# Spectral and image analysis

Luca Gregoratti

Sincrotrone Trieste SCpA, Area Science Park, SS14-Km163.5, 34012 Trieste, Italy

email: luca.gregoratti@elettra.trieste.it

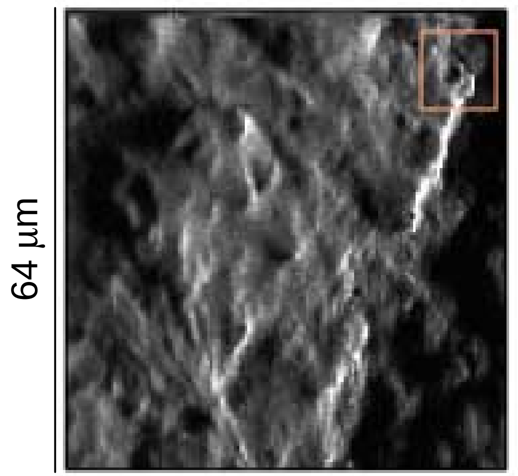
# Contrast mechanisms in a photoemission image

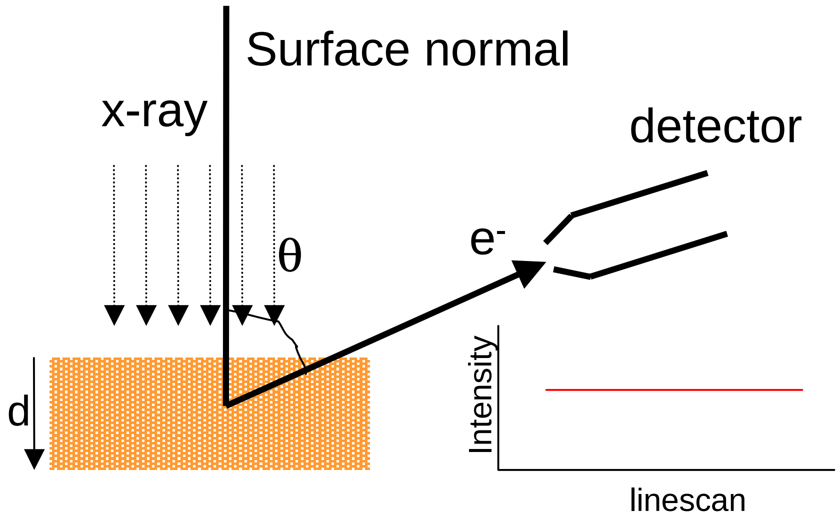
- Topography

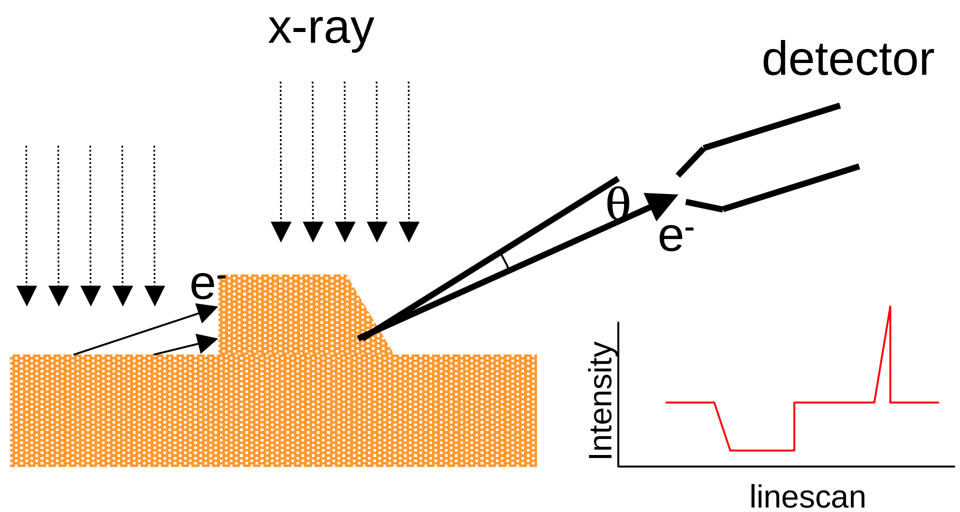
$$I = I_0\, e^{-\frac{d}{\lambda \cos\theta}}$$

λ = inhelastic mean free path

Blob of C nanotubes



## • Chemical inhomogeneity

Ni islands on Si

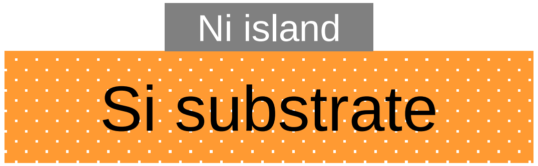



Image on Ni

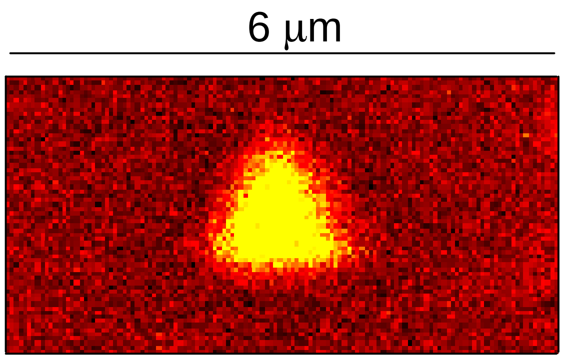
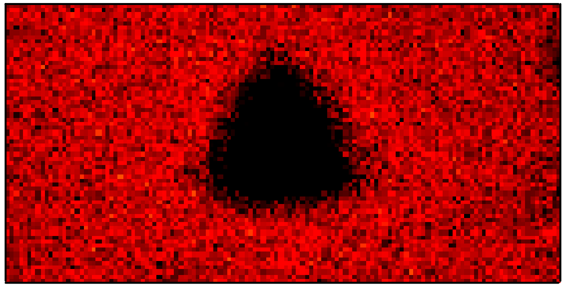



Image on Si



Au patch on Rh(110)


Image on Rh

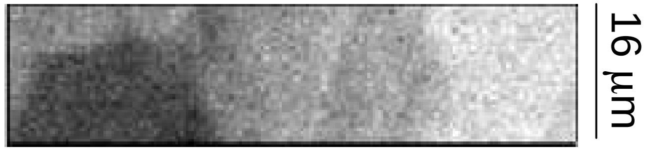
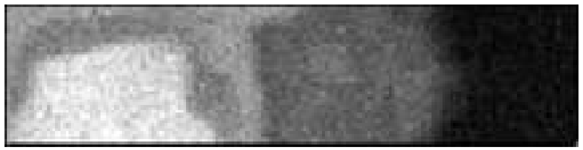
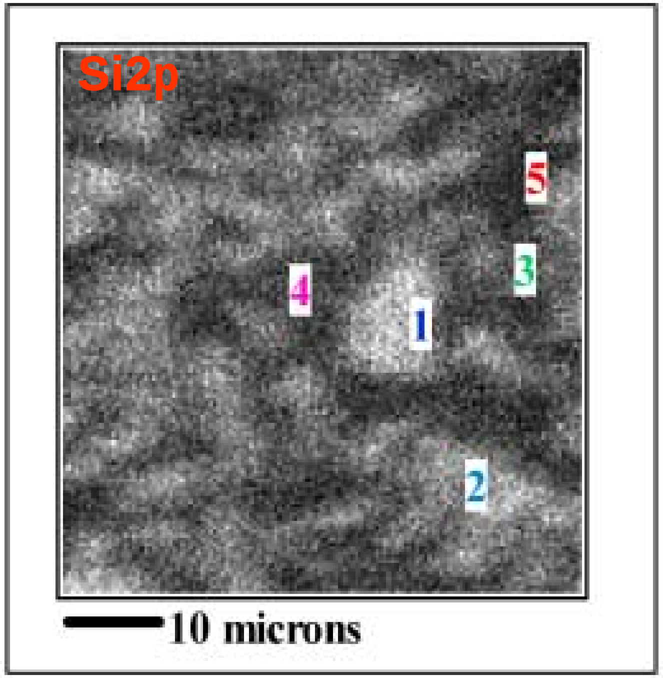


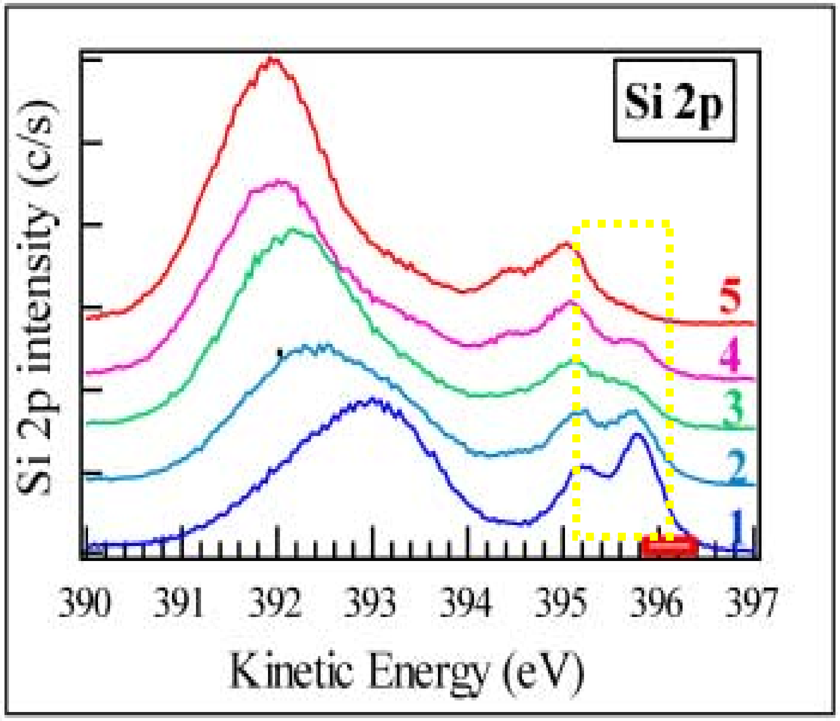

Image on Au



## • Other sources of contrast

charging



# Getting the chemical information out of the artefacts

## Artefacts

1. Topography
2. Beam induced effects:
   - C deposition (residual gases)
   - $O_2$ reduction
   - Charging
3. Background level

## General formulas:

$$I = \frac{I_{peak} - I_{bkg}}{I_{peak} + I_{bkg}}$$

$$I = \frac{I_{peak} - I_{bkg}}{I_{bkg}}$$

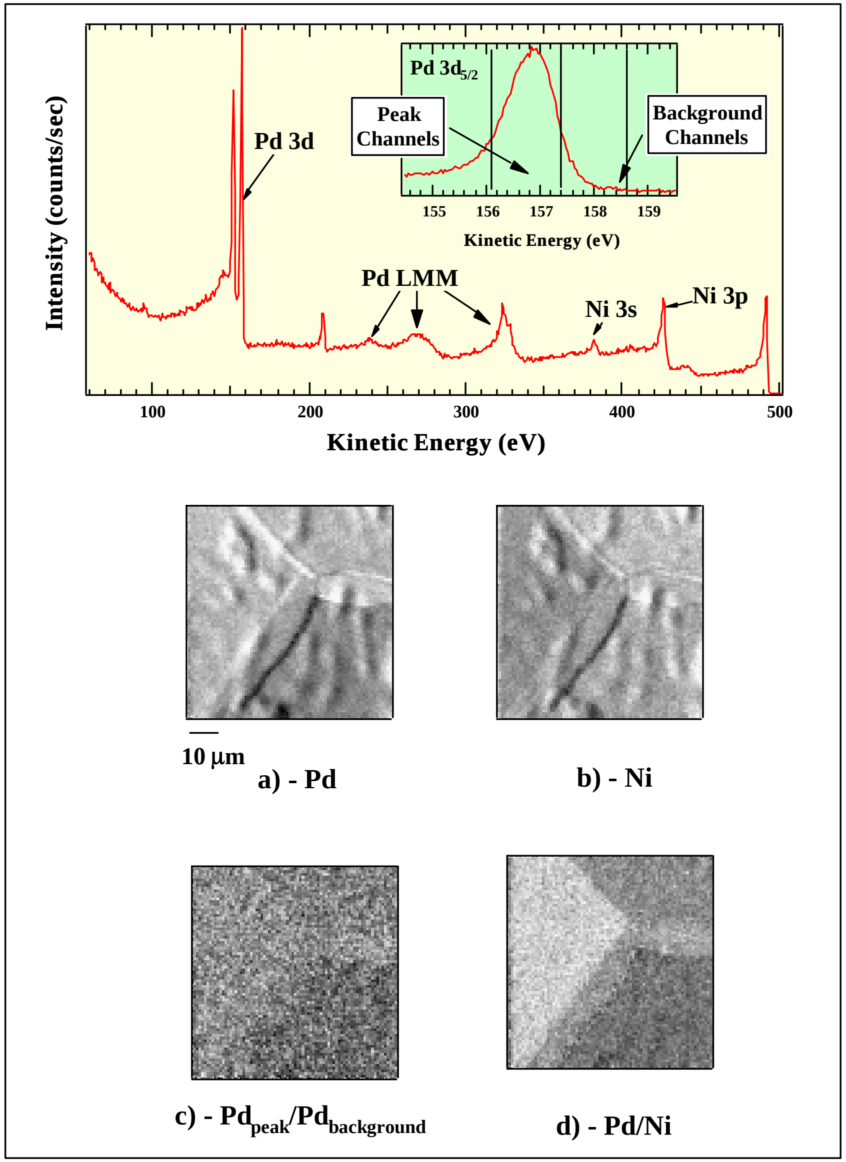
$$I = \frac{I_{peak}}{I_{bkg}}$$

sometimes only:

$$\frac{I_{peak1}}{I_{peak2}}$$

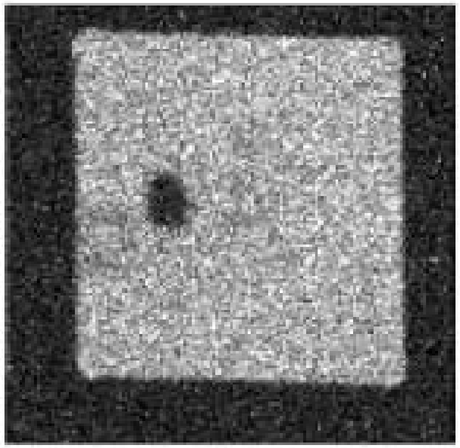
Which $I_{bkg}$ ?

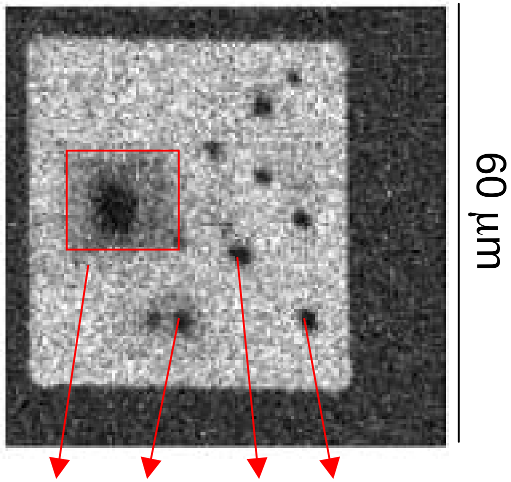
- $I_{bkg\ left}$
- $I_{bkg\ right}$
- $I_{bkg\ (left+right)}$
- *secondaries*



# C growth

$SiO_x$ sample
Si2p maps

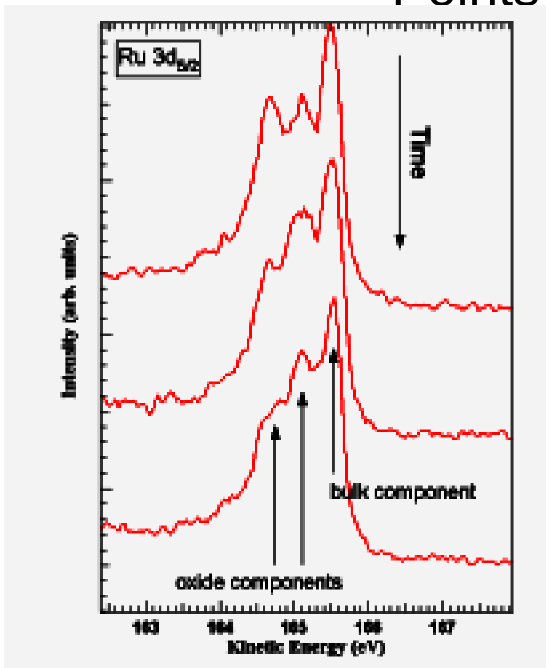





Points irradiated (>10 min)

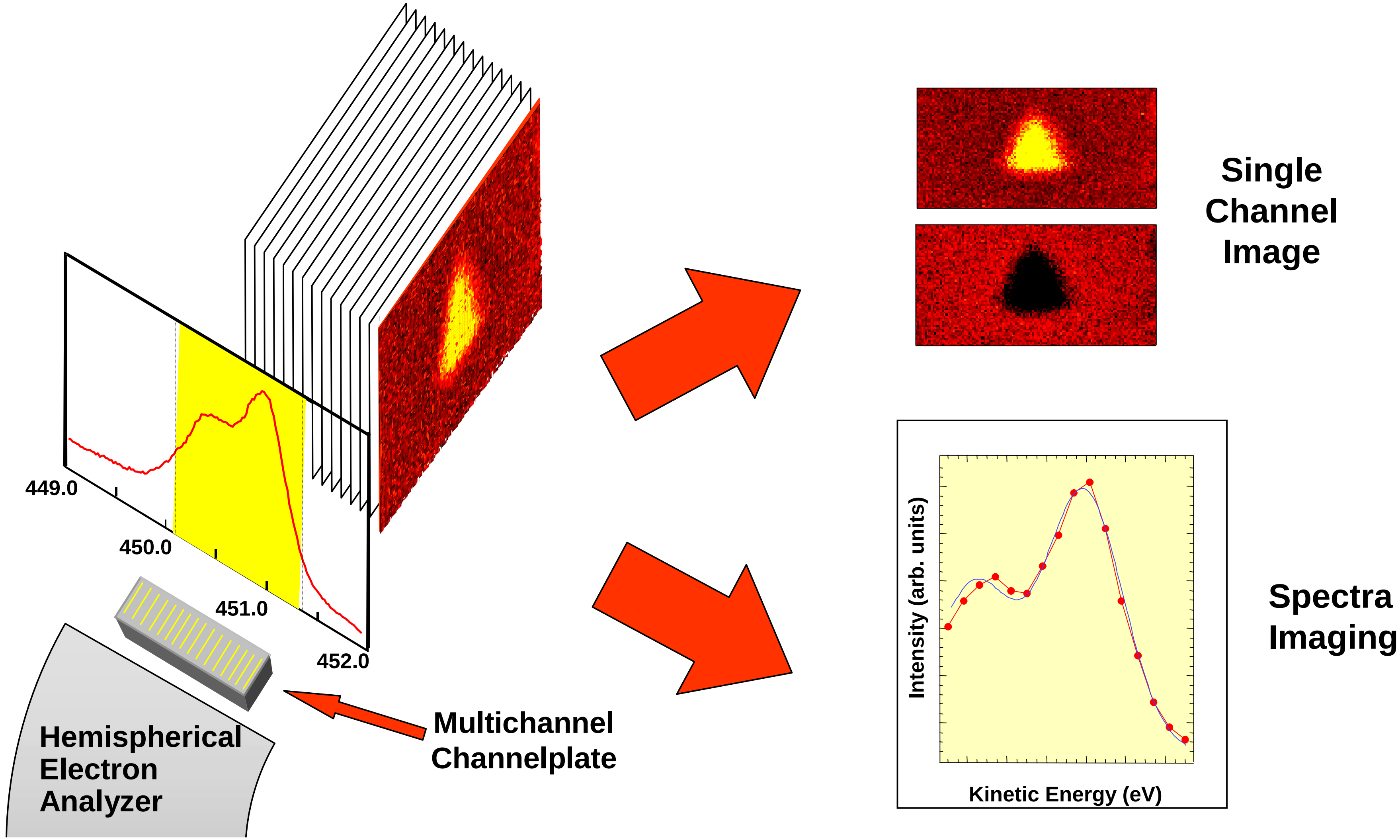
# $O_2$ reduction

$RuO_x$ sample




Each spectrum every 1 min

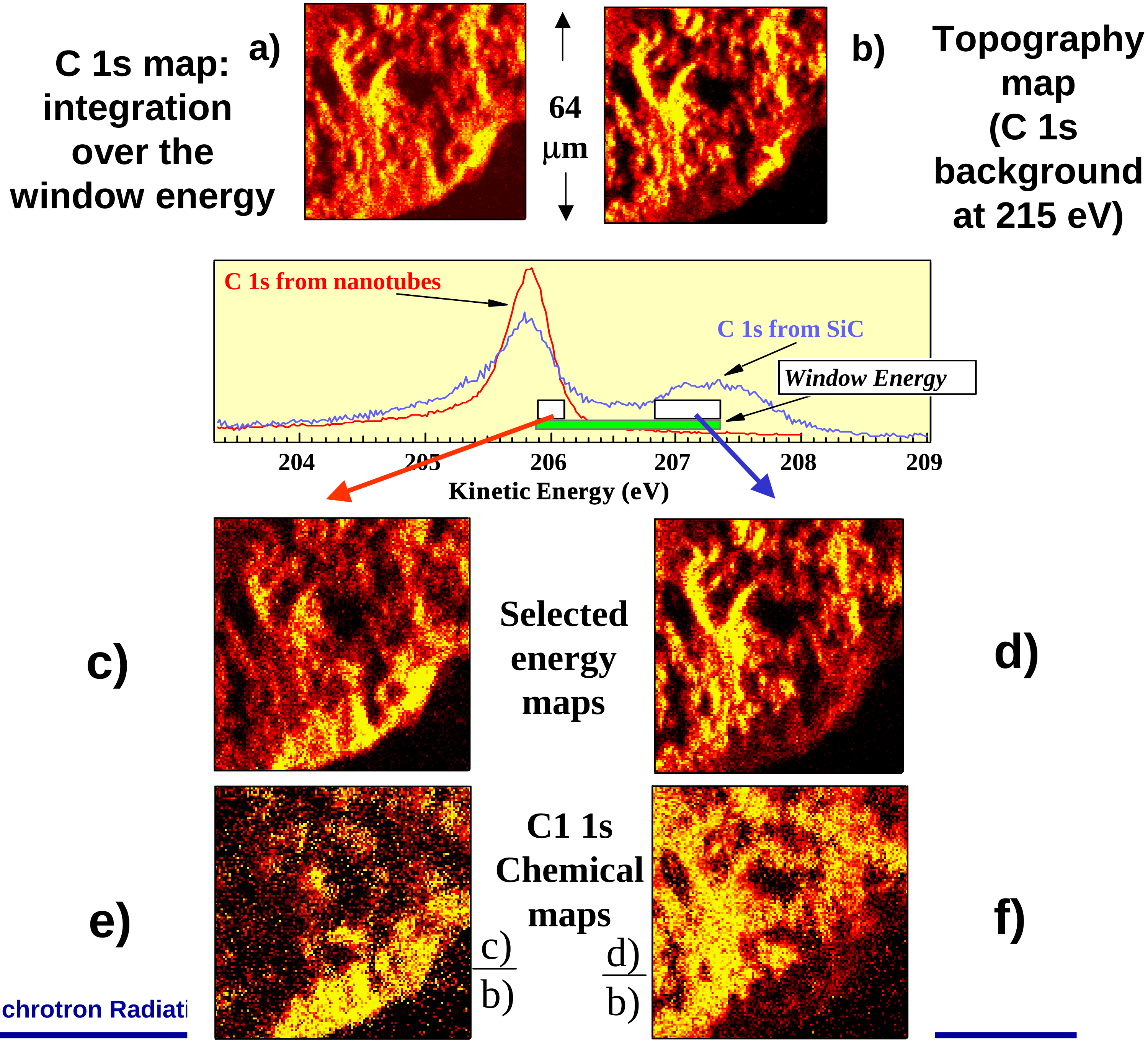
# Multichannel detection



# Single Channel Analysis

## Carbon nanotubes on SiC

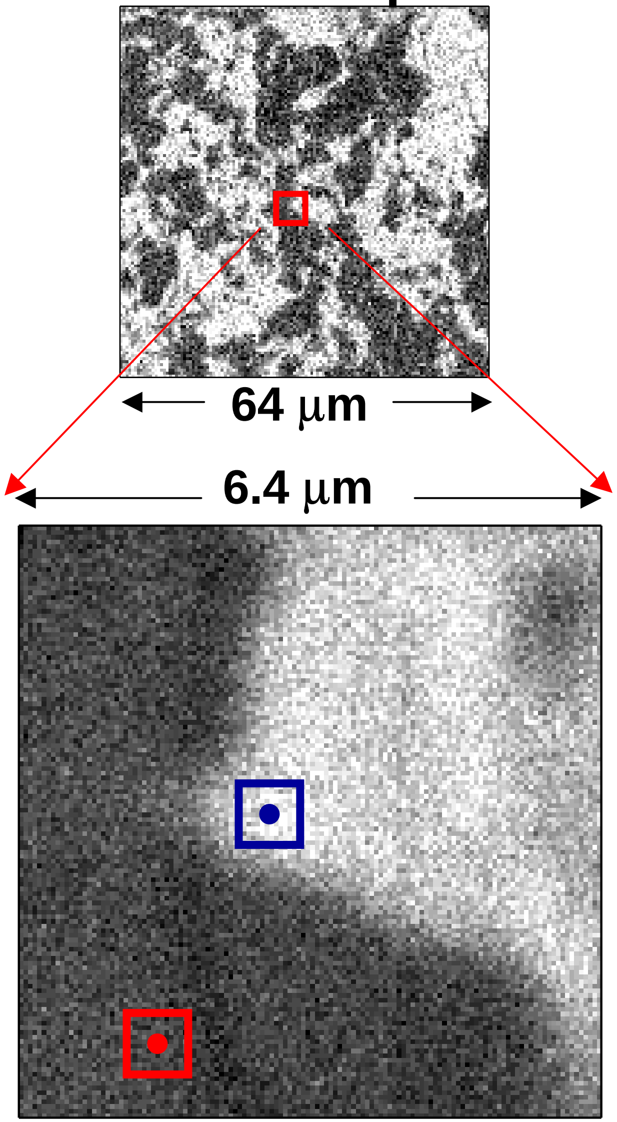
R. Larciprete – Enea - Italy



# Spectra Imaging

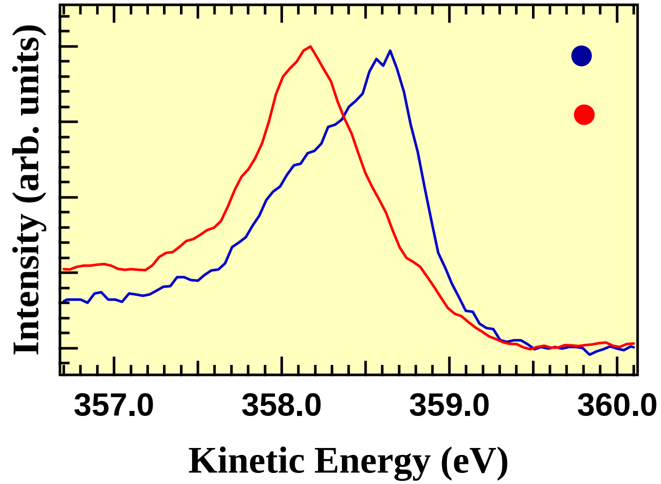
**Ru(0001) oxidation**
H. Conrad – FHI - Germany

## Ru 3d maps

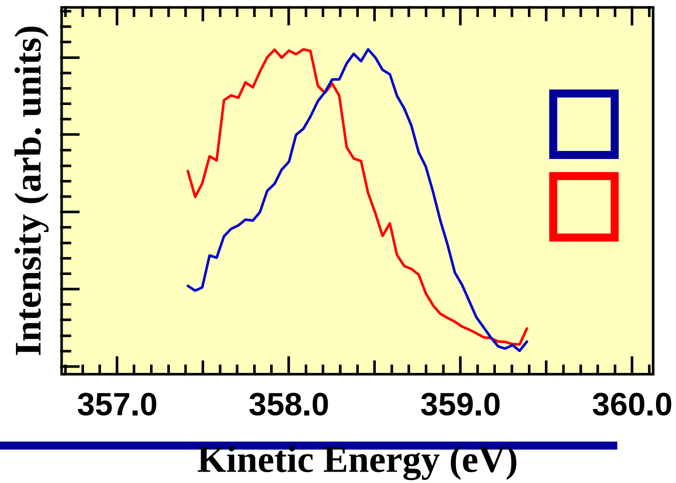



## Ru 3d$_{5/2}$ spectra

Conventional Scanning Spectroscopy (48 points - 70 sec)

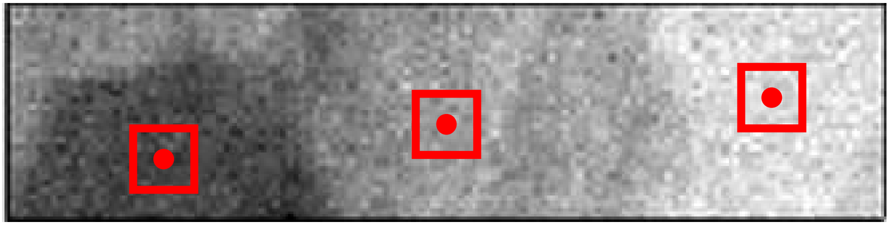



Inherent Dispersion Energy Spectroscopy (48 points - 10 sec)



# Spectra Imaging

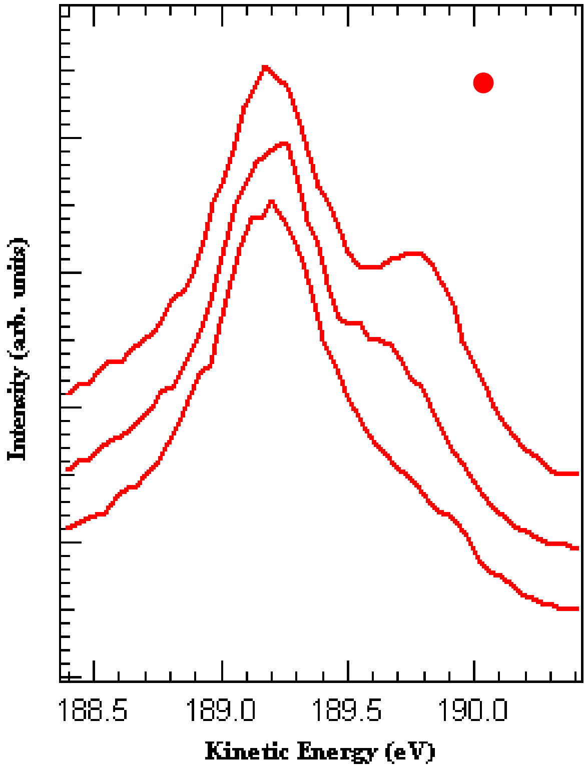
Rh 3d map

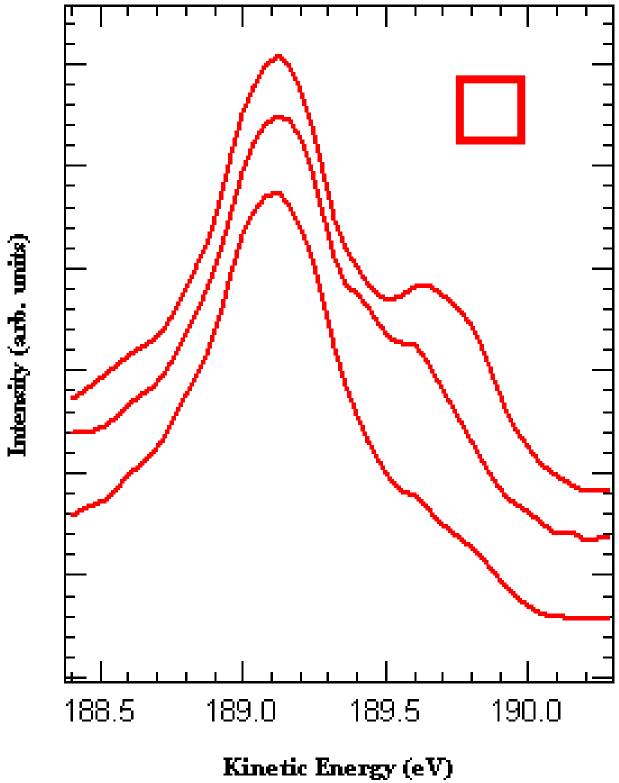


Conventional Scanning Spectroscopy

Inherent Dispersion Energy Spectroscopy

Rh $3d_{3/2}$ spectra



# Spectra analysis

Natural linewidth  or core hole lifetime (Lorentzian)

Good for insulators and semiconductors

$$L(E) = \frac{1}{\left(1 + 4\left(\frac{E - E_L}{\Gamma_L}\right)^2\right)}$$

$E_L$ = centroid
$\Gamma_L$ = FWHM

Instrumental resolution and phonon broadening (Gaussian)

$$G(E) = \exp\left[-4\ln 2\left(\frac{E - E_G}{\Gamma_G}\right)^2\right]$$

$E_G$ = centroid
$\Gamma_G$ = FWHM

Convolution of the Gaussian and the Lorentzian  (Voigt)

$$I(E_G) = \int_{-4\sigma}^{+4\sigma} \exp\left[-4\ln(2)\left(\frac{E - E_G}{\Gamma_G}\right)^2\right] \times \frac{1}{\left(1 + 4\left(\frac{E - E_L}{\Gamma_L}\right)^2\right)} \mathrm{d}E$$

Natural linewidth or core hole lifetime (Doniach-Sunjic)

Good for metals

$$DS(E) = \frac{Gamma(1-\alpha)\cos\left[\frac{\pi\alpha}{2} + (1-\alpha)\arctan\left(2\left(\frac{E-E_L}{\Gamma_L}\right)\right)\right]}{\left((E-E_L)^2 + 4\Gamma_L^2\right)^{\frac{1-\alpha}{2}}}$$

$E_L$ = centroid

$\Gamma_L$ = FWHM

$\alpha$ = asymmetry

Lineshape for metals

$$I(E_G) = \int_{-4\sigma}^{+4\sigma} \exp\left[-4\ln(2)\left(\frac{E-E_G}{\Gamma_G}\right)^2\right] \times DS(E)\mathrm{d}E$$

# Fitting procedure

## Background removal

Background functions:

- Tougaard

$$F(E) = j(E) - \lambda \int_E^{\infty} dE' K(E' - E) j(E')$$

$F(E)$=primary excitation spectrum
$j(E)$=flux of emitted electrons
$K(E,T)$=probability for an electron of loosing energy
$\lambda$=mean free path for inelastic scattering

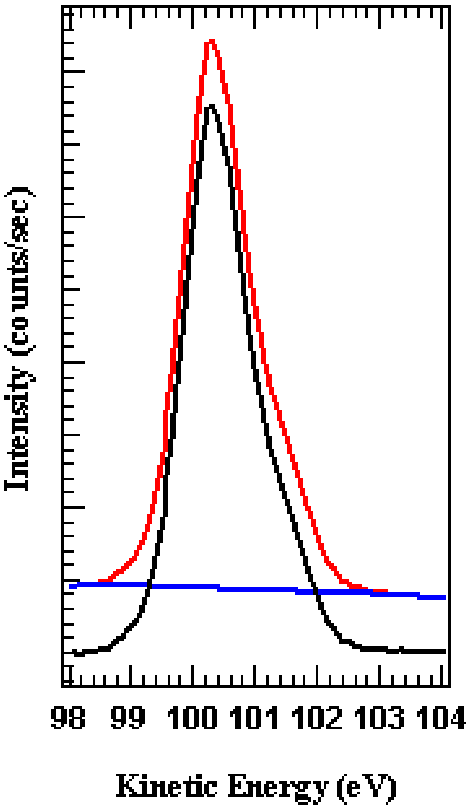
- Shirley

$$b_i = k \sum_{j=i+1}^{N} p_j$$

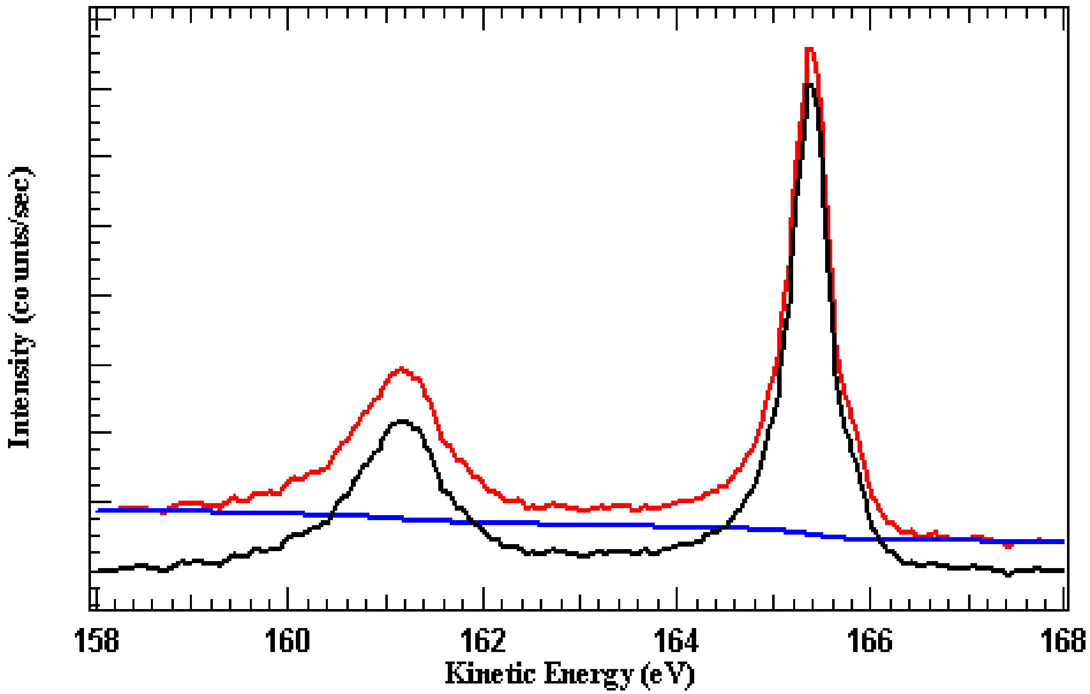
$b_i$=background of the point $i$
$p_j$=signal of the point $j$
$N$=highest kinetic energy
k=constant

- Linear
- Cubic

Linear background: N1s



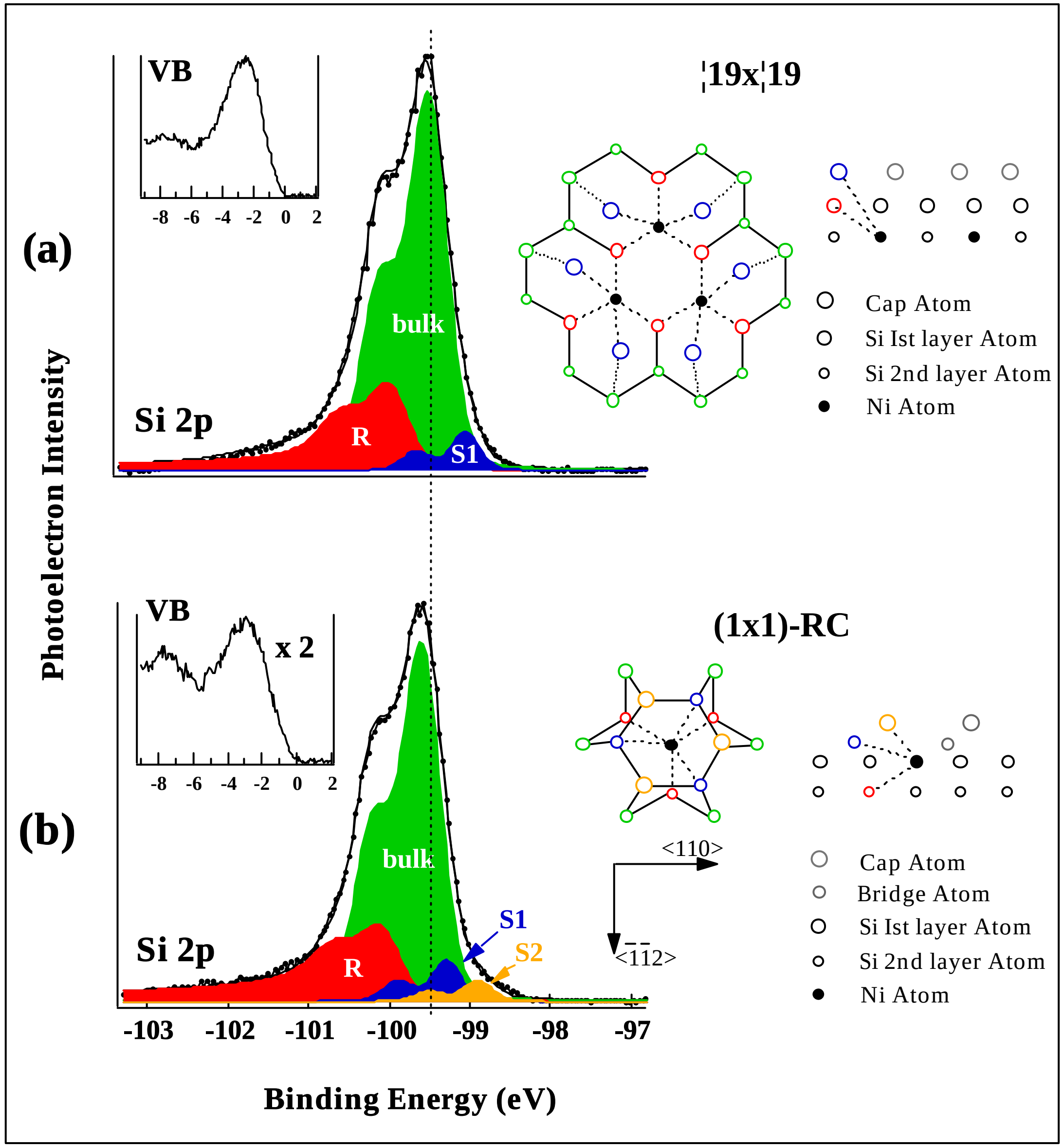

Shirley background: Rh3d



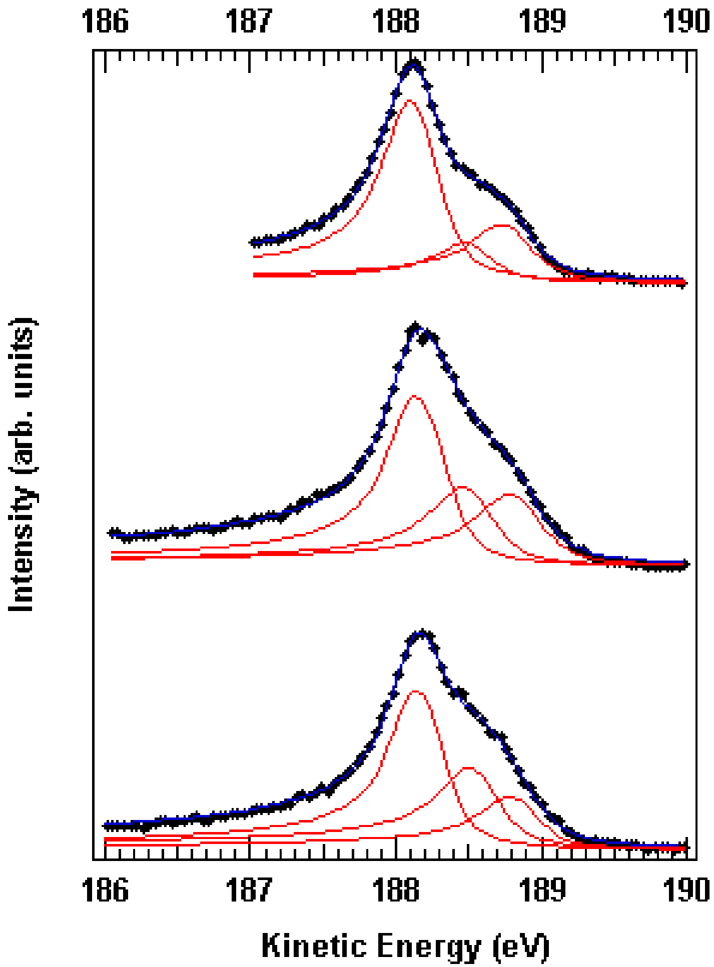
# Fitting

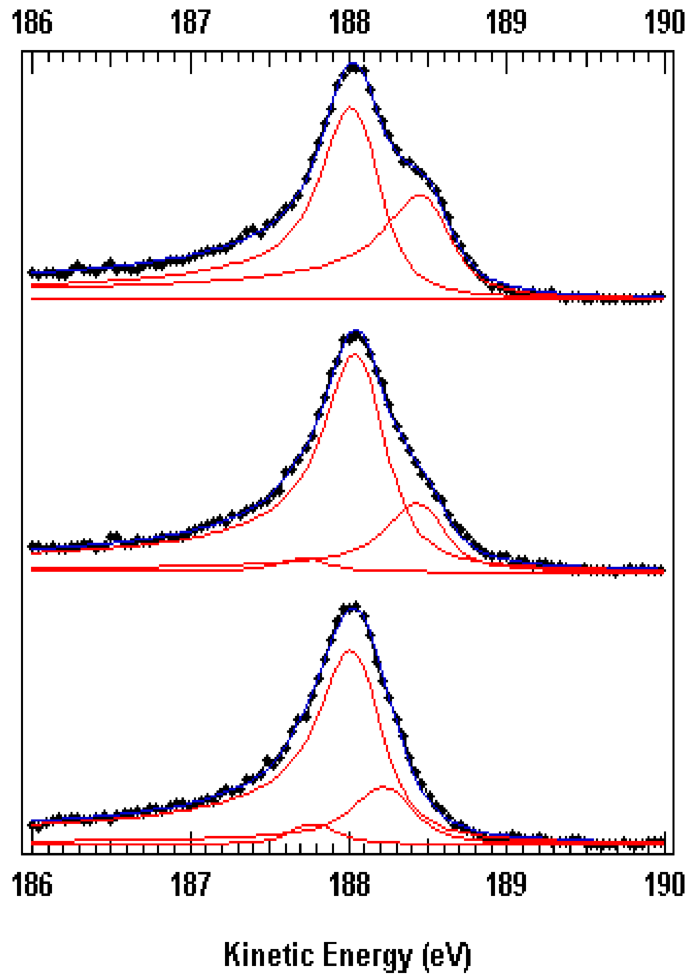
Ni/Si(111)
2D recostructions

Si2p
spectra



# Rh $3d_{3/2}$ fitting procedure (same experiment)



## References

S. Gunther, A. Kolmakov, J. Kovac, M. Kiskinova, “Artefact formation in scanning photoelectron emission microscopy”, Ultramicroscopy 75 35-51, (1998).

J.J. Joice, M. Del Giudice and J. H. Weaver, “Quantitative analysis of synchrotron radiation photoemission core level data”, J. of Elec. Spectr. And Relat. Phenom. 49 31-45 (1989).

Stefan Hufner, “Photoelectron spectroscopy, principles and applications”, Springer