

Infrared spectroscopic study of chromium film growth on single crystal diamond



Robert Lovrincic and Annemarie Pucci
Kirchhoff-Institut für Physik der Universität Heidelberg



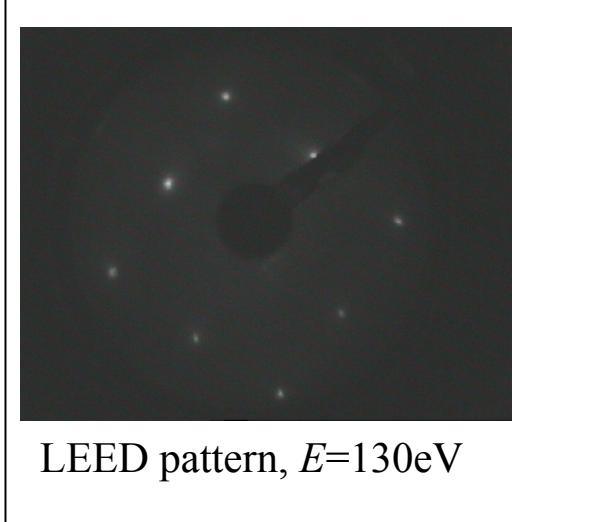
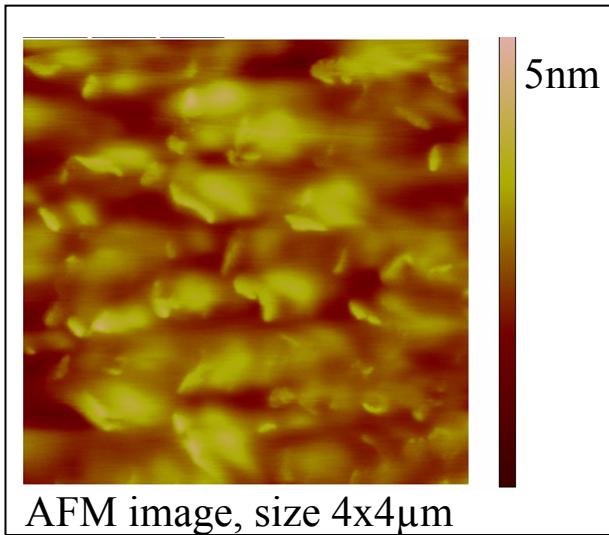
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Outline

- The diamond (100) – Cr interface
- Optical properties of thin metal films in the IR
- Experimental setup
- Experimental results and discussion

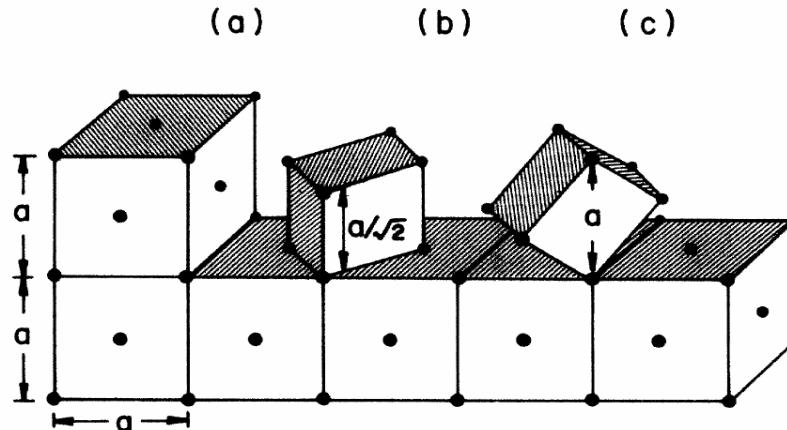
Substrate: Diamond (100)-(1x1)

- Commercial CVD single crystal diamond supplied by Element 6
- Surface: (100), cleaned in boiling $\text{HNO}_3 + \text{H}_2\text{SO}_4 + \text{HClO}_4$ *
- Size: 4.5x4.5x0.5mm³



*according to Yokoba et al., J. Appl. Phys. **81**, 1997

Epitaxial growth of Cr on diamond



Schematic representation of possible epitaxial arrangements of Cr on C(100): (a) (100) fcc Cr; (b) (100) bcc Cr; (c) (110) bcc Cr

Lattice mismatch Cr - diamond:

$$a_{\text{fcc}} = 3.62 \text{ \AA}$$

$$a_{\text{bcc}} = 2.88 \text{ \AA}$$

$$a_{\text{dia}} = 3.57 \text{ \AA}$$

$$a_{\text{dia}}/\sqrt{2} = 2.52 \text{ \AA}$$

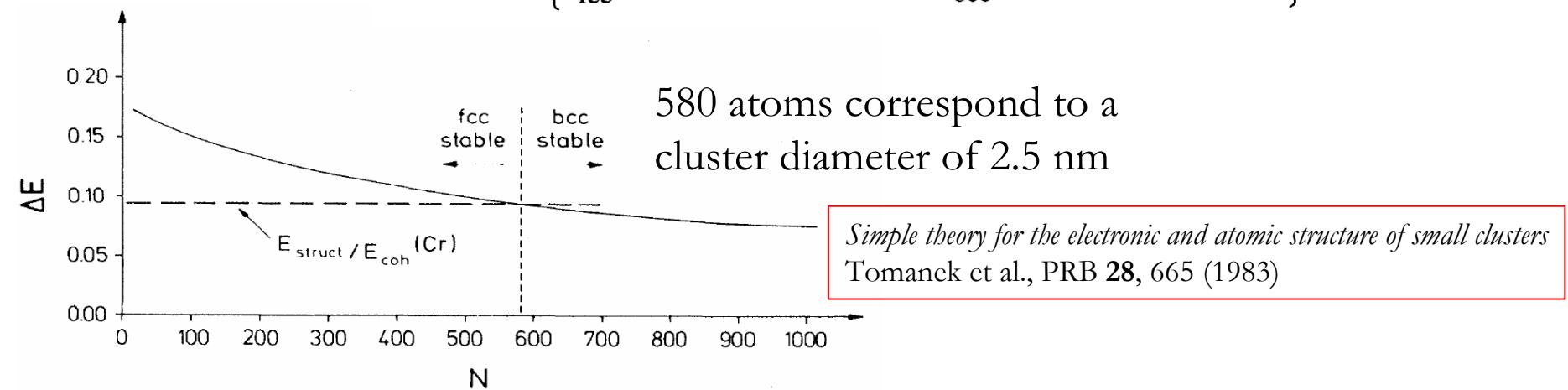
$$\Delta_{\text{fcc}} = 1.4\%$$

$$\Delta_{\text{bcc}} = 14.3\%$$

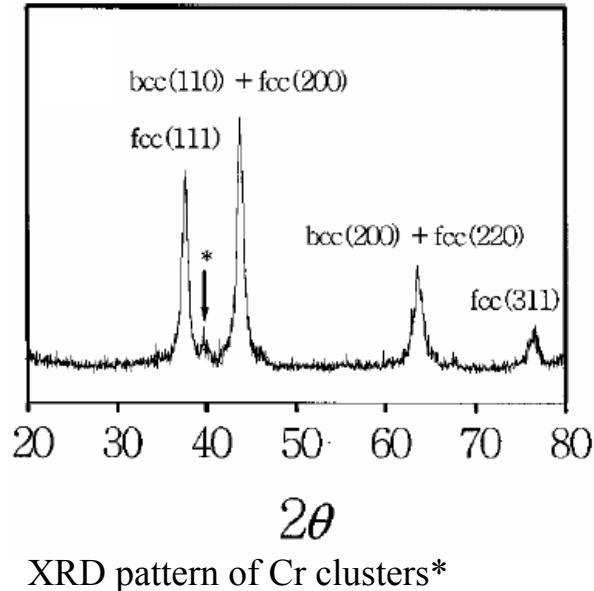
Structural stability of Cr clusters

- Stable fcc phase of Cr clusters due to lower surface energy

$$\frac{E_{coh,b}(\text{bcc}) - E_{coh,b}(\text{fcc})}{E_{coh,b}} = \frac{1}{N} \left[\sum_{\substack{i=1 \\ \text{fcc}}}^{N_s} [(Z_i/Z_b)^{1/2} - 1] - \sum_{\substack{i=1 \\ \text{bcc}}}^{N_s} [(Z_i/Z_b)^{1/2} - 1] \right]$$

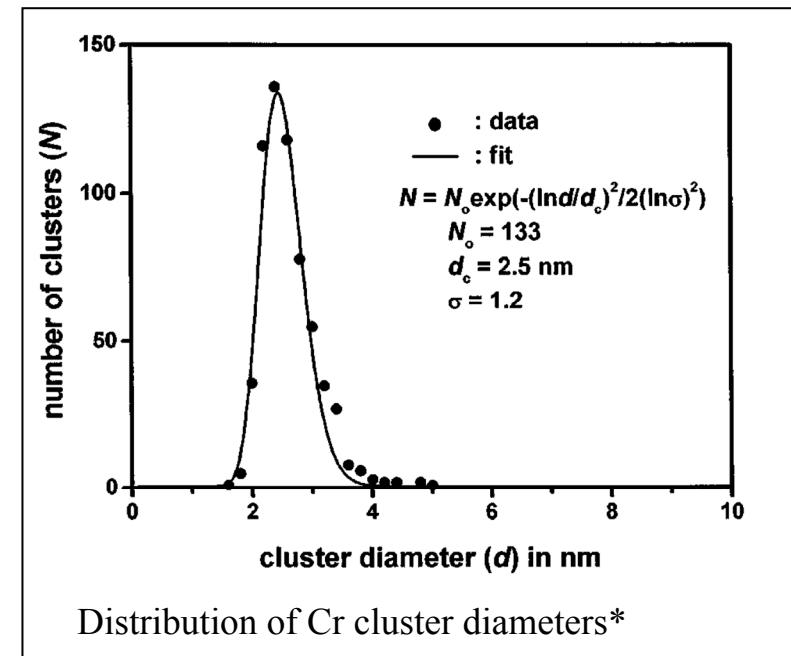


Cr clusters



XRD pattern of Cr clusters*

- A coexistence of fcc and bcc phase can be found for Cr clusters



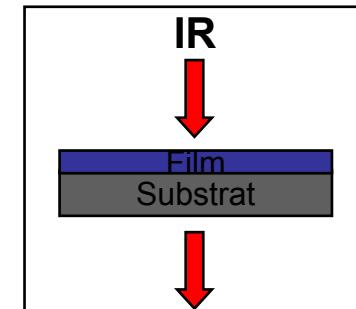
Distribution of Cr cluster diameters*

*Huh et al., Phys. Rev. B **62**, 2937 (2000)

Thin films

- Transmittance at normal incidence for thin films:

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



- Metal films below the onset of interband transitions: $\epsilon(\omega)$ can be described by Drude model
- $\epsilon(\omega)$ connected to electrical conductivity

Thin metal films in IR region: Drude model

$$\epsilon(\omega) - \epsilon_{\infty} = \frac{i\sigma_{\text{film}}(\omega)}{\omega\epsilon_0} = -\frac{\omega_p^2}{\omega^2 + i\omega\omega_{\tau}} \quad \omega_p = \sqrt{\frac{ne^2}{\epsilon_0 m_{\text{eff}}}}, \omega_{\tau} = \frac{1}{\tau}$$

$$\omega_{\tau} \rightarrow \omega_{\tau}(d) = \omega_{\tau}^{\text{bulk}} + \omega_{\tau}^{\text{surf}}(d)$$

due to scattering of electrons at defects and surfaces, depends strongly on roughness

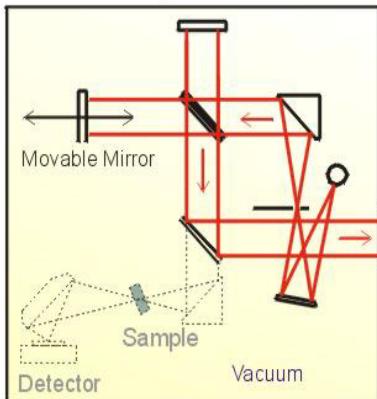
$$\omega_p \rightarrow \omega_p(d) = \beta(d) \cdot \omega_p^{\text{bulk}}$$

can account for depolarization effects, contributions from surface states

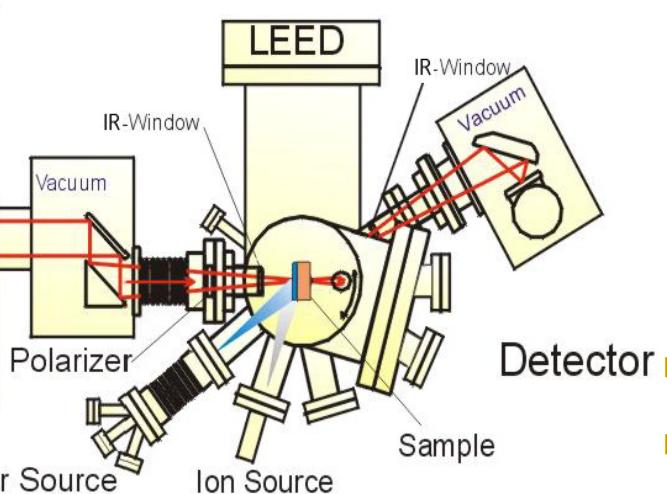
$$\rightarrow \epsilon(\omega, d) = \epsilon_1(\omega, d) + i\epsilon_2(\omega, d)$$

Experimental details

FTIR-Spectrometer

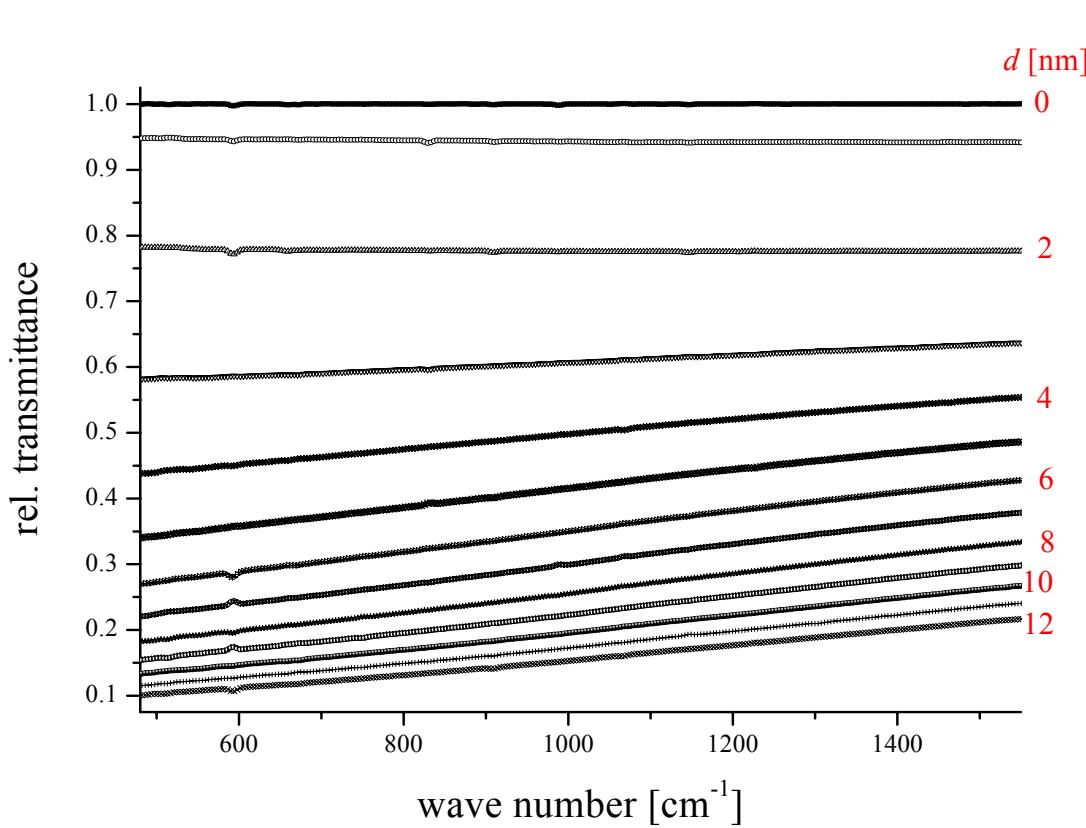


UHV-Chamber



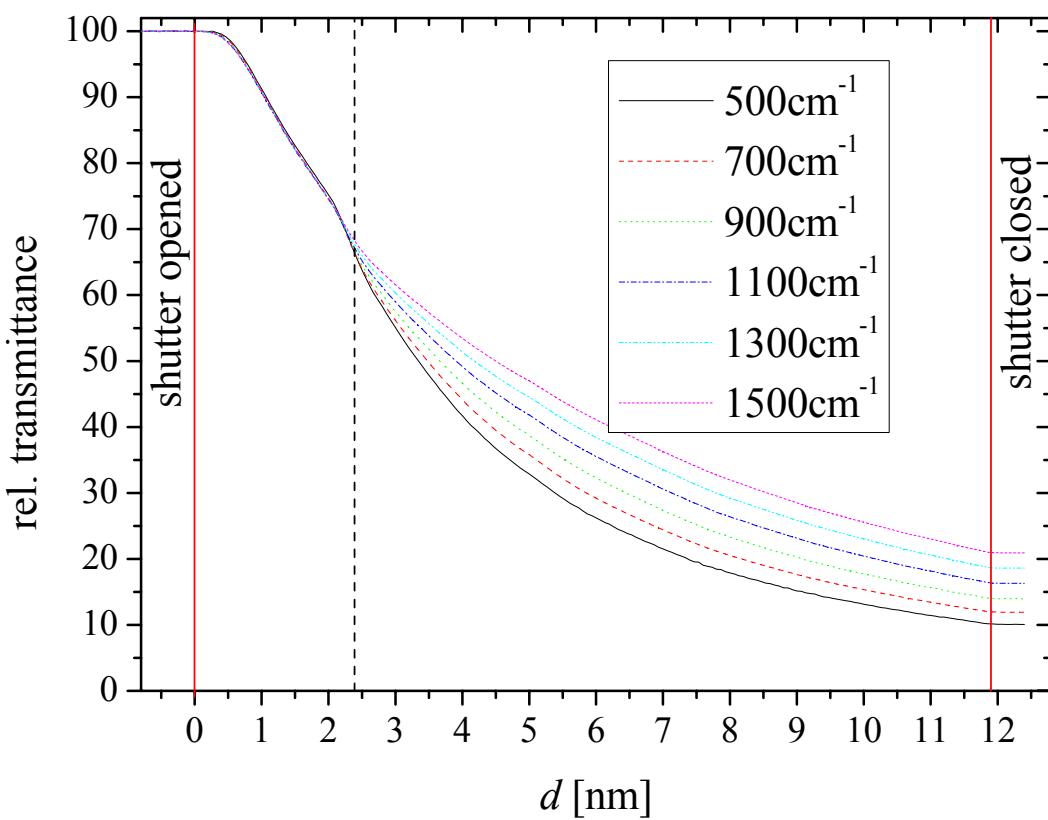
- Substrate: C(100)-(1x1):O, wet-chemical treated with $\text{H}_2\text{SO}_4 + \text{KNO}_3$, $\text{H}_2\text{SO}_4 + \text{HNO}_3 + \text{HClO}_4$ and cleaned in UHV by heating to $\sim 300^\circ\text{C}$ for some hours
- Base pressure: 1×10^{-10} mbar
- Pressure during evaporation: $\sim 2 \times 10^{-10}$ mbar
- Evaporation rate: $\sim 600\text{s/nm}$, calibrated with quartz micro balance

IR-transmittance of Cr deposited on C(100) at $T=300\text{K}$



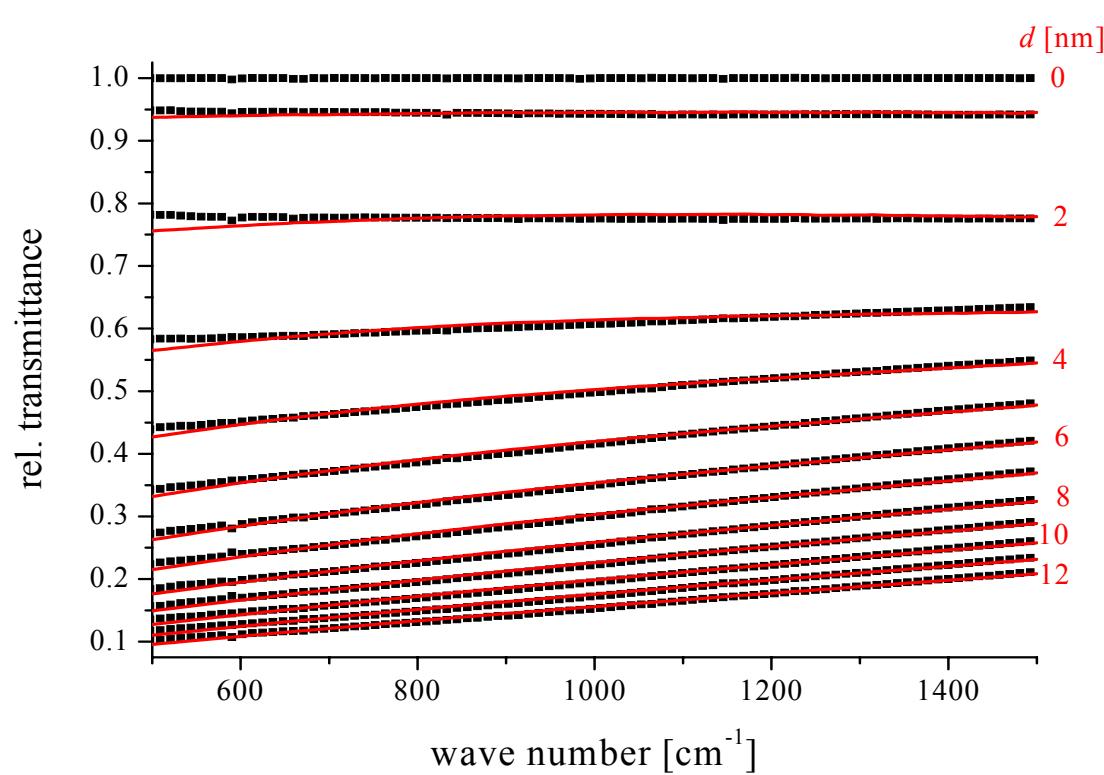
- IR spectra measured in-situ during evaporation of Cr, only small selection is shown

IR-transmittance of Cr deposited on C(100) at $T=300\text{K}$



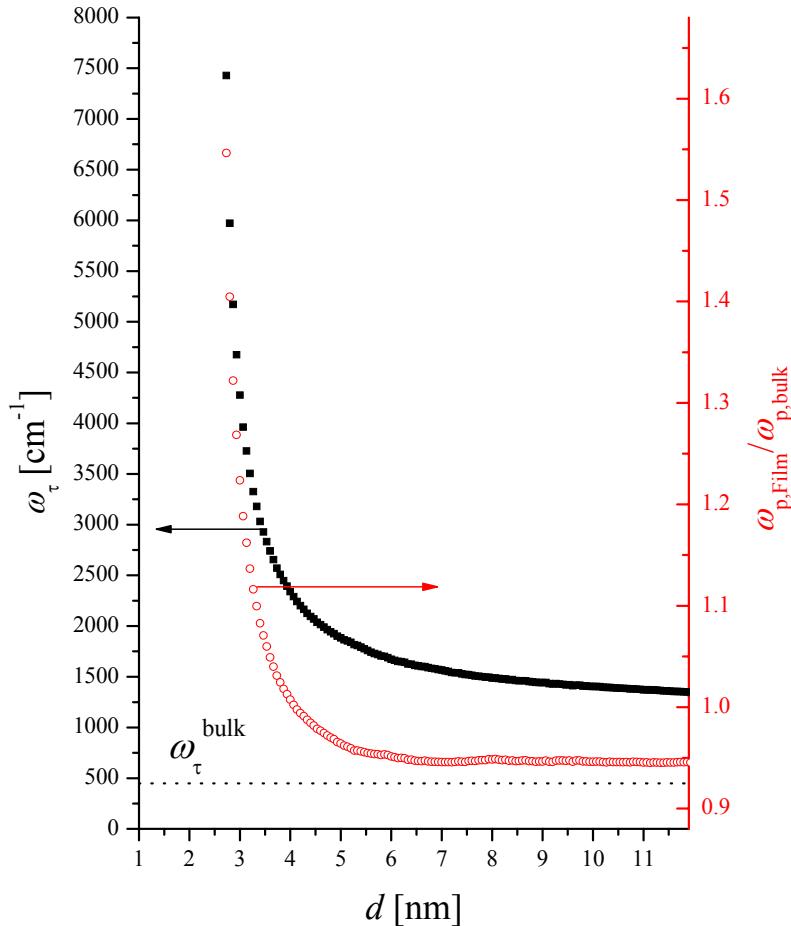
- The transmittance is frequency independent up to a thickness of about $d_{\text{crit}}=2.5\text{nm}$. Beyond this point, the decrease in transmission is stronger for smaller wave numbers, indicating metallic behaviour.

Calculation of spectra using extended Drude model



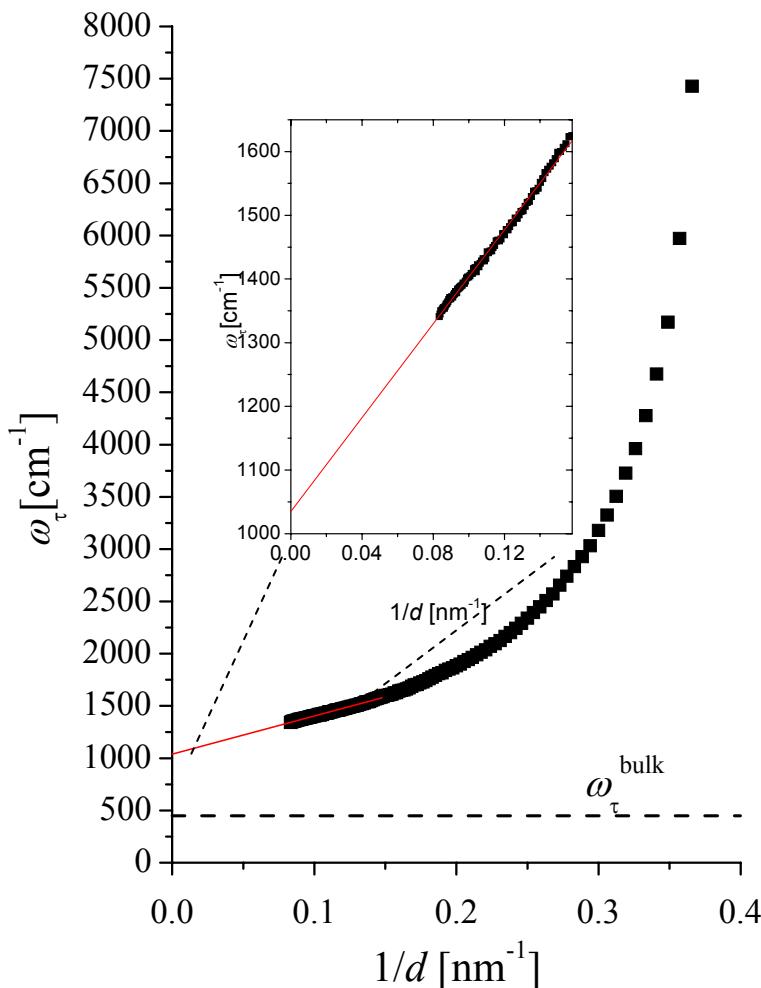
- Using a commercial software package the spectra are fitted with above described model
- Fit parameters: ω_P and ω_τ
- Good accordance can be found

Fit results for Drude parameters



- For $d < 2.5 \text{ nm}$ the parameters take unreasonable values, film does not show metallic behaviour
- This can be explained by a layer consisting of small grains that coalescence when reaching a diameter of 2.5 nm
strong hint for presence of fcc Cr

$d > 2.5 \text{ nm}$



- Linear relationship at higher d is expected from classical size effect* describing scattering of electrons at interfaces
- Extrapolation for d vs. ∞ does not result in bulk value

*Sondheimer, Adv. Phys. **1**, p. 1 (1954)

Summary

- Relaxation rate even for highest thickness bigger than bulk value, indicating defect-rich film
- Cr films on C(100) show non-metallic behaviour up to a thickness of 2.5nm
- This comparably thick amorphous layer is probably related to a coexistence of fcc and bcc phases of Cr

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Enhanced ω_p for ultra-thin Fe films

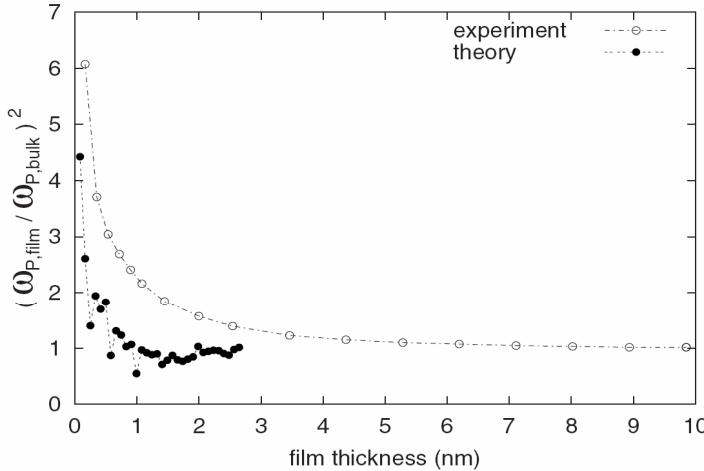


FIG. 5. Experimental data and theoretical results of the film plasma frequency $\omega_{P,film}$ relative to the bulk value $\omega_{P,bulk}$ for Fe/Si(111).

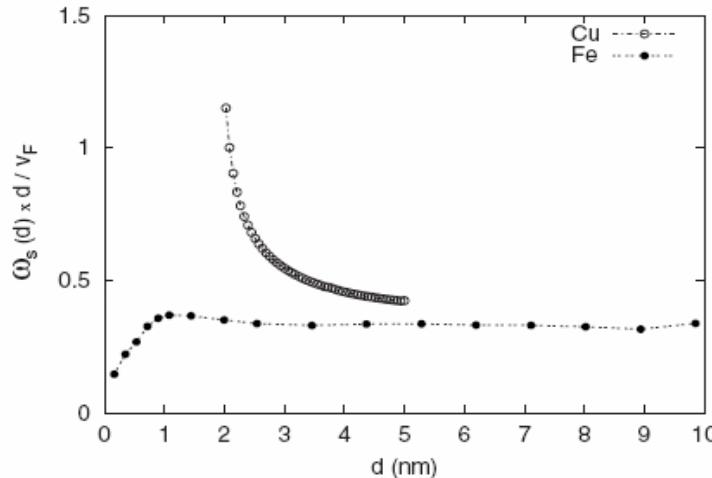


FIG. 3. The thickness dependence of the surface contribution to the scattering rate for Cu/Si(111) and Fe/Si(111).

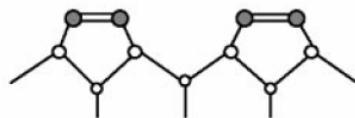
- related to the increase of the Fermi velocity caused by the large contribution of surface states and resonances

- Fe/Si: Reasonable Drude parameters for all thicknesses

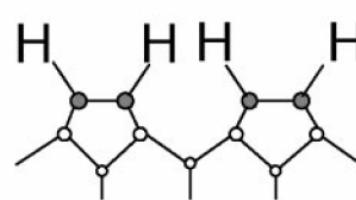
The diamond (100) surface

Not only the metallization, but also the diamond surface plays a key role in the device performance.

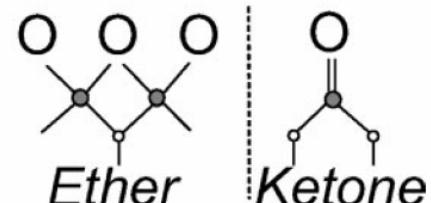
C(100)-(2x1)



C(100)-(2x1):H



C(100)-(1x1):O



Maier et al., PRB 64, 165411 (2001)

Electron affinity χ of diamond surfaces with different terminations.

	χ [eV]
C(100)-(2x1)	0.5
C(100)-(1x1):O	1.7
C(100)-(2x1):H	1.3

Pb on Si

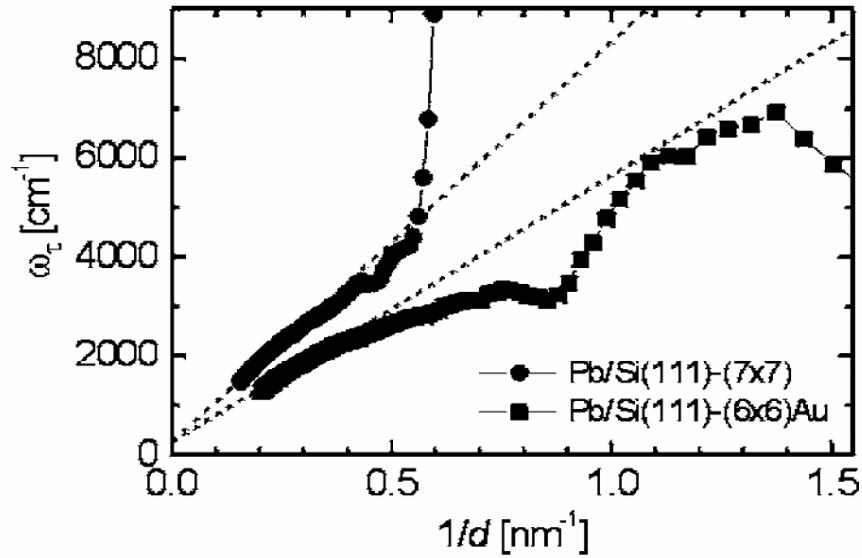


FIG. 5. Relaxation rates versus inverse Pb thickness $1/d$. The linear relationship at higher thickness d indicates the dominating CSE, its extrapolation is shown as a broken line.

Length scales for Cr

- Local optics: skin depth must be larger than distance which electron propagates during cycle of IR-field

$$\delta(\omega) > l_p(\omega)$$

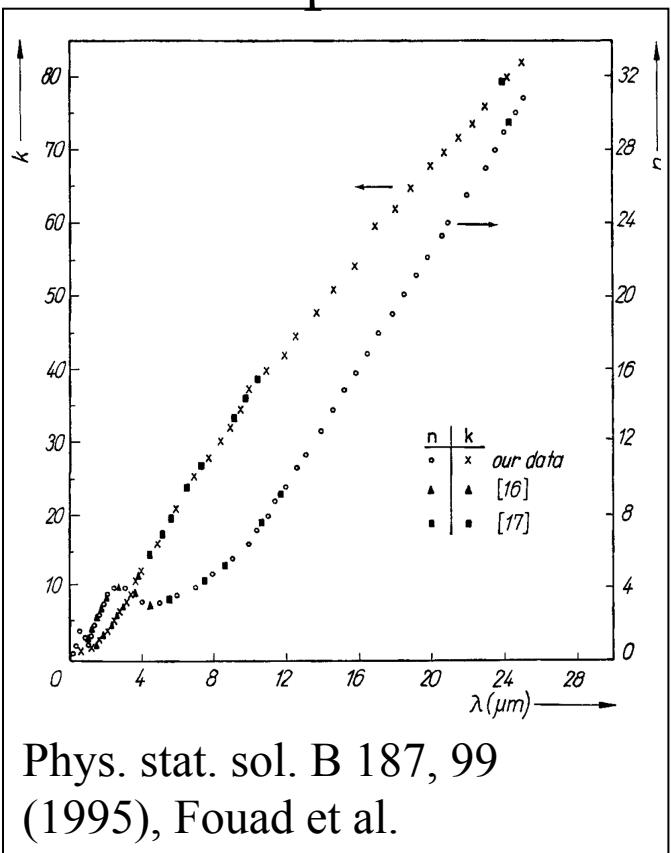
$$\frac{c}{\omega_p(\omega)} > \frac{v_F}{\omega}$$

$$\Rightarrow \omega > 210\text{cm}^{-1}$$

- Only for thicknesses below the mean free path of electrons a homogeneous conductivity within the metal can be assumed

$$d < \lambda_f \Rightarrow d < 20\text{nm}$$

Cr: $\omega_p(\omega)$ and $\omega_\tau(\omega)$ from bulk data



Phys. stat. sol. B 187, 99
(1995), Fouad et al.

