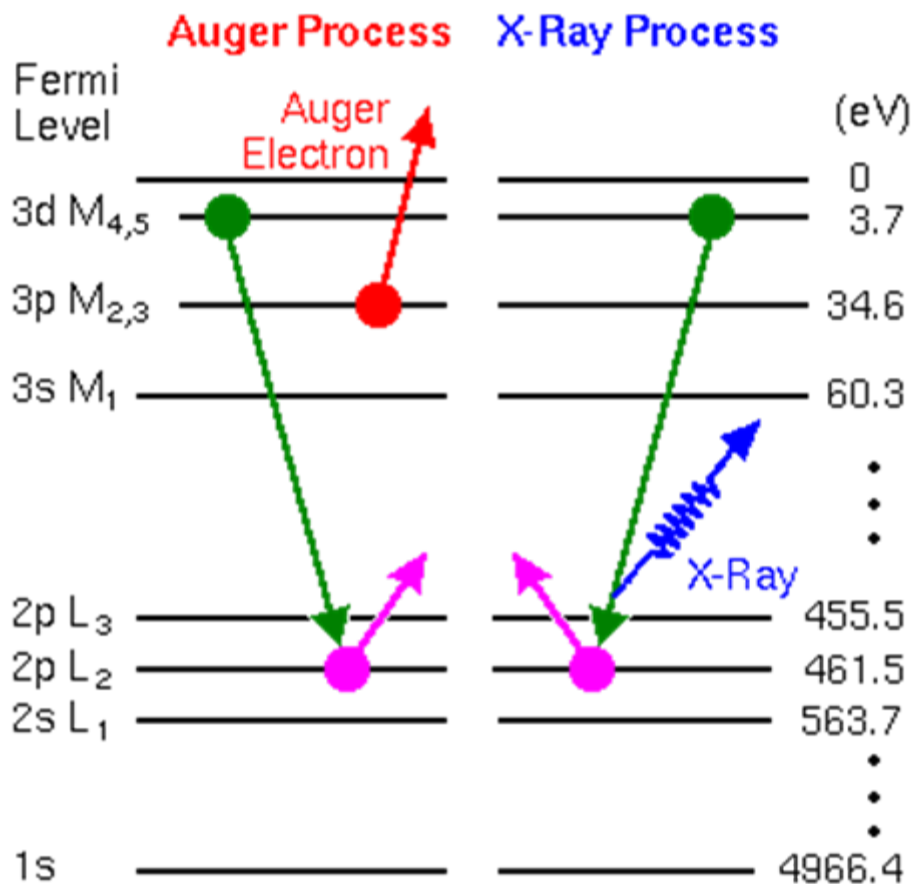# Auger and radioactive relaxation in the case of Titanium

An electron core (violet arrow) of a titanium film is excited by an external electron probe. The two possible relaxation processes are the Auger electron emission or the X-ray emission. Calculate the energy of the emitted Auger electron or the emitted photon

**Auger Process    X-Ray Process**

Fermi
Level

Auger
Electron

(eV)

0

3d $M_{4,5}$    3.7

3p $M_{2,3}$    34.6

3s $M_1$    60.3

$\vdots$

X-Ray

2p $L_3$    455.5
2p $L_2$    461.5
2s $L_1$    563.7

$\vdots$

1s    4966.4

## Solution:  Auger and radioactive relaxation in the case of Titanium

The illustrated LMM Auger electron energy is ~423 eV ($E_{Auger} = E_{L2} - E_{M4} - E_{M3}$) and the X-ray photon energy is ~457.8 eV ($E_{hv} = E_{L2} - E_{M4}$).
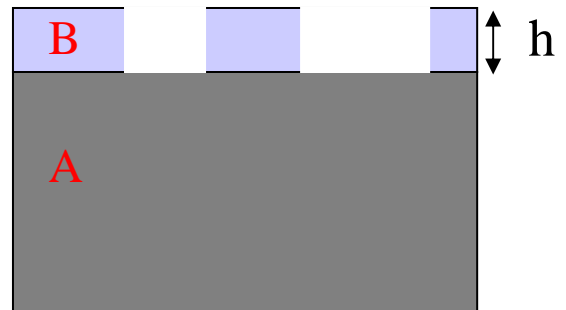
**Auger intensity**

Consider an electron beam of intensity I(0) impinging with an angle θ on the surface of a thick sample.

a) Assuming an absorption factor $r$ for each atomic plane which is the intensity J(z) of the electron beam at the depth $z$?

b) Which is the intensity of the resorting beam measured by a detector? (note that the adsorption factor for the Auger electrons is in general different from that of the impinging electrons. Why?)

c) You want to monitor by Auger spectroscopy the growth of a thin film (element B) on the sample surface (element A). Which is the evolution of the intensity of the Auger peaks for element B and A as a function of the film thickness h assuming a layer-by-layer growth and h < 4-5 ML (very thin film)?



d) Which is the evolution of the intensity of the Auger peaks for element B and A as a function of the film thickness h if the film grows in a discontinuous way (keep the assumption of very thin film)?



θ fraction of the surface covered by the film

# Solution:  AUGER intensity

**a)** The intensity arriving on the first atomic plane is I, the one on the second atomic plane is $J(2)=I(0)/r$, on the third is $J(3) = I(0)/r^2$, ... . In general $J(z) = I(0)\, r^{-z/d}$ if d is the atomic layer thickness.

**b)** Similarly to point a) the intensity of the Auger electrons emitted at a depth z and measured by the detector at the surface will be $I(z) = I(0)\, r^{-z/d}\, s^{-z/d}$ where s is the attenuation factor for the out-coming electrons. The previous formula can also be written in the usual form $I(z) = I(0)\, \exp(-z/d\, \ln(rs)) = I(0)\, \exp(-z/\lambda)$ with $\lambda = d/\ln(rs)$ the electron mean free path. The total intensity measured by the detector is the summation over the contribution of all the atomic planes which means $I = \int_0^z I(z)\, dz = I(0)\, \lambda\, (1-\exp(-z/\lambda))$. Actually the measured intensity depends by an other multiplicative factor taking into account the effective ionization section which depends on the material i.e. $I = I^\infty (1-\exp(-z/\lambda))$.

Note that we can define an impinging mean free path $\lambda_i = d/\ln(r)$ and an Auger mean free path $\lambda_{Auger} = d/\ln(s)$ in such a way that $1/\lambda = 1/\lambda_i + 1/\lambda_{Auger}$. Because the energy of the impinging electrons is of the order of 3 KeV while typically Auger electrons have energy of 100-500 eV, $\lambda_i \gg \lambda_{Auger}$ meaning that the mean free path $\lambda$ is the one of the Auger electrons

**c)** The intensity due to the element B is
$I_B = \int_0^h I(z)\, dz = C_B\, \lambda_B(E_B)\, (1-\exp(-h/\lambda_B(E_B)))$ where the multiplicative factor due to the ionization section is explicitly included and $\lambda_B$ depends on the attenuation factor for the element B and the energy $E_B$ of the Auger electrons emitted by atoms of type B.

Concerning the element A we have to take into account the assumption of very thin film. This implies that the impinging electrons travel practically undisturbed the element B and that the signal measured by the detector is than due to the Auger electrons generated in A attenuated due to the traveling in B.

The intensity due to the element A at the interface A-B is
$I_{A-B} = \int_0^\infty I(z)\, dz = C_A\, \lambda_A(E_A)$ . This intensity is attenuated during traveling in B. The intensity on the detector is $I_A = I_{A-B}\, \exp(-h/\lambda_B(E_A))$ where $\lambda_B$ depends on the attenuation factor for the element B and the energy $E_A$ of the Auger electrons emitted by atoms of type A.


d) The intensity due to the element B is now proportional to the fraction of the surface covered by the film. Using the previous result
$I_B = \theta\, C_B\, \lambda_B(E_B)\, (1-\exp(-h/\lambda_B(E_B)))$

Similarly $I_A = C_A\, \lambda_A(E_A)\, [(1-\theta) + \theta\, \exp(-h/\lambda_B(E_A))]$ where the $(1-\theta)$ term takes into account the uncovered A surface

**Alloying during epitaxial growth of Ni on Au(100)**

The room temperature growth of Ni on Au(100) has been studied by Auger spectroscopy as a function of the film thickness $n$. The experimental data and the fits with different models are shown in Fig1.

a) Model 0. Assuming the Ni growing in a layer-by-layer fashion, give an expression for the normalized Au Auger intensity as a function $n$. The monitored Au Auger peak is at 69 eV. Assume an equal mean free path $\lambda$ for electrons traveling Au and Ni. Is the model fitting the experimental data?

b) Model I. We assume that alloying takes place with mixing between gold and nickel atoms limited to the first surface plane. We also introduce a parameter K representing the fraction of the Au atoms of the topmost surface plane that are mixed with the Ni incoming atoms. The model is schematically represented in fig. 2. Give an expression as a function of K and $A = \exp(-1/\lambda)$ for the normalized Auger intensity after depositing 1 ML of Ni?

c) Using the model I, which is the expression for the normalized Auger intensity after depositing 2 ML of Ni?

d) Can you find a recurrence relation between the intensity measured after $n$ and $n+1$ deposited layers?

e) Assuming $\lambda = 2$ ML try to estimate the value of K using the experimental points
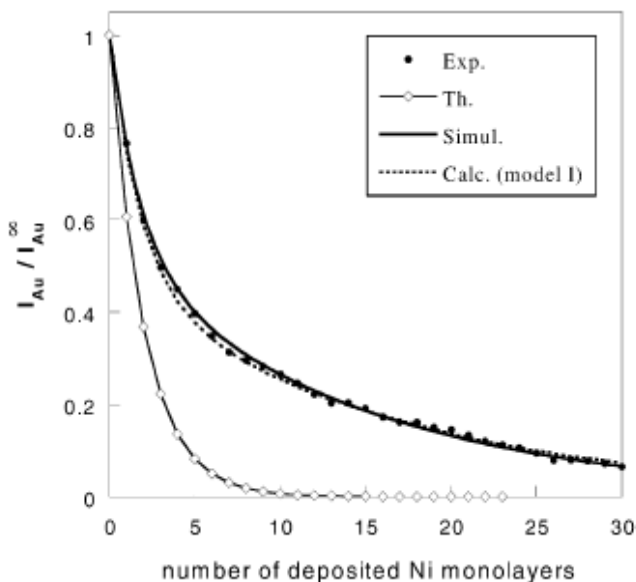


Fig.1 Normalized Au Auger intensity $(I_{Au}/I^{\infty}_{Au})$ as a function of the number $n$ of deposited Ni ML: experimental data (*), theoretical intensity in the absence of segregation effects (model 0), simulated intensity obtained by adjusting the parameter K to the experimental data for each $n$ (model I).
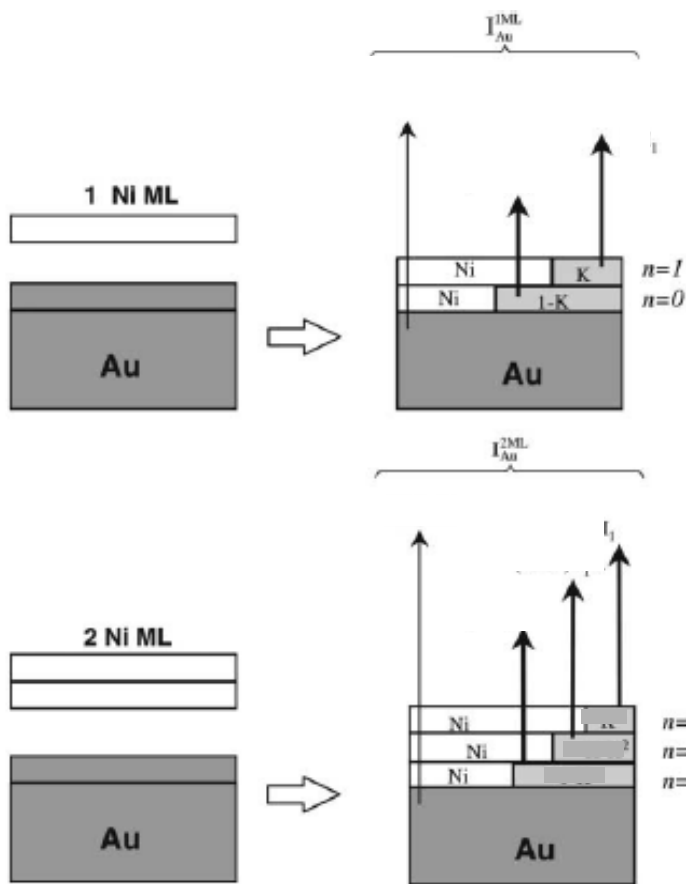
Fig. 2. Schematic representation of the alloying model used to calculate the Au Auger intensities for one (I1ML Au ) and two (I2ML Au ) Ni ML deposited on Au (n = 0 refers to the topmost Au surface plane before the Ni deposition, K is the atomic exchange coefficient between the Au atoms of the topmost surface plane and the incoming Ni atoms, A the attenuation factor relative to one atomic layer).

λ (electron mean free path) as a function of the electron energy
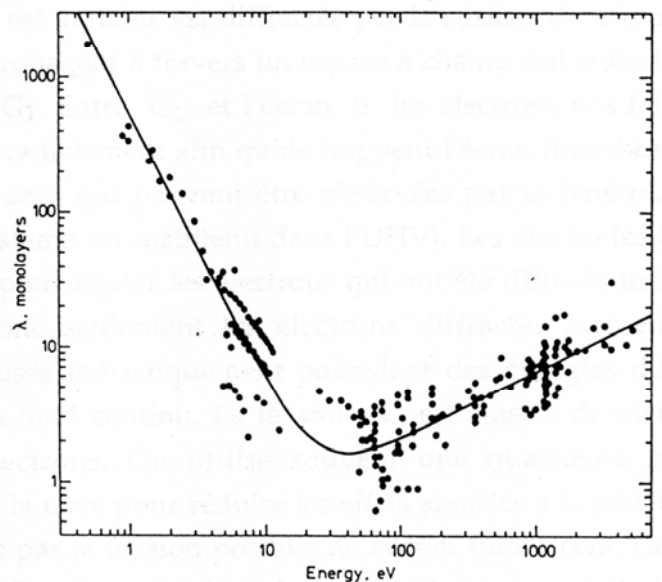
# Solution: Alloying during epitaxial growth of Ni on Au(100)

**a)**  $I(n) = I_{Au}^{\infty} \exp(-n/\lambda)$ with $\lambda = 2$ ML for an energy of 69 eV

**b)**  Indicating with A the quantity $\exp(-1/\lambda)$ and looking to fig.2 we have a fraction K of the surface giving $I^{\infty}$, a fraction (1-2K) giving $I^{\infty}A$ and a fraction K giving $I^{\infty}A^2$. The normalized intensity is than given by $J(1) = K + (1-2K)A + K A^2 = A + (1-A)^2K$

**c)**  The mixing is confined to the topmost layer meaning that a fraction K of the previous K fraction of surface Au (i.e. $K^2$) stays at the new surface (n=2 in fig2) and a fraction (1-K) of the previous K fraction (i.e. $K-K^2$) stays in the first sub-surface layer (n=1 in fig2), while the previous (1-K) fraction stays unchanged (n=0 in fig2). The normalized intensity is than given by $J(2) = K^2 + (K-2K^2)A + (1-2K+K^2)A^2 + KA^3 = A [A + (1-A)^2K] + (1-A)^2K^2 = A J(1) + (1-A)^2K^2$

**d)**  Generalizing  $J(n+1) = A J(n) + (1-A)^2 K^{n+1}$

**e)**  Assuming $\lambda = 2$ ML we get A=0.605.
Using the formula calculated in b) and c) one obtains K=1.06 and K=0.93.
The best fit using all the experimental data points gives A = 0.57 or $\lambda$ = 1.8 ML and K = 0.94
Note the strange value for K in the case of just one monolayer (K has to be inferior to 1). A better agreement is obtained refining the alloying model and assuming that the alloying concerns the two topmost surface planes.