) V

The morphology of the epitaxial overgrowth:

There are three basically different growth morphologies of the epitaxial overgrowth. These are classified according to the dimensionality principle:

1. Frank- van der Merwe (FM, two-dimensional or layer by layer growth)
2. Volmer-Weber (VW, three-dimensional or island growth)
3. Stransky-Krastanow (SK, layer by layer growth, followed by islanding)

The first approach to understand these behaviours is to consider the wetting of the substrate by the film.

If $\sigma_F + \sigma_I > \sigma_S$ then three dimensional growth occurs, ($\sigma_F + \sigma_I \cos\alpha = \sigma_S$), for $\sigma_F + \sigma_I < \sigma_S$ two dimensional growth is expected. and

for $\sigma_F + \sigma_I = \sigma_S$ the Stransky-Krastanov mechanism occurs.

(F: film, S: surface, I: interface, σ: surface tension)

In this picture the role of the substrate and film is not interchangable. If the condition of two dimensional growth is fulfilled for the growth of A on B, then in the reversed case B will grow in three dimensional way on A. So, the growth of e.g. multilayers in these picture seems to be not easy. For example, Ge/Si is SK mode, Si/Ge is VW growth [1-3].

There are two ways of avoiding islanding of films during growth:

a) restrict growth kinetics either by lowering growth temperature or increasing deposition rate

b) using surfactants to alter the surface energy of the growing layers [4]

Surfactants are thought to influence surface reconstructions of the growing surface. Reconstructions in the interfaces similar to those observed on surfaces have only been

receantly observed in the $CoSi_2/Si(001)$ interface by elektron microscopic techniques [5].

Epitaxial layers are strained because of differences in lattice parameters between film and substrate. The strain energy is accumulating with increasing film thickness, and leads to different effects. The changeover from 2D to 3D growth in the SK growth mode is also related to the accumulation of strain energy in the film and substrate, which is then relaxed by the change to a 3D mode. So, the strained layer is expected to undergo relaxations at a critical thickness h_c, estimated in different ways [7]. The critical thicknesses can be estimated from the energetic balance of the strain energy of the film and the energy of the interface [6]. At the critical thickness the introduction of dislocations into the interface and increasing by this its energy will be compensated for by the decrease of the strain energy of the film.

Another approach was taken by Matthews and Blakeslee [58] when the introduction of dislocations was calculated from the condition of bending the threading dislocations into the interface by the film stress against the line tension of the dislocation. If the two forces are balanced, a critical thickness can be calculated:

$$h_c = \frac{b(1-\nu\cos^2\alpha)}{8\pi\varepsilon(1+\nu)\cos\lambda}\left(\ln\frac{h_c}{b}+1\right)$$

Where ν is the Poisson ratio

λ is the angle between the slip direction of the of the dislocation and the slip plane normal projected into the interface

α is the angle between the dislocation line and its Burgers vector **b**

ε is the misfit

If dislocation generation is accounted for at the interfaces in Si/SiGe system the results fit better to the experimental value:

$$h_c \approx \left(\frac{1-\nu}{1+\nu}\right)\left(\frac{b^2}{16\pi\alpha\varepsilon\sqrt{2}}\right)\ln\left(\frac{h_c}{b}\right)$$

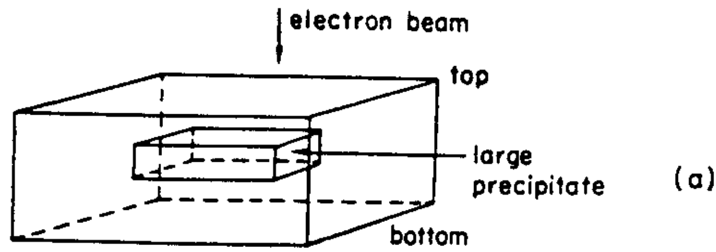
The critical thicknesses range fom a few monolayers to a few nm, depending very much on the misfit.

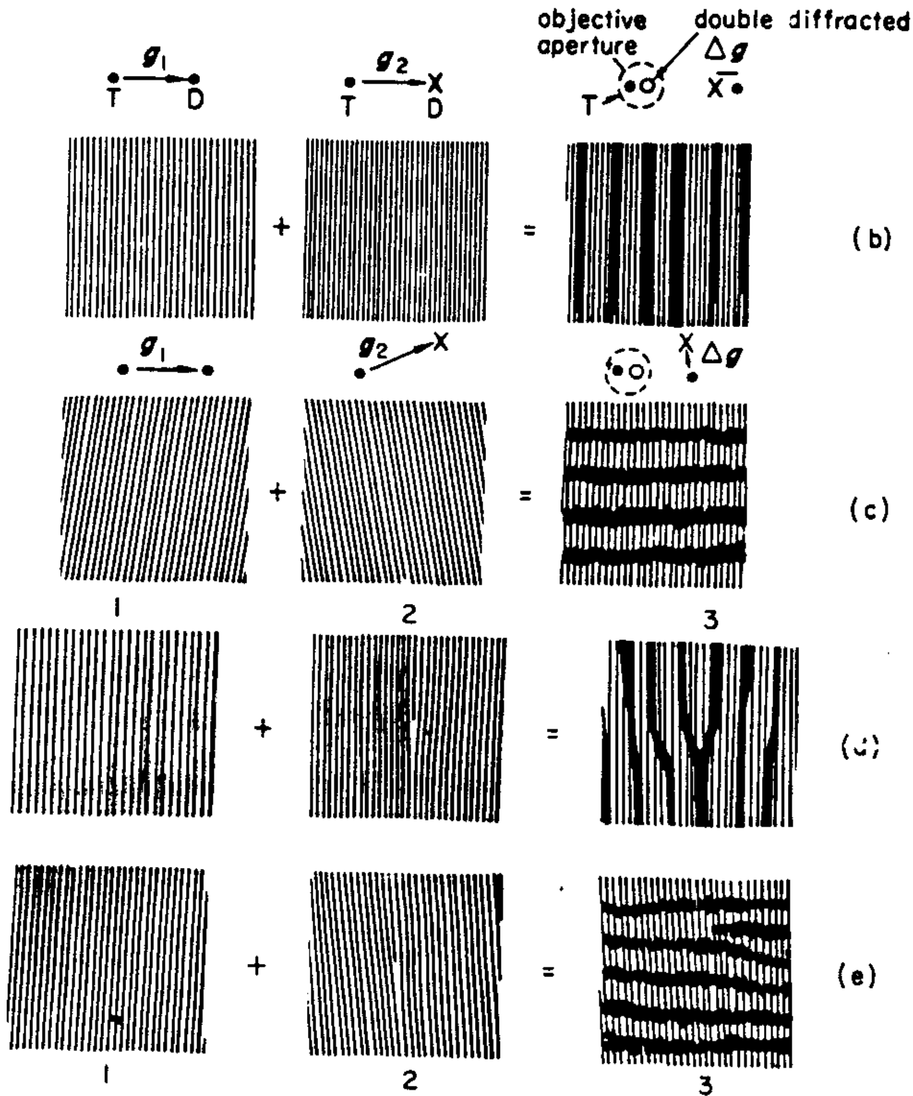
These theories do not give good agreement with the experimental ones for h_c for different systems. The agreement is relatively good for metals, and worse for semiconductors. This is due to the difference in frictional forces of dislocations, which is small for FCC metals and large for covalent semiconductors.

References

1. P.M.J.Marée et al. Surf. Sci. **191** (1987), 305.
2. S.S Iyer et al. Appl. Phys. Lett. **54** (1989), 219.
3. E. Kasper. H. Jorke, in Chemistry and Physics of Solid Surfaces,(ed. R. Vanselow, R.F. Howe). Springer Verlag, Berlin, (1988),p. 557.
4. M. Copel et al., Phys. Rev Lett., **63** (1989), 632 and Phys. Rev. B., **42** (1990), 11682.
5. D. Loretto et al. Phys. Rev. Lett., **63** (1989) 298.
6. J. H. van der Merve, J. of Appl. Phys., **34** (1963), 123.
7. W. A. Jesser. J. H. van der Merve in Dislocations in Solids (ed. F. R. N. Nabarro). Vol. 8. Elsevier (1989)pp. 421-460.

Misfit disloc.
Moire*



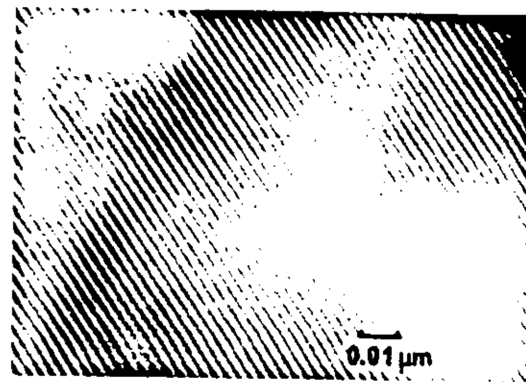


$$\Lambda_{\perp} = \left| \frac{d_1 d_2}{d_1 - d_2} \right|$$

$$\Lambda = \left| \frac{d_1 d_2}{d_1 - d_2} \right|^{*}$$

$$\Lambda = \frac{d}{\theta} \; *$$

$$\Lambda_{\perp} = \frac{b}{\theta}$$



(f)

Figure 3.57 (a) A schematic diagram illustrating a large precipitate lying parallel to the foil surface. Optical analogues demonstrating the formation of (b) parallel and (c) rotational Moire patterns by two overlapping line gratings. Diffraction patterns are also shown. Similar optical analogues showing the influence of dislocations on (d) parallel and (e) rotational Moires. (f) A rotational Moire pattern from overlapping graphite flakes

In Practical Electron Microscopy (Philips) written by:
by Edington Vol. 3. p. 83.

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InP/GaAs
overlapof moiré fringes aua misfit dislocations in plan-veiw.

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Radnóczi Gy.
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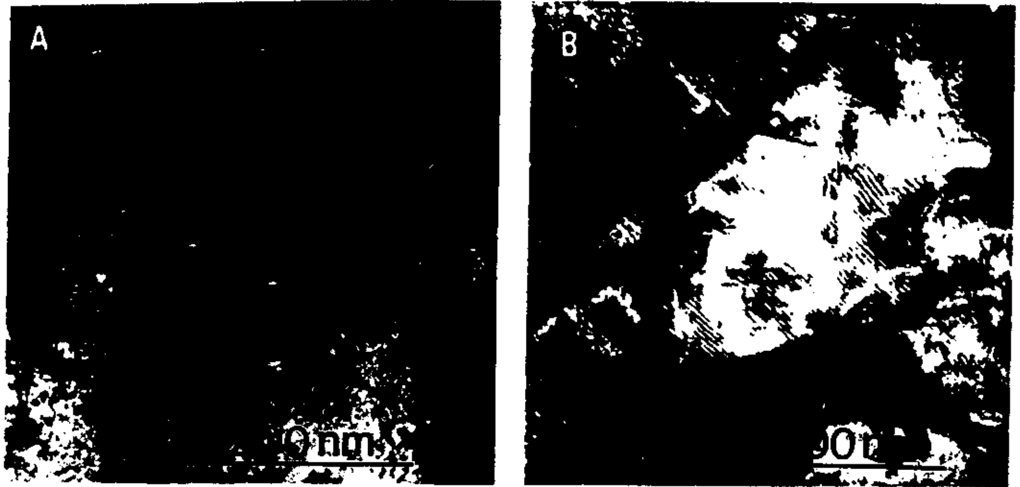


Fig. 1. Plan-view TEM images of samples 1 (a) and 2 (b).

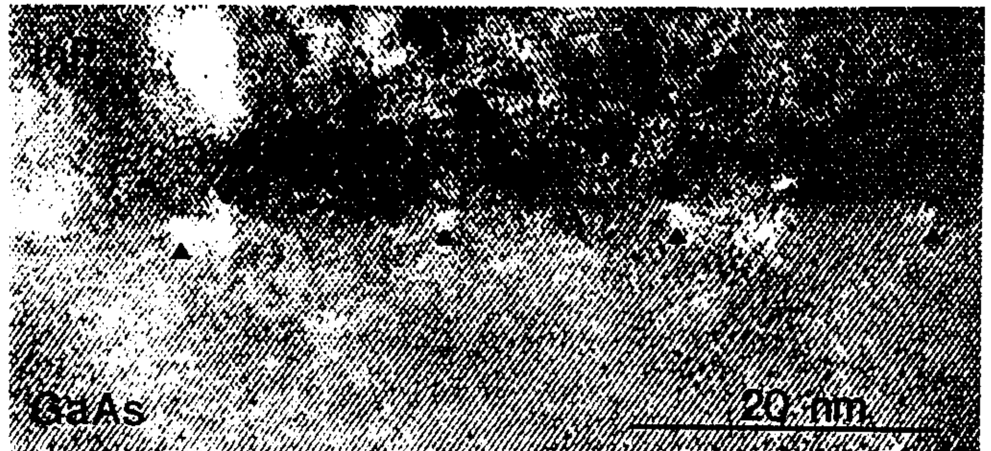
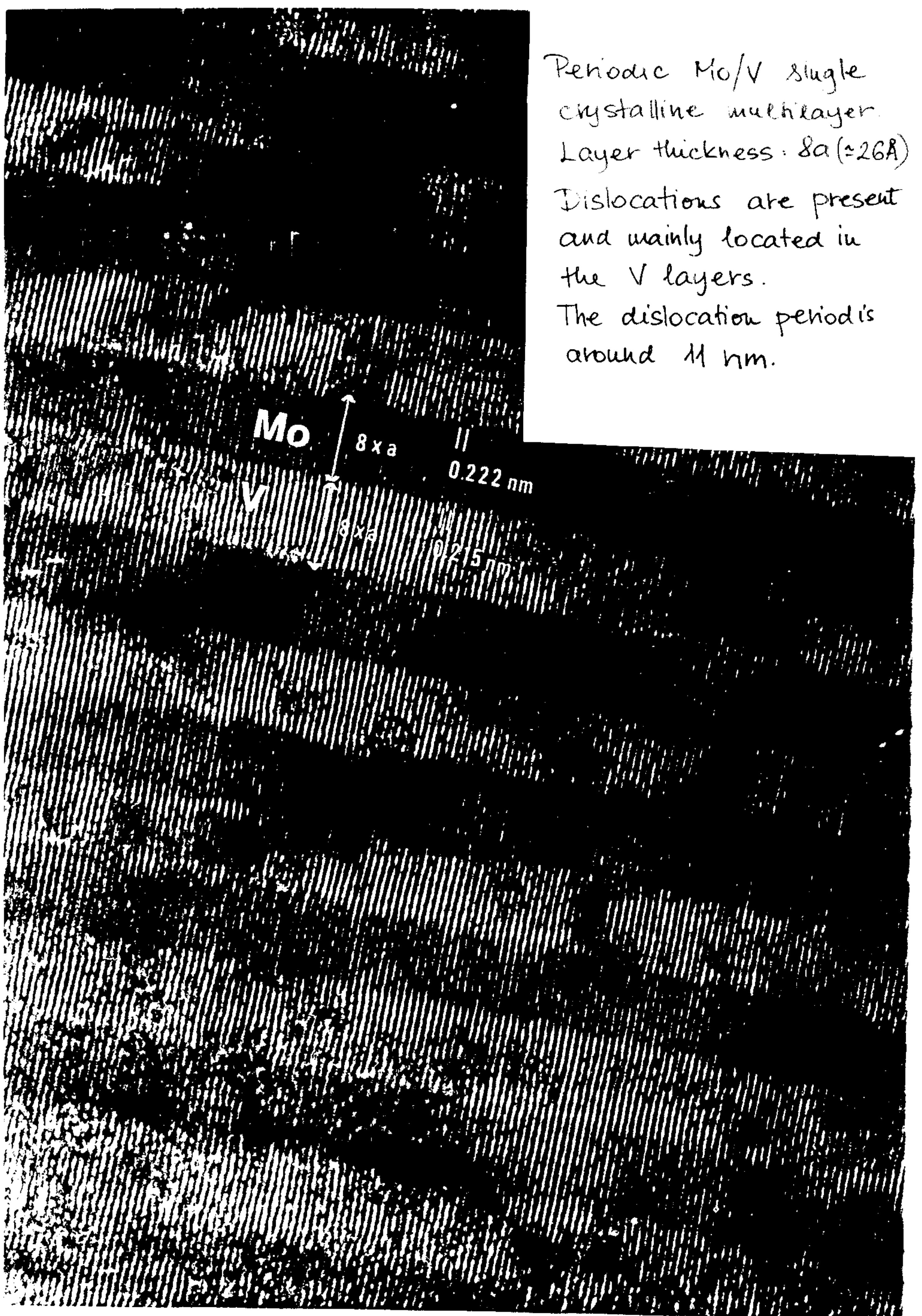
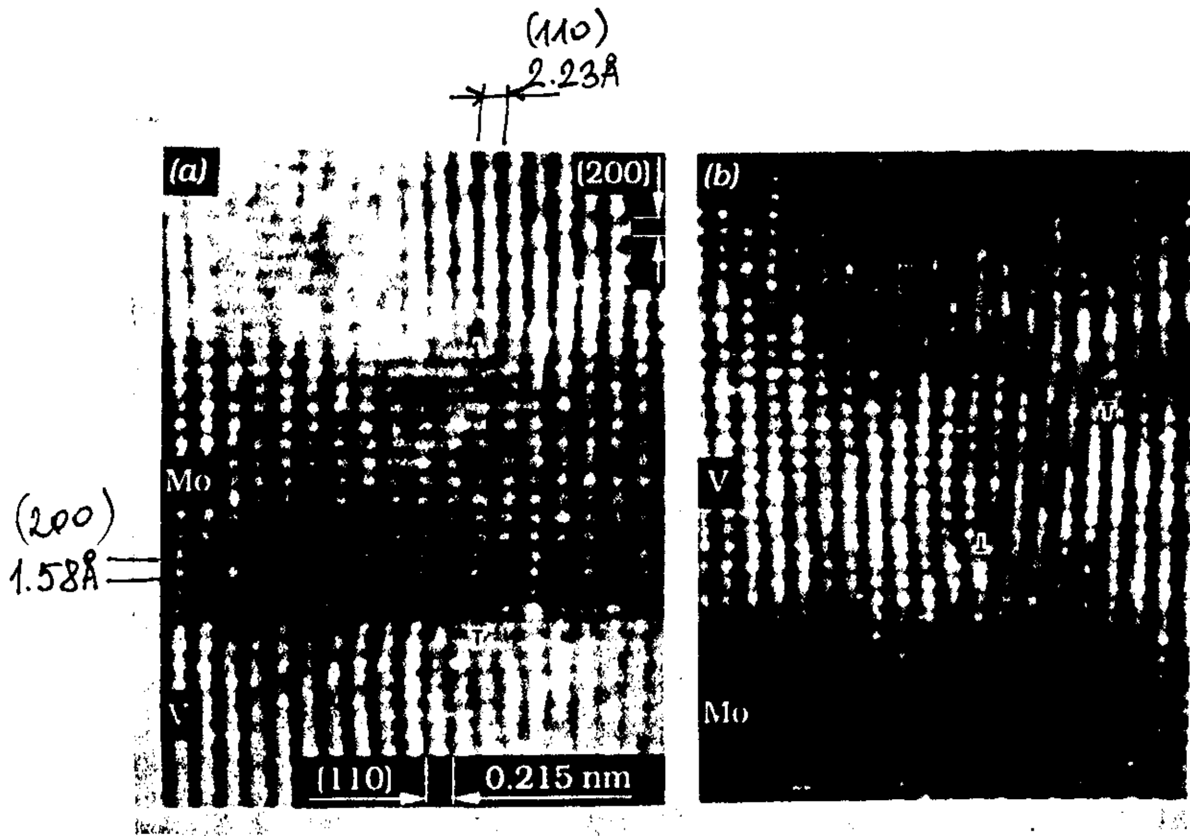


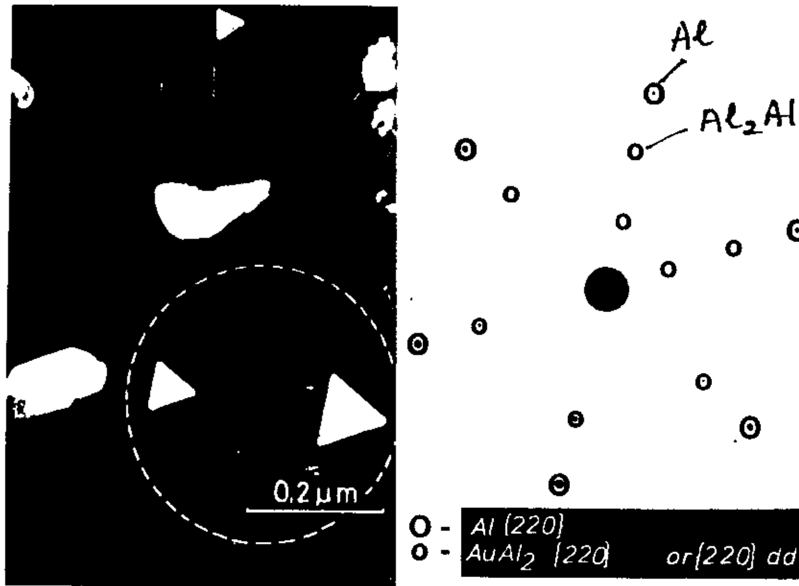
Fig. 2. High-resolution cross-sectional TEM image of the interface of sample 2. The dislocations, which are all of pure edge type, are indicated with arrows.



Periodic Mo/V single crystalline multilayer.
Layer thickness: 8a (≃26Å)
Dislocations are present and mainly located in the V layers.
The dislocation period is around 11 nm.



Misfit dislocations in a Mo/V multilayer viewed edge on.
The strongly deformed area is ± 3-4 lattice spacings in both directions.
The misfit in the Mo/V system is 3.9%
a(Mo) = 3.15 Å a(V) = 3.02 Å

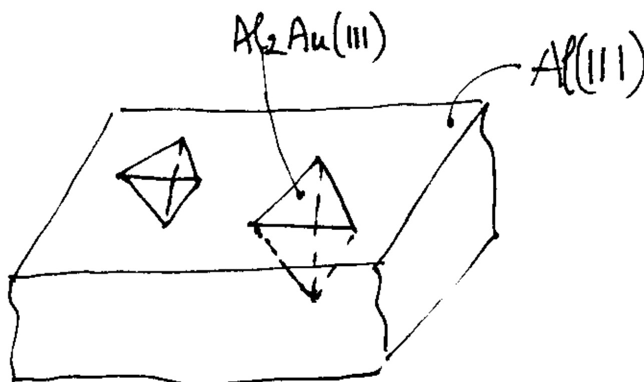


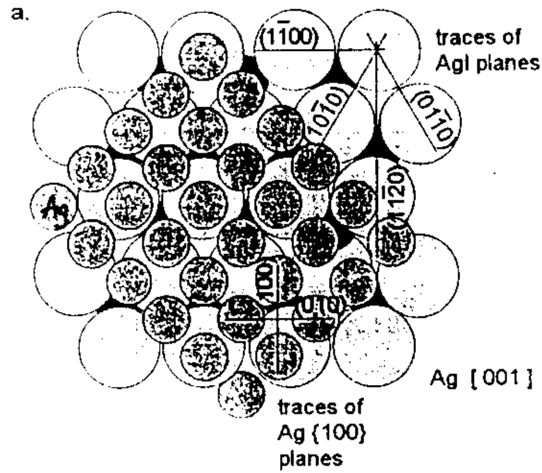
Al_2Au tetraeders grown into the substrate Al grain. The interface is commensurate:

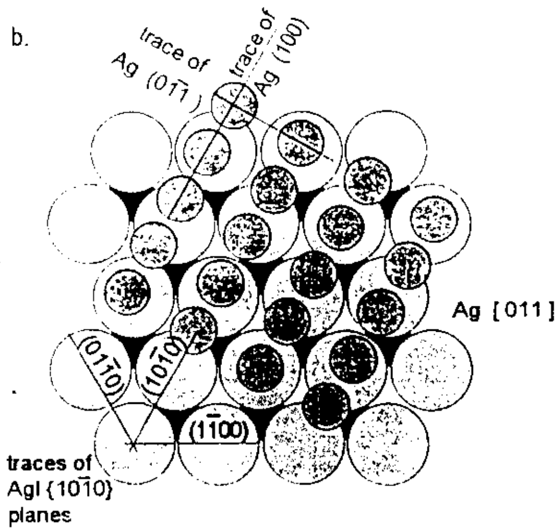
$3d\{220\}_{Al} = 2d\{220\}_{Al_2Au}$ deduced from the diffraction pattern

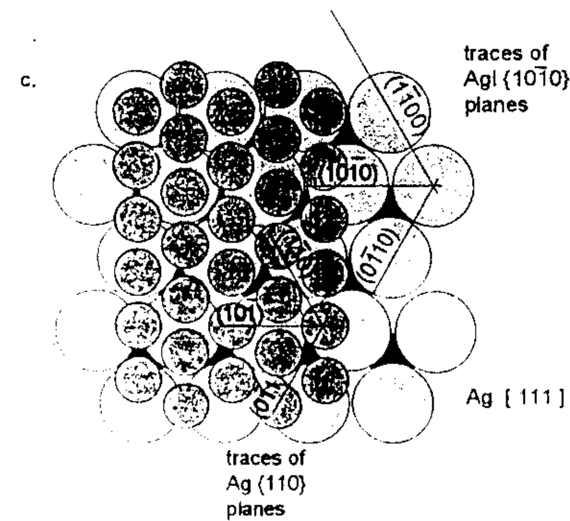
i.e.

$$3d\{110\}_{Al} = 3d\{110\}_{Al_2Au}$$









Incommensurate interfaces between Ag and AgI.
An epitaxial relationship always exists.
G. Sáfrán et al.: Thin Solid Films 259 (1995) 96.

TS/21

The development of grain structure during growth of thin films

1) FORMATION OF GRAINS IN SINGLE COMPONENT FILMS

A) NUCLEATION + GROWTH

B) COALESCENCE

C) CHANGES ACCOMPANIING FILM THICKENING

A) DEPEND ON: T, v_{dep}, material T_M, substrate ...

ORIENTED → texture, single cryst., epitaxy

RANDOM →

GROWTH: RESULTS IN PERFECT(!) SINGLE CRYSTALS

Containination: can stop growth, anizotropically, → secondary nucleation

ADATOM MIGRATION!

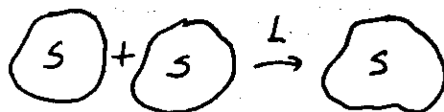
B) DEPEND ON: T, material (T_M), substrate, contamination, V_{dep}, nucleus orientation ...

Liquid like (phase): crystallites melt partly or completely

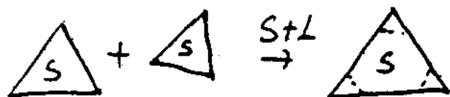
↓

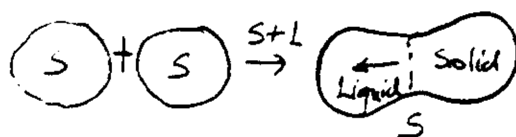
GB: either does not form or is eliminated

ΔT from surf. energy ~100°C



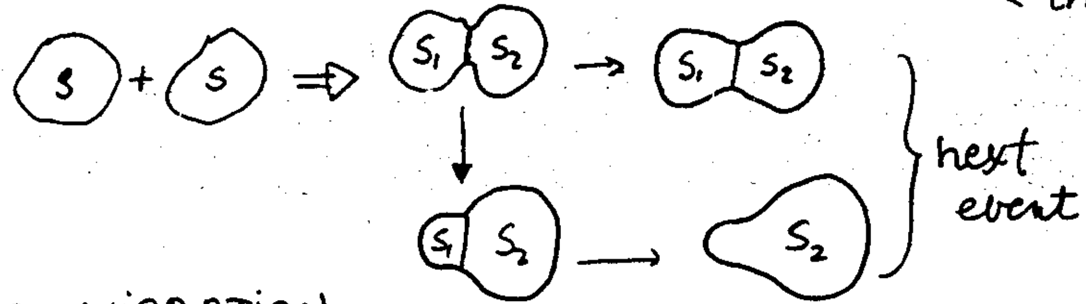
LIQUID FLOW (Solid)





GB goes out, before the next event, one part of island melts

SOLID PHASE COALESCENCE : THE GB → out
↘ in



GB MIGRATION

DRIVING FORCE : ↓ γ_S , ↓ γ_{GB} ↓ γ_{IF}

ORIENTATION RELATIV TO SUBSTRATE – epitaxy

GRAIN SIZE, GB orientations

LOT OF GB-S ELIMINATED – SELECTION OF ORIENTATIONS

↓

GB STRUCTURE,

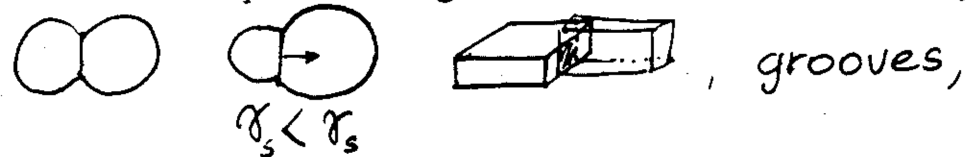
special GB-s (twins)

(Al)
(Au)

c) CHANELL - STRUCTURE 100-200 Å : f(T)

CONTINUOUS FILMS ~ 200-400 Å → ↑ f(T)

GB movements are made easier in cont. films (geometrical reasons)

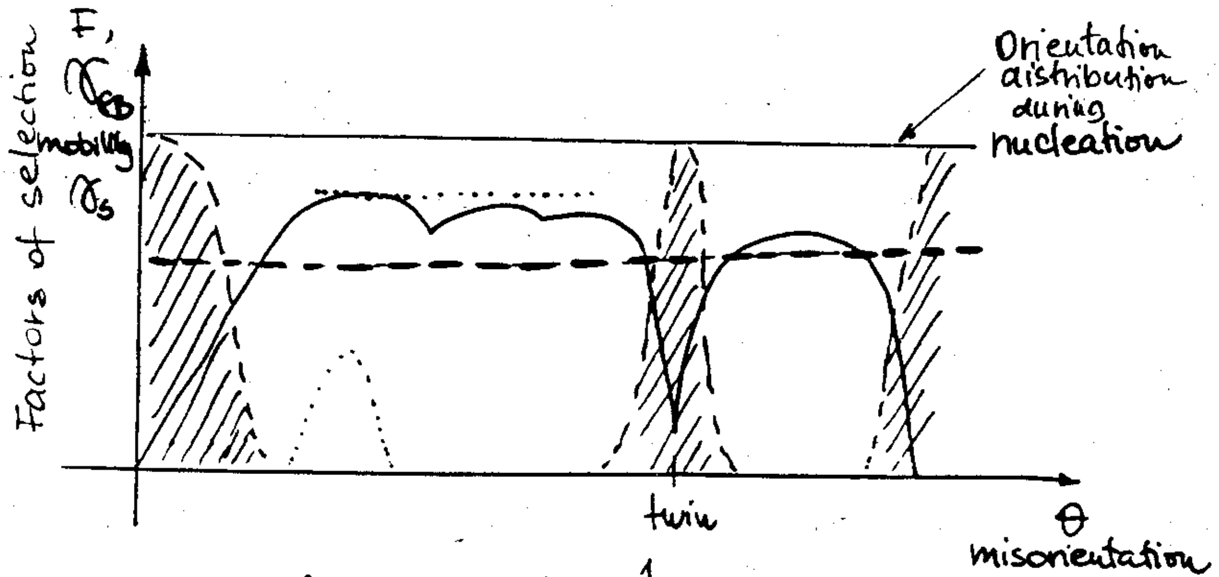


, grooves,

Capillarity driven GB migration during growth (grain growth) → "uniform growth"

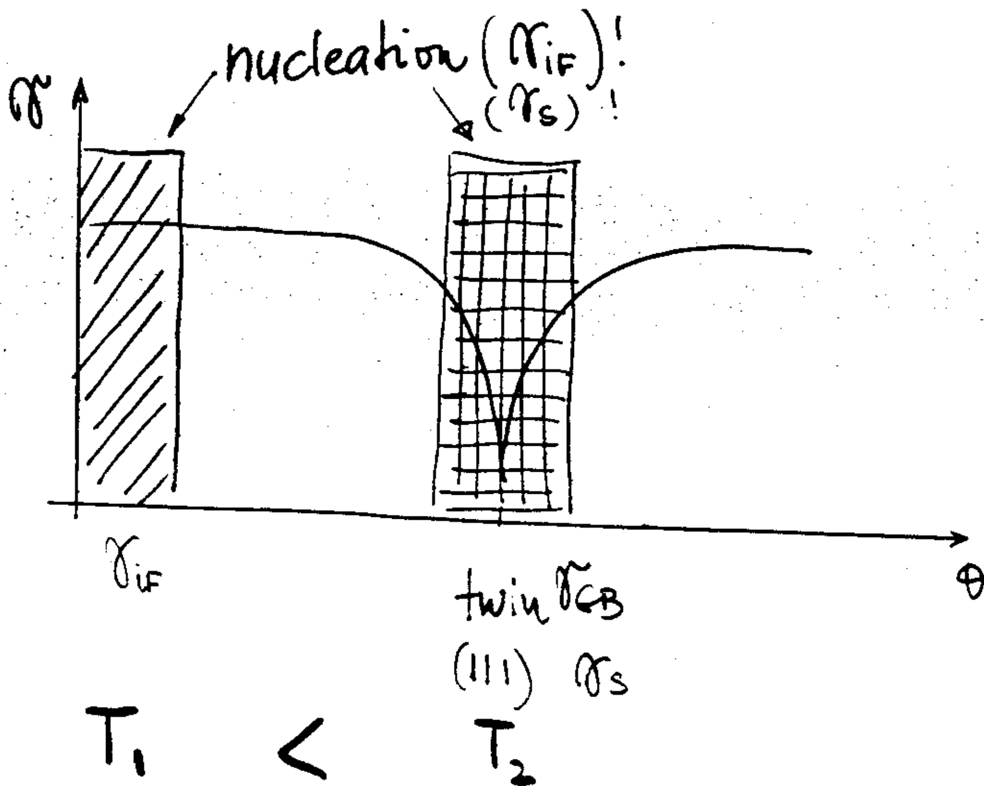
↘ secondary recrystallization (bimodular grain size distr.)

Orientation selection during coalescence



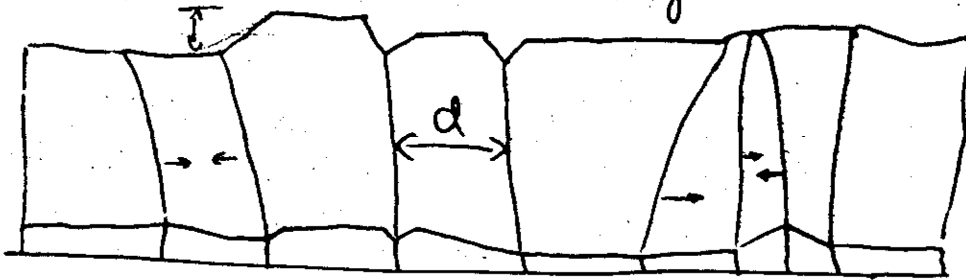
$$F = \text{Driving force} \sim \gamma_{GB} \cdot \frac{1}{d}$$

$$\sim \gamma_s \cdot \frac{1}{d}$$



$T_1 < T_2$

Film thickening



$\sum_i \gamma_S F_S \simeq$ const
$\sum_i F_i \gamma_{IF} \simeq$ const
$\sum_{GB} \gamma_{GB} G_{GB} \sim t \uparrow$

GB movements, alignments
grain growth

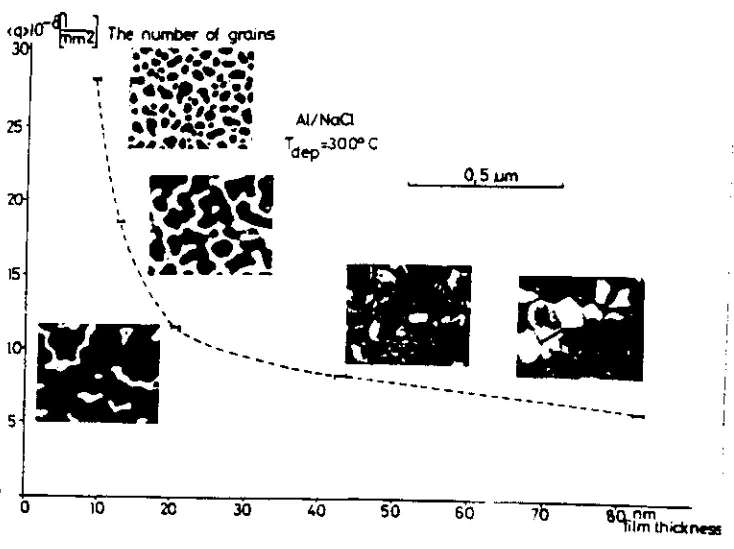
Surface anizotropy can become more important → effects accumulate during time.

Grooving – growth
contamination
energy equilibrium

Driving force on GB $\sim \gamma_{GB} \cdot \frac{1}{d}$ –

Retarding forces: grooves
Long columns: shape anizotropy, istability

The number of Al grains decreasing with the growth of the film thickness.
A lot of grains and orientations can be lost due to this process.



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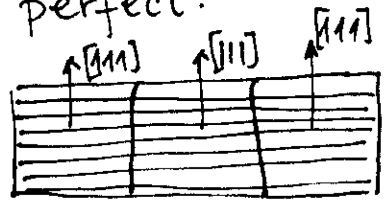
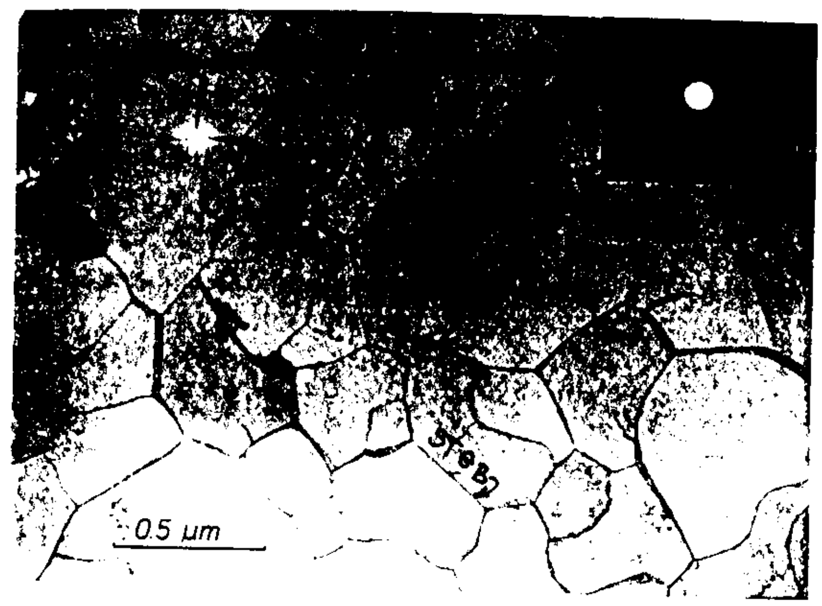
Uniformly oriented grains in Al film grown on mica.
[111]Al || [0001]mica
This orientation is perfect.





(111) planes go through GB continously.
The GB-s are pure tilt, a few are also symmetrical (STGB)

1681

Captured lattice dislocations and ledges in a GB of Al

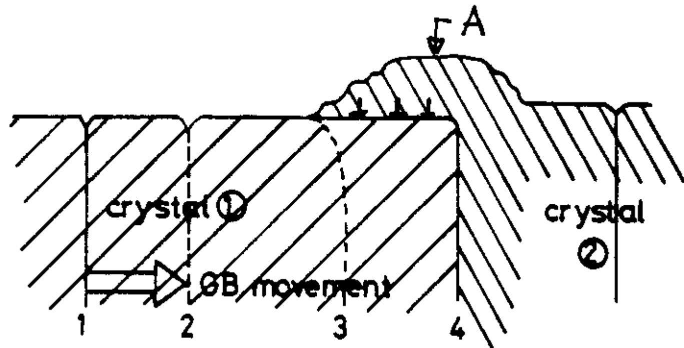
5F 633

Al H88 ox + Pt

350° C
2500 Å
100 Å/s

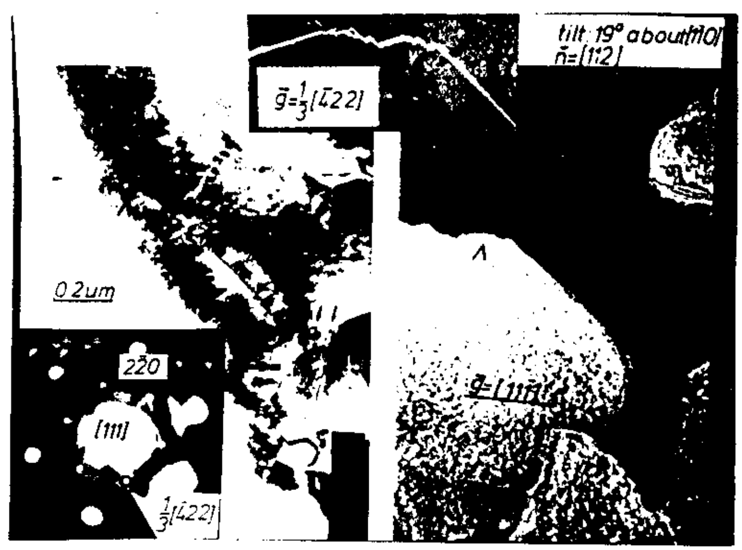
1668.

The interaction of a (twin) GB with a growth surface hill (A) in Al
Dislocation are observed in the undercut region



~~Szöveg: 1606 ...~~

Special (twin) GB in Al.
GB steps
GB dislocations
stacking reversal



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1701.

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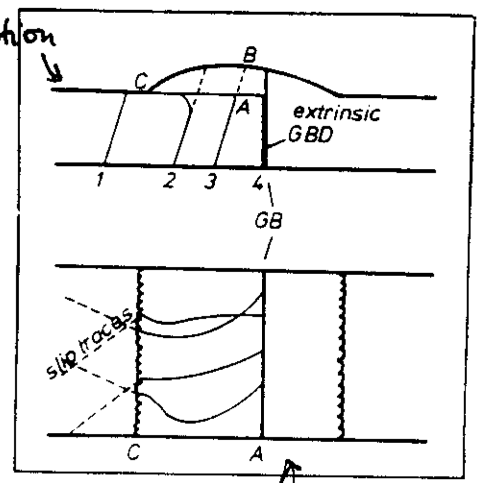
0

Schematic drowing of interaction of dislocations and GB, observed in Al film. Threding dislocation tails are left below the GB hills.

cross section

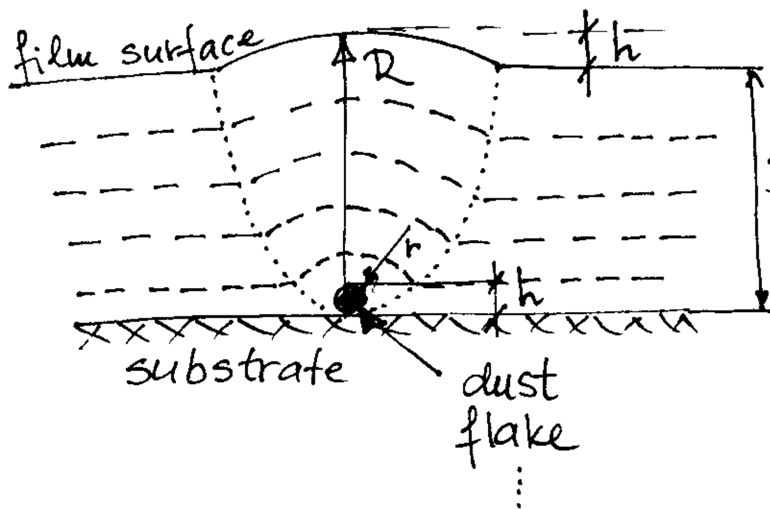


top view

1691.

Nodes in NiCr film, grown on Si (native oxide).
Strong shadowing effect is present during growth → no smoothening occurs.

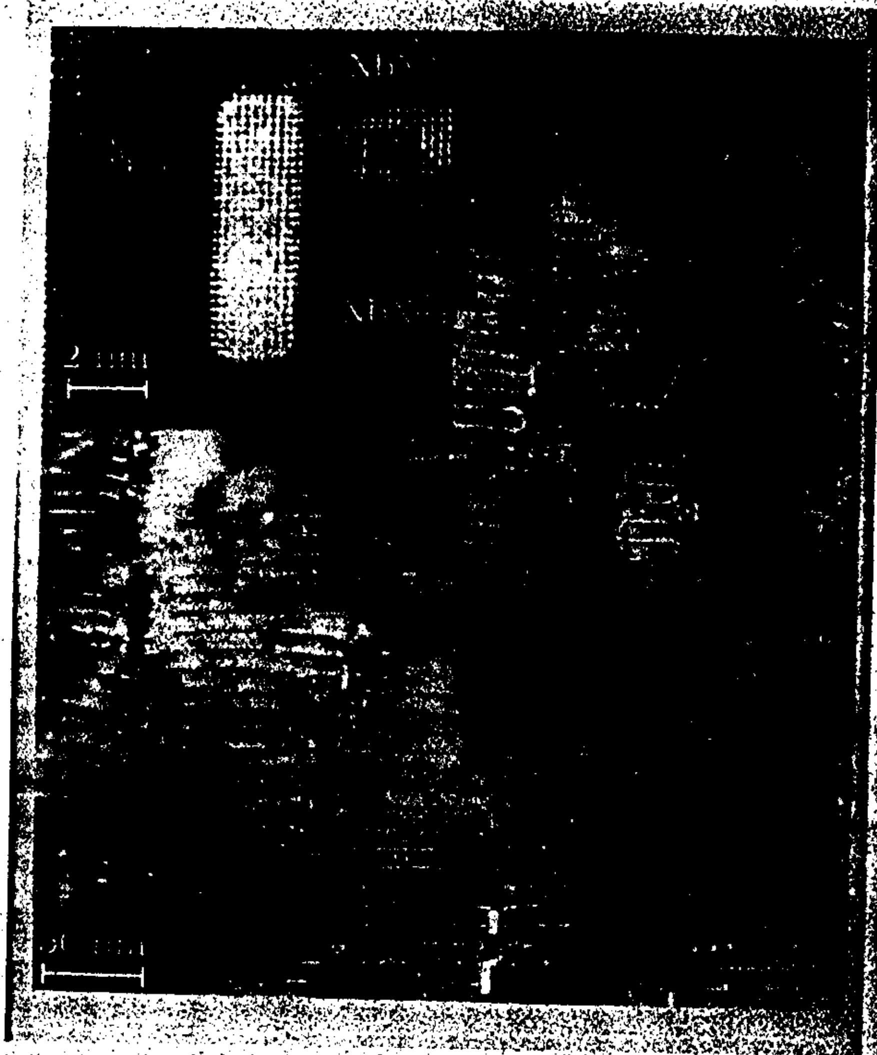
Nodes grow on substrate inhomogenities.
Node geometry



1) $R = r + D$

2) ...... is a paraboloid

3) Apparent smoothening occurs.



L. Hultman et al. J. Vac. Sci. Technol. A 10(4) (1992) 1618

Columnar structure of single crystalline NbN/TiN multilayer, grown by DC magnetron sputtering on MgO.

Cause: low surface mobility + oblique deposition effects.

The shadowed region mixes, voids form.

Cu/Ag 10 nm period polycrystalline multilayer (~300K, DC magnetron sputtering onto Si wafer)

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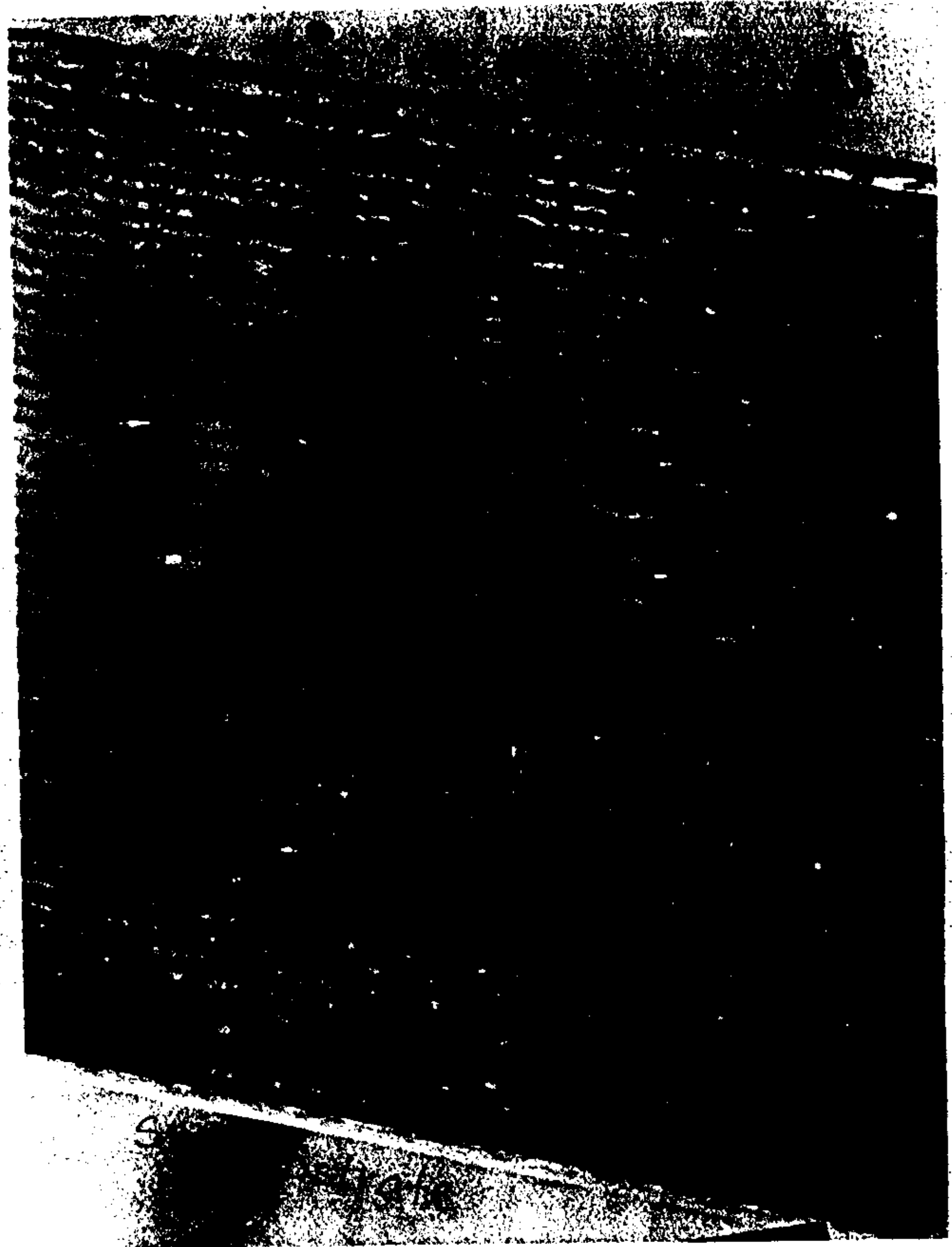
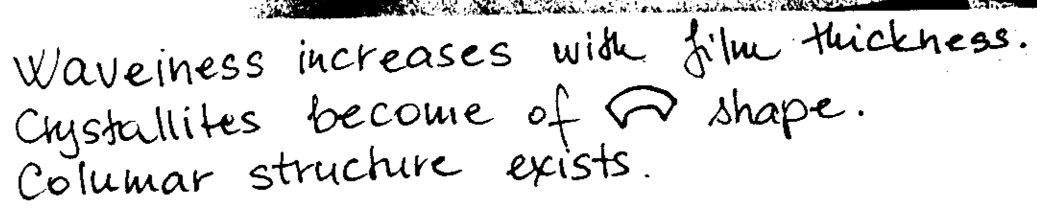




Waveiness increases with film thickness.
Crystallites become of ⌒ shape.
Columar structure exists.

White columns of Ag/Cu multilayer, showing the single crystalline nature of the columns (dark field TEX image, cross cection)

Mo/V superlattices

DC magnetron sputtering:

$5x10^{-9}$ mbar
$3\text{-}5x10^{-3}$ mbar Ar, Ø50 mm targets
0,1 nm/sec
MgO (100), 970K
D(V, Mo)≤ 10 nm

The grown film: V/Mo single crystal,

V[001]| |MgO[001]

V[100]| |MgO[110]

Periodic, quasiperiodic (Fibonacci) superlattices:

Methods: TEM, X-ray diffr.

Results:

Geometry of the phase boundaries (growth: 2D, 3D)
Interface thickness (a=0,31 nm)
Misfit dislocations in V, L=11 nm)
X-ray line width, $\beta=f(\Lambda)$
V: 2D⇒3D transition critical thickness $D_c=f(\Gamma,\eta)$
non-cumulative waviness, The 3D layers became
again smooth if $D_V<D_c$
Mo shows always 2D growth

GROWTH MODES

Frank- van der Merve:	2D	$\gamma_f+\gamma_i<\gamma_s$	
Volmer-Weber:	3D	$\gamma_f+\gamma_i>\gamma_s$	(1)
Stranski-Krastanow:	2D+3D	$\gamma_f+\gamma_i\approx\gamma_s$	

	γ mJ/m^2	T_M
Mo	2250	2880 K
V	1950	2173 K

At 973K:

$\gamma(T)=1{,}2\gamma(T_M)+0{,}45(T_M-T)$ according to empirical rule

$\gamma_{Mo}=3560$ mJ/m^2
γ_V $=2880$ mJ/m^2

Lorentz-Berthelot rule:

$$E_i=\gamma_i=\gamma_{Mo}+\gamma_V-2(\gamma_{Mo}\gamma_V)^{1/2}=36 \text{ mJ/m}^2 \quad (2)$$

According to (1): Mo: 3D
V: 2D

Experimental observation: Mo: 2D, always
V : 2D, if $D_V>D_c$, 3D

If the elastic energy and the energy of crystal defects are also incorporated into γ_i, the condition for 2D growth according to (1) becomes:

$$\gamma_i = E_i + E_D + E_\varepsilon = \gamma_s - \gamma_f, \qquad (1)$$

E_i based on (2):

$$E_i = \gamma_{Mo} + \gamma_V - 2\sqrt{\gamma_{Mo}\gamma_V} \qquad (2)$$

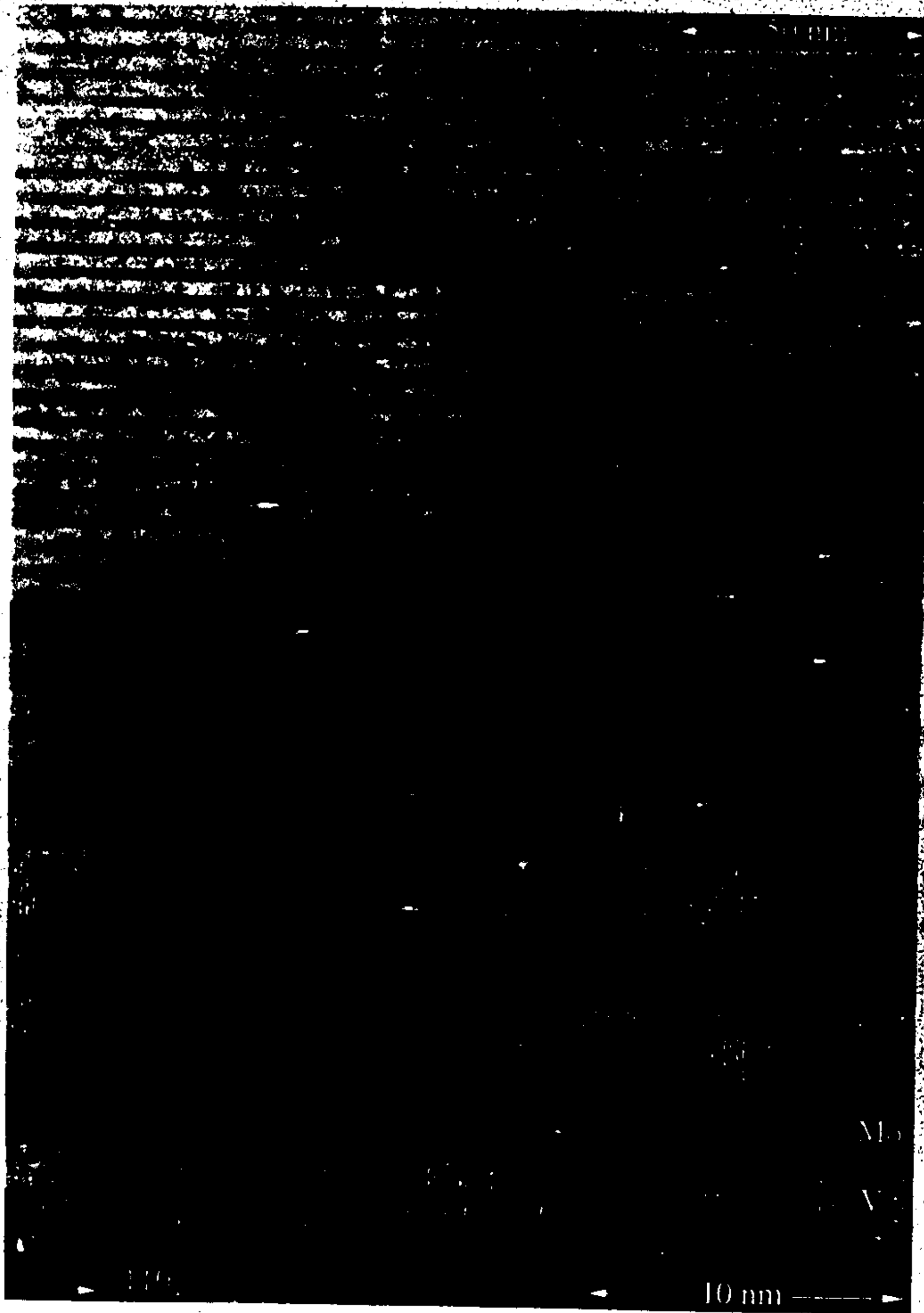
36 mJ/m2

$$E_D = (\eta_0 - \varepsilon)\frac{Gb}{2\pi(1-\nu)}\ln\left(\frac{D}{b}+1\right) \qquad (3)$$

$$E_\varepsilon = \frac{2G(1+\nu)}{1-\nu}\varepsilon^2 D \qquad (4)$$

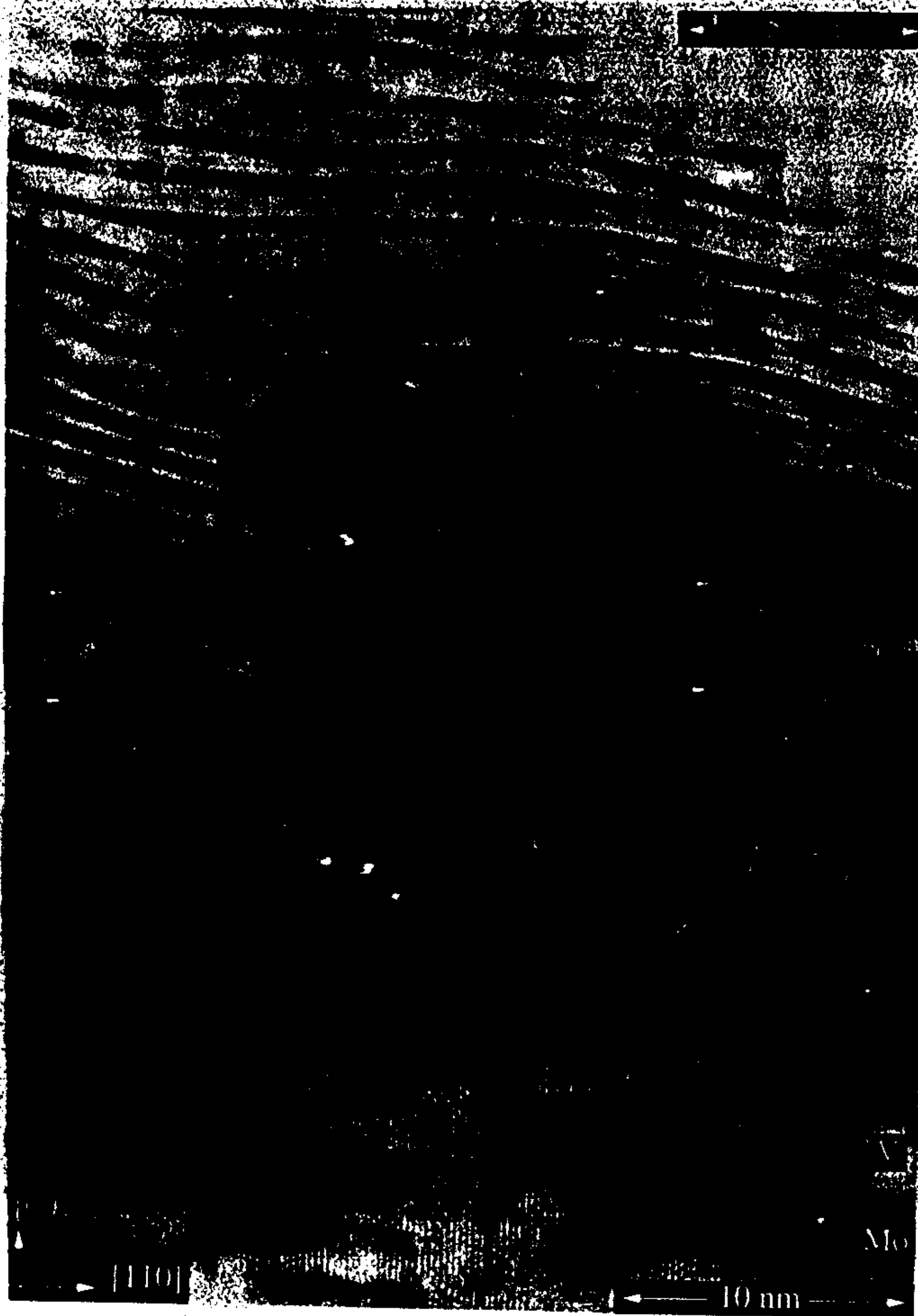
D-layer thickness,
G- shear modulus
b- Burgers' vector length
ε-residual elastic strain
η_0- misfit
ν- Poisson const.

On the basis of (1), (2), (3) and (4): The limiting value for D_V(2D) is 30-50 nm.



} $\Lambda = 5{,}0$ nm

Planar layers, 2D growth in Mo/V



3D growth of V, initiated by surface strain effect of
2D growth of Mo misfit dislocations.

CONCLUSIONS

V layers:
The possibility to switch to the 3D growth mode is due to the fulfilment of the condition: $T_R(V)>T_S(V)$

The direct cause of the 2D$\Rightarrow$ 3D transition is the surface deformation caused by the misfit dislocations and the corresponding driving force causing thickness fluctuations in the V layer.

The surface deformation for $\Gamma=0.25$ and $\Gamma=1$ is the same and about 3,5%. With decreasing $|\eta V|$ and increasing layer thickness the surface deformation caused by the dislocations decreases, D_C increases.

The resulting surface waviness is not cumulative.

The surface smoothens as Λ decreases: 2D growth, steps.

Mo layers:
The causes of the 2D growth mode :

the decrease of γ due to surface segregation,
kinetically limited 2D growth