Metal-film formation studied with IR spectroscopy

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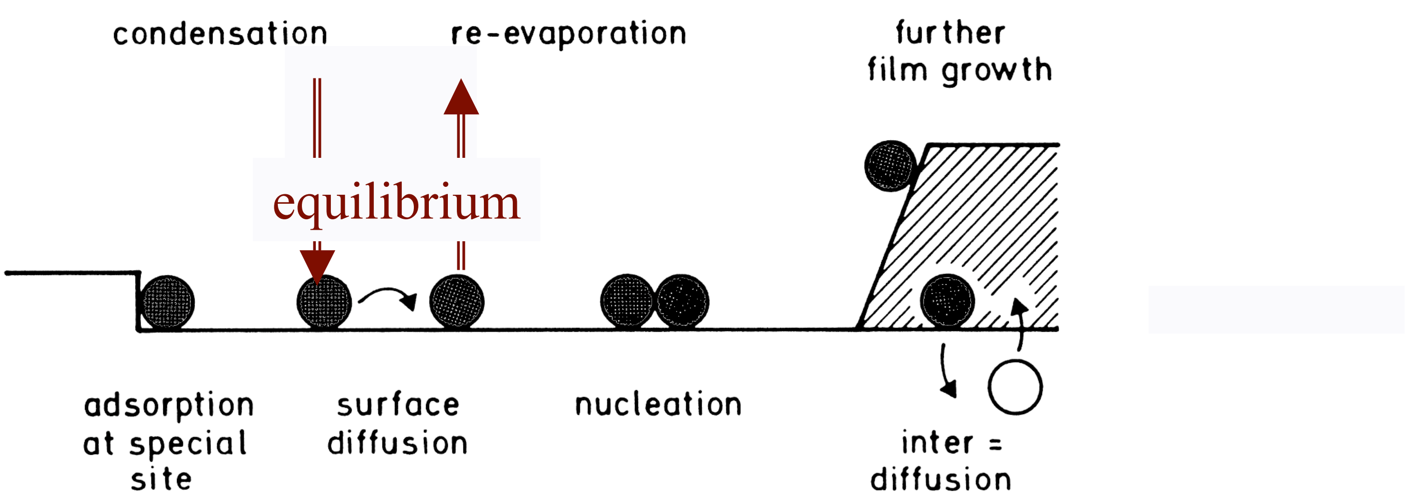
1. Film-growth basics
2. Our experimental set up and what we measure
3. IRS of metal films
4. SEIRA and AFM as additional probes

Film-growth basics

Equilibrium phenomena are described by **thermodynamics**. An equilibrium effect is the vapor pressure of a crystal. However, in film growth the rate of change of metastable structures is dominant; **kinetics** is important.

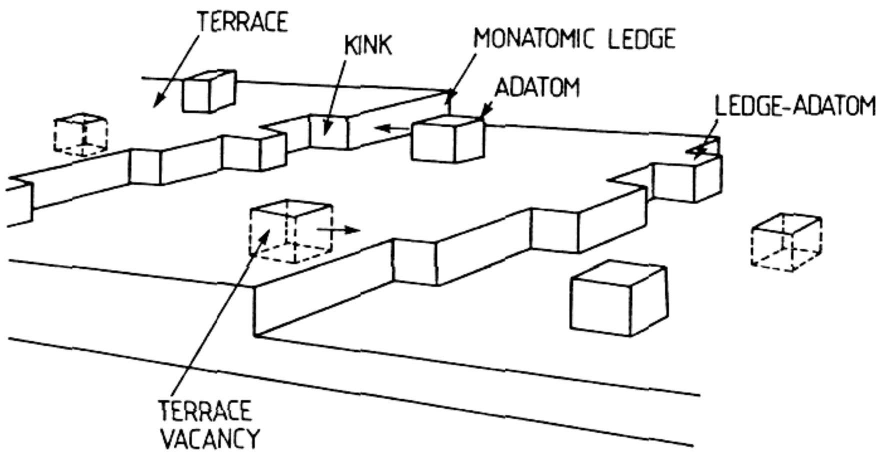


Schematic representation of atomic processes involved in film growth on a solid substrate. Film atoms shown as dark circles, substrate atom as open circle

Film-growth basics

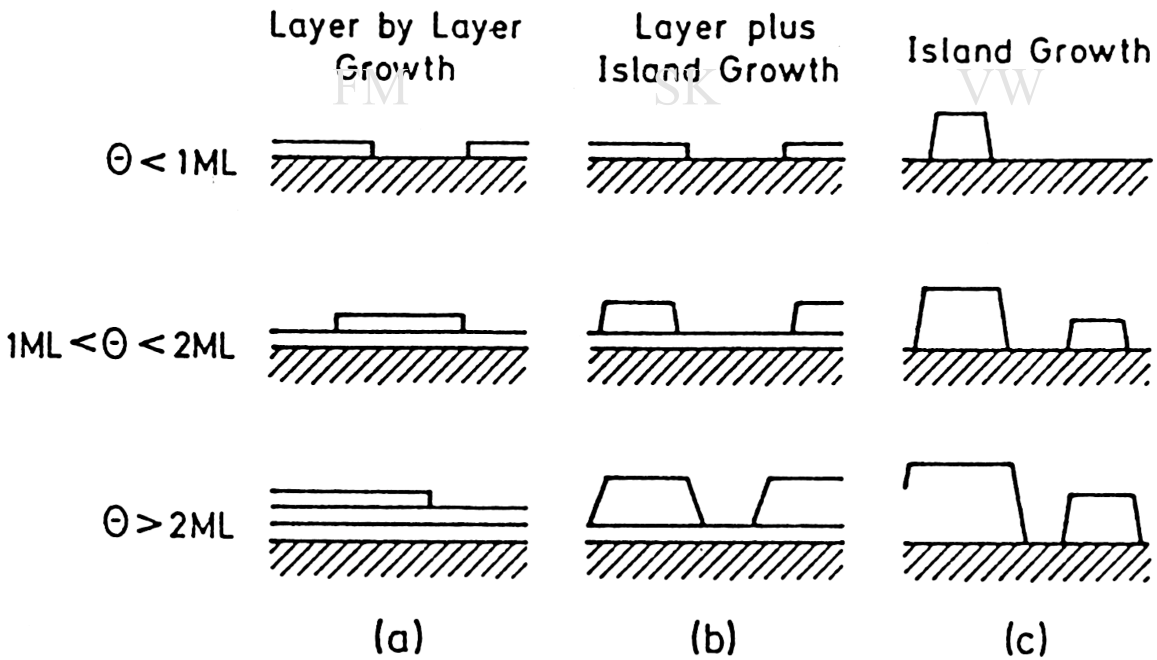
Kinetics of crystal growth

We have to consider the presence of defects!



Schematic drawing of various defects that may occur on a solid surface

Film-growth basics



Schematic representation of the three important growth modes of a film for different coverage (θ) regimes (ML means monolayer). **(a)** Layer-by-layer growth (Frank-von der Merve, FM). **(b)** Layer-plus island growth (Stranski-Krastanov, SK). **(c)** Island growth (Vollmer-Weber, VW)

Growth modes, only close to equilibrium determined by surface and interface energy.

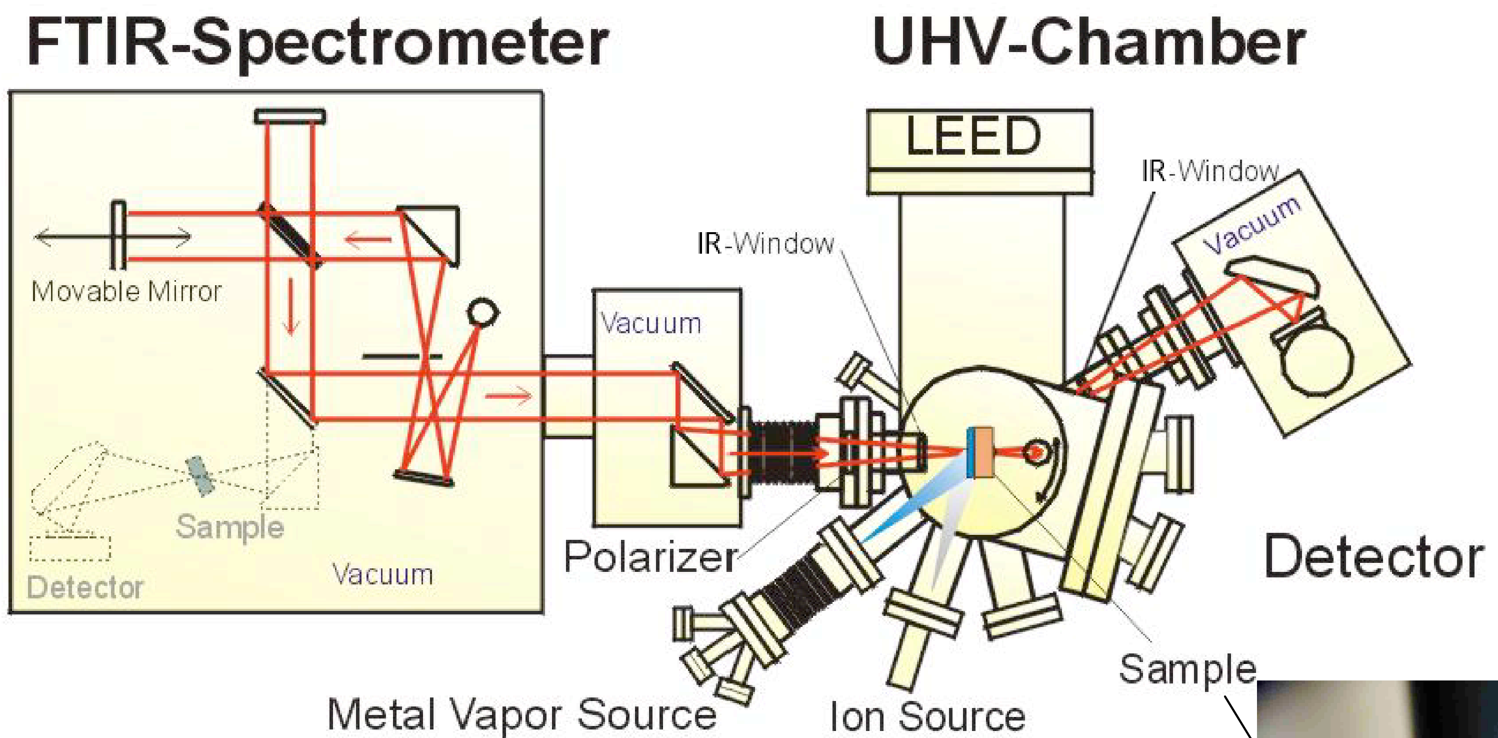
Film-growth basics

Film growth is a non-equilibrium process =>

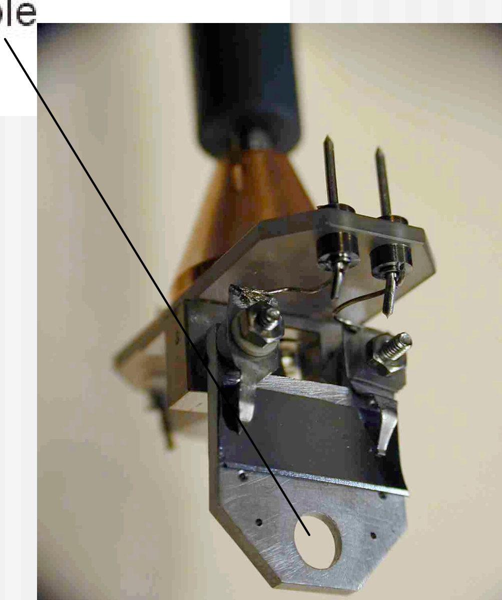
- Dependent on several preparation conditions a film can be “trapped” in a variety of equilibrium conditions.
- This allows control of morphology by intelligent manipulation of deposition parameters (pressure*, temperature, substrate structure, radiation, additional gases,..)
- However, one must recognize that a non-equilibrium structure is always prone to rearrangement.
- **Understanding the mechanisms and kinetics of growth and rearrangement is necessary to be successful in achieving a sufficiently stable well-defined structure.**

*Rate versus diffusion constant has a great effect!

Our experimental set up ...



surface preparation	cleavage, heating, sputtering
accessible sample temperatures	40 K to 1300 K
evaporation rates (by quartz microbalance)	0.1 to 0.4 nm/min
base pressure	$< 2\cdot10^{-10}$ mbar



Sample holder for Si substrates

. . . and what we measure

Dielectric function for free electrons in a 3D metal

$$\varepsilon(\omega)-\varepsilon_{\infty}=\frac{\mathrm{i}\sigma_{\mathrm{st}}}{\varepsilon_0\omega(1-\mathrm{i}\omega\tau)}=-\frac{ne^2}{m^*}\frac{1}{\varepsilon_0\left(\mathrm{i}\omega/\tau+\omega^2\right)}$$

squared plasma frequency follows from band structure

$$=-\frac{\omega_{\mathrm{p}}^2}{\left(\mathrm{i}\omega/\tau+\omega^2\right)}$$

Drude-type dielectric function

… and what we measure

- Mostly transmittance at normal incidence
- For ultrathin films $\left(d \ll \lambda / n_{\text{film}}\right)$

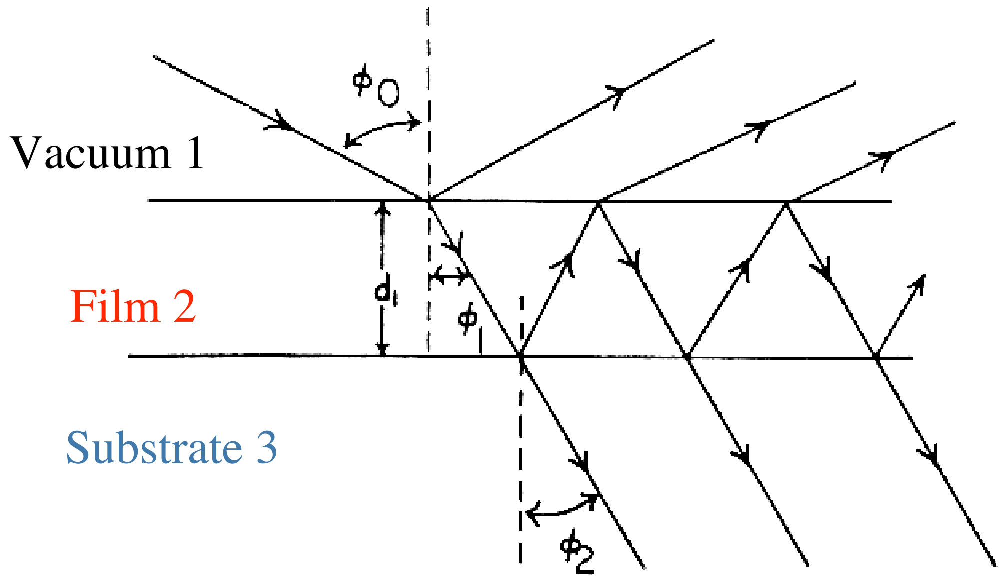
relative transmittance

$$\frac{T_{\text{film/substrate}}}{T_{\text{substrate}}} \approx 1 - \frac{2 \cdot d \cdot \omega \cdot \mathrm{Im}\,\varepsilon_{\text{II film}}(\omega)}{c \cdot (1 + n_{\text{substrate}})},$$

$$\varepsilon_{\text{film}} - \varepsilon_{\infty} = \frac{i\sigma(\omega)}{\omega\varepsilon_0}$$

$\Rightarrow$ Conductivity measurement without electrical contacts

… and what we measure

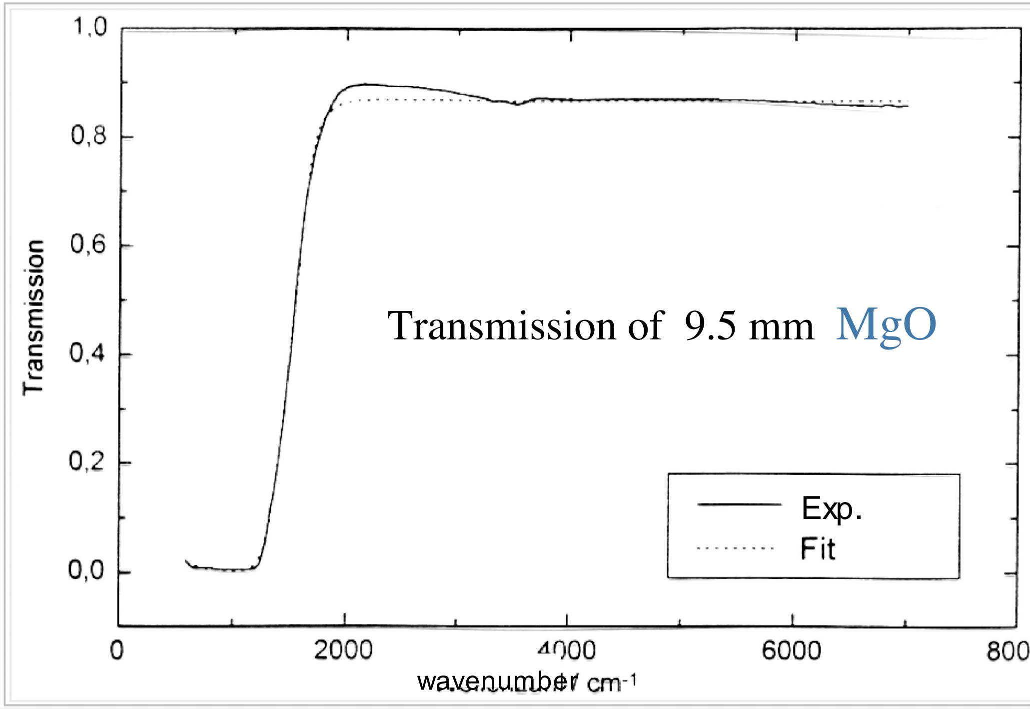


Local optics of layer systems including interferences

$$t_{123} = \frac{t_{12} \cdot t_{23} \cdot e^{-i2\pi \frac{d}{\lambda}\sqrt{\varepsilon_2}}}{1 + r_{12} \cdot r_{23} \cdot e^{-i4\pi \frac{d}{\lambda}\sqrt{\varepsilon_2}}}$$

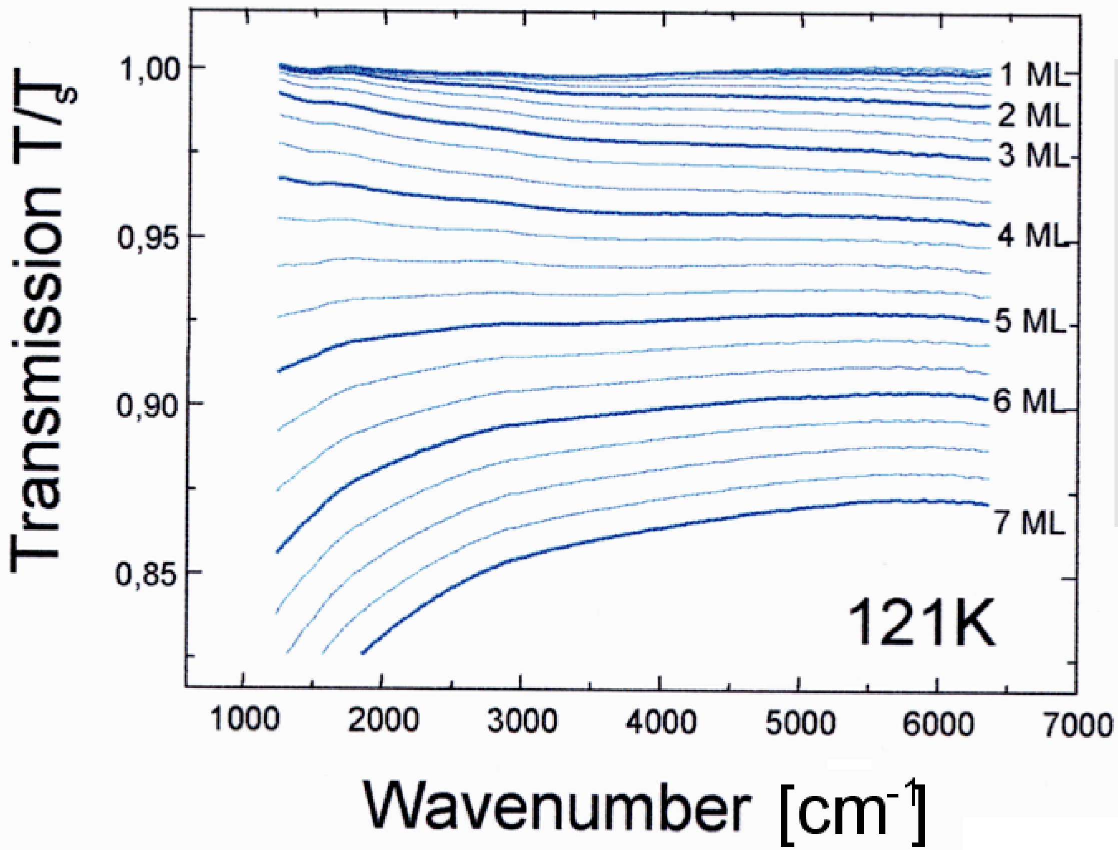
Limited transmittance of a typical ionic crystal substrate

Reference example



IRS of metal films

Layer growth on a cold substrate - submonolayer sensitivity



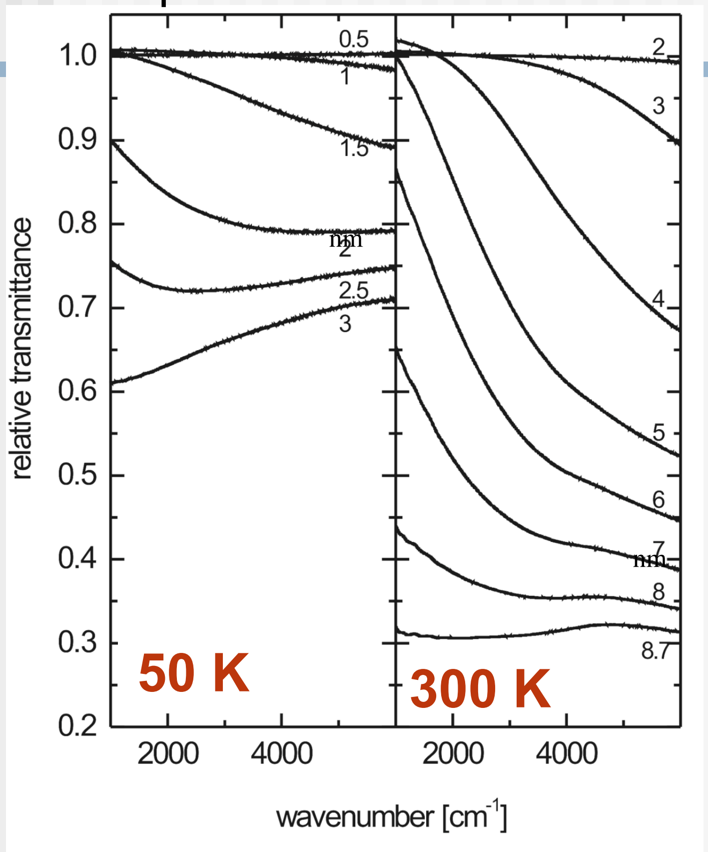
Relative IR transmittance of **Fe** layers on **MgO(001)**, normal incidence of light, deposition and spectroscopy at 121K

G. Fahsold, A. Bartel, O.Krauth, and A. Lehmann, Surface Science **433-435,** 162 (1999)

IRS of metal films

role of mean fee path

IR spectra of **Cu island films** up to percolation



Mean free path of diffusing adatoms $l \approx (D/R)^{1/6}$
with ratio of diffusion "constant" *D* to deposition rate *R*
(mean-field assumption, only isolated atoms mobile on the surface, pre-exponential factors omitted)

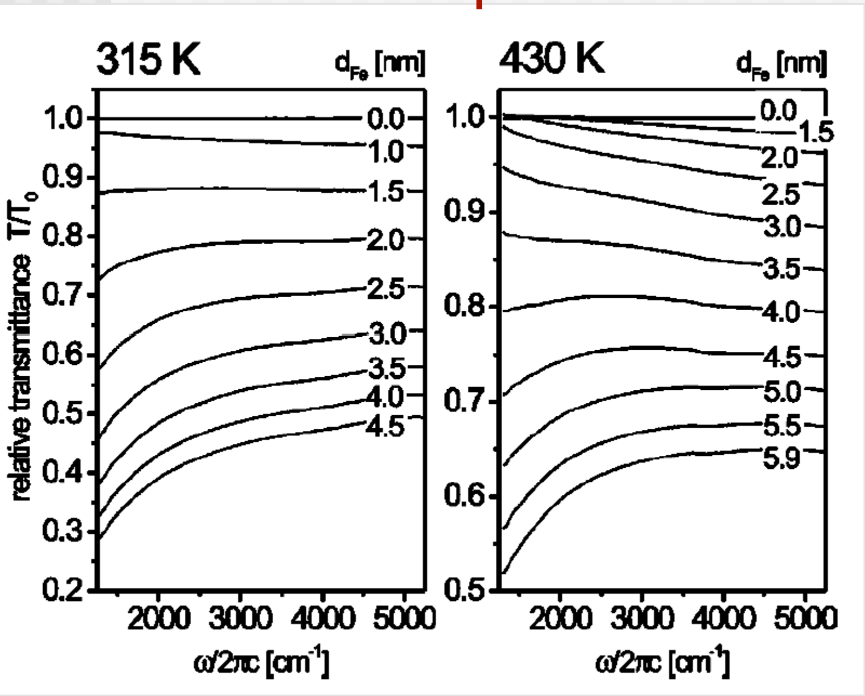
H. Brune, Surf. Sci. Reports 1998

- At 50 K islands with atomically rough surface are formed.

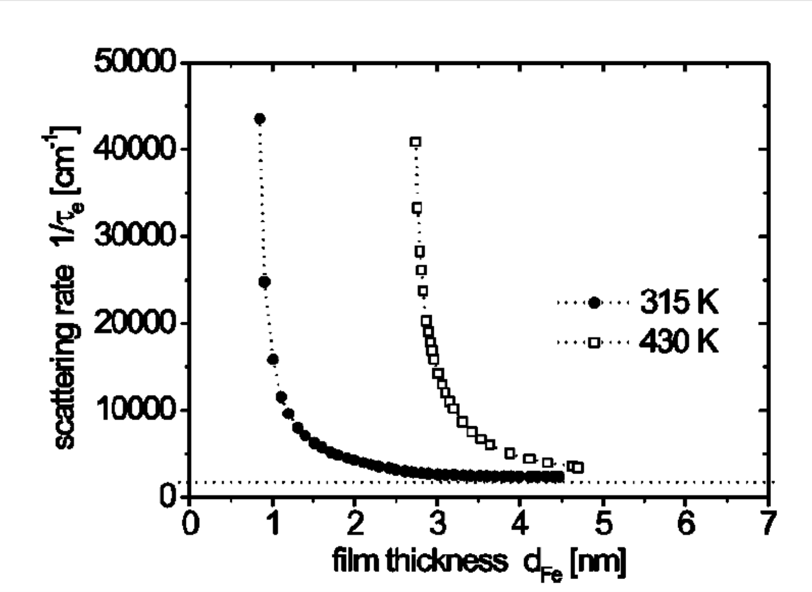
$$\frac{l(50K)}{l(300K)} \approx \begin{cases} 10^{-7} & \text{Cu on Cu with } E_D \approx 0.5\text{eV} \\ 0.2 & \text{Cu on KBr, } E_D \approx 0.05\text{eV assumed (value for Ag on MgO)} \end{cases}$$

IRS of metal films

islands and percolation



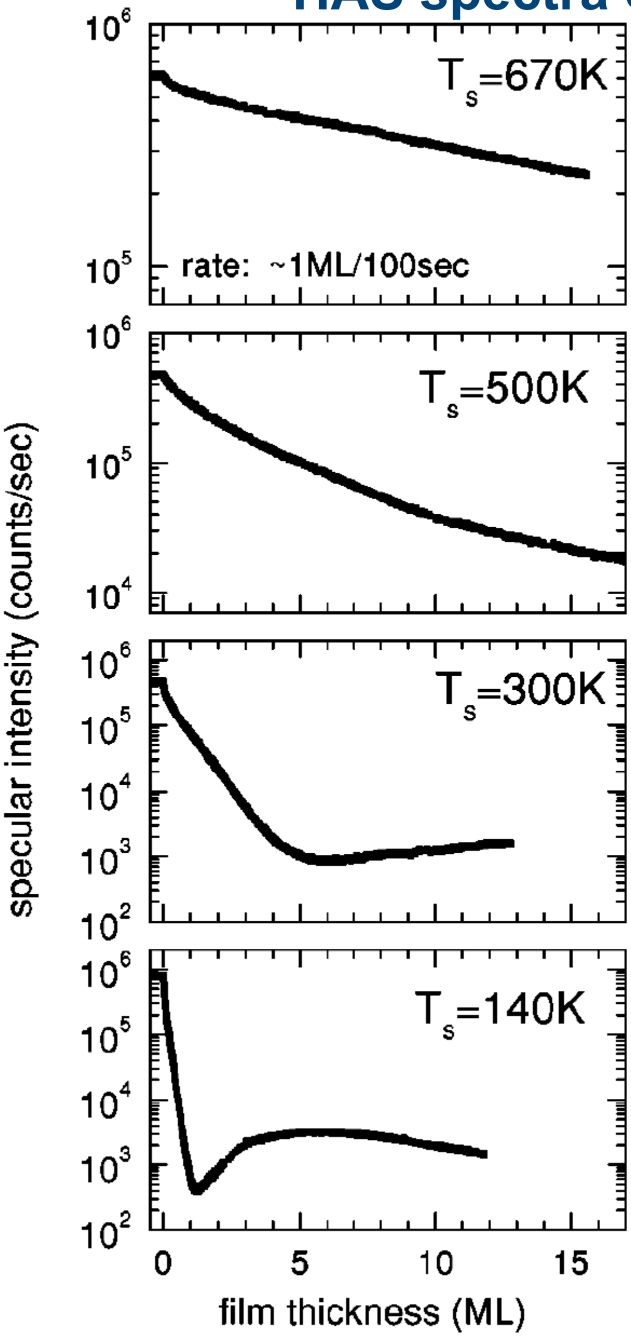
Fe on MgO(001):
IR and scattering rates



- At the percolation threshold the breakdown of the Drude-type model is indicated by the huge increase of the average scattering rate.

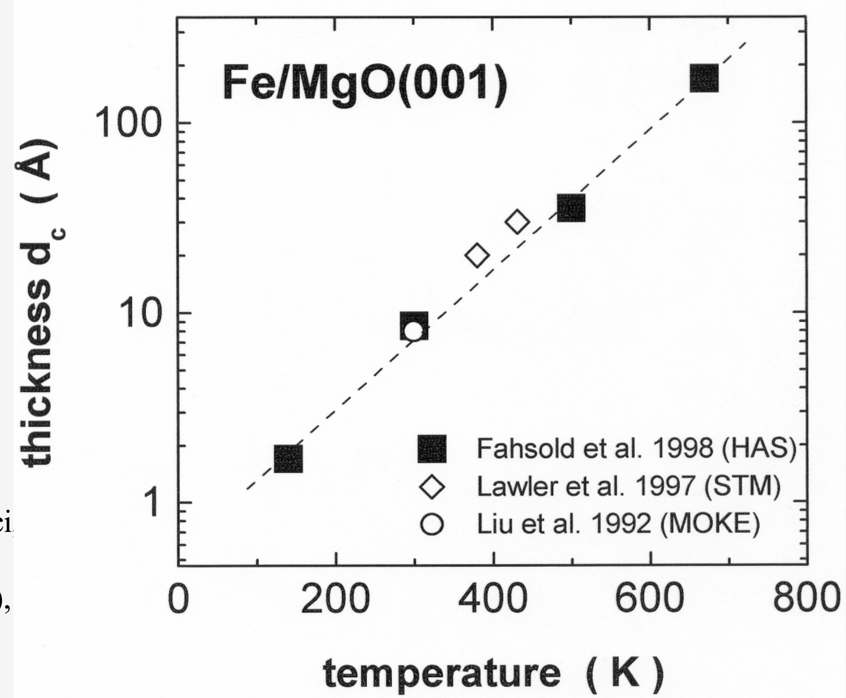
O. Krauth, G. Fahsold, N. Magg, and A. Pucci, J. of Chemical Physics **113** (2000) , 6330

HAS spectra of Fe/MgO(001) for comparison



Development of specular intensity *I* with average Fe thickness *d* on MgO(001) at different temperatures.
1ML thickness means 1.33 Å.

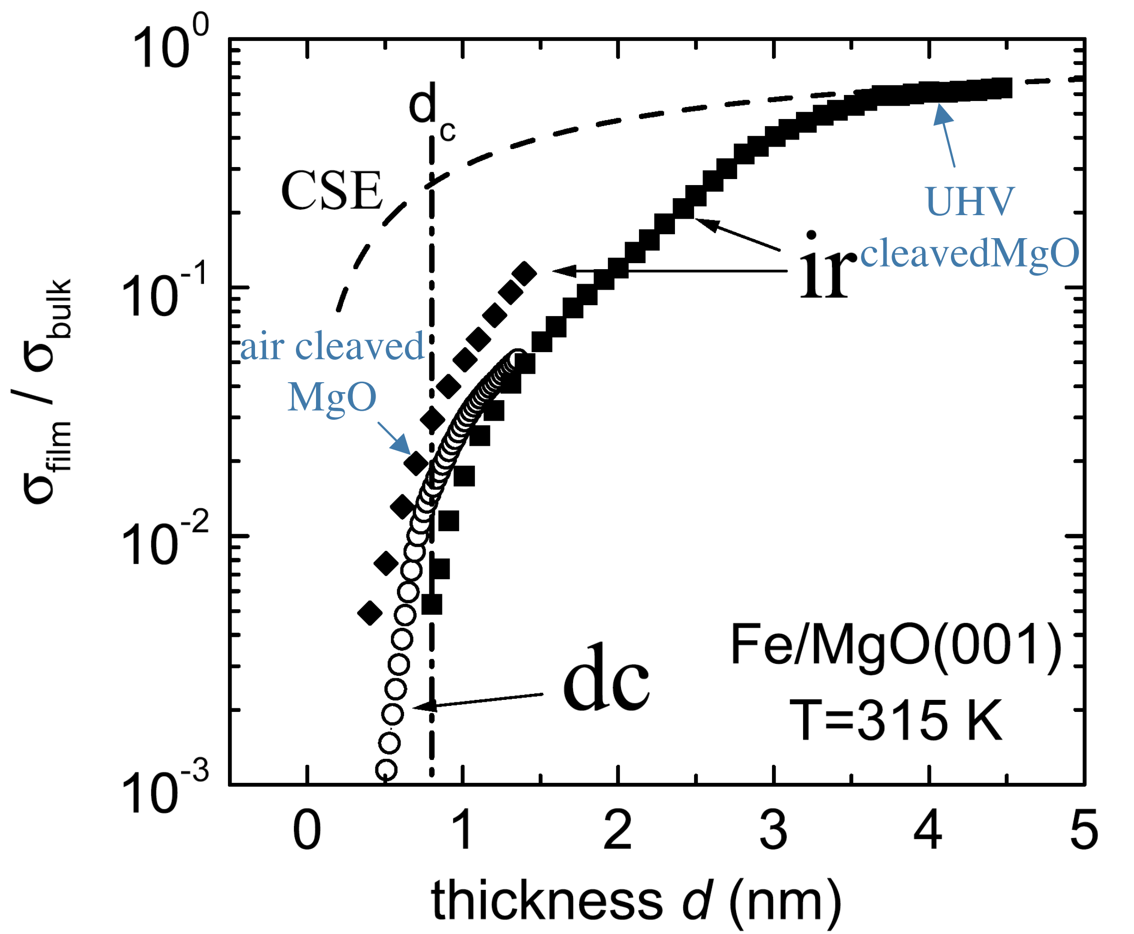
- The average thickness d_c for complete coverage of MgO with islands gives the maximum roughness and the minimum specular intensity ≅ percolation threshold



Fahsold, Pucci, Rieder, PRB61(2000), 4875.

IRS of metal films

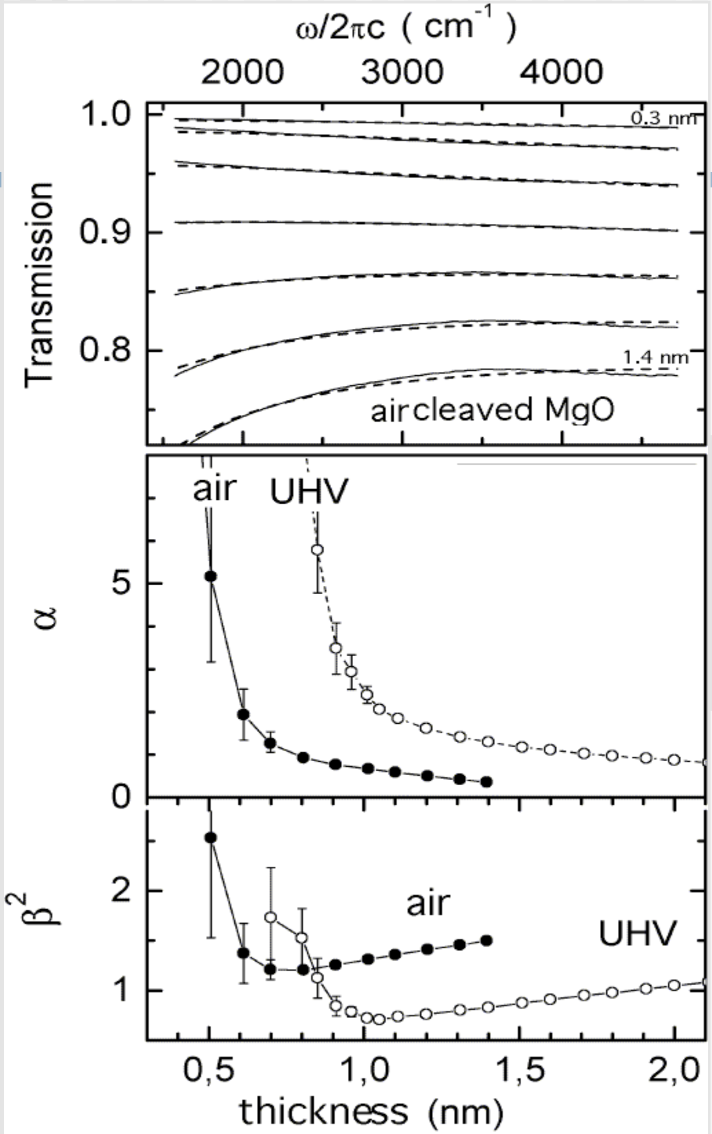
comparison of IR and dc data



G. Fahsold, A.Priebe, N. Magg, A. Pucci, Thin Solid Films **428** (2003) 107.

Conductivity of **iron films on MgO(001)**, experimental data (circles and squares) and calculation for smooth films with CSE (broken line). At the thickness d_c percolation of the island-like films on UHV cleaved MgO(001) starts.

IRS of metal films



role of substrate surface

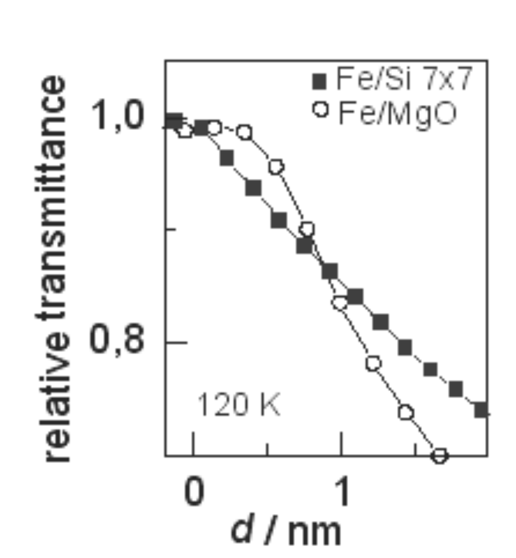
Fe/MgO at 300K

- Lowering of the percolation threshold due to increased density of nucleation centers at the MgO surface cleaved in air

G. Fahsold, A. Priebe and A. Pucci, Appl. Phys. **A 73**, 39 (2001)

IRS of metal films

Initial transmittance change in dependence on substrate surface



Relative IR transmittance versus average thickness for **Fe on two different surfaces**; initial change of transmittance at 200cm^{-1}.

After 2 Å the MgO(001) surface is completely covered by iron. Above about 4 Å a Drude-type conductivity is found.

- For Fe on Si(111)7x7 at 120K the Drude-type conductivity sets in immediately and the plasma frequency is increased.

$$\frac{\dfrac{T_{\text{film/MgO}}}{T_{\text{MgO}}}-1}{\dfrac{T_{\text{film/Si}}}{T_{\text{Si}}}-1} \approx \frac{\operatorname{Im}\varepsilon_{\text{film on MgO}}}{\operatorname{Im}\varepsilon_{\text{film on Si}}} \cdot \frac{(1+n_{\text{Si}})}{(1+n_{\text{MgO}})}$$

... AFM as additional probe...

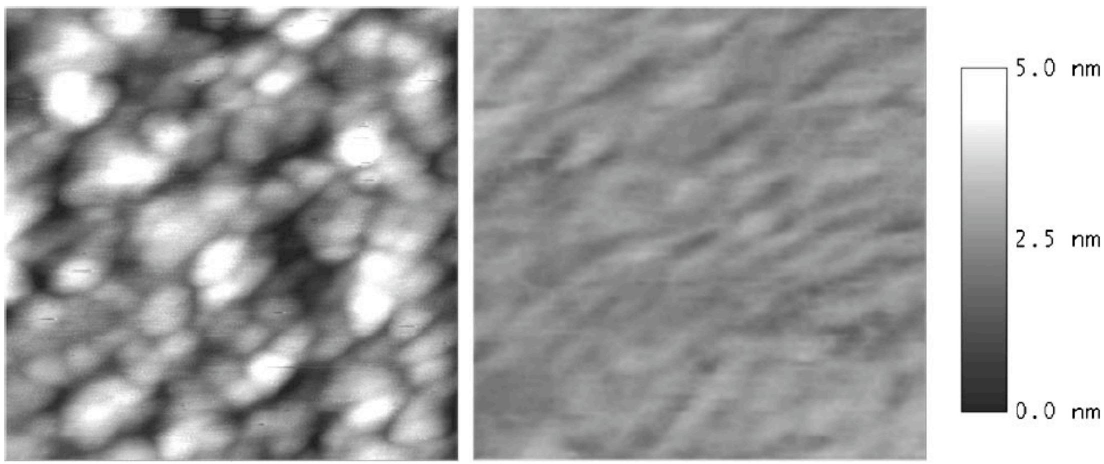


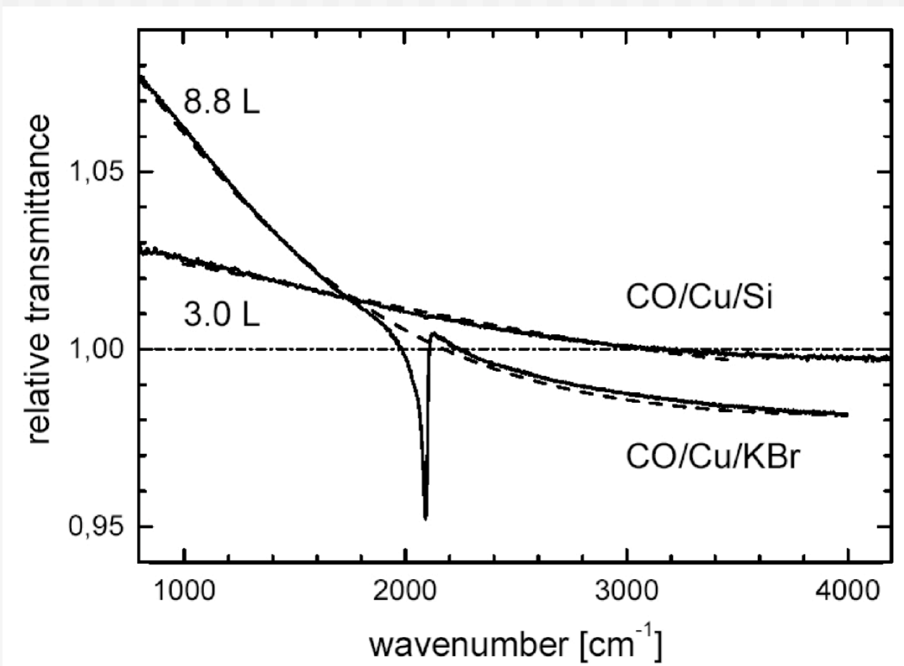
FIG. 5. AFM images of mesoscopically rough Cu films on KBr(001) (left) and of smooth Cu films on Si(111)[II] (right). Film thickness is 5.5 nm for both films. Imaging is done in air at room temperature, scan size is 200 nm × 200 nm. Both films are grown at 100 K.

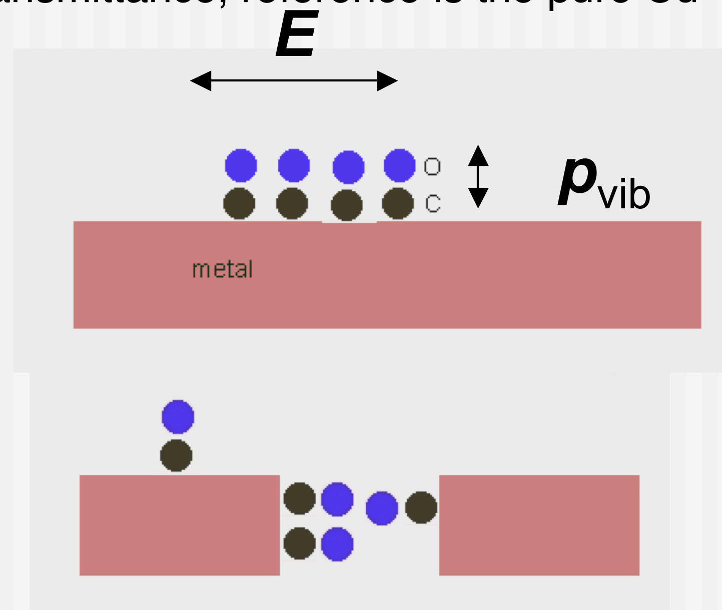
The pictures were taken at room temperature ex situ. Therefore, the first monolayers on the cold-deposited films are annealed. From IR spectra we deduced a smoothening of facets.

G. Fahsold, M. Sinther, A. Priebe, S. Diez, and A. Pucci, Phys. Rev B 2004

SEIRA .. as additional probe..

- CO adsorption on Cu films at 100K, relative transmittance, reference is the pure Cu film

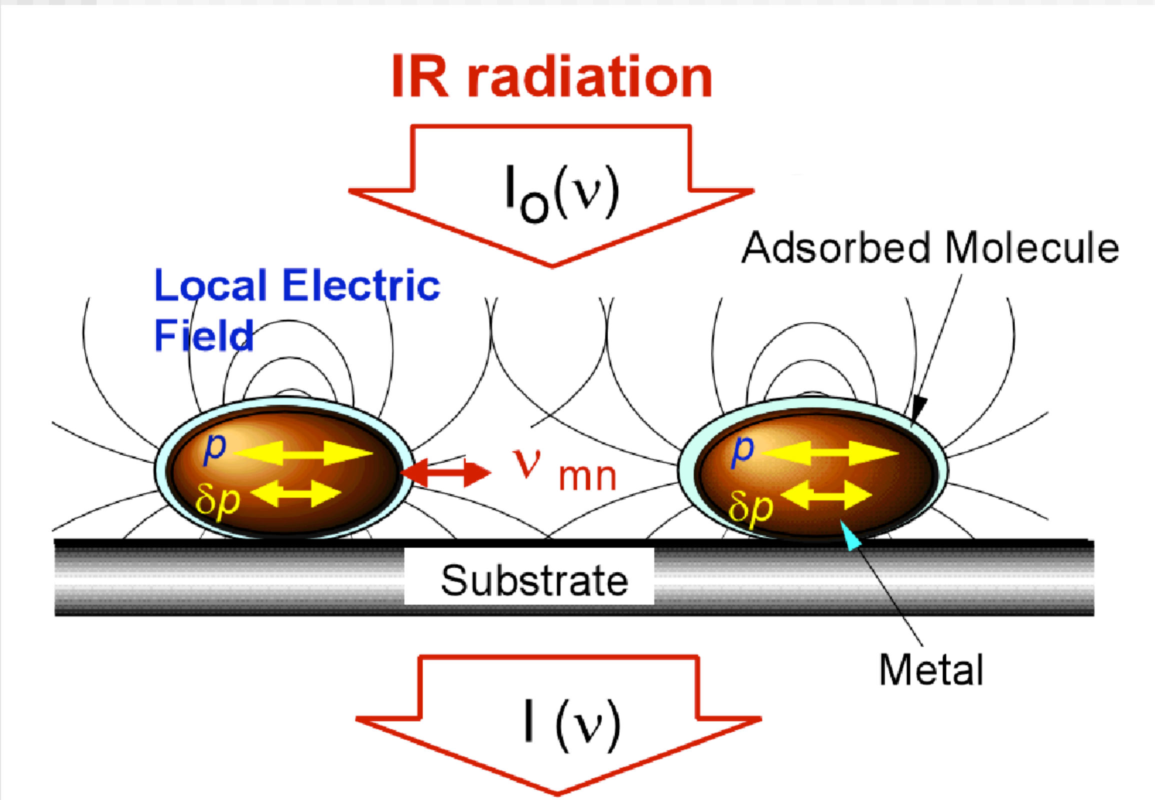


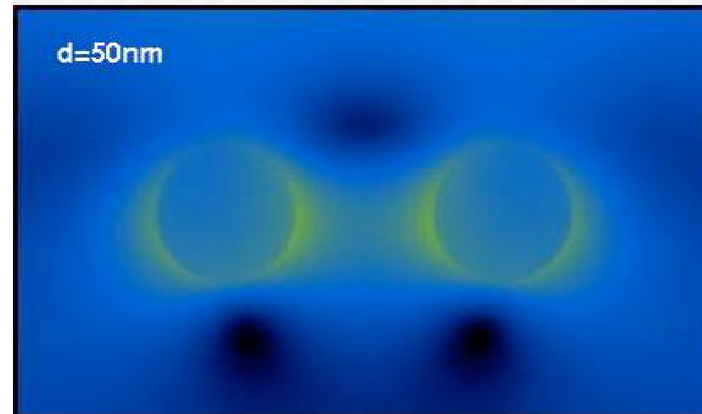


G. Fahsold, M. Sinther, A. Priebe, S. Diez, and A. Pucci, Phys. Rev B **70** (2004) 115406

SEIRA ... as additional probe...

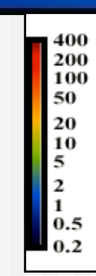
Field enhancement in Surface Enhanced IR Absorption





J.P.Kottmann, O.J.F. Martin, OPTICS EXPRESS 8 (2001) 655

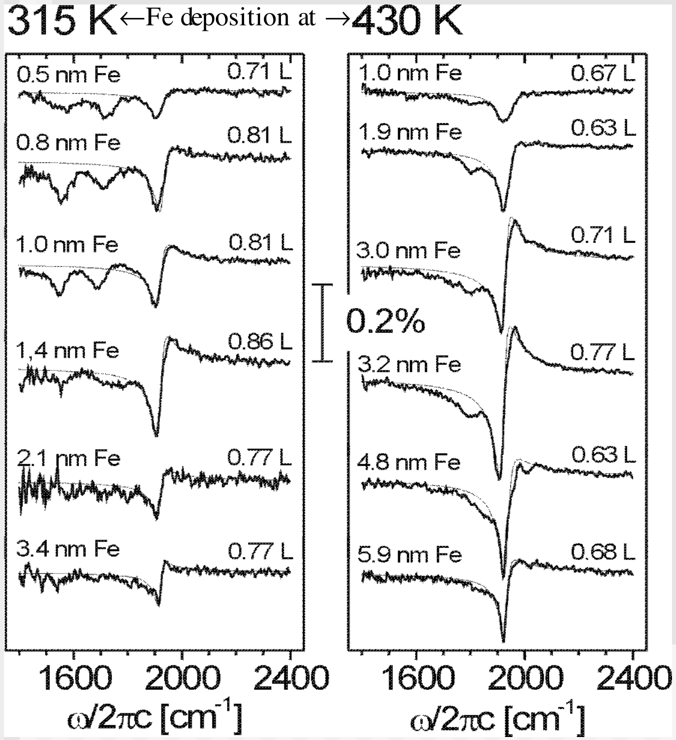
$$\left|\frac{E_{local}}{E_0}\right| \propto \frac{D+d}{d}$$



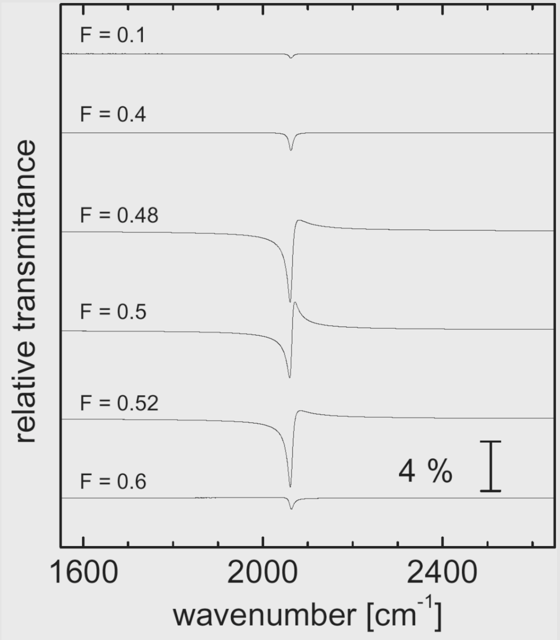
- SEIRA signal from molecules at sidewalls of islands with closest distance

SEIRA ... as additional probe...

- Maximum signal and asymmetry of SEIRA lines for *d* at percolation!
- Orientation of facets from CO-vibration frequency



O. Krauth, G. Fahsold, N. Magg, A. Pucci, J. of. Chem. Phys. **113**, 6330 (2000)

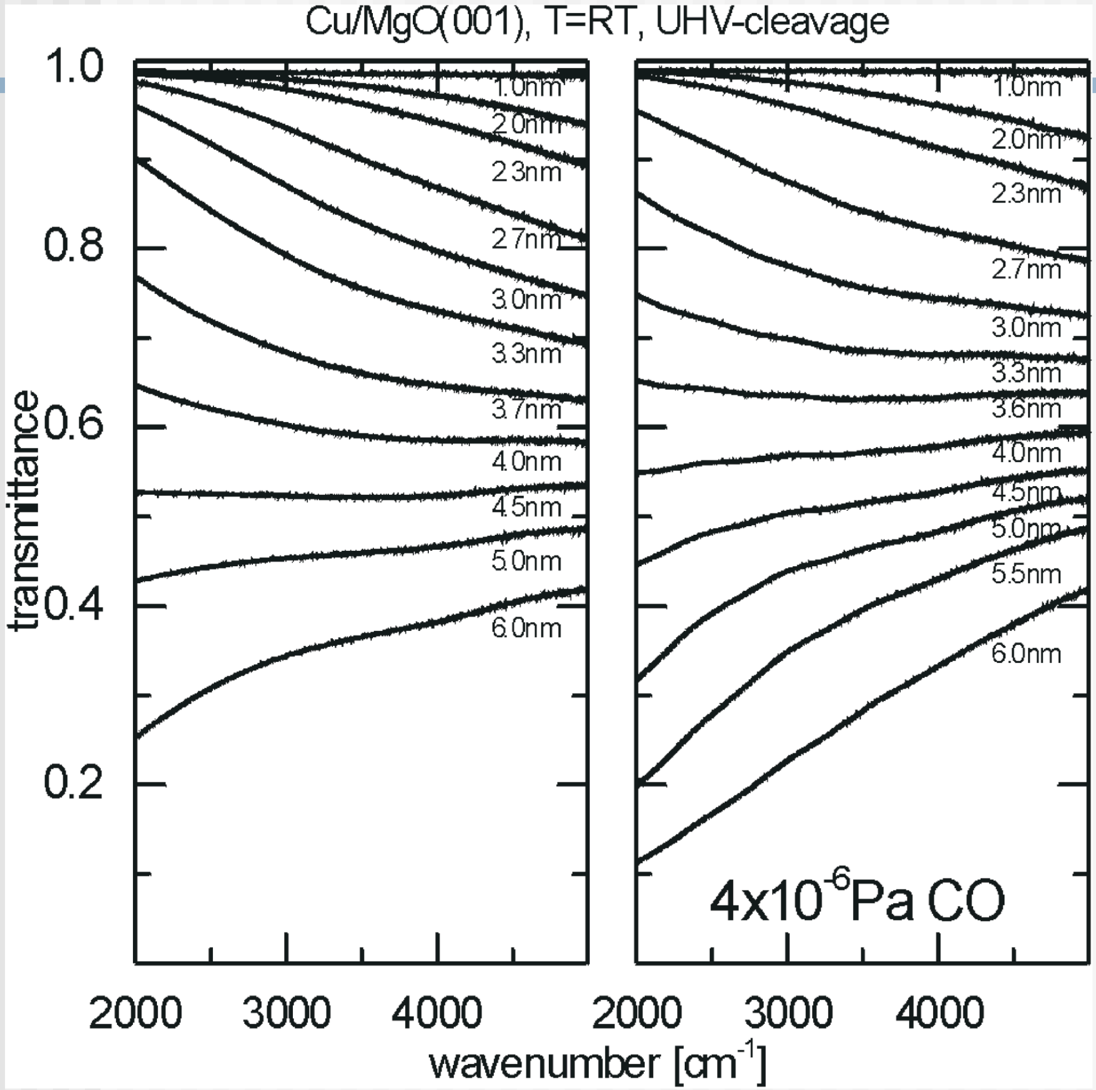


Calculation, 2D Bruggeman, one oscillator, filling factor *F* as parameter

A. Priebe, M. Sinther, G. Fahsold, and A. Pucci, J. of Chemical Physics. **119** (2003) 4887

SEIRA and AFM as additional probes

to study the role of residual pressure, CO as "surfactant"



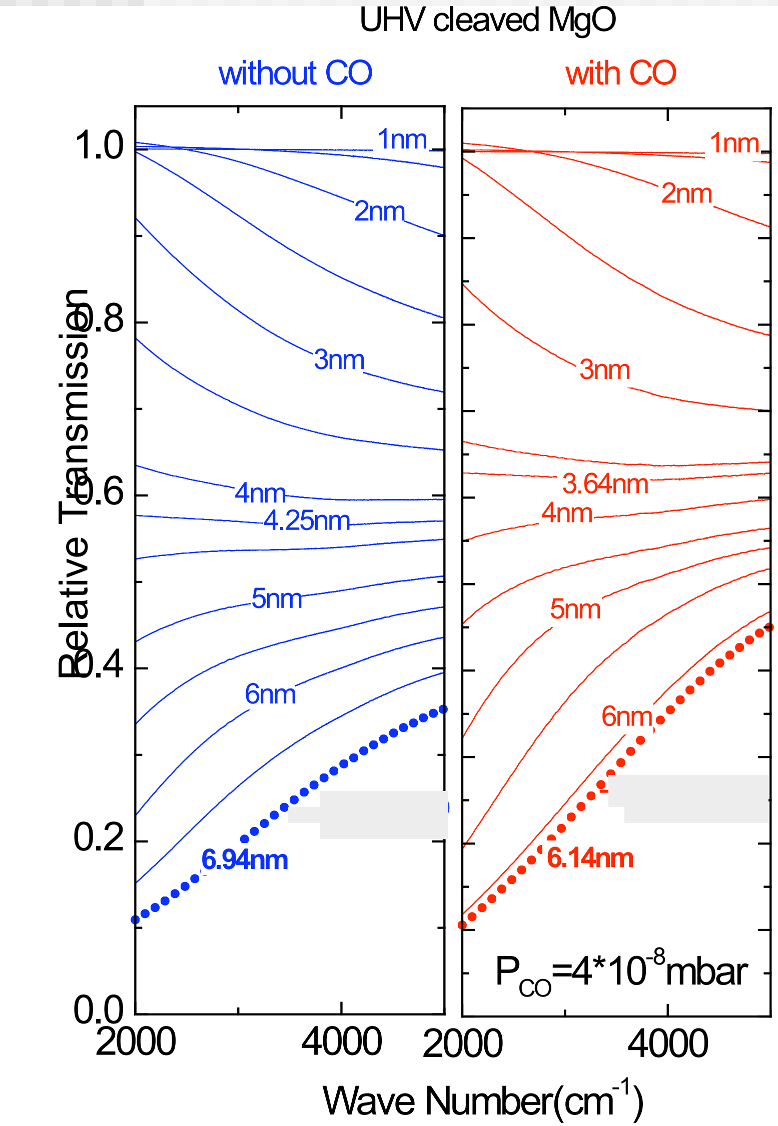
Development of relative IR transmittance during Cu-film growth on UHV cleaved MgO(001),

- effect of CO exposure during growth.

M. Lust, A. Priebe, G. Fahsold, and A. Pucci, Surface and Interface Analysis **33** (2002) 487.

SEIRA and AFM as additional probes

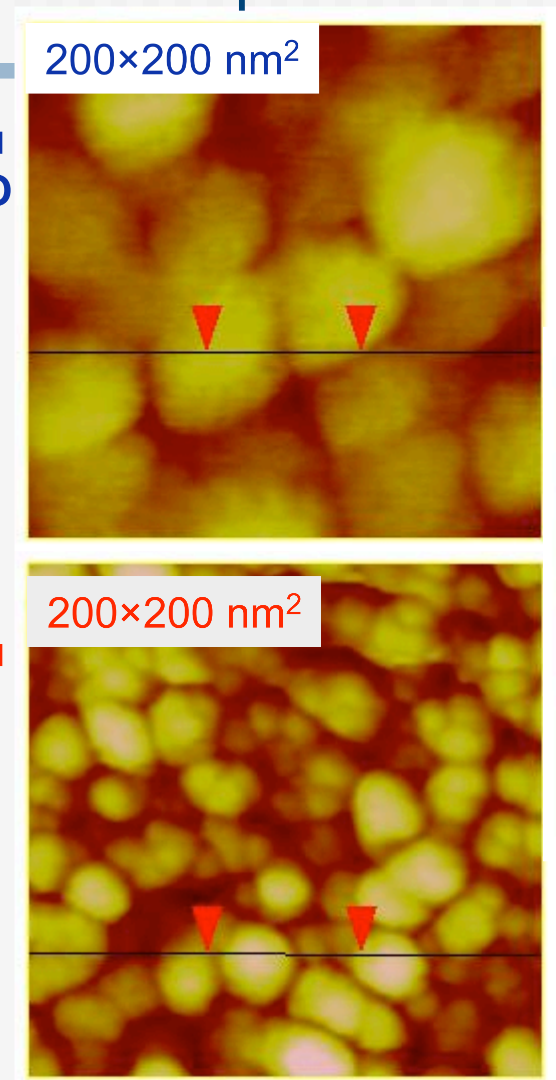
...role of residual pressure, CO as "surfactant"

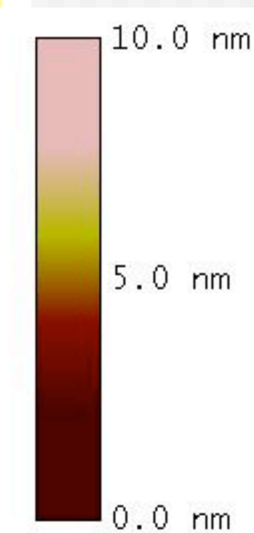


AFM pictures

6.84 nm Cu Without CO

6.14 nm Cu With CO

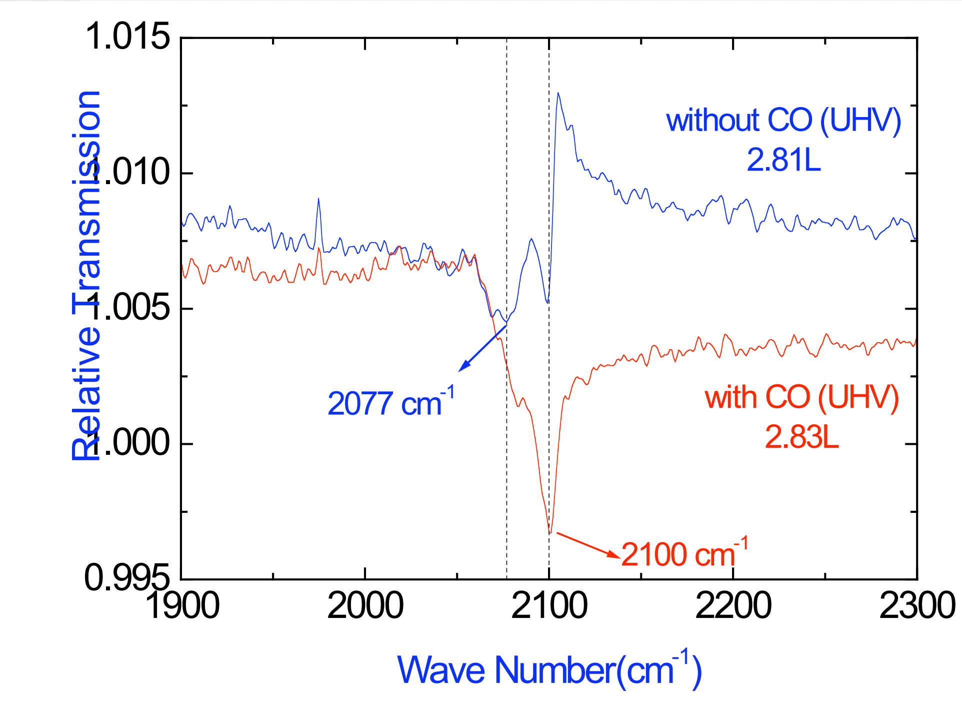




A. Priebe, F. Meng, A. Pucci, Asian J. Phys. 2005, submitted.

SEIRA and AFM as additional probes

...role of residual pressure, CO as "surfactant”, SEIRA spectra



SEIRA spectra of CO on Cu films grown at 300 K on MgO(001), CO saturation exposure, 100 K.

- For smaller Cu islands more IR intensity is transferred to the higher frequency (dipole-dipole interaction for dipoles perpendicular to the array plane)

2077 cm^{-1} ⇔ **CO/Cu (111)**

2100 cm^{-1} ⇔ **CO/Cu (110)**

A. Priebe, F. Meng, A. Pucci, Asian J. Phys. 2005, submitted.

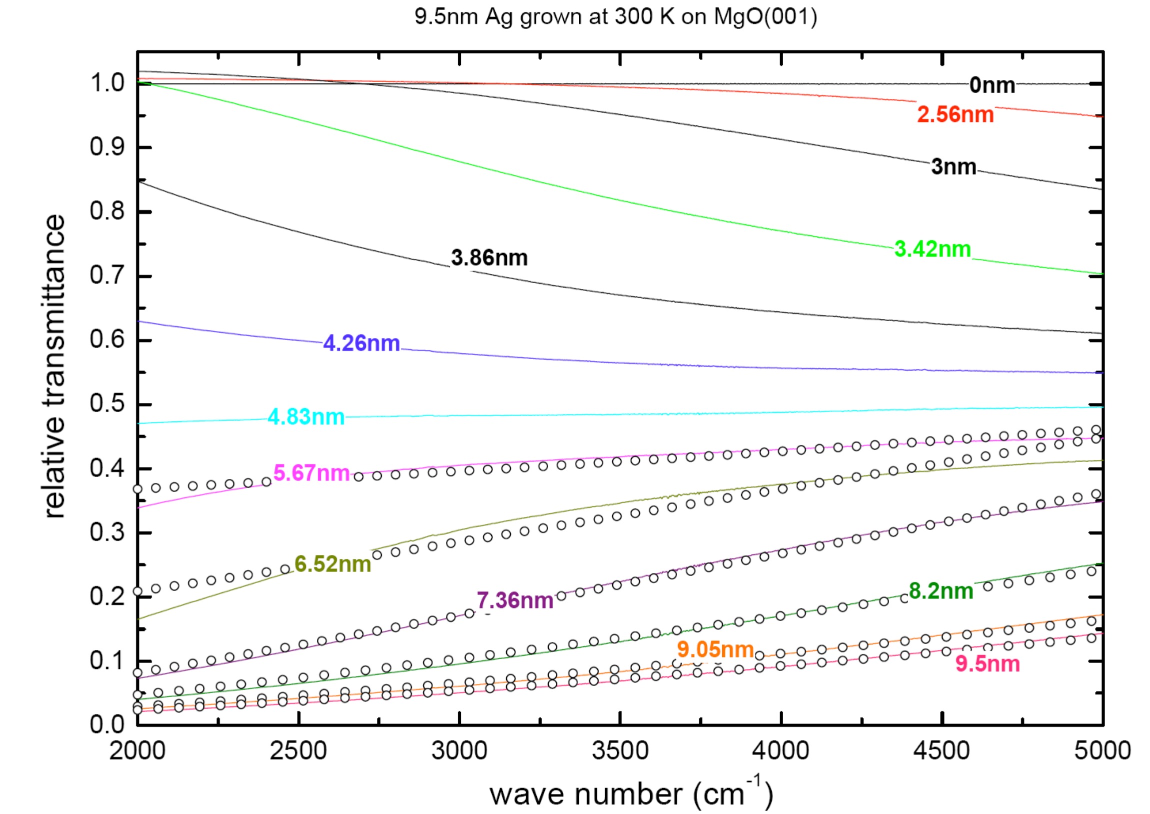
SEIRA and AFM as additional probes

for the study of silver growth on MgO(001)

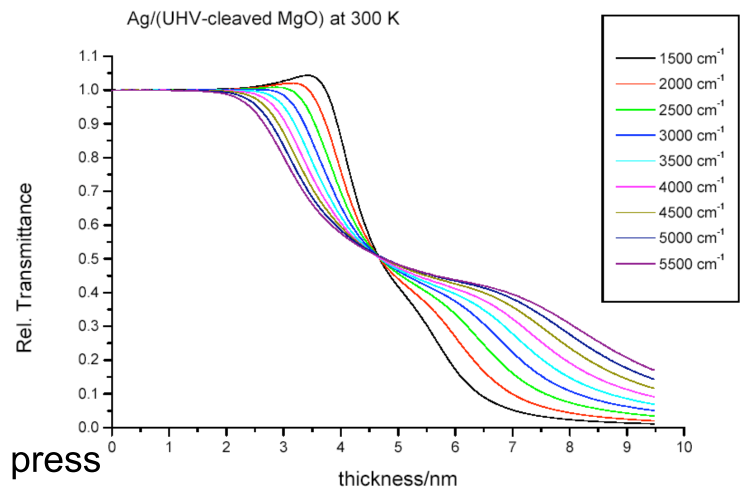
- surface energies of both the materials are about 1-2 J/m^2
- lattice mismatch at 300 K: 2,98 %
- diffusion barriers:
  - Ag on Mg0(001): about 0.05 eV
  - Ag on Ag: about 0.5 eV

SEIRA and AFM as additional probes

...Ag on MgO(001) at 300 K - T/T_0 compared to Drude-type model



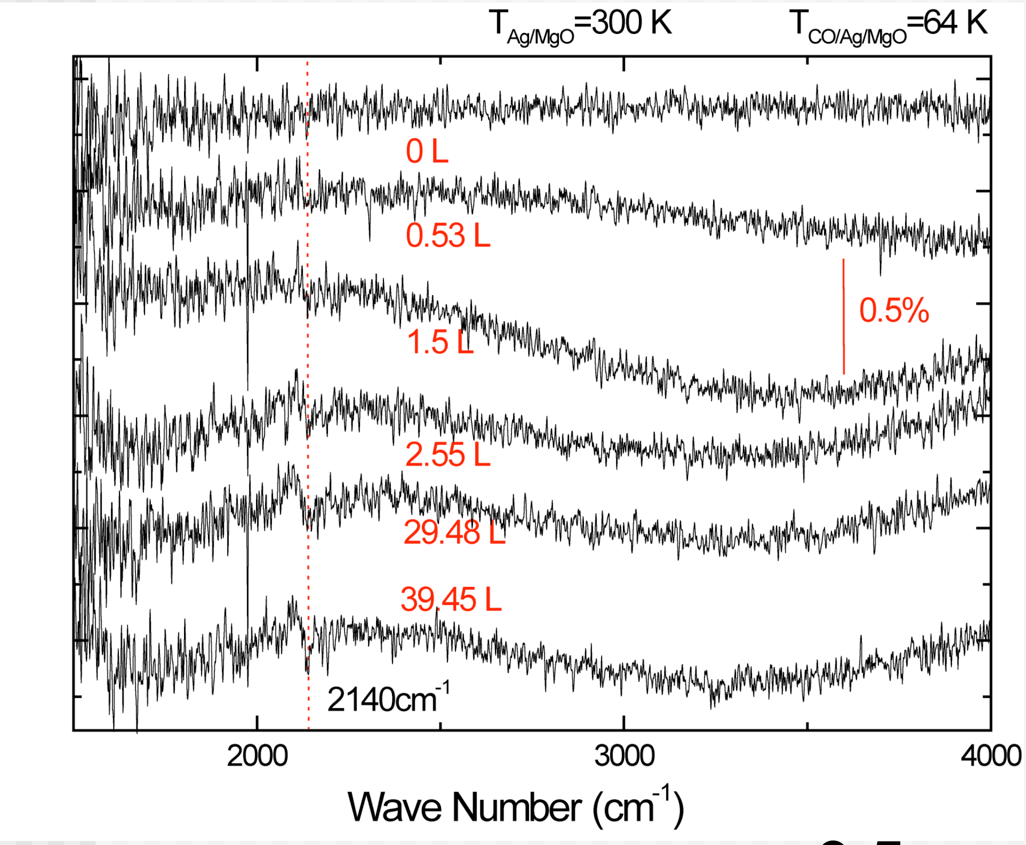
- Silver grows island-like on MgO
- Percolation threshold at about 4.5nm, not changed by CO exposure during growth
- From the Drude-type fit (°) follows that **at about 9 nm the bulk conductivity is reached**



F. Meng, G. Fahsold, A. Pucci, physica status solidi (c) 2005, in press

SEIRA and AFM as additional probes

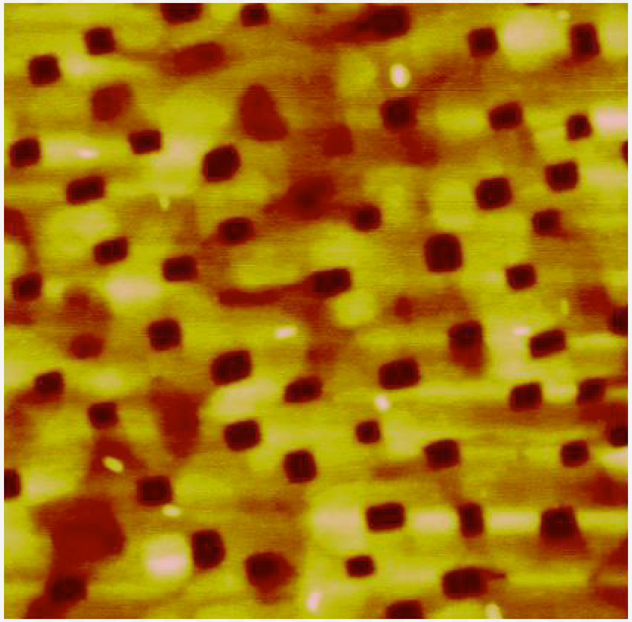
……SEIRA of CO on the 300K-silver film



- Small signal indicates smooth film
- No signal at 100 K detected

9.5 nm Ag

SEIRA and AFM as additional probes
Ag on MgO(100) grown at 300 K - AFM

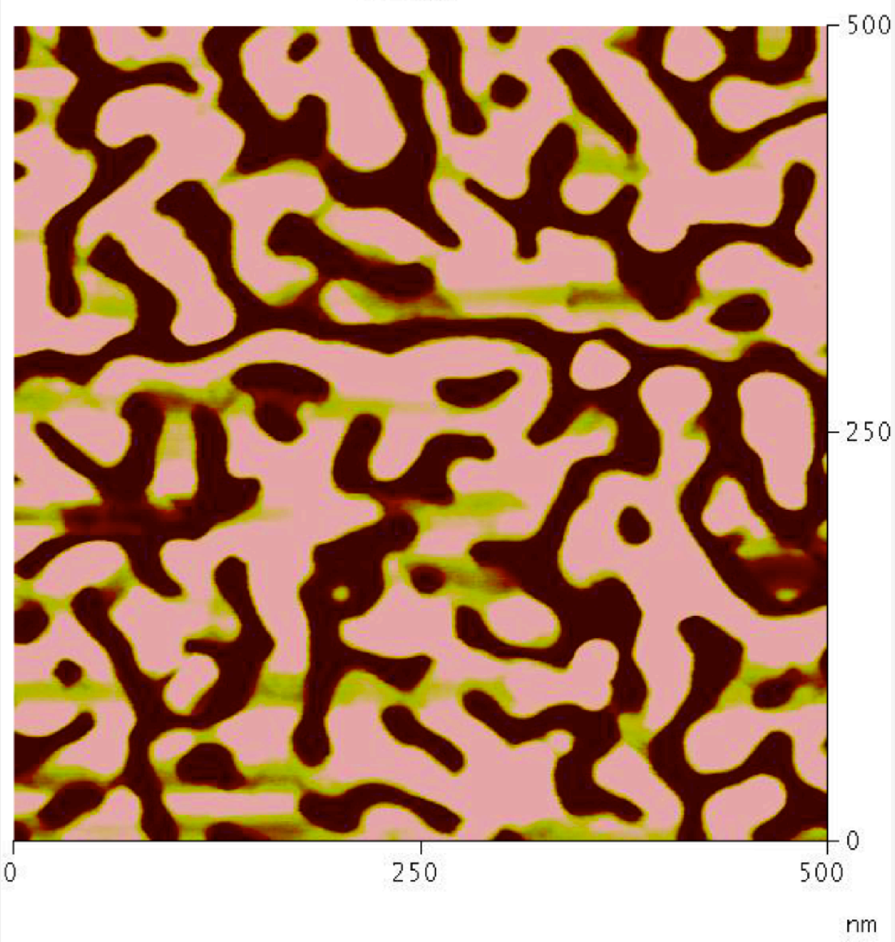


500 nm x 500 nm AFM picture of about 10 nm **Ag on MgO**

F. Meng and D. Seibel, 2004

- Strain is released by the formation of rectangular shallow holes.
- The holes do not disappear at higher Ag coverage
- The holes do not enable SEIRA $\Rightarrow$ too shallow
- Finding corroborates IR transmittance data.

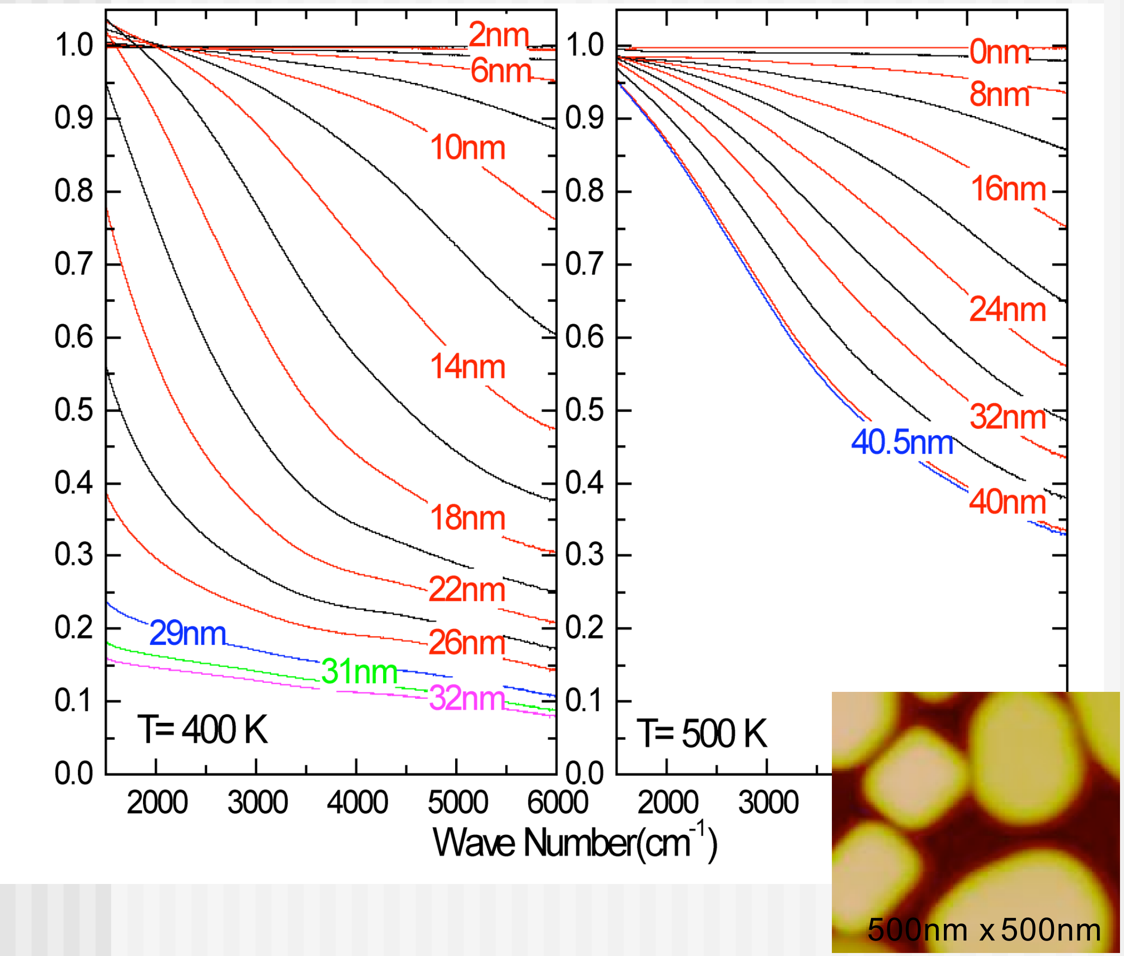
SEIRA and AFM as additional probes
Ag on MgO(001) at 300 K just beyond percolation



- AFM image for 5.3 nm average thickness, 500nmx500nm

... AFM as additional probe..

Ag on Mg0(001) at 400 K and 500 K - IR transmittance *T/T_0*

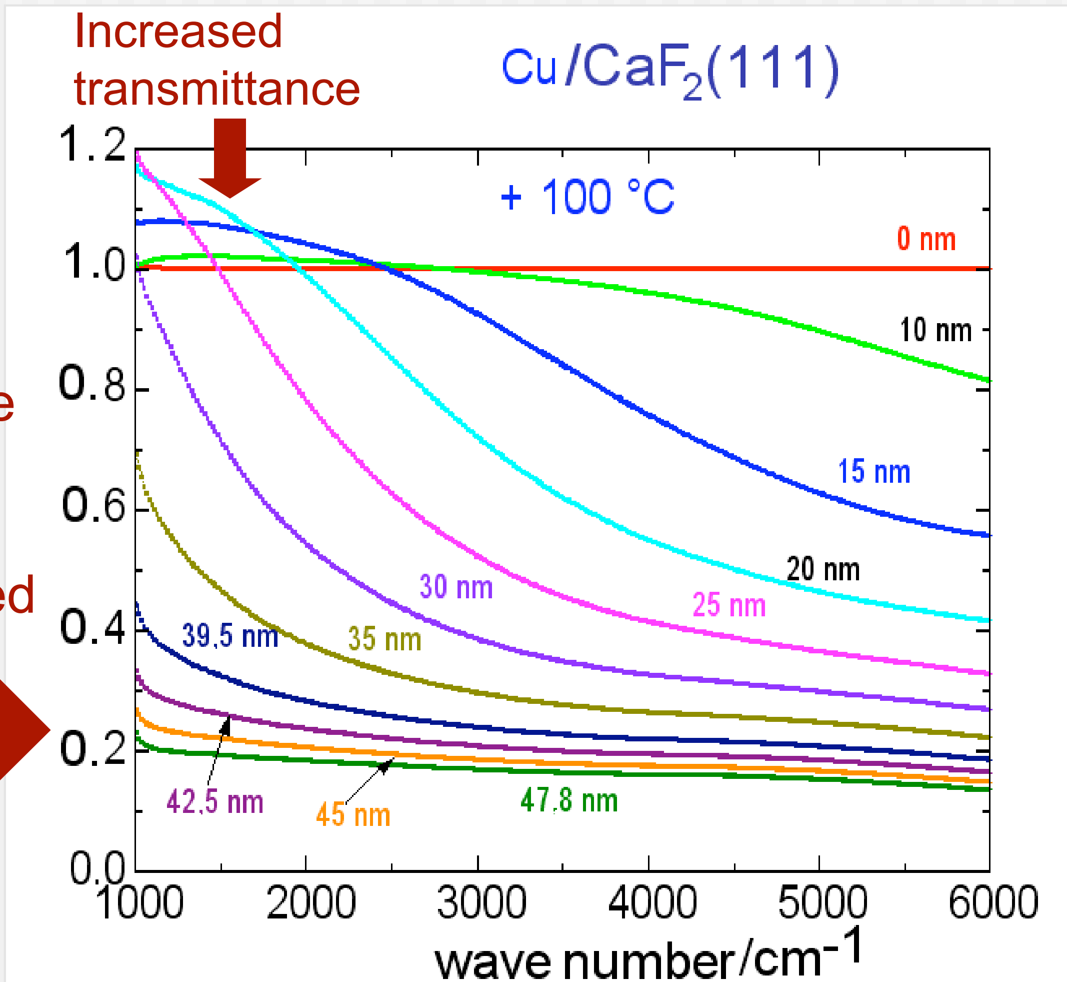


- Extended island growth at higher temperature,
- Thickness given as determined for 300 K, in fact coverage is lower because of reduced sticking of Ag on MgO.
- The films will never become continuous.

F. Meng and D. Seibel, 2004

... AFM as additional probe..

Cu on CaF_2(111) at 100°C - IR transmittance T/T_0

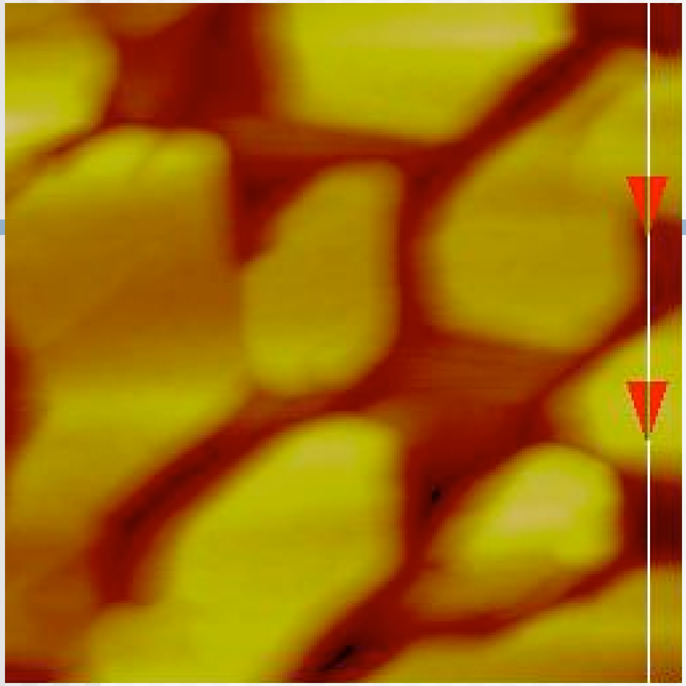


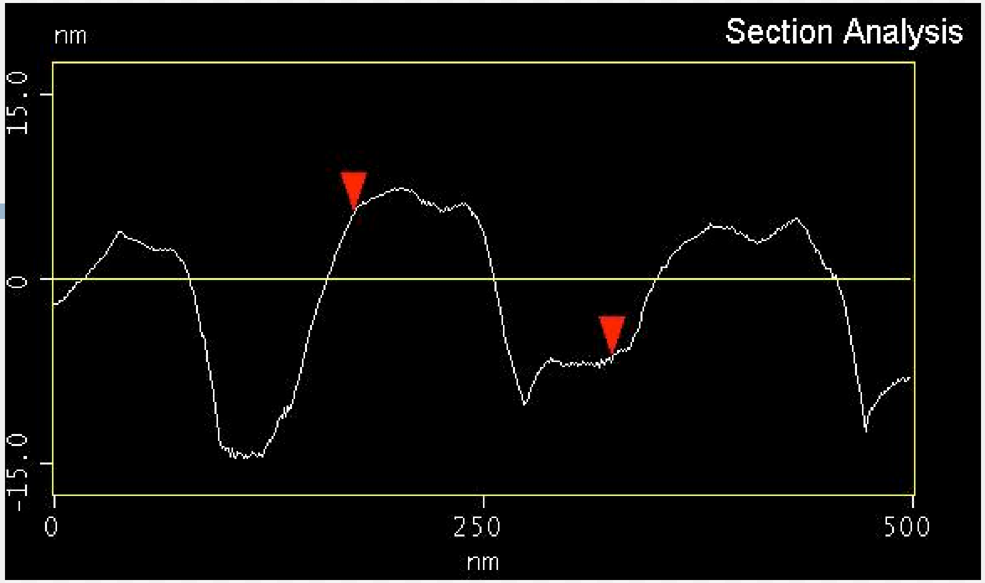
Extreme island growth observed in IRS

Relative transmittance at normal incidence for Cu grown on UHV cleaved CaF_2 at 100°C.

B. Gehring, diploma thesis, Heidelberg 2004

... AFM as additional probe... Cu on CaF_2(111) grown at 100°C





AFM image (500nm x 500nm) and a height scan of about 50 nm Cu deposited onto CaF_2(111) at 100°C

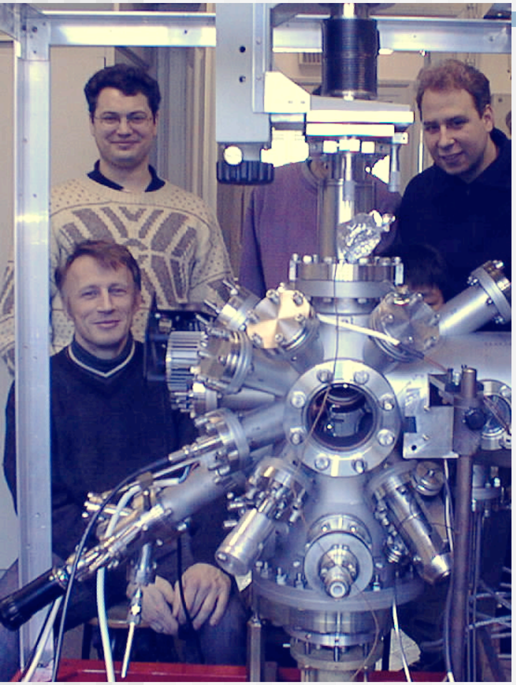
B. Gehring, diploma thesis, Heidelberg 2004

The ES barrier hinders diffusion downwards from the islands.

General conclusions

- IR transmittance spectroscopy enables control of film growth and conductivity information.
- SEIRA and AFM combined give information on film morphology.

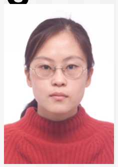
Acknowledgement



G. Fahsold

O. Krauth
A. Priebe
J. Solbrig
M. Sinther
M. Lust

O. Skibbe
D. Enders
T. Kolb
F. Meng



A. Bartel,
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