Secondary electrons production with EUV synchrotron radiation: experiment and modeling

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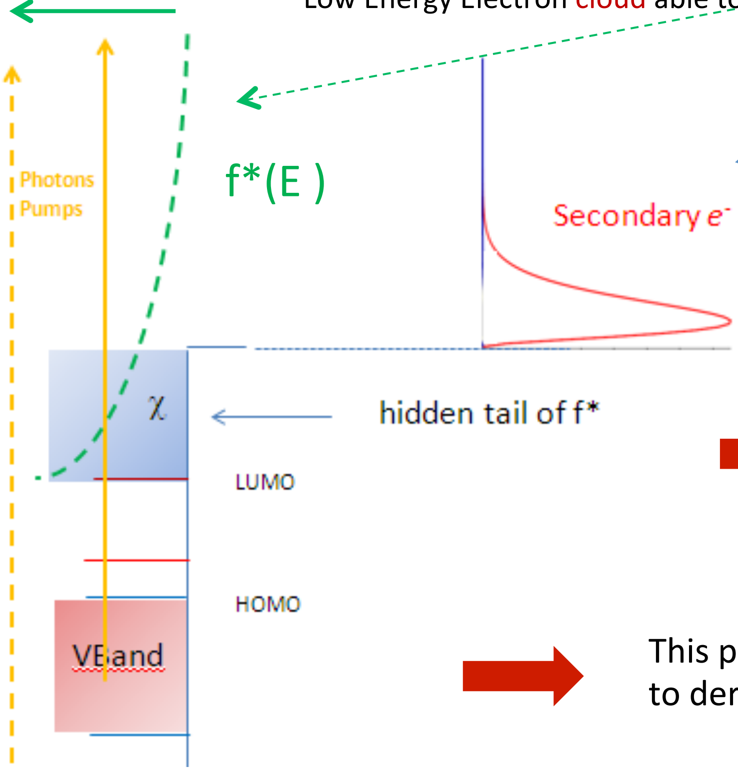
The phenomenology of interest in our case

Our group (IOM-CNR, IMEC, UniCam) is currently concentrated on two classes of phenomena both involving non-resonant (i.e. with specific bonds of material) photons absorption and Low Energy Electrons

- *photosensitive materials* (*solubility switching of photoresists*)
- *photon damage of optical elements* (*typically synchrotron radiation optics/case of BEAR*)

The origin of *non resonant* photo-sensitivity
is related to the creation of photo-electrons (e.g. by 92 eV photon for photoresists)
and to the subsequent electron cascade with the formation of a
Low Energy Electron cloud able to induce reactions in the material (*facts to be understood*)



Secondary electrons are the image, though deformed by *electron scattering* and by the solid-vacuum *barrier crossing*, of the low energy distribution inside material

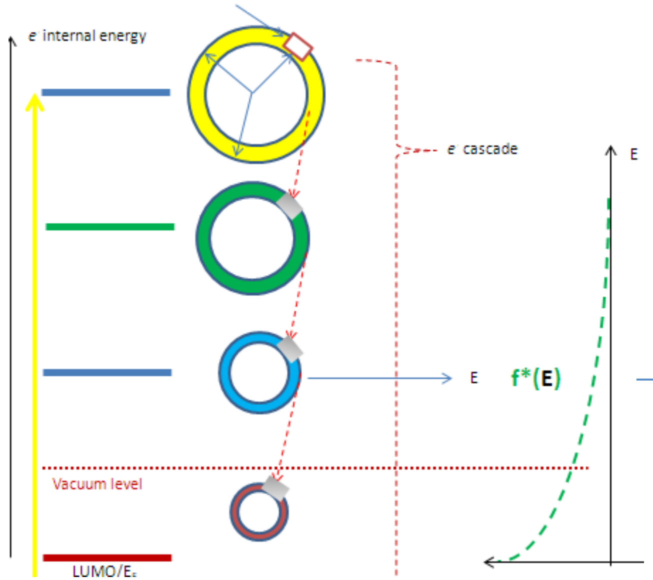
the out of thermal equilibrium distribution function f*(E) is identified as a quantity able to describe this state of things

This presentation deals with to construction of a model to derive f*(E) from the experimental secondary spectra

The physical picture : isotropic free electron gas ($g(E) \propto m^{\frac{3}{2}}\sqrt{E}$)in stationary conditions

- impinging photon partially fills up the volume elements of *p-space* $dV_p \simeq p^2 d\theta_V d\phi_H dp$ of the highest reachable p-FEG sub shell

- then emptying processes start including:
  - elastic diffusion maybe toward the surface → XPS/UPS (*not now*)
  - radiative de-excitation (*not included in the model*)
  - multiple scattering and e^- cascade at issue here



E_K=E-χ

The emission rate at E_K is a point function of the energy *E* of electron involving the occupation function *f*(E) of its state* [~*kinematics description*]

Though it could be instructive to give a look to a dynamical description based on a Boltzmann equation

Boltzmann equation providing the **f*(E)** – *some hints*

[e.g. *G. F. Amelio J Vac Sci Technol 7, 593 (1970)*]

$$\frac{\delta}{\delta t} f^*(z,\cos\theta,E) + \frac{\vec{p}}{m}\cdot\nabla f^*(z,\cos\theta,E) = S - \frac{|\vec{p}|}{m}\frac{f^*(z,\cos\theta,E)}{\Lambda} + \int \frac{|\vec{p}'|}{m}\frac{f^*(\vec{r},\vec{p}',t)}{\Lambda(\vec{p}')} f^*(\vec{p},\vec{p}')d\vec{p}'$$

stationary conditions

excitation function /written for a single *e^-beam* (axial)
→spherical distribution of e^-beams instead in the cases of interest
→to be adapted to the present case where excited atoms constitute a
suite of distributed electron guns turned on by the photon absorption

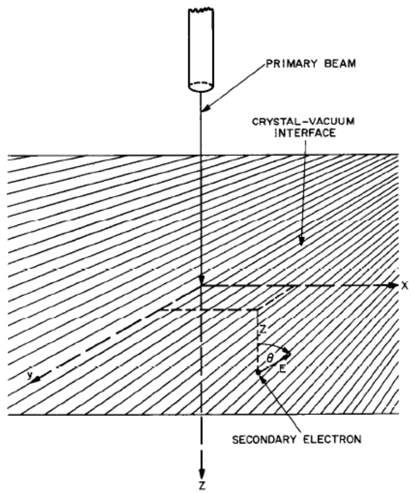


FIGURE 1. Typical experimental geometry showing coordinates and energy of a secondary electron.

Over all goal

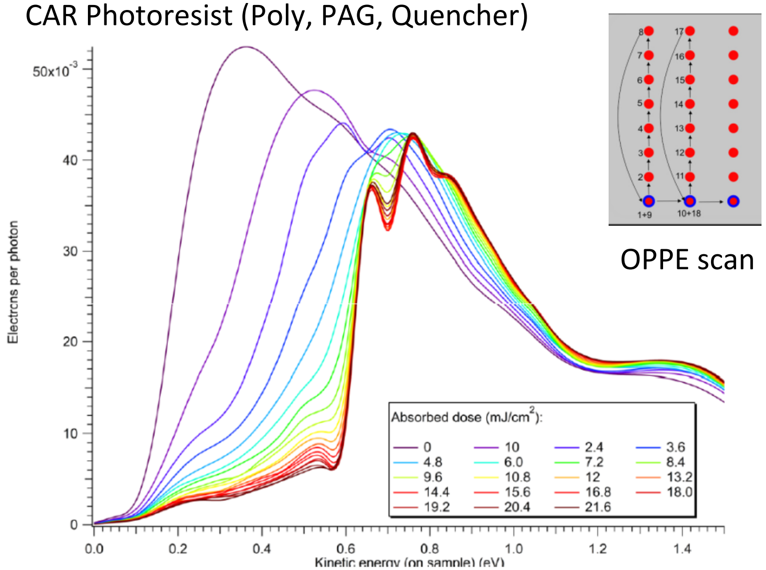
• The Goal is to get a quantitative – *tough naïve, but manageable* - expression linking the distribution in energy *E* of secondary electrons under illumination involving the experimental parameters and those of the material to the out-of-equilibrium distribution function **f*(E)** : *just a picture of the sate of things*

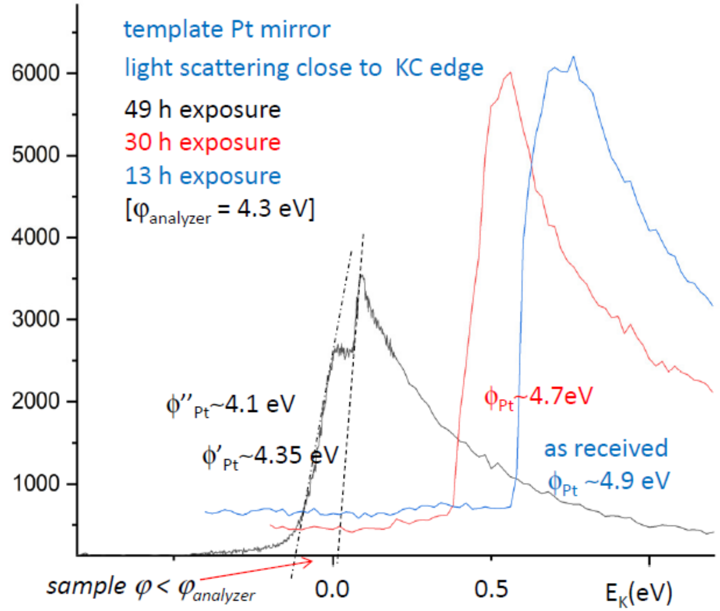
• then as a first step to get oriented the difficulties due to complexity have been put aside to concentrate instead on the description of the emission process choosing a stable system - *that is a non-photosensitive material*

• in doing that also attention to single out difficulties, limits and their origin to get a quantitative expression

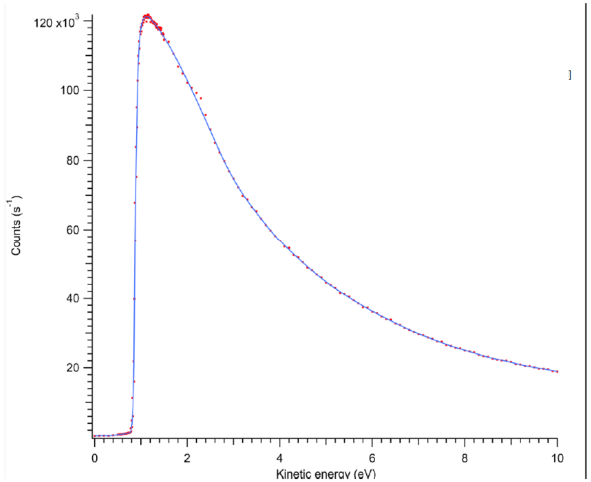
in fact things quickly turn to complex

CAR Photoresist (Poly, PAG, Quencher)





to start with: Au[100] sputtered (*not annealed surface*)

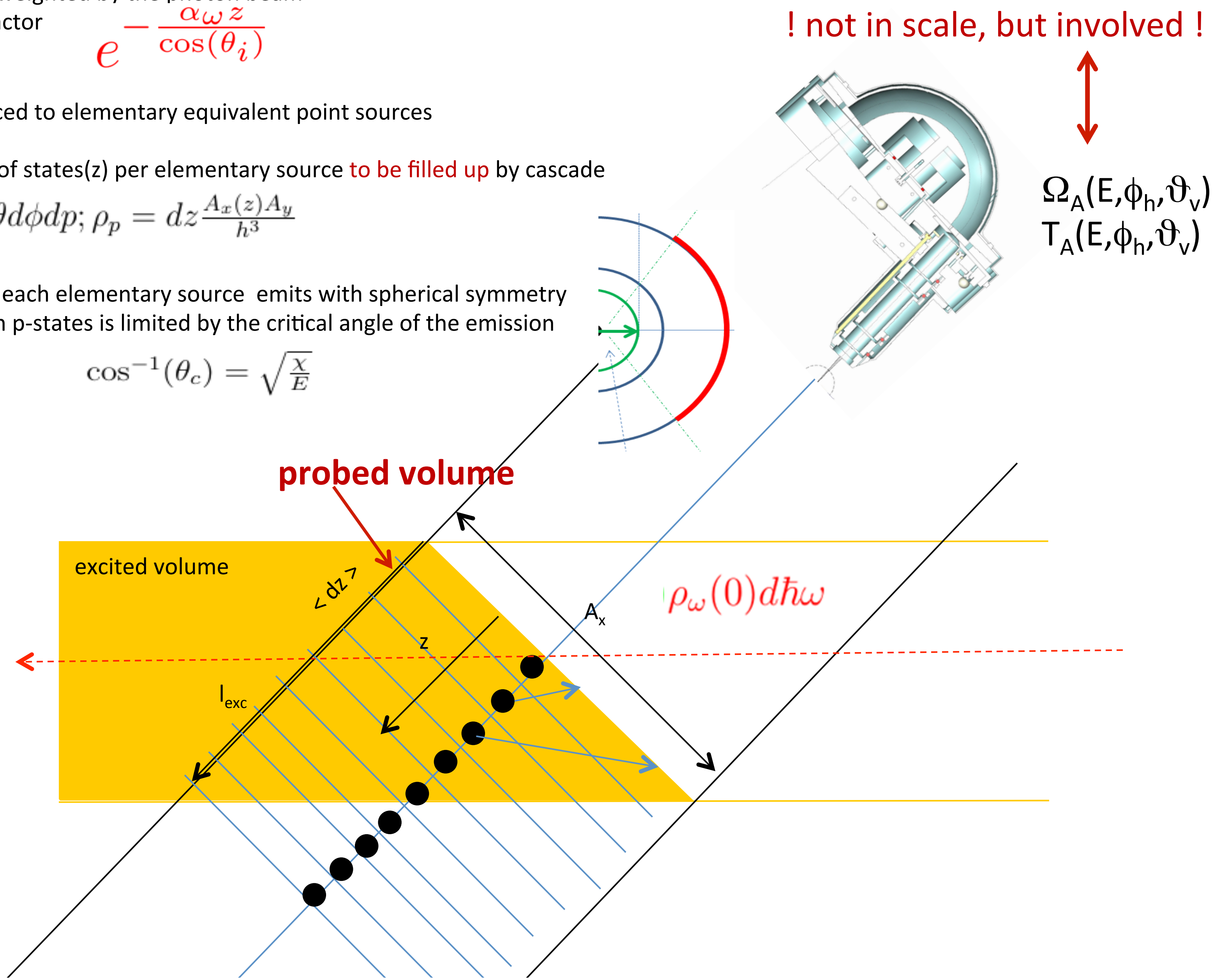


#101

$\hbar\omega$=92 eV
$\Delta\hbar\omega$=20 meV (100 μ)
ΔE_k (meV)= 100 (12-15.5 eV)/10 (15.5-16.5)/100(16.5-107)
I_0(92 eV) = 8 x10^{10} ph/s
filter = Si
polarization=~ linear/horizontal [sel pol = -0.945 mrad; + 0.95 mrad]
incidence = 45° / *s* polarization incidence
S_h= 400 μm
S_v= 100 μm
E_p= 5 eV
ΔE_k=38 meV
V_{bias}=15 V
I_{drain}~

The play ground (*the volume problem*)

- the probed volume is divided into elementary slices
- the slices are weighted by the photon beam attenuation factor $e^{-\frac{\alpha_\omega z}{\cos(\theta_i)}}$
- slices are reduced to elementary equivalent point sources
- the number of states(z) per elementary source to be filled up by cascade
  $V_p \simeq p^2 d\theta d\phi dp; \rho_p = dz\frac{A_x(z)A_y}{h^3}$
- [anticipating] each elementary source emits with spherical symmetry emission from p-states is limited by the critical angle of the emission cone
  $$\cos^{-1}(\theta_c) = \sqrt{\frac{\chi}{E}}$$

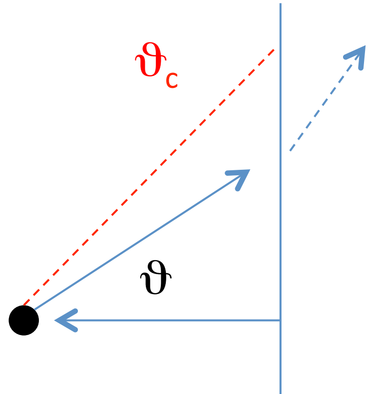


Equations from emission rate (*the surface problem*) to f*(E)

$$d^5 n_\omega(E,\theta,\phi,z,\omega) = d\phi \times f^*_{ph\omega} d\hbar\omega \rho_\omega(z=0)$$

$$dz e^{-\alpha(\omega)z} \sqrt{2} m^{\frac{3}{2}} \sqrt{E} dE \times \frac{A_x(z)A_y}{h^3} \times$$

$$d\theta e^{-\frac{z}{\Lambda(E)\cos(\theta)}} \times \frac{4\sqrt{E\cos^2(\theta)} \times \sqrt{E\cos^2(\theta)-\chi}}{[\sqrt{E\cos^2(\theta)} + \sqrt{E\cos^2(\theta)-\chi}]^2}$$

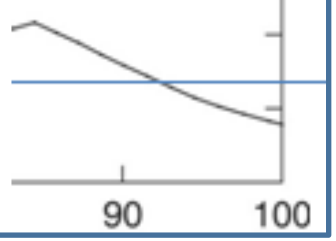


~cylindrical symmetry around z
$\int d\phi = 2\pi$

$$f^*_{ph\omega}(E)\rho_\omega(0)d\hbar\omega = \frac{d^2 n_\omega(E,\omega)}{\left\{ 2\pi\sqrt{2} m^{\frac{3}{2}} \sqrt{E} \frac{A_y}{h^3} dE \int_0^{l_{exc}} dz e^{-\frac{\alpha_\omega z}{\cos(\theta_i)}} A_x(z) \int_0^{\theta_c} d\theta e^{-\frac{z}{\Lambda(E)\cos(\theta)}} \frac{4\sqrt{E\cos^2(\theta)} \times \sqrt{E\cos^2(\theta)-\chi}}{[\sqrt{E\cos^2(\theta)} + \sqrt{E\cos^2(\theta)-\chi}]^2} \right\}}$$

from experiment
[Reflectivity not included yet]

$\alpha(92)$ ~0.45x10^{-6} cm^{-1}



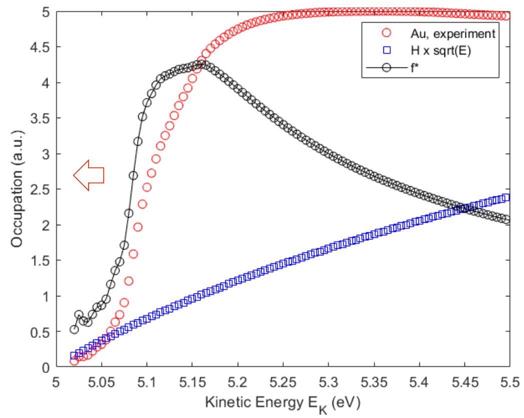
CXRO data bas

$$\lambda_i = \frac{A_i}{E^2} + B_i E^{1/2}$$

Seah and Dench (SIA paper)

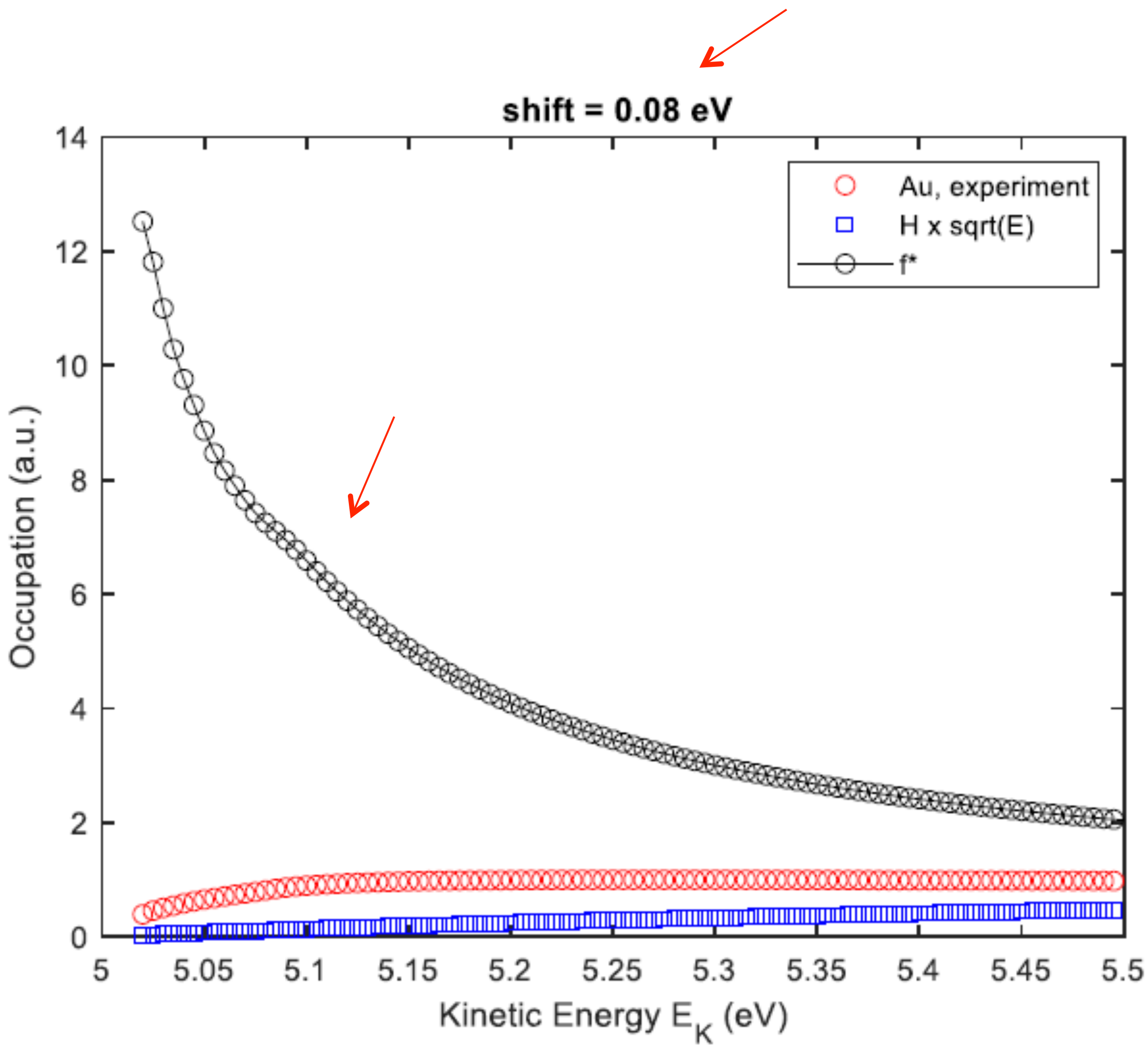
A_x,A_y and impinging intensity from experiment

input χ_{Au}=5 eV → Shift exp. 0f -0.08 eV



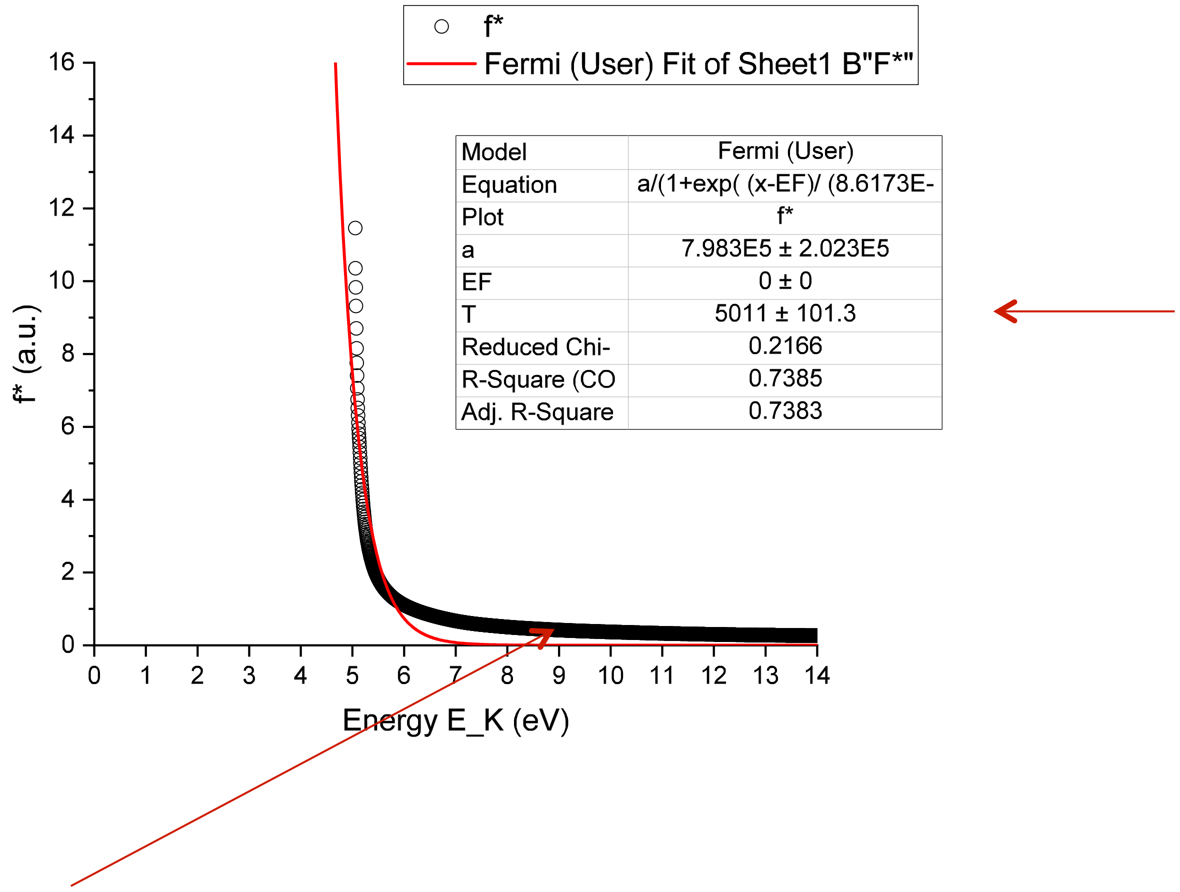
critical alignment at onset:
Physics (barrier) or model (or experimental error)?

Experimental distribution function (arbitrary units)



matlab code R.Fallica - IMEC

Thermal fit to experiment (Fermi function)



non-thermal behavior

Summary and open issues

A simple expression (even naïve) for the kinetic energy distribution of secondary electrons has been written in terms of the experimental parameters and of the material properties with the double goals of analyzing the experimental spectra and at contextually testing the difficulties and limits of a quantitative description and where they come from

The model shows that the occupation function of the states above the vacuum level in the presence of photon excitation can be obtained by combining the experimental data with the expression obtained from the calculation

It has been applied to the simple case of a Au crystal

The distribution function was obtained in *arbitrary units* a limit that currently involves both the description of the emission process itself and the electron collection (solid angle and transmission)

Suitable normalizations are need: among others TEY (drain current $\int dE_K$...) could be of use

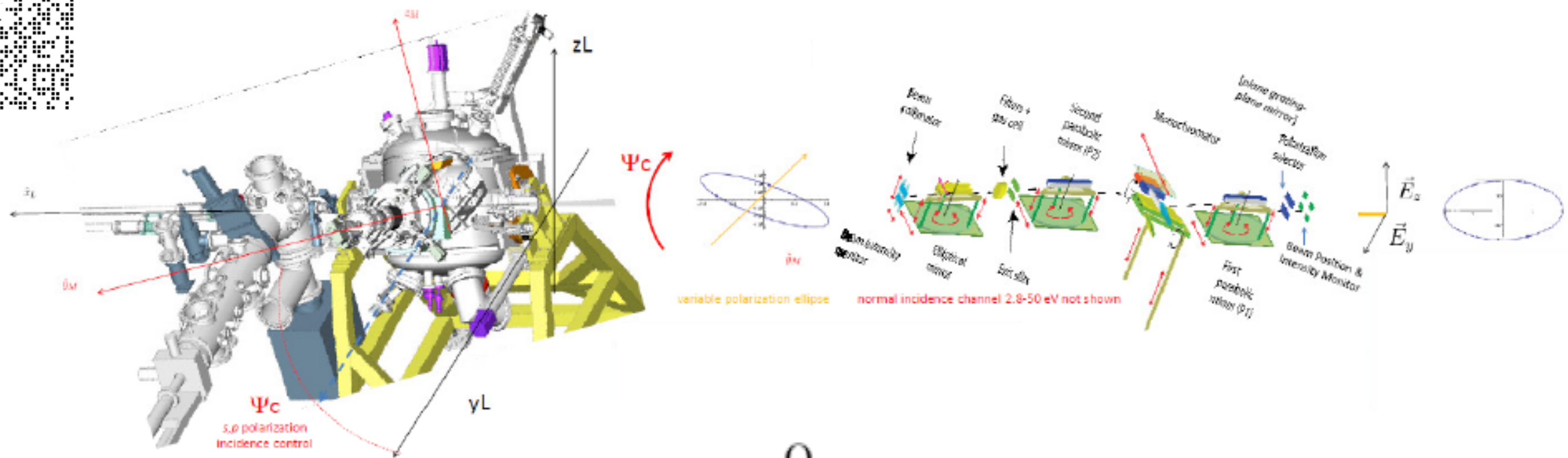
This result, *if confirmed by subsequent experiments*, could be of use, in in application-oriented contexts to monitoring the processes depending on the extent of formation of LEE cloud (e.g. photoresists)

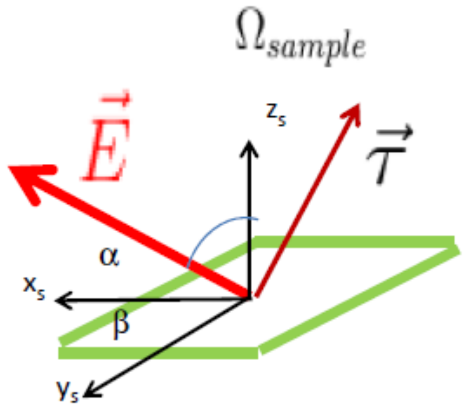
From the emission line-shape a temperature of the electron gas (5000K) was inferred together with the evidence of a disagreement with a thermal excitation

This approach does not allow a direct access to the "hidden tail" of the LEE whose occupancy could anyway described by extrapolating the $f^*(E)$ for $E < \chi$ or seeking for alternate experimental approaches to test the occupation of the states below the vacuum level up to LUMO or Fermi level (*no lack of ideas – but to figure out an experiment numbers are needed*) .

BEAR overview – IOM-CNR beamline at Elettra

[https://www.elettra.trieste.it/elettra-beamlines/bear.html]





BEAR contributes to the BABE unit (Resp.Elena Magnano - https://babe.iom.cnr.it/about-us)
belonging to
AHEAD2020 (Integrated Activities in the High Energy Astrophysics Domain)

L.Pasquali(Dept. of Eng.E. Ferrari, Univ.Modena and R.E. leads a number of activity at BEAR related with the electron yield specifically in the field of materials for aerospace

People involved

- Roberto Fallica IMEC-Belgium

- Georghii Tchoudinov UniCam
- Javid Rezvani

- Angelo Giglia IOM-CNR
- Nicola Mahne
- Marco Malvezzi