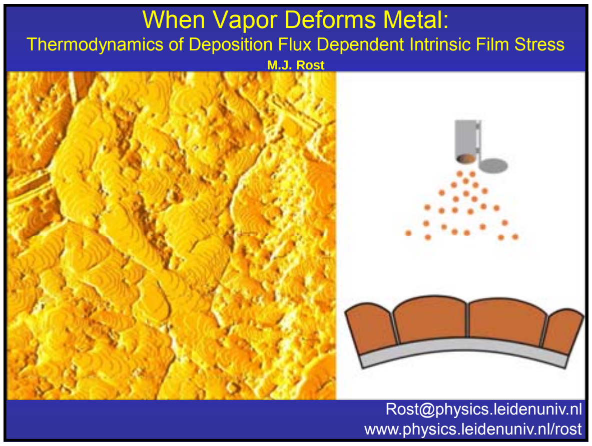
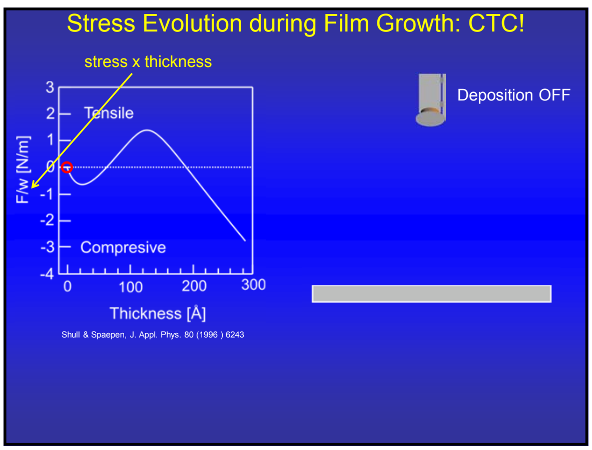
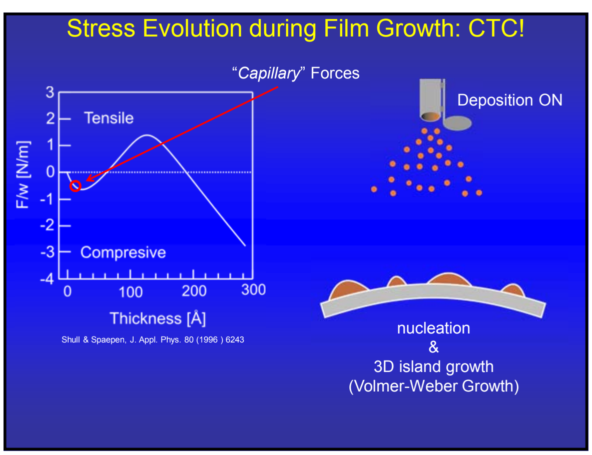
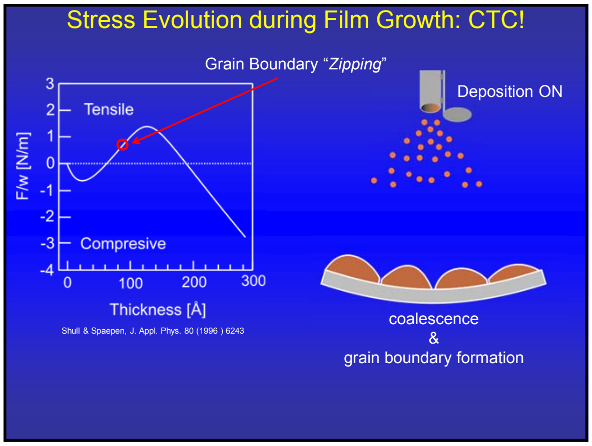
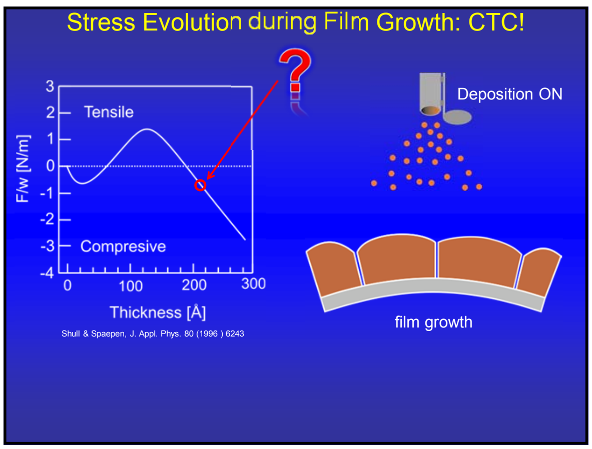
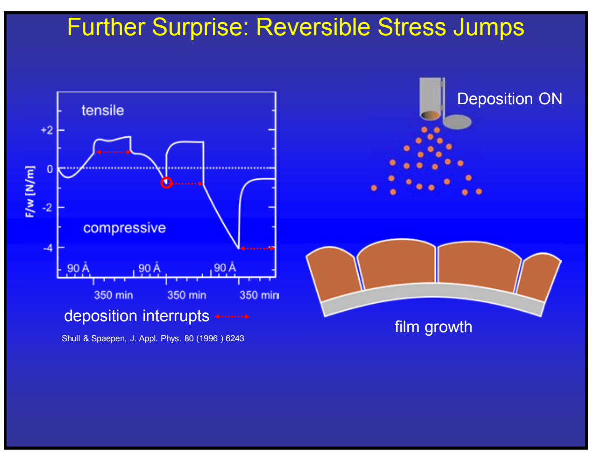

When Vapor Deforms Metal:
Thermodynamics of Deposition Flux Dependent Intrinsic Film Stress
M.J. Rost
Rost@physics.leidenuniv.nl
www.physics.leidenuniv.nl/rost

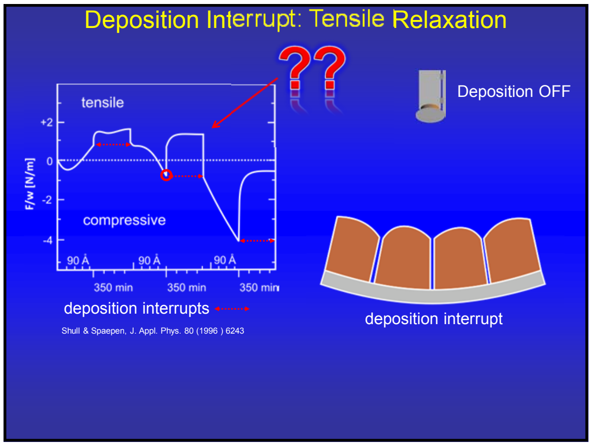

Stress Evolution during Film Growth: CTC!
stress x thickness
Tensile
Compresive
F/w [N/m]
Thickness [Å]
3
2
1
0
-1
-2
-3
-4
0
100
200
300
Shull & Spaepen, J. Appl. Phys. 80 (1996) 6243
Deposition OFF

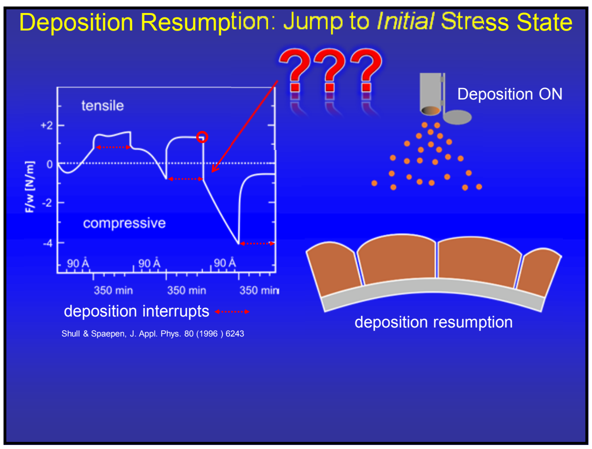

Stress Evolution during Film Growth: CTC!
"*Capillary*" Forces
Tensile
Compresive
F/w [N/m]
Thickness [Å]
3
2
1
0
-1
-2
-3
-4
0
100
200
300
Shull & Spaepen, J. Appl. Phys. 80 (1996) 6243
Deposition ON
nucleation
&
3D island growth
(Volmer-Weber Growth)

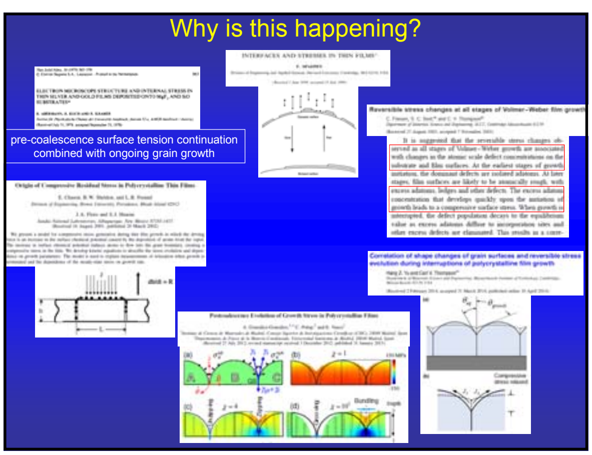

Stress Evolution during Film Growth: CTC!
Grain Boundary "Zipping"
Tensile
Compresive
F/w [N/m]
Thickness [Å]
Shull & Spaepen, J. Appl. Phys. 80 (1996) 6243
Deposition ON
coalescence
&
grain boundary formation

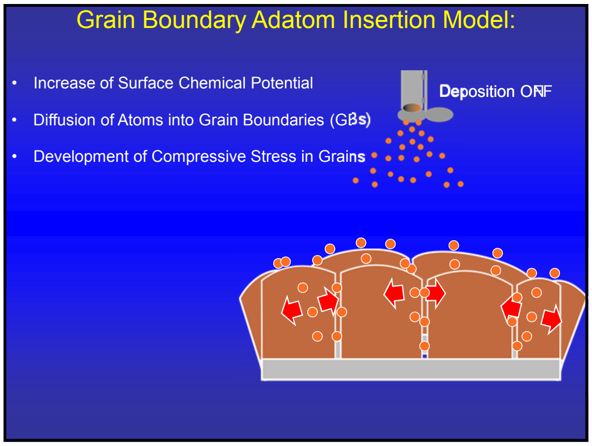

Stress Evolution during Film Growth: CTC!
Tensile
Compresive
F/w [N/m]
Thickness [Å]
Shull & Spaepen, J. Appl. Phys. 80 (1996) 6243
Deposition ON
film growth

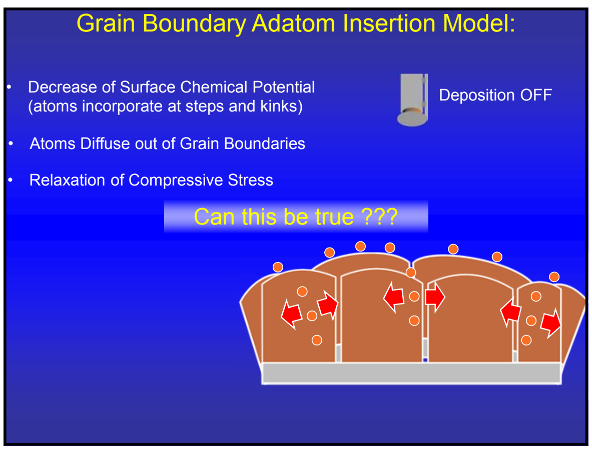

Further Surprise: Reversible Stress Jumps
tensile
compressive
F/w [N/m]
90 Å
350 min
deposition interrupts
Shull & Spaepen, J. Appl. Phys. 80 (1996) 6243
Deposition ON
film growth

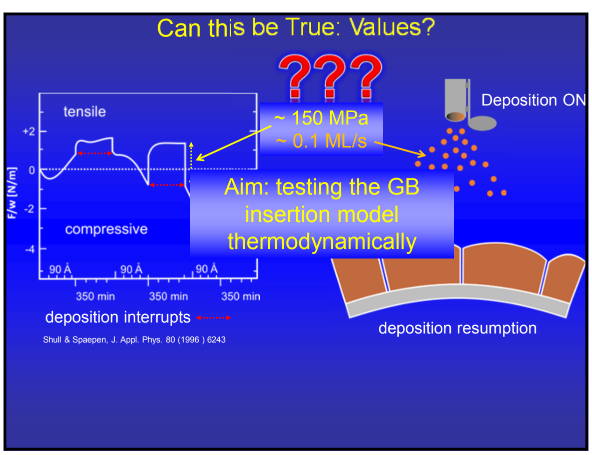

Deposition Interrupt: Tensile Relaxation
??
Deposition OFF
tensile
compressive
F/w [N/m]
+2
0
-2
-4
90 Å
90 Å
90 Å
350 min
350 min
350 min
deposition interrupts
Shull & Spaepen, J. Appl. Phys. 80 (1996) 6243
deposition interrupt

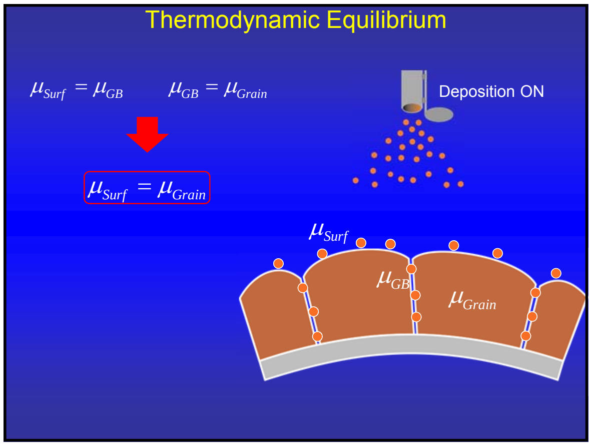

Deposition Resumption: Jump to *Initial* Stress State
???
Deposition ON
tensile
compressive
F/w [N/m]
+2
0
-2
-4
90 Å
90 Å
90 Å
350 min
350 min
350 min
deposition interrupts
Shull & Spaepen, J. Appl. Phys. 80 (1996) 6243
deposition resumption

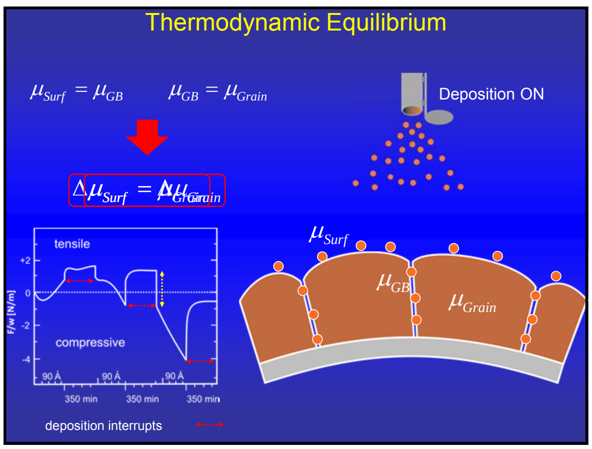

Why is this happening?
pre-coalescence surface tension continuation
combined with ongoing grain growth
Reversible stress changes at all stages of Volmer–Weber film growth
Correlation of shape changes of grain surfaces and reversible stress evolution during interruptions of polycrystalline film growth

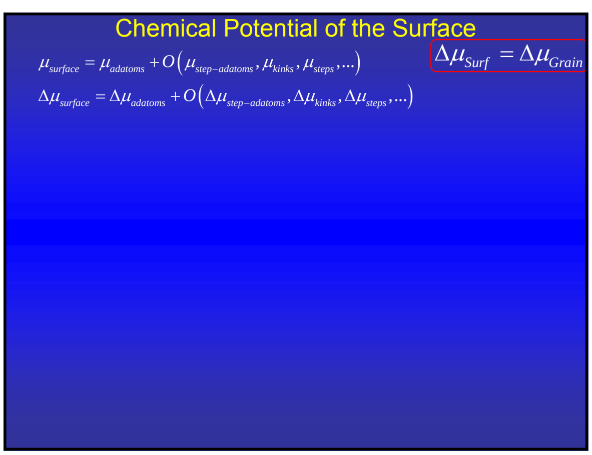

Grain Boundary Adatom Insertion Model:
Increase of Surface Chemical Potential
Diffusion of Atoms into Grain Boundaries (GBs)
Development of Compressive Stress in Grains
Deposition ON


Grain Boundary Adatom Insertion Model:
Decrease of Surface Chemical Potential
(atoms incorporate at steps and kinks)
Atoms Diffuse out of Grain Boundaries
Relaxation of Compressive Stress
Deposition OFF
Can this be true ???


Can this be True: Values?
???
~ 150 MPa
~ 0.1 ML/s
Deposition ON
tensile
compressive
F/w [N/m]
+2
0
-2
-4
90 Å
90 Å
90 Å
350 min
350 min
350 min
Aim: testing the GB insertion model thermodynamically
deposition interrupts
deposition resumption
Shull & Spaepen, J. Appl. Phys. 80 (1996) 6243


Thermodynamic Equilibrium
$\mu_{Surf} = \mu_{GB}$
$\mu_{GB} = \mu_{Grain}$
Deposition ON
$\mu_{Surf} = \mu_{Grain}$
μ_{Surf}
μ_{GB}
μ_{Grain}


Thermodynamic Equilibrium
$\mu_{Surf} = \mu_{GB}$
$\mu_{GB} = \mu_{Grain}$
Deposition ON
$\Delta\mu_{Surf} = \Delta\mu_{Grain}$
tensile
compressive
F/w [N/m]
+2
0
-2
-4
90 Å
90 Å
90 Å
350 min
350 min
350 min
deposition interrupts
μ_{Surf}
μ_{GB}
μ_{Grain}

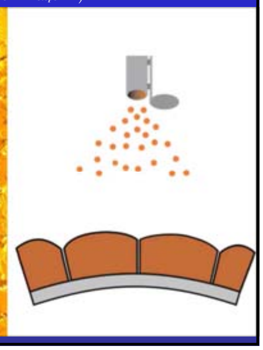

Chemical Potential of the Surface
$\Delta\mu_{Surf} = \Delta\mu_{Grain}$
$\mu_{surface} = \mu_{adatoms} + O\left(\mu_{step-adatoms}, \mu_{kinks}, \mu_{steps}, ...\right)$
$\Delta\mu_{surface} = \Delta\mu_{adatoms} + O\left(\Delta\mu_{step-adatoms}, \Delta\mu_{kinks}, \Delta\mu_{steps}, ...\right)$

Chemical Potential of the Surface

$$\Delta\mu_{Surf} = \Delta\mu_{Grain}$$

$$\mu_{surface} = \mu_{adatoms} + O\left(\mu_{step-adatoms}, \mu_{kinks}, \mu_{steps}, \ldots\right)$$

$$\Delta\mu_{surface} = \Delta\mu_{adatoms} + O\left(\Delta\mu_{step-adatoms}, \Delta\mu_{kinks}, \Delta\mu_{steps}, \ldots\right)$$



μ_{Surf} due to Adatoms

$$\Delta\mu_{Surf} = \Delta\mu_{Grain}$$

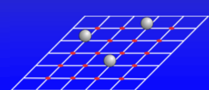
$$\mu_s = \left(\frac{\partial F_s}{\partial N}\right)_{T,V} = \frac{\partial U_{adatom}}{\partial N} + \frac{\partial U_{inter}}{\partial N} - \frac{\partial S}{\partial N}T$$

Ignoring Interactions between Adatoms

θ: Coverage

- Adatom *Lattice* Model

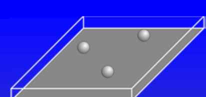
$$\mu_{Ad.Latt.} = E_{ad} + kT\ln\left(\frac{\theta}{1-\theta}\right)$$



- 2D Adatom *Gas* Model

$$\mu_{2DAG} = E_{ad} + kT\left[\ln\left(\frac{\Lambda^2}{A_{ad}}\frac{\theta}{1-\theta}\right) + \frac{\theta}{1-\theta}\right]$$

$$\Lambda = \frac{h}{\sqrt{2\pi mkT}}$$ thermal de Broglie wavelength

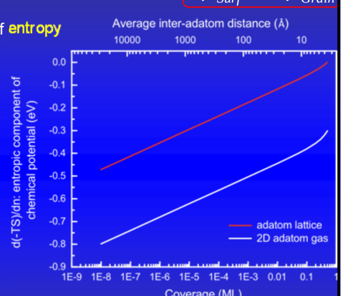


μ_{Surf} due to Adatoms

$$\Delta\mu_{Surf} = \Delta\mu_{Grain}$$

- Difference in *absolute* value of **entropy**
- *Same* slope for θ < 0.1ML
- Important: interest in $\Delta\mu_{Surf}$
- For θ < 0.1ML:

$$\Delta\mu_{adadtom} \approx kT\ln\left(\frac{\theta_2}{\theta_1}\right)$$ Eq. 1



$$\mu_{Ad.Latt.} = E_{ad} + kT\ln\left(\frac{\theta}{1-\theta}\right)$$

$$\mu_{2DAG} = E_{ad} + kT\left[\ln\left(\frac{\Lambda^2}{A_{ad}}\frac{\theta}{1-\theta}\right) + \frac{\theta}{1-\theta}\right]$$

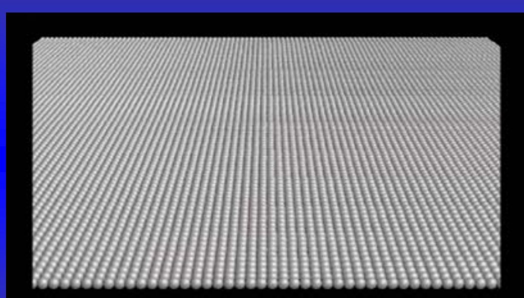
$$\Delta\mu_{Surf} = \Delta\mu_{Grain}$$

$$\Delta\mu_{adadtom} \approx kT \ln\left(\frac{\theta_2}{\theta_1}\right) \quad \text{Eq. 1}$$

distribution of θ
during growth ?

Island Nucleation

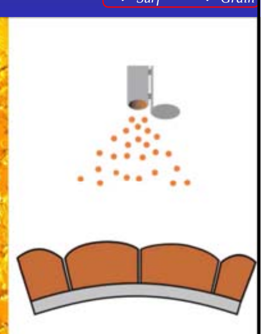
$$\Delta\mu_{Surf} = \Delta\mu_{Grain}$$



Kinetic Monte Carlo Simulation of Film Growth:
with courtesy of Vladimir Kaganer, Paul-Drude-Institut für Festkörperelektronik
(see also https://www.youtube.com/watch?v=NsGRKSV8yH8)

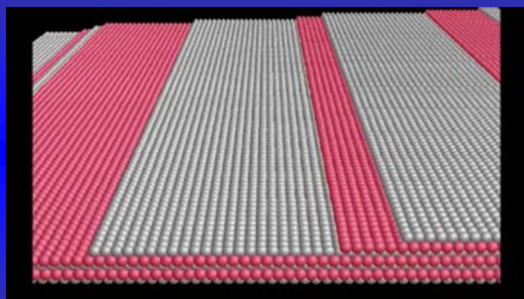
Step Flow Growth

$$\Delta\mu_{Surf} = \Delta\mu_{Grain}$$



Step Flow Growth

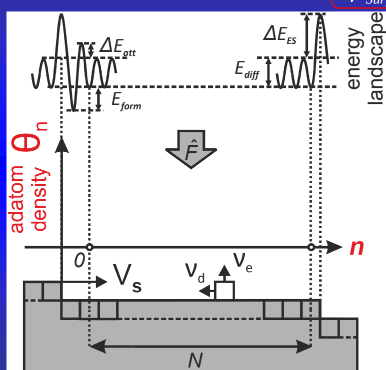
$\Delta\mu_{Surf} = \Delta\mu_{Grain}$



Kinetic Monte Carlo Simulation of Film Growth:
with courtesy of Vladimir Kaganer, Paul-Drude-Institut für Festkörperelektronik
(see also https://www.youtube.com/watch?v=NsGRKSV8yH8)

Adatom Density on a Terrace

$\Delta\mu_{Surf} = \Delta\mu_{Grain}$

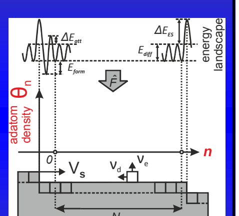


Adatom Density on a Terrace

$\Delta\mu_{Surf} = \Delta\mu_{Grain}$

$$\frac{\partial\theta_n}{\partial t} = v_d \frac{\partial^2\theta_n}{\partial n^2} + V_s \frac{\partial\theta_n}{\partial n} - v_e\theta_n + \hat{F}$$

diffusion ↑ step movement ↑ evaporation ↑ deposition flux ↑



Simplifications:

- room temperature: $v_e \approx 0$
- for typical deposition situations: $V_s \approx 0$

Adatom Density on a Terrace

$\Delta\mu_{Surf} = \Delta\mu_{Grain}$

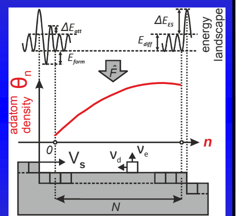
Definitions:

$\theta_{eq} = \exp\left(-E_{form}/kT\right) \qquad \nu_d = \nu_0 \exp\left(-E_{diff}/kT\right)$

$s = s_0 \exp\left(-\Delta E_{ES}/kT\right) \qquad a = \exp\left(-\Delta E_{att}/kT\right)$

Result:

$$\theta_n = \theta_{eq} + \frac{\hat{F}N(an+1)(sN+2)}{2\nu_d\left(asN+a+s\right)} - \frac{\hat{F}n^2}{2\nu_d} \qquad \text{Eq. 2}$$



Cu(111):

$\nu_0 = 10^{12}\,Hz \qquad E_{diff} = 0.040eV$
$s_0 = 15$
$\Delta E_{ES} = 0.224eV$
$\Delta E_{att} = 0eV$

experimentally determined

$E_{form} = 0.714eV$

$\Delta\mu_{Surf} = \Delta\mu_{Grain}$

$$\Delta\mu_{adadtom} \approx kT\ln\left(\frac{\theta_2}{\theta_1}\right) \qquad \text{Eq. 1}$$

$$\theta_n = \theta_{eq} + \frac{\hat{F}N(an+1)(sN+2)}{2\nu_d\left(asN+a+s\right)} - \frac{\hat{F}n^2}{2\nu_d} \qquad \text{Eq. 2}$$

chemical potential
of a
grain under stress?

Chemical Potential of Grain Interior

$\Delta\mu_{Surf} = \Delta\mu_{Grain}$

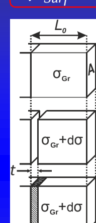
$\sigma = E_0 \cdot \varepsilon$ *stress-strain relation*

$$\mu_{grain} = \left(\frac{\partial F_{grain}}{\partial N}\right)_{T,V,N_t=0} = \lim_{t\to 0}\left(\frac{\partial W_t}{\partial N_t}\right)$$

$$W_t = -\int_0^t \left(\sigma(\varepsilon)\cdot A\right) dL$$

$$\mu_{grain} = \lim_{t\to 0}\left(\frac{\partial W_t}{\partial N_t}\right) = \lim_{t\to 0}\left(-\sigma_{grain}\Omega - \frac{E}{L_0}\Omega t\right)$$

$$\Delta\mu_{grain} = \lim_{t\to 0}\left(-\sigma_2\Omega - \frac{E_2}{L_0}\Omega t\right) - \lim_{t\to 0}\left(-\sigma_1\Omega - \frac{E_1}{L_0}\Omega t\right)$$

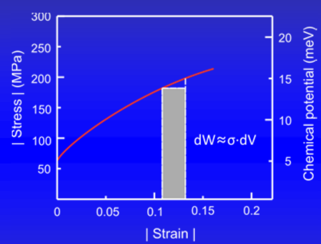


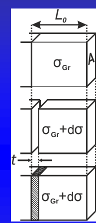
$$\Delta\mu_{grain} = \Delta\sigma \cdot \Omega \qquad \text{Eq. 3}$$

Chemical Potential of Grain Interior

$$\Delta\mu_{grain} = \Delta\sigma \cdot \Omega \quad \text{Eq. 3}$$

$$\Delta\mu_{Surf} = \Delta\mu_{Grain}$$





R. Sandström, J. Hallgren, J. Nuc. Mater. 422 (2012) 51

$\Delta\mu_{Surf} = \Delta\mu_{Grain}$

$$\Delta\mu_{adadtom} \approx kT \ln\left(\frac{\theta_2}{\theta_1}\right) \quad \text{Eq. 1}$$

$$\theta_n = \theta_{eq} + \frac{\hat{F}N(an+1)(sN+2)}{2\nu_d\left(asN+a+s\right)} - \frac{\hat{F}n^2}{2\nu_d} \quad \text{Eq. 2}$$

$$\Delta\mu_{grain} = \Delta\sigma \cdot \Omega \quad \text{Eq. 3}$$

Combining the Equations

$$\Delta\mu_{Surf} = \Delta\mu_{Grain} \quad \Rightarrow \quad kT \ln\left(\frac{\theta_2}{\theta_1}\right) = -\Delta\sigma \cdot \Omega$$

$$\theta_n = \theta_{eq} + \frac{\hat{F}N(an+1)(sN+2)}{2\nu_d\left(asN+a+s\right)} - \frac{\hat{F}n^2}{2\nu_d}$$

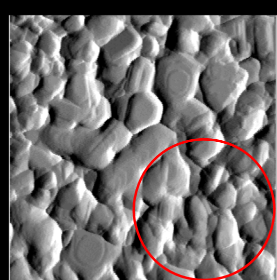
$$\left|\Delta\sigma_{comp}\right| \le \frac{kT}{\Omega} \ln\left(1 + \frac{\hat{F}N(an+1)(sN+2)}{2\nu_d\left(asN+a+s\right)\theta_{eq}} - \frac{\hat{F}n^2}{2\nu_d\theta_{eq}}\right)$$

which terrace position *n*?

Surface Equilibrium Structure

Phys.Rev.Lett. 91 (2003) 026101

from 125⁰C to 175⁰C in 394 min.

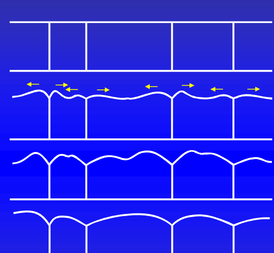


350 nm 125 ⁰C

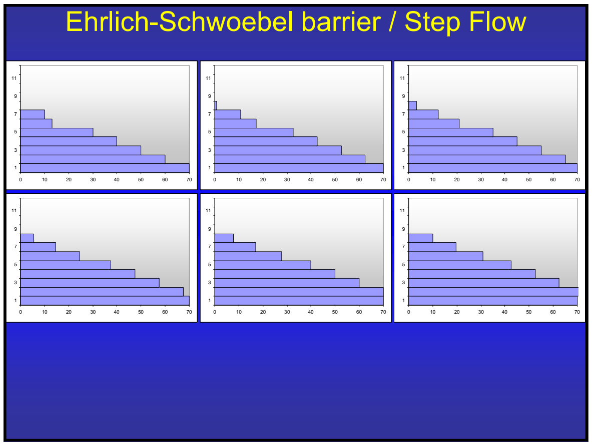
[film coarsening]

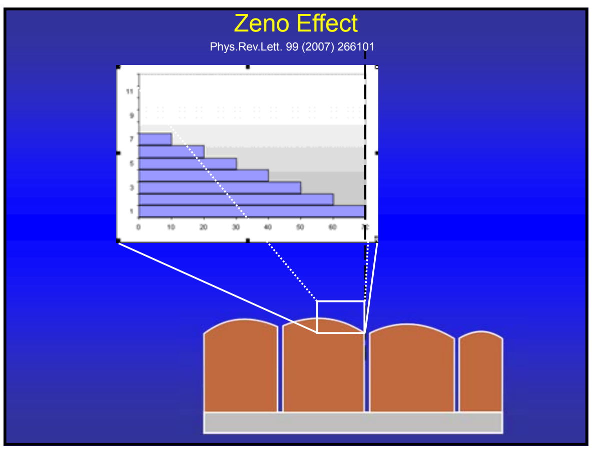
Surface Equilibrium Structure

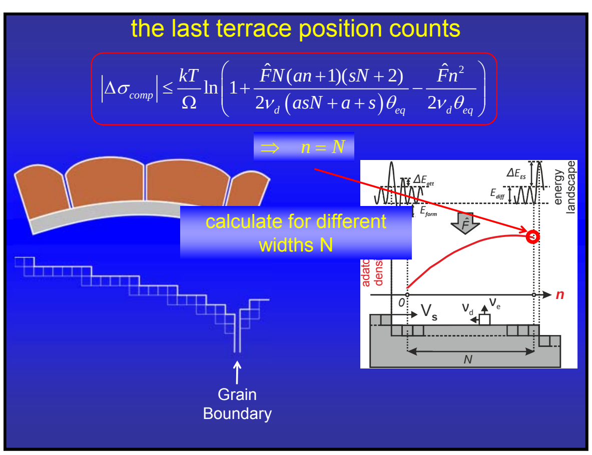
Phys.Rev.Lett. 91 (2003) 026101



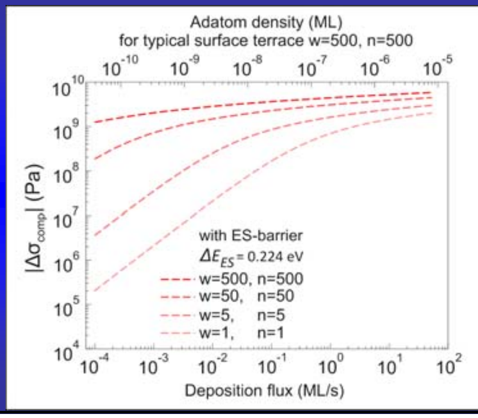
surface in **equilibrium**
⇒ grains with **convex** shape


Ehrlich-Schwoebel barrier / Step Flow

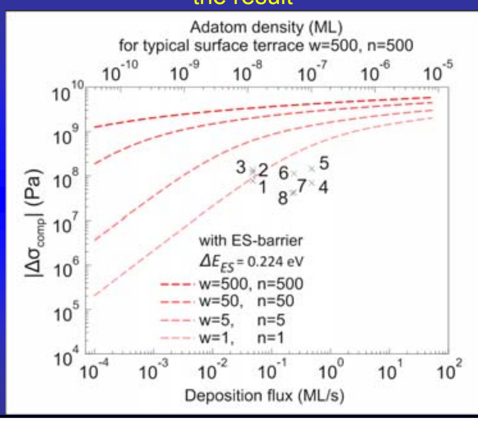

Zeno Effect
Phys.Rev.Lett. 99 (2007) 266101


the last terrace position counts
$$|\Delta\sigma_{comp}| \le \frac{kT}{\Omega}\ln\left(1+\frac{\hat{F}N(an+1)(sN+2)}{2\nu_d\,(asN+a+s)\,\theta_{eq}}-\frac{\hat{F}n^2}{2\nu_d\theta_{eq}}\right)$$
$\Rightarrow \quad n = N$
calculate for different widths N
energy landscape
n
N
Grain Boundary

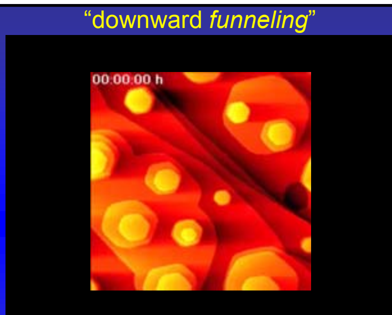
the result



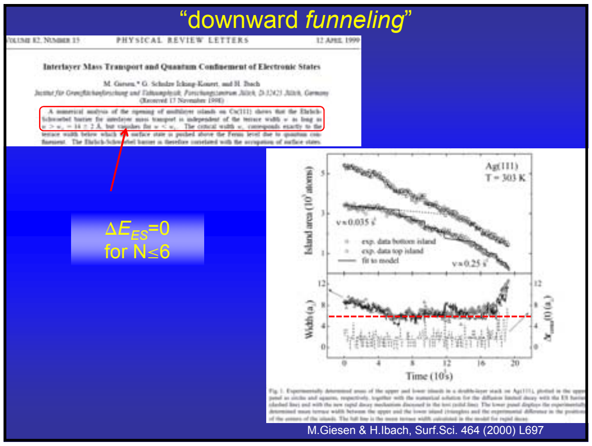
the result

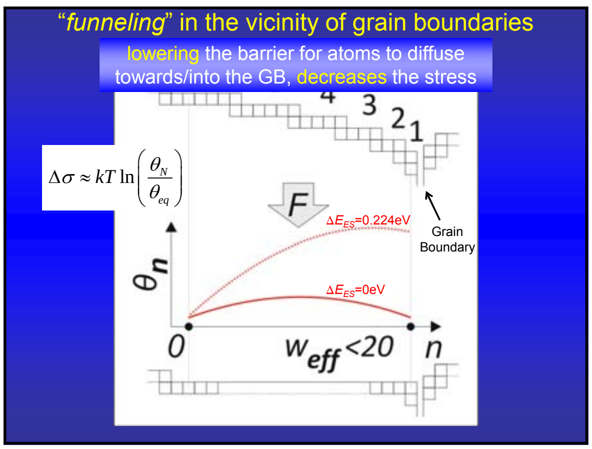


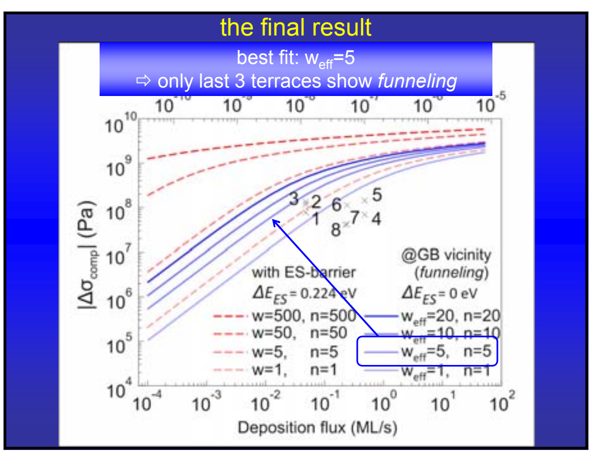
“downward *funneling*”



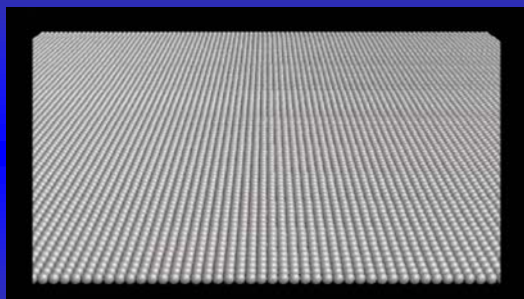
M.Giesen, G. Schulze Icking-Konert, H.Ibach,
Phys.Rev.Lett. 82 (1999) 3101


"downward funneling"
VOLUME 82, NUMBER 15 PHYSICAL REVIEW LETTERS 12 APRIL 1999
Interlayer Mass Transport and Quantum Confinement of Electronic States
ΔE_ES=0
for N≤6
Ag(111)
T = 303 K
Island area (10³ atoms)
Width (a_s)
Time (10³s)
M.Giesen & H.Ibach, Surf.Sci. 464 (2000) L697


"funneling" in the vicinity of grain boundaries
lowering the barrier for atoms to diffuse towards/into the GB, decreases the stress
$\Delta\sigma \approx kT \ln\left(\frac{\theta_N}{\theta_{eq}}\right)$
4 3 2 1
F
ΔE_ES=0.224eV
ΔE_ES=0eV
Grain Boundary
θ_n
0
w_eff<20
n

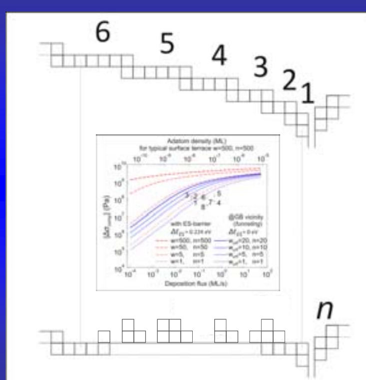

the final result
best fit: w_eff=5
⇨ only last 3 terraces show funneling
|Δσ_comp| (Pa)
Deposition flux (ML/s)
with ES-barrier
ΔE_ES = 0.224 eV
w=500, n=500
w=50, n=50
w=5, n=5
w=1, n=1
@GB vicinity
(funneling)
ΔE_ES = 0 eV
w_eff=20, n=20
w_eff=10, n=10
w_eff=5, n=5
w_eff=1, n=1

Roughening instead of Step Flow Growth

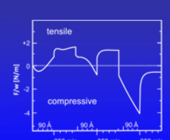


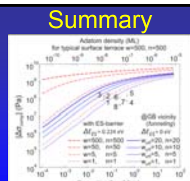
Kinetic Monte Carlo Simulation of Film Growth:
with courtesy of Vladimir Kaganer, Paul-Drude-Institut für Festkörperelektronik
(see also https://www.youtube.com/watch?v=NsGRKSV8yH8)

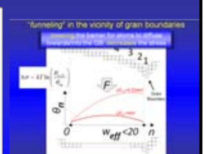
Roughening instead of Step Flow Growth



Summary







A.Saedi & M.J. Rost,
Nature Communication 2016

huge stress
entropic effect

~ 150 MPa
~ 0.1 ML/s