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Characterization of Nickel Diffusion in Gold

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U.S. DEPARTMENT OF ENERGY NNSA

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PURPOSE

To understand nickel diffusion in gold and impacts on low temperature aging.

To verify and cross-reference surface analysis quantification.

To develop quantitative HAXPES with application to the gold/nickel system.

<u>HAXPES performed at NSLS (only HAXPES end-station in USA)</u>

NSLS is a DOE user facility at Brookhaven Ntl. Labs

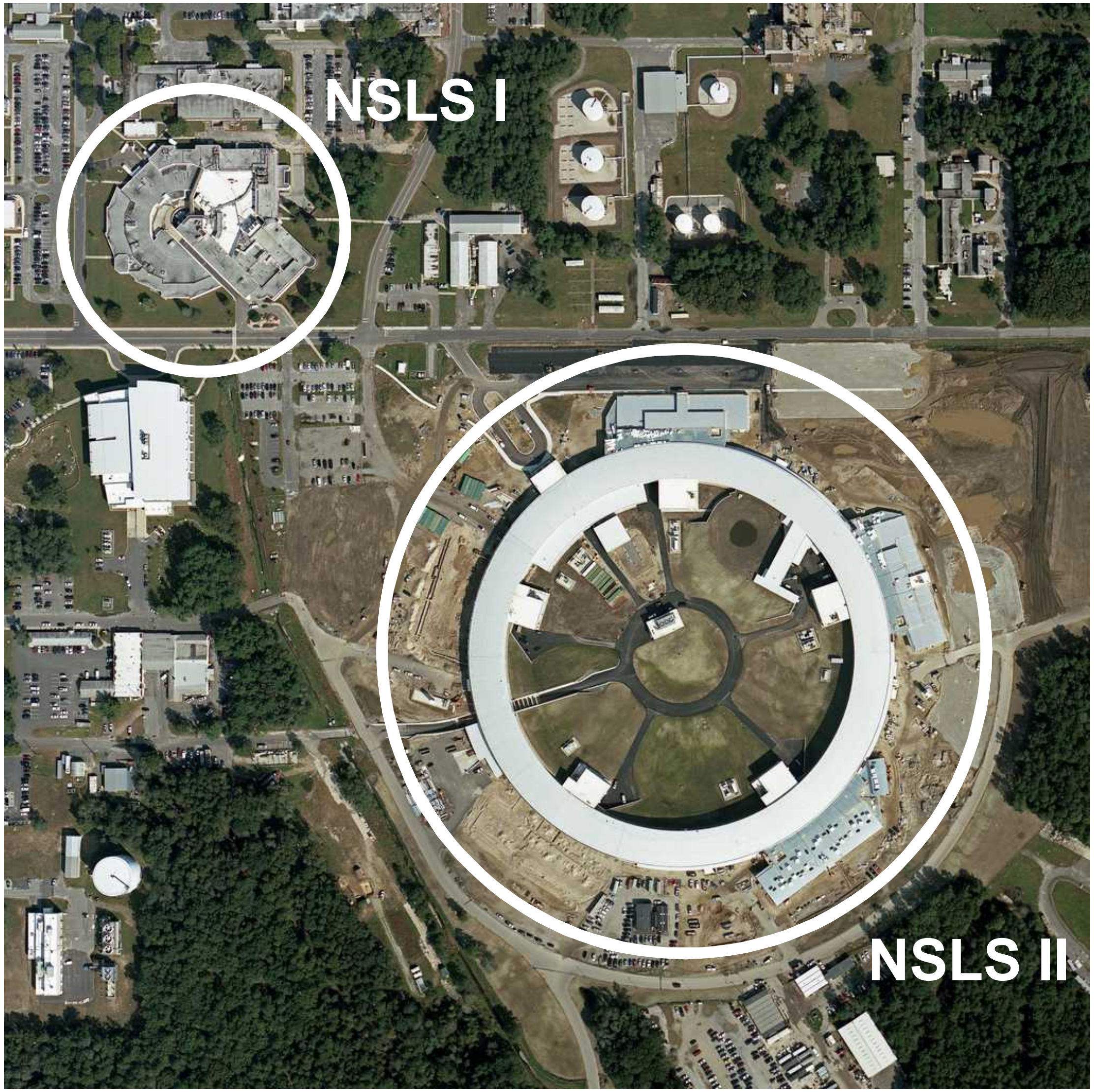
Operational since 1982

Provides high-brightness radiation from far-infrared to 100 keV X-rays.

49 beamlines on the X-ray ring

16 beamlines on the VUV-IR ring.

NSLS II

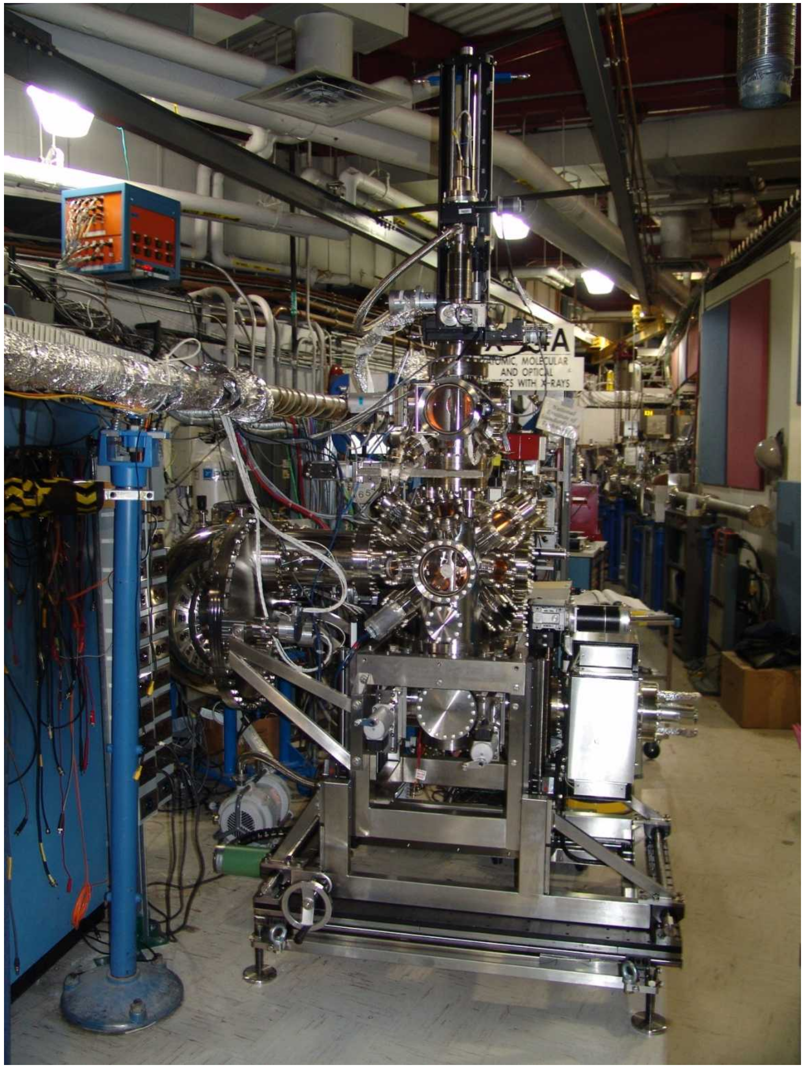


NSLS II (scheduled for 2015)

"NSLS-II will be a new state-of-the-art, medium-energy electron storage ring (3 billion electron-volts) designed to deliver world-leading intensity and brightness, and will produce x-rays more than 10,000 times brighter than the current NSLS."

www.bnl.gov/ps/nsls2/about

HARD X-RAY PHOTOELECTRON SPECTROSCOPY HAXPES



In laboratory XPS instruments, the energy of the excitation source is fixed (commonly 1487 or 1254 eV).

At beamline X24A, the energy of the light source can be tuned across a broad range (2000-5000 eV) with higher brightness and better resolution.

<u>Advantages of HAXPES</u>

Study samples from air; i.e., real samples!

Tune information depth for experimental system.

Variable kinetic energy XPS (VKE-XPS) for depth profiling and chemical speciation.

Bulk and surface sensitive core lines accessible for the same element.

Eliminate Auger interferences.

Photoemission and other techniques (SSXPS).

SURFACE ANALYSIS

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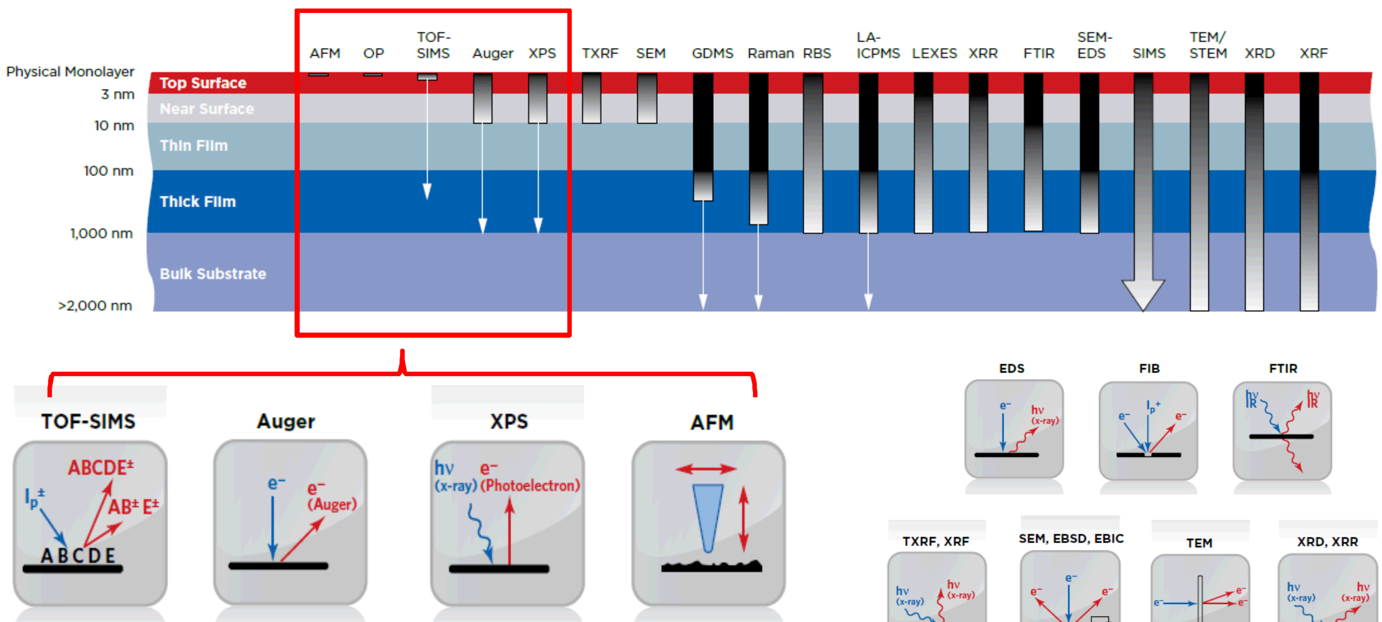
Analytical techniques with sensitivity to the uppermost nanometers of a material providing vertically resolved chemical analysis.

laboratory - XPS, AES, SIMS, ...

synchrotron - NEXAFS, VKE-XPS, ...



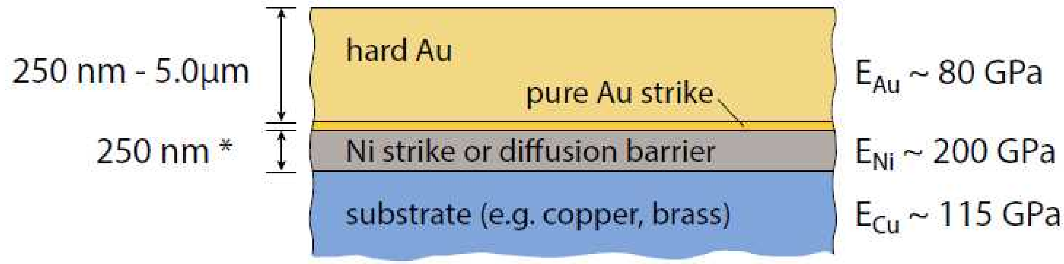
Evans Analytical Group, www.eaglabs.com/

HARD GOLD FOR ELECTRICAL CONTACTS

What is Hard Gold? (defined in ASTM B488-11 / MIL-DTL-4520D)

hard gold films are defined by the following three numbers (specifications):

1. type (purity)
2. code or grade (hardness)
3. class (minimum thickness)



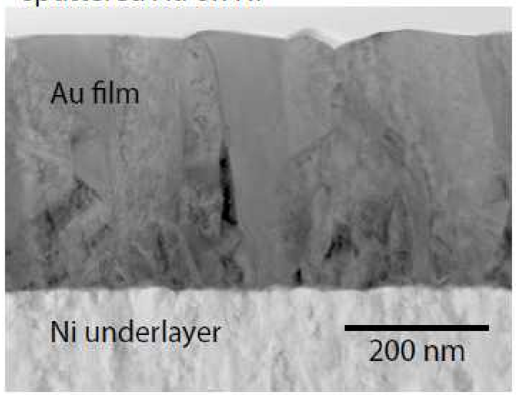
* if operating at high temperature and on a Cu substrate then > 1.2 µm is recommended

	purity	type	suggested applications (ASTM)
	> 99.7% Au	I	general-purpose, high-reliability electrical contacts
(hardest)	> 99.0% Au	II	general-purpose, wear resistance; low temperature only
(softest)	> 99.9% Au	III	soldering; limits impact of oxidation of codeposited material
		IIIA	semiconductor components, nuclear eng., high temperature

more Ni/Co/Fe content (in the 0 to 2 vol. %) → *increased hardness* → *reduced wear and increased electrical contact resistance*

TYPES OF DIFFUSION

sputtered Au on Ni



L.G. Harrison defined three behavior regimes for experimental diffusivity measurement.

where,

$$d = grain\ size\ (m)$$
$$t = aging\ time\ (s)$$
$$\delta = grain\ boundary\ width \cong 0.5\,nm$$
$$D_L = lattice\ diffusivity\ (cm^2/s)$$

$\sqrt{D_L t}$ *is approx. the* ***diffusant penetration depth into the lattice***

type A (lattice dominated) diffusion

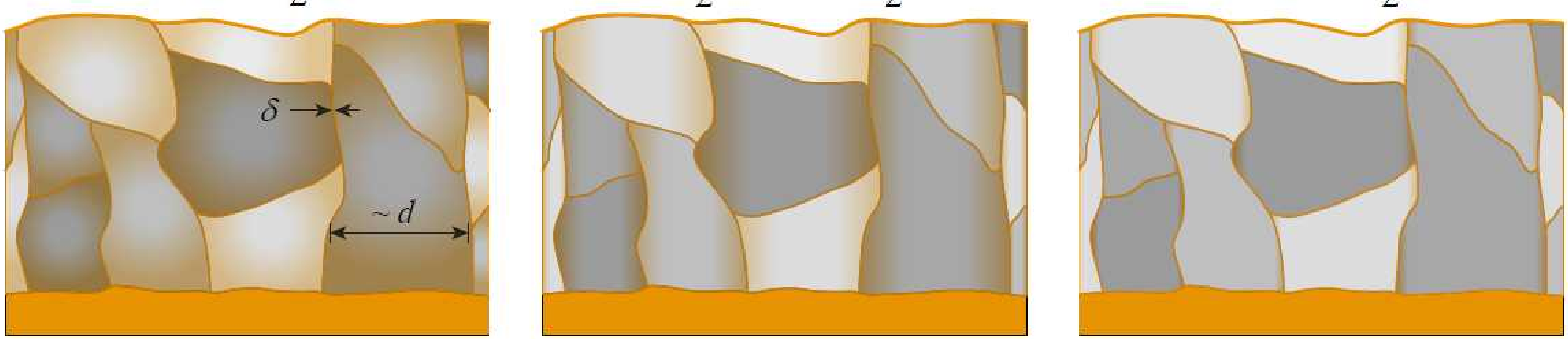
$$\sqrt{D_L t} \geq \frac{d}{2}$$

type B (mixed lattice/G.B.) diffusion

$$\frac{\delta}{2} < \sqrt{D_L t} < \frac{d}{2}$$

type C (grain boundary dominated) diffusion

$$\sqrt{D_L t} \leq \frac{\delta}{2}$$



decreasing ***temperature*** *or* ***aging time***

Reference: L.G. Harrison, Trans. Faraday Soc., **57** (1961) 1191.

DIFFUSION IN GOLD

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Temperature Activated Process

Diffusivity coefficient (D) is an empirical parameter shown to follow Arrhenius behavior.

$$D_{GB} = D_{o,GB} \exp\left(-\frac{E_a}{RT}\right)$$

Diffusion Regimes

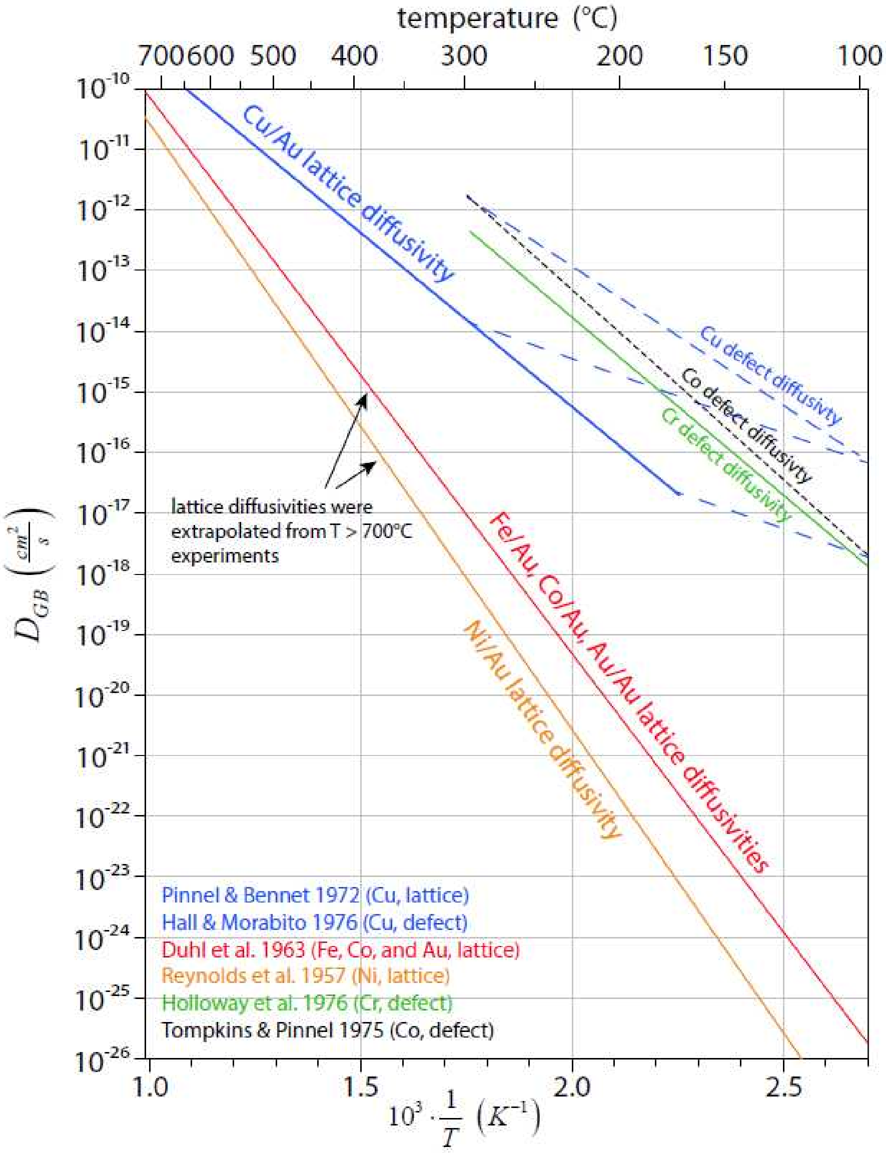
Metal interdiffusion occurs by four mechanisms, each described by a unique diffusion coefficient:

- D_L *inter-granular lattice diffusion*
- D_{GB} *grain boundary diffusion*
- D_P *pipe diffusion through dislocation cores*
- D_S *surface diffusion*

where: $D_L << D_{GB} \sim D_P << D_S$

Low Temperature Defect Dominated Diffusion

The volumetric density of defects (dislocations and grain boundaries) plays the dominant role in low temperature diffusion degradation



AGING AND CONTACT RESISTANCE

Hwang-Balluffi Model

$$\frac{c_s}{c_a} = 1 - \exp\left[-s(t - t_o)\right]$$

where, $s = \dfrac{2 w_b D_b}{w_s l d}$

w_b is width of a GB

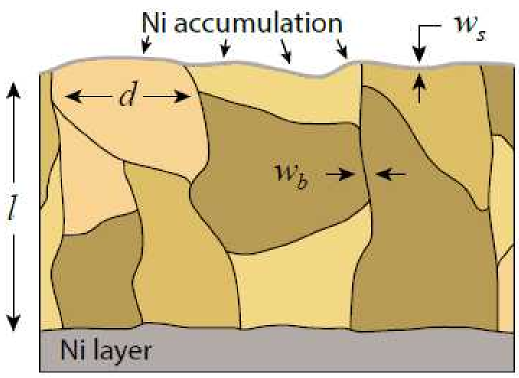
D_b is GB diffusivity

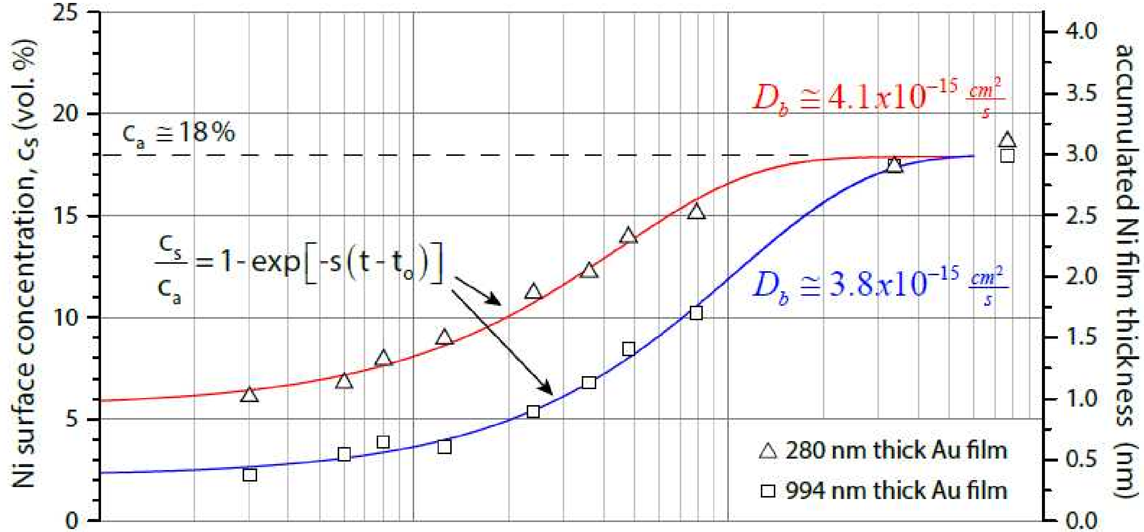
w_s is accum. film thickness

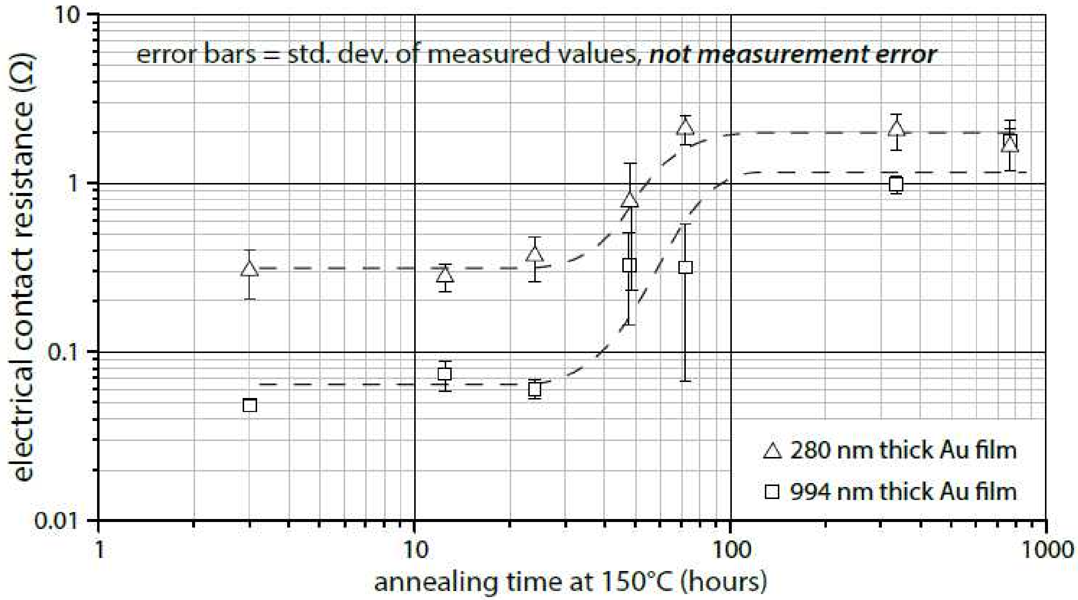
l is Au film thickness

d is avg. grain size

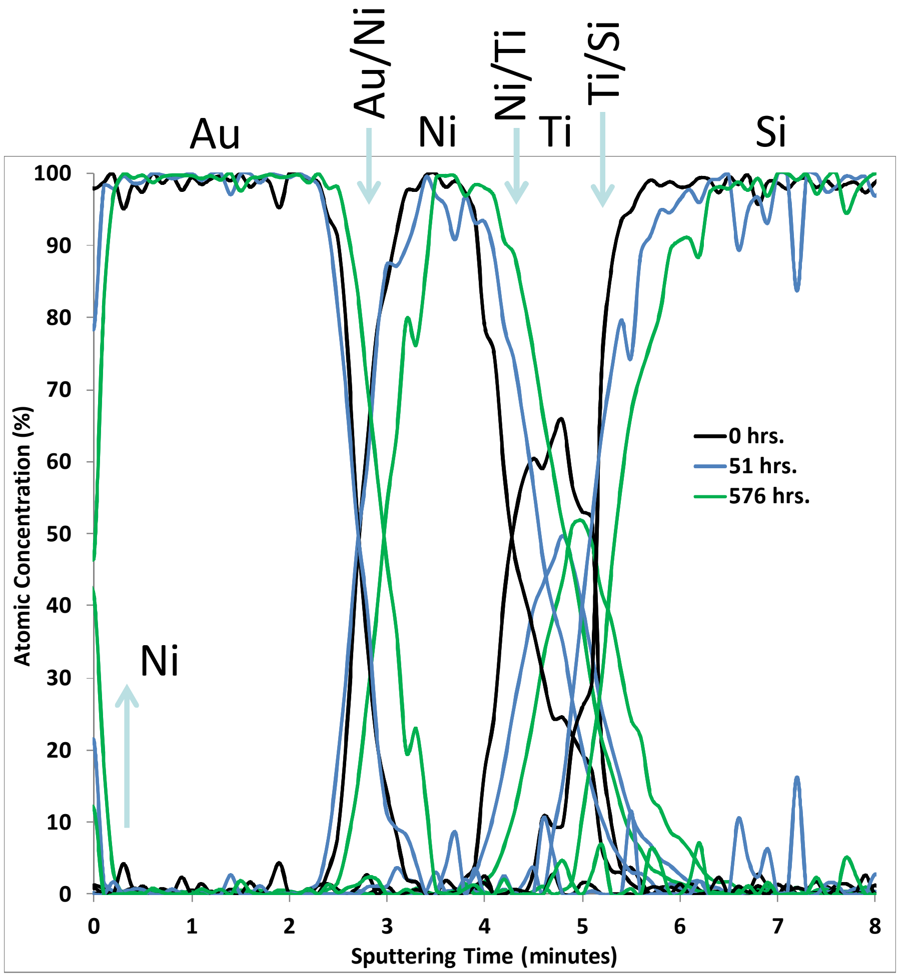
Reference: Hwang and Balluffi, JAP, **50**-3 (1979)







AUGER ELECTRON SPECTROSCOPY



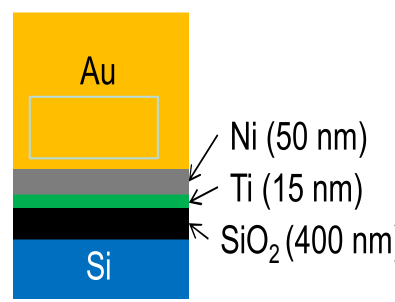
	Sputtering rate
Gold	1.5 nm/s
Titanium	0.3 nm/s
Nickel	0.5 nm/s

Auger depth profiles of aged thin film stacks show:

1) Nickel concentration increases at the surface.

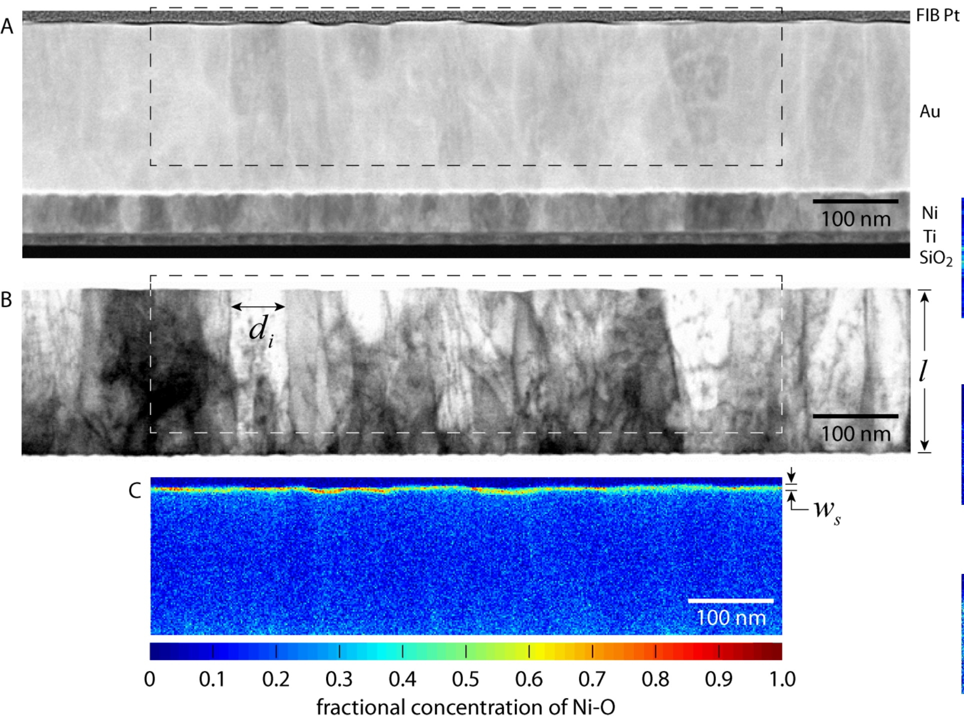
2) The Au/Ni interface is unaffected until longer aging times where it shows some broadening.

3) The Ni/Ti and Ti/Si interfaces become mixed.

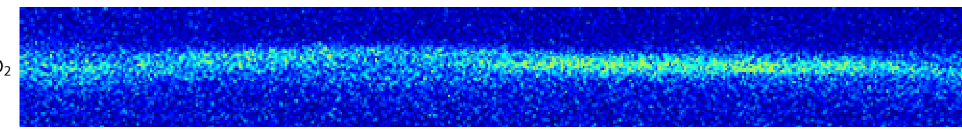


TEM OF NICKEL SURFACE LAYERS

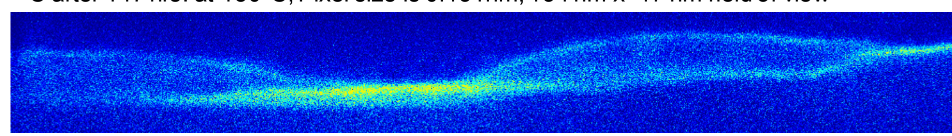
Ni content was confirmed as a thin surface layer on top of the gold via AC-STEM.



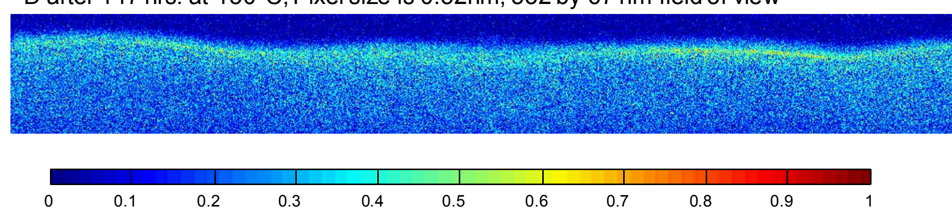
B after 147 hrs. at 150°C, Pixel size is 0.092nm, 94 x 12 nm field of view



C after 147 hrs. at 150°C, Pixel size is 0.131nm, 134 nm x 17 nm field of view



D after 147 hrs. at 150°C, Pixel size is 0.52nm, 532 by 67 nm field of view



QUANTIFICATION COMPARISONS

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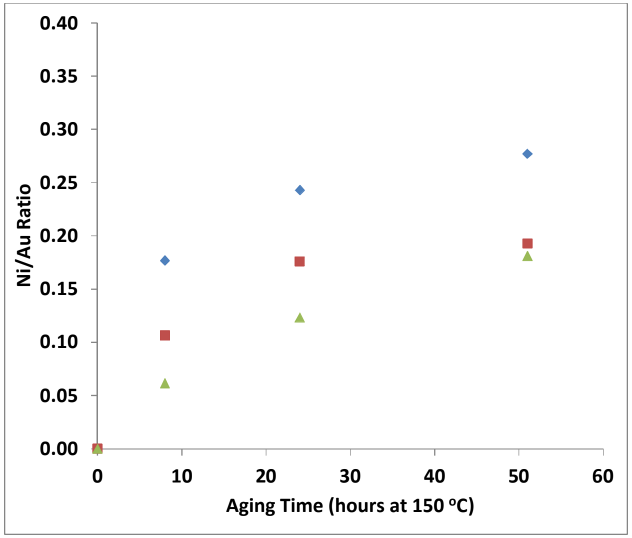
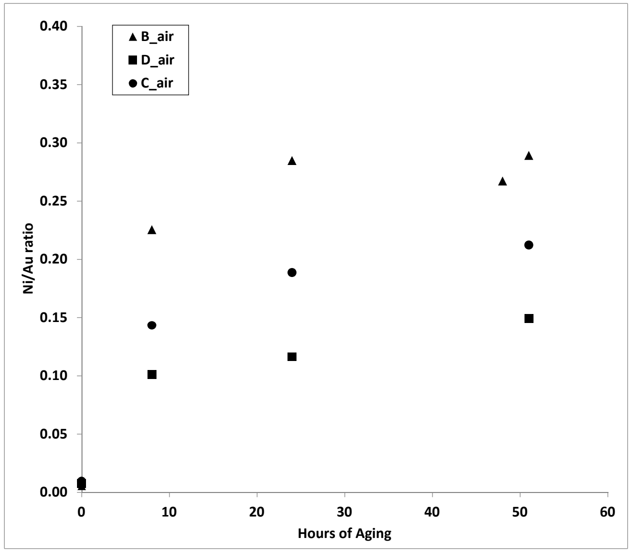
Quantifications from Auger and XPS are very similar.

XPS



Auger



Quantifications from grazing incidence X-ray diffraction are unreliable. The depth of penetration is too large to provide useful surface information.

(Au lattice parameter – measured lattice parameter)/5.548e^{-3} = atomic % Ni substitution

	% Ni - GIXRD			% Ni – normal XRD		
	0 hrs.	**8 hrs.**	**147 hrs.**	**0 hrs.**	**8 hrs.**	**147 hrs.**
A	1.6	-0.7	1.0	0.1	0.5	1.4
B	0.6	-0.1	-0.3	-0.1	1.9	2.5
C	1.0	0.0	-0.2	0.4	1.7	2.1
D	1.0	-0.7	0.3	1.1	1.9	2.5

QUANTIFICATION IN XPS

The intensity of a photemission peak (I_a) is dependent on a number of parameters.

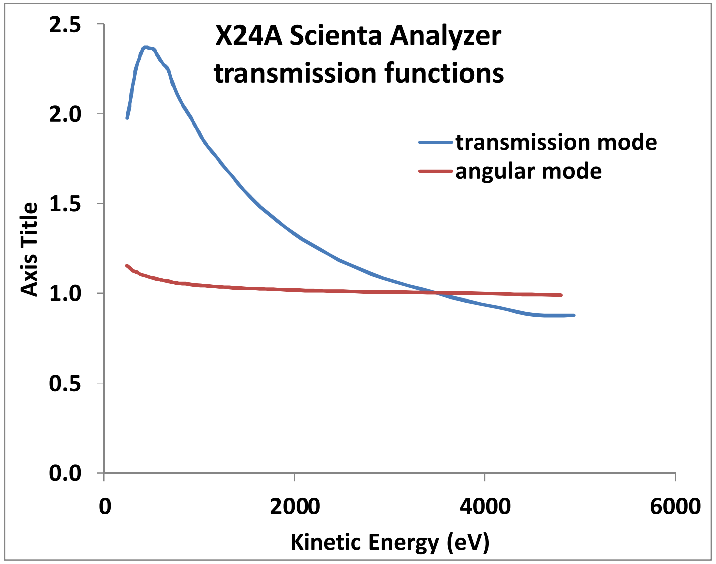
$$I_a = \Phi C_a \sigma \lambda A T$$

Φ = X-ray flux
C_a = concentration of element a
σ = subshell ionization cross-section
λ = probability of no-loss escape (IMFP)
A = angular acceptance of analyzer
T = transmission function of analyzer

The parameters must be determined to make quantification possible.

$$I_a = \Phi C_a \sigma \lambda A T$$

T = transmission function of analyzer



PHOTOIONIZATION AND ELECTRON ESCAPE DEPTH

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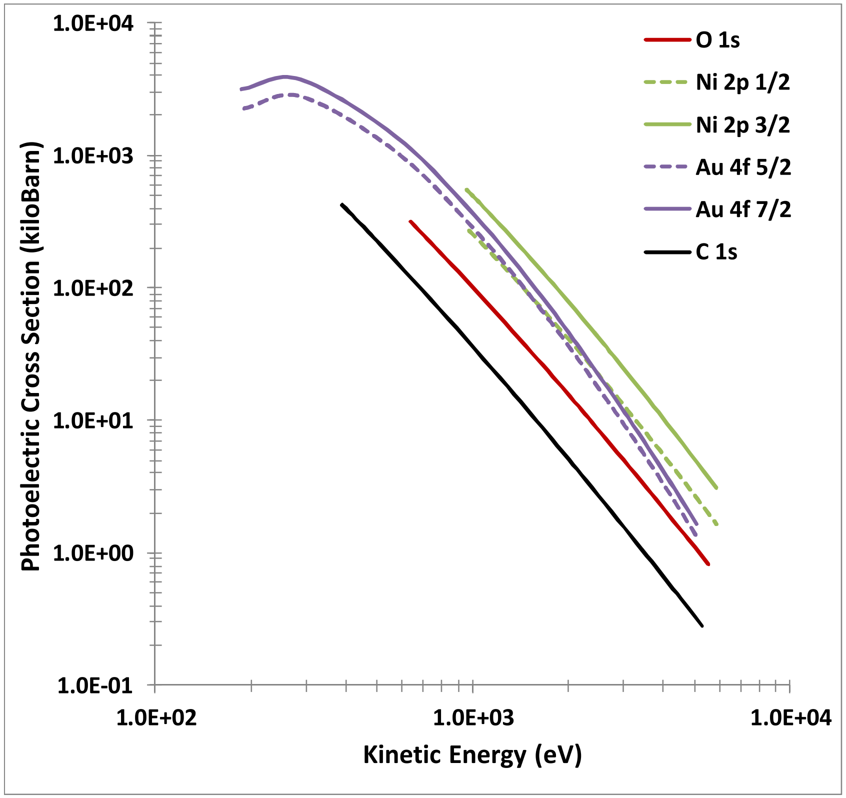
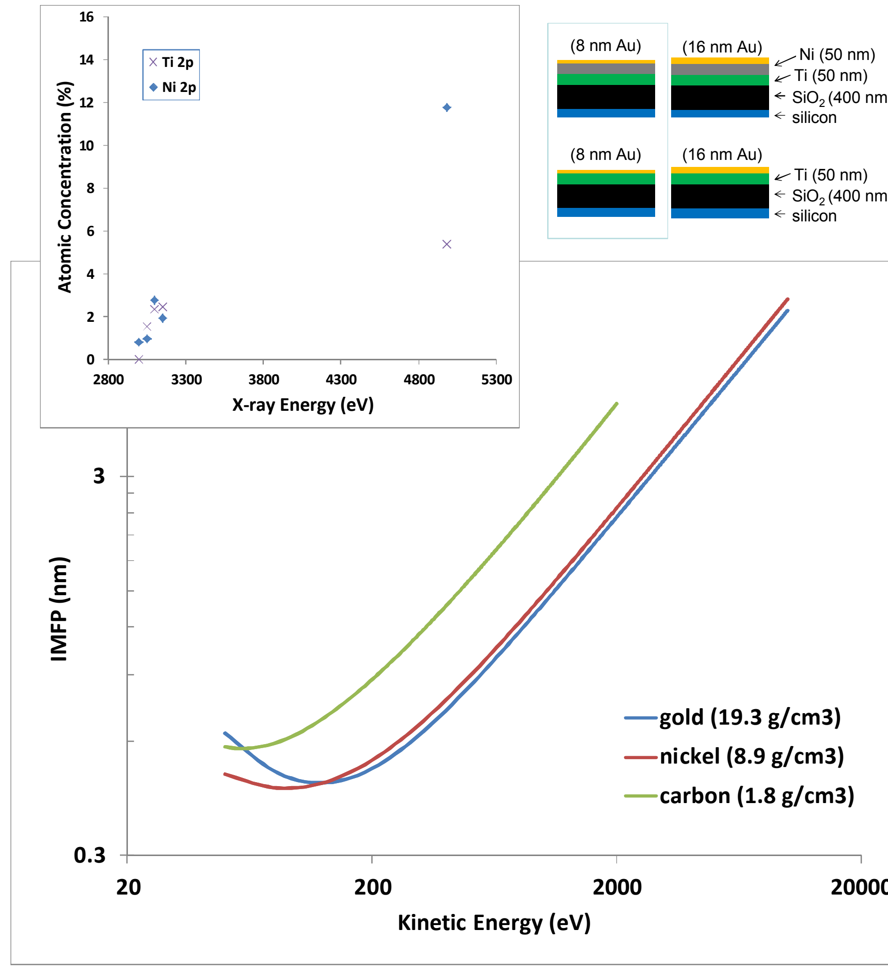
$$I_a = \Phi C_a \sigma \lambda A T$$

σ = subshell ionization cross-section



$$I_a = \Phi C_a \sigma \lambda A T$$

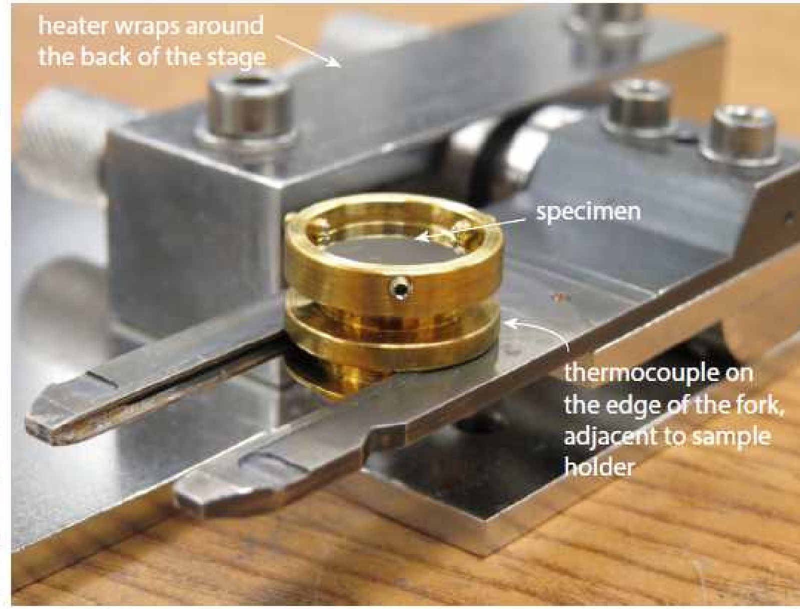
λ = probability of no-loss escape (IMFP)

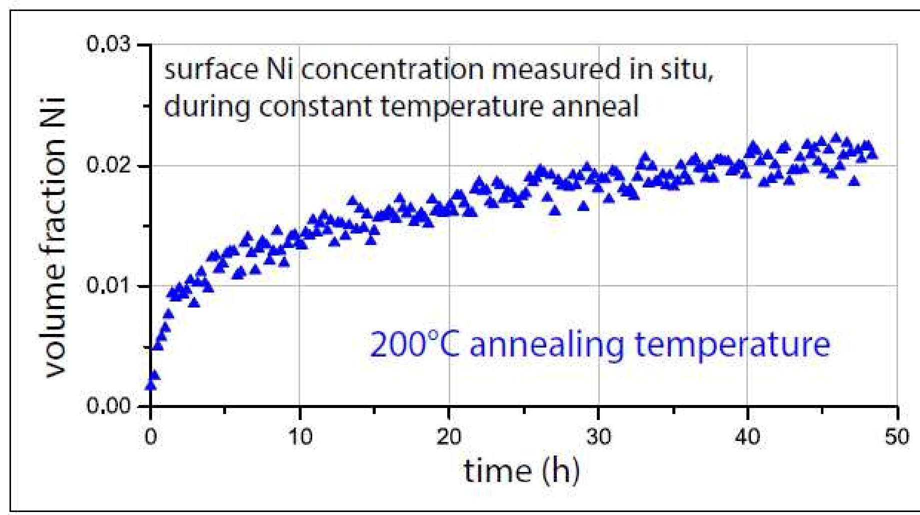


ON-GOING WORK – IN SITU DIFFUSION STUDIES

In situ thermal aging in XPS developed

Kratos Axis Ultra DLD XPS/UPS





ON-GOING WORK – ACTIVATION ENERGIES

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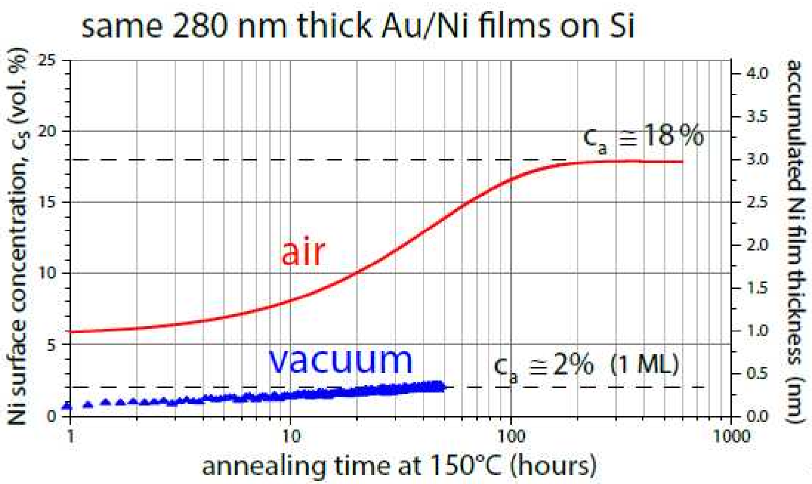
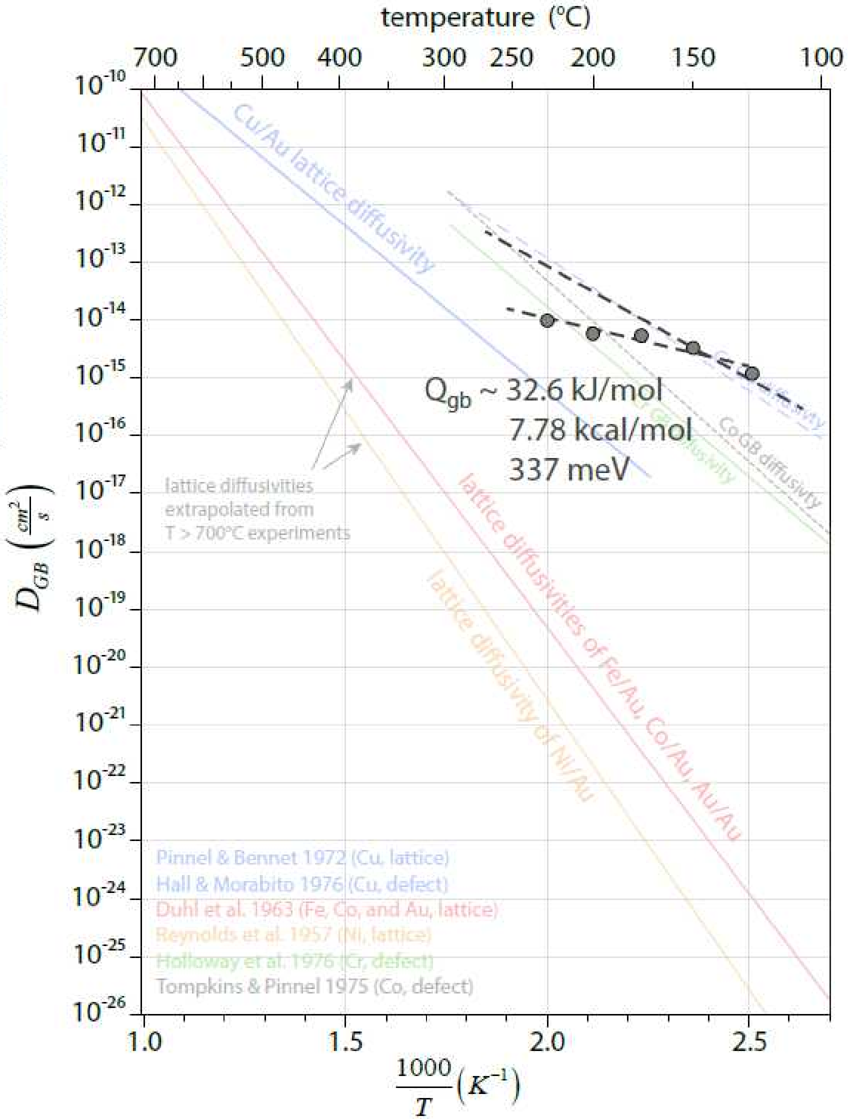


oxidation is a "sink" for arriving Ni

activation energy is unusually low... strain effect?



SUMMARY

Conclusions

- Underlayers, such as Ni strikes, are key participants in diffusion related aging
- A simple predictive model for the rate of material accumulation has been identified (Hwang-Balluffi) assuming some information about the films (thickness, grain size, temperature, etc.)
- Surface accumulation behavior was asymptotic
- For Ni (and presumably other systems) the thickness of the accumulation layer will exhibit a thickness of 1-3 nm and non-uniform coverage, greatly affecting ECR
- Oxide debris accumulation is also a concern (potential for "contact chatter")