Application and Development of Surface Analysis for Investigating of Surface Products and Thin Films

Surface Analysis

- Definition of Solid Surface: Outer-most atomic layers
- Importance of Surface:
  - Properties differ from those of the bulk
  - Solid interacts with their surroundings through surfaces
- Main Techniques
  - ***Electron Spectroscopies***

    XPS: X-ray Photoelectron Spectroscopy

    AES: Auger Electron Spectroscopy

    EELS: Electron Energy Loss Spectroscopy
  - ***Ion Spectroscopies***

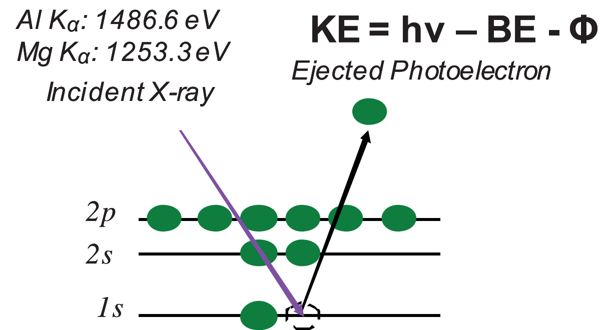
    SIMS: Secondary Ion Mass Spectrometry

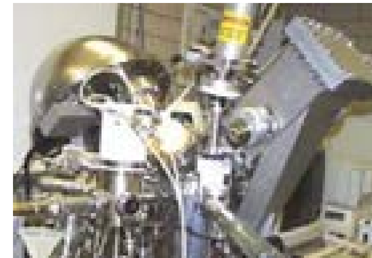
    SNMS: Sputtered Neutral Mass Spectrometry

    ISS: Ion Scattering Spectroscopy
  - ***Compliment***: SEM, AFM, XRD and so on.

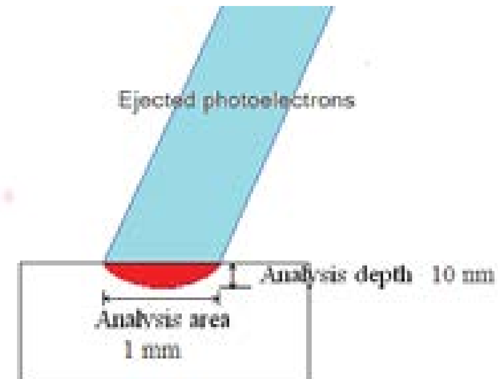
Surface Analysis---XPS

X-ray Photoelectron Spectroscopy
or Electron spectroscopy for Chemical Analysis (ESCA)



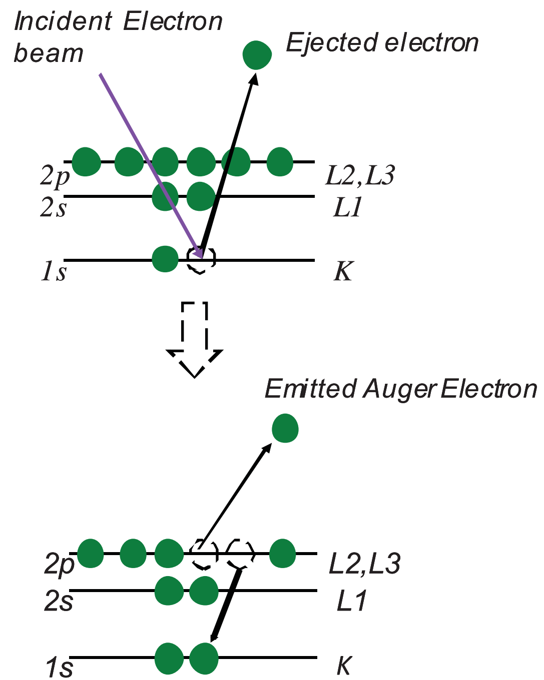


- In: X-ray
- Out: Photoelectron
- Info: a) Chemical composition and states
  b) Film thickness
  c) Distribution of elements in depth
- Lateral resolution: ~ 1 mm



Surface Analysis---AES

Auger electron spectroscopy

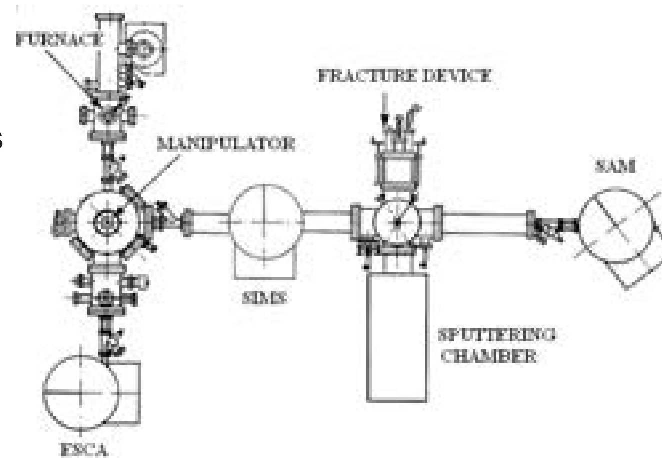


- In: Electron beam
- Out: Auger electron
- Info: a) Chemical composition of small features
  b) Chemical states (some)
  c) Distribution of elements in depth
- High lateral resolution:
  a) ~ 7 nm (SEM)
  b) ~ 12 nm (SAM)

Comparison of XPS and AES

- Both XPS and AES are surface sensitive; can indentify the elements present.

- XPS:
  - Major strength: chemical analysis
  - Low spatial resolution
  - Quantitation straightforward
  - Applicable to insulators



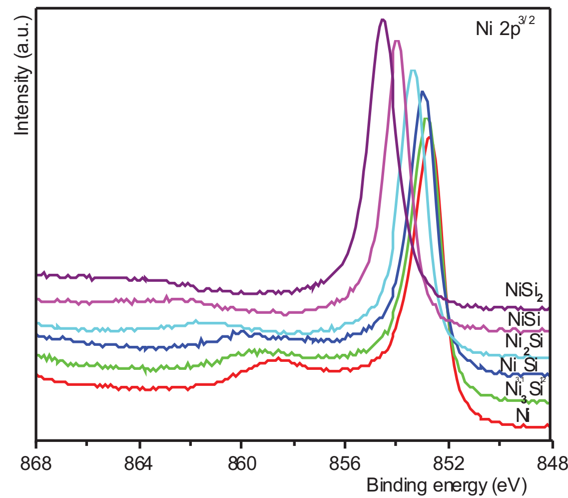
- AES
  - High spatial resolution
  - Quantitation is complex

1. Application on Silicide Thin Films

Chemical Shifts and Auger Parameters

What is Chemical Shift?

- Changes in electron energy resulted from different chemical environment



- Increasing Si content shifts Ni $2p_{3/2}$ core level to higher BE position with respect to Ni metal

$NiSi_2$:	1.9 eV
NiSi:	1.2 eV
Ni_2Si:	0.7 eV
$Ni_{31}Si_{12}$:	0.3 eV
Ni_3Si:	0.1
Ni	0

Formulating of the E_B (Ni $2p_{3/2}$)- C_{Si} (at%) relation

$C_x = (I_x/S_x)/(\Sigma I_i/S_i)$ I_x : intensity in area; S_x: sensitivity factor

Silicide	Stoichiometric composition [1]		Relative concentration (Ni $2p_{3/2}$)		Relative concentration (Ni 3p)	
	Si (at %)	Ni (at %)	Si (at %)	Ni (at %)	Si (at %)	Ni (at %)
$NiSi_2$	66.7	33.3	69.9	30.1	67.9	32.1
NiSi	50	50	60.5	39.5	53.6	46.4
Ni_2Si	33.3	66.7	44.3	55.7	37.7	62.3
$Ni_{31}Si_{12}$	27.9	72.1	31.4	68.6	25.3	74.7
Ni_3Si	22.8-24.5	77.2-75.6	21.9	78.1	17.3	82.7

Boltzmann relation:

$E_B = A_2 + (A_1-A_2)/(1 + \exp((C_{Si}-x_0)/d_x))$

A_1 852.6 ± 0.08

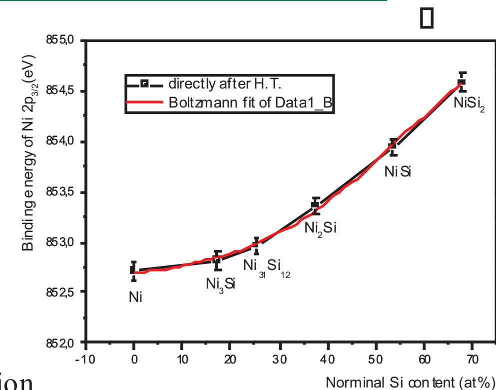
A_2 855.4 ± 0.49

x_0 55.1 ± 5.49

d_x 15.8 ± 3.11

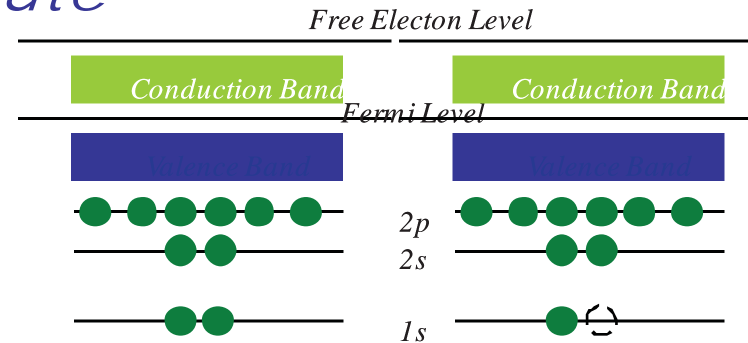
R^2 = 0.99858

Using Ni 3p and Si 2p for quantification



Why do core level shift?

Both initial state and final state effect contribute

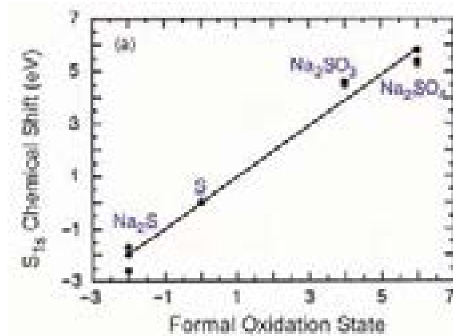


- Initial state effect:
  - Prior to photoemission
  - Other electrons "frozen"
- Final state effect:
  - Following photoelectron emission
  - Re-arrangement of other electrons

    --- minimize the energy

Why do core level shift? --- Initial State Effect

Example 1



Example 2

C-F: 2.9 ev
CF_2: 5.9 eV
CF_3: 7.7 eV

Example 3

Decreasing 3d-electron population with increased Si concentration

Ni_2Si $3d^{8.7}4sp^{1.2}$
NiSi $3d^{8.6}4sp^{1.3}$
$NiSi_2$ $3d^{8.3}4sp^{1.5}$
less dense crystal structure.

- *Ionicity;*
- *Valence orbital transformation;*
- *Valence electron configurations*

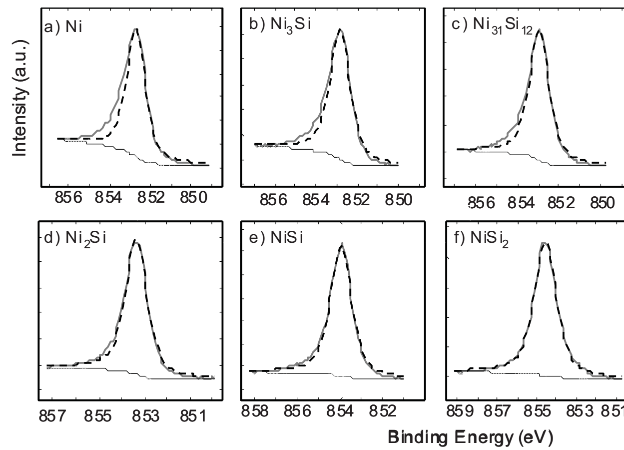
} Distribution and density of electrons

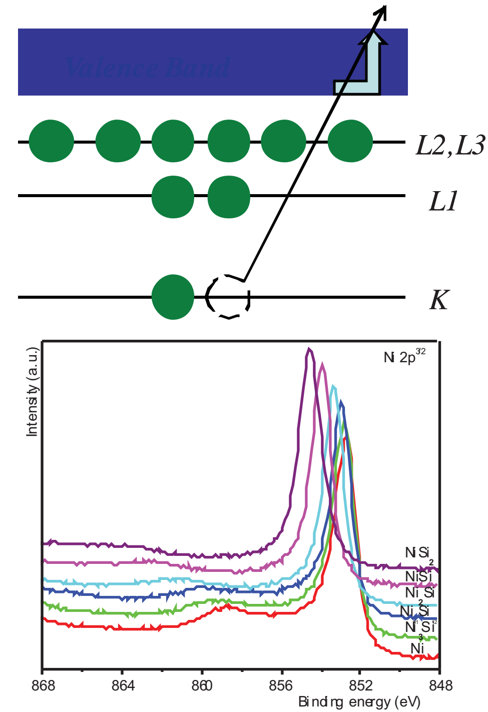
Why do core level shift?--- *Final State Effect*

- Relaxation: energy reduction caused by rearrangement of electrons, lowing $E_{B.}$
- Mostly rearrangement of outer shell
- Positive shift between most metals and their compound.
- Exception: negative 2 eV between Ce and CeO_2
- Other types: shake up, multiplet splitting

Electronic structure information

Shake-up: valence electron excited to a higher energy level

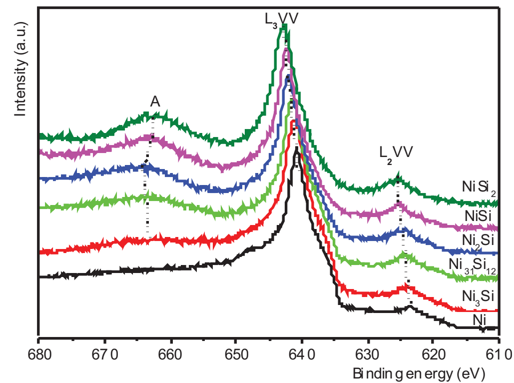


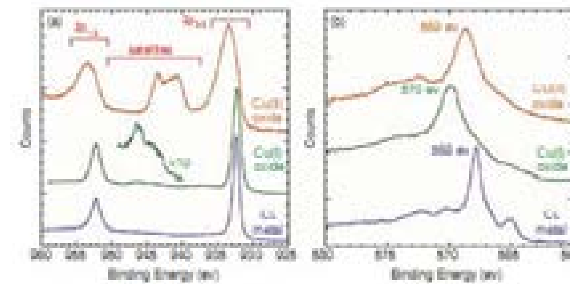


How to estimate the initial and final state effect ?

Estimation of Final State Effect

Auger peaks





Parameter	Ni	Ni_3Si	$Ni_{31}Si_{12}$	Ni_2Si	NiSi	$NiSi_2$
Peak shift of Ni $2p_{3/2}$	0	0.1	0.3	0.7	1.2	1.9
Peak shift of Ni L_3VV	0	0.3	0.7	1.3	1.5	1.9

- Bigger chemical shift than core level peaks, especially for Ni-rich silicides.

$2p_{3/2}$ Cu^0 : 532.5 eV
Cu^{+1} : 532.5 eV
LVV Cu^0: 568 eV
Cu^{+1} : 570 eV

Estimation of Final State Effect

- Auger parameter Definition: $\alpha = E_B + E_K$

$$\left.\begin{array}{ll} \text{Ni } 2p_{3/2}: & E_B = 852.7 \\ L_3VV: & E_K = 1486.6 - 640.8 \end{array}\right\} \alpha = E_B + E_K = 1698.5$$

- Independent of electrostatic charging of the specimen.
- Representive of relaxation energies

$\Delta\alpha = 2\Delta R$

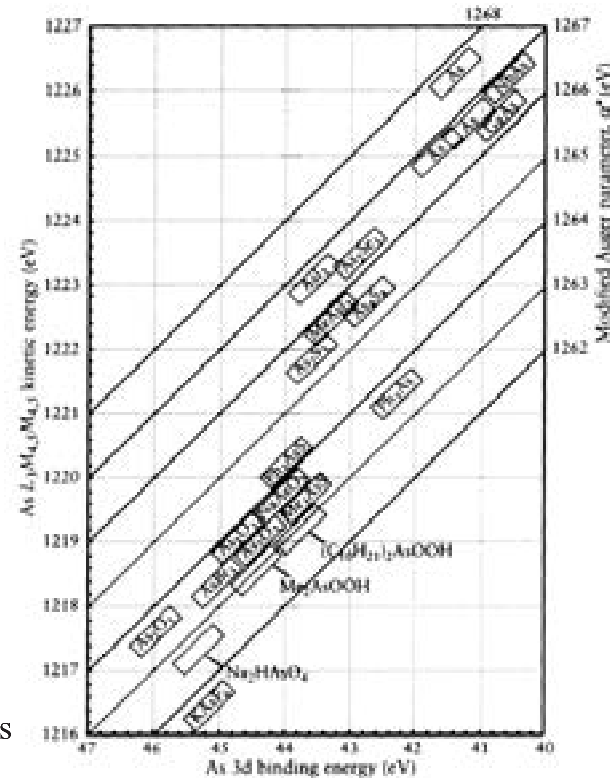
ΔR: difference in final state relaxation energies between chemical states

Wagner plot for final state effect

$$E_k = \alpha - E_b$$

Ordinate: Auger kinetic energy
Abscissa: photoelectron binding energy oriented in the negative direction

α: intercepts of straight lines with slope -1 on the right ordinate



Wagner chemical state plot for arsenic compounds (John F. Watts, *An Introduction to Surface Analysis by XPS and AES*)

Chemical state information provided as well

Ni Auger peaks

- Decreased α (Δα = 2ΔR) indicates that relaxation of the photoholes is less favourable in Ni_3Si, $Ni_{31}Si_{12}$, Ni_2Si and NiSi.

Normalized Ni LVV Auger peaks

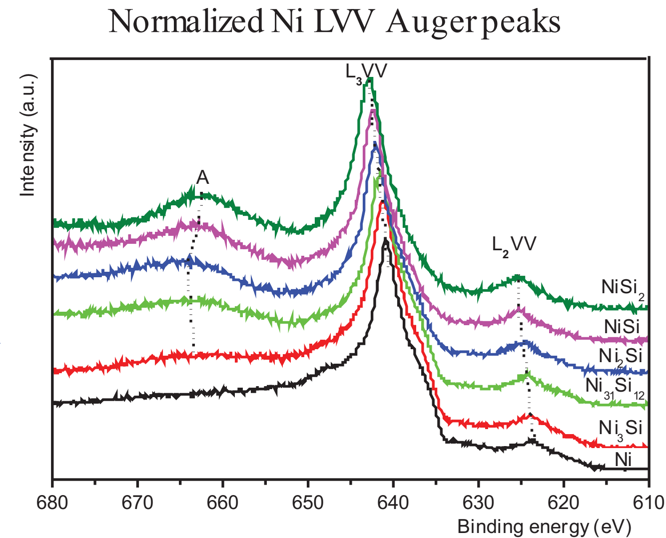
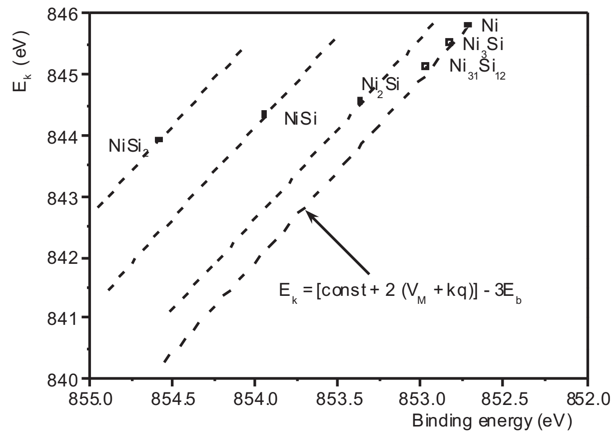


Table. Auger Ni L_3VV peak position, shift and Auger parameter α (eV)

Parameter	Ni	Ni_3Si	$Ni_{31}Si_{12}$	Ni_2Si	NiSi	$NiSi_2$
Peak shift of Ni $2p_{3/2}$	0	0.1	0.3	0.7	1.2	1.9
Peak shift of Ni L_3VV	0	0.3	0.7	1.3	1.5	1.9
α (Ni $2p_{3/2}$-L_3VV)	1698.5	1698.3	1698.1	1697.9	1698.3	1698.5
Δα (Ni $2p_{3/2}$-L_3VV)	0	-0.2	-0.4	-0.6	-0.2	-0.0

Wagner plot for initial state effect



$$E_k = [\underline{const + 2\,(V_M + kq)}] - 3E_b$$

⇩

Initial state effect Auger parameter β

⇩

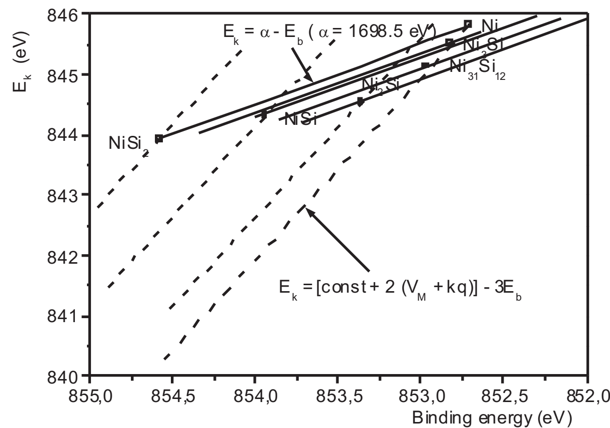
intercept of the straight line with slope –3 in Wagner plot

Why do core level shift? ---Wagner plot in Ni- Silicides

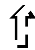
$E_k = \alpha - E_b$ (1)

$E_k = \beta - 3E_b$ (2)

$\Delta E_b = ½ (\Delta\beta - \Delta\alpha)$ (3)



Dash line Solid line

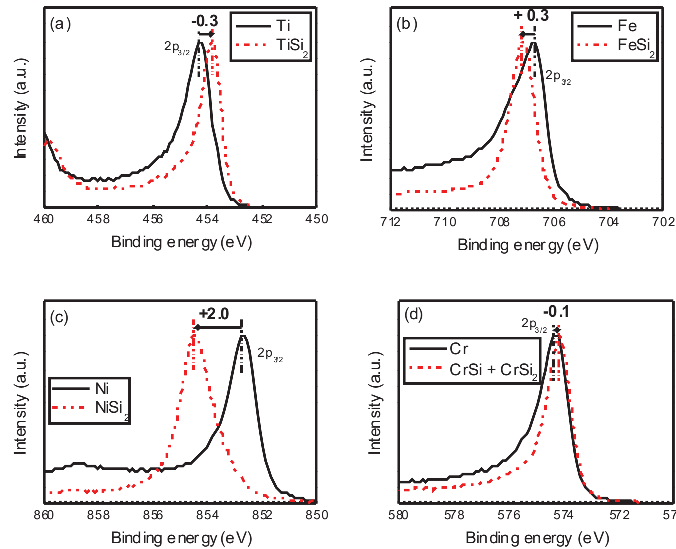


➢Both initial and final state effect can be seen from the figure!

Factors for Ni $2p_{3/2}$ core level shift are related to the type of silicide.

- Similar initial state effect for Ni metal and $Ni_{31}Si_{12}$ and Ni_3Si. Final state effect contribute to the small shift.
- Initial state effect is the governing factor in $NiSi_2$, important for $NiSi_2$ and NiSi.
- Both initial and final state effects in Ni_2Si and NiSi; while initial state effect more important for NiSi.

Why do core level shift? Transition Metal - Silicides

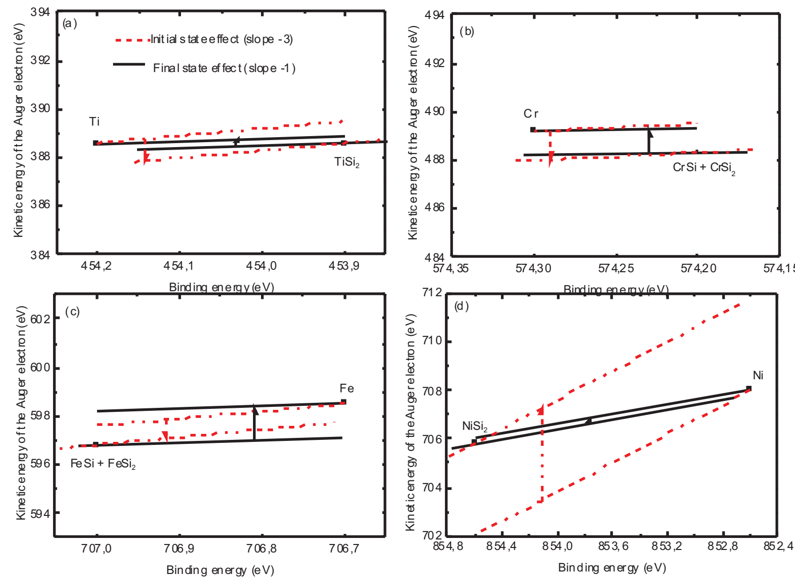


$$E_k = \alpha - E_b \quad (1)$$

$$E_k = \beta - 3E_b \quad (2)$$

$$\Delta E_b = ½ (\Delta\beta - \Delta\alpha) \quad (3)$$

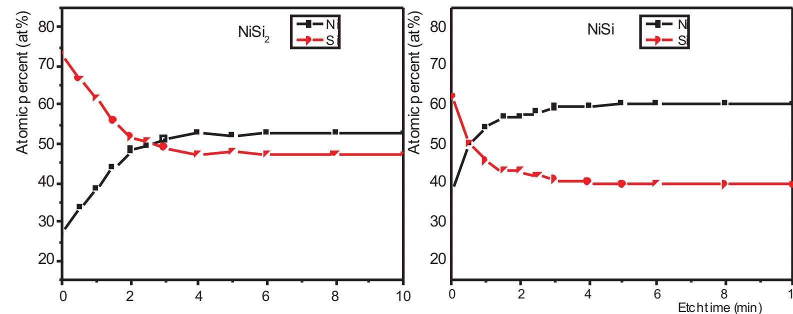
Why do core level shift? ---Wagner plot in Transition Metal - Silicides

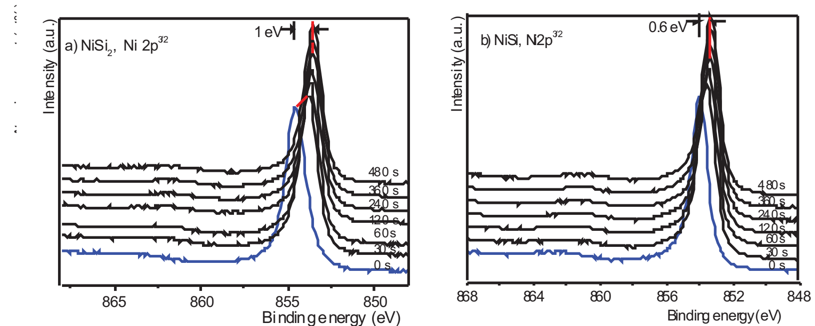


Wagner plot for core level $2p_{3/2}$ line and $L_3M_{23}M_{23}$ Auger peaks in different silicides studied. The arrows represent twice the core level shifts with respect to metal reference caused by the final state effects (solid arrow) and initial state effects (dashed arrow), respectively.

- Final state effects shift core level positively; less important for Ti and Ni.
- $NiSi_2$ exhibits the highest positive core level binding energy shift due to large Δβ
- Initial states effects in other silicides cause negative shift, which can cancel the positive shift caused by final state effect partly or totally, resulting in shift in small amounts either negatively (Ti and Cr silicides) or positively (Fe silicide).

Results: Argon ion etching of Ni silicides -- chemical state and composition



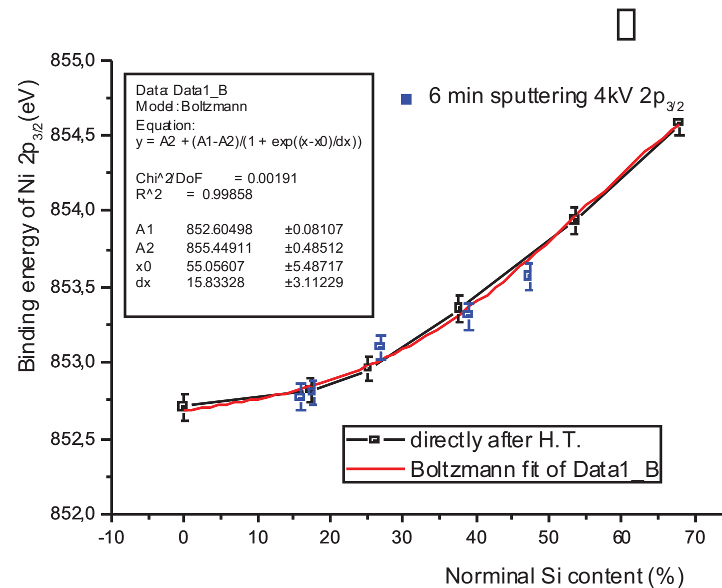


Argon ion etching produces preferential removal of Si; (increases with increasing Si content of silicide)

Argon ion sputtering shift Ni $2p_{3/2}$ peaks to lower BE until steady state reached.

$NiSi_2$: 1 eV ,
NiSi: 0.6 eV
Ni_2Si: 0.4 eV
$Ni_{31}Si_{12}$: 0.2 eV

E_B (Ni $2p_{3/2}$)- C_{Si} (at%) relation after Argon ion etching



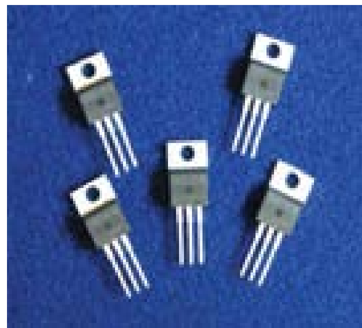
- Boltzman relation still works!
- Boltzman relation between E_B and Si atomic content works for both as-annealed and argon ion etched Ni silicides.

2. Contact Formation on SiC by use of Ni and Ta film

Depth profiling

Background: Applications of SiC

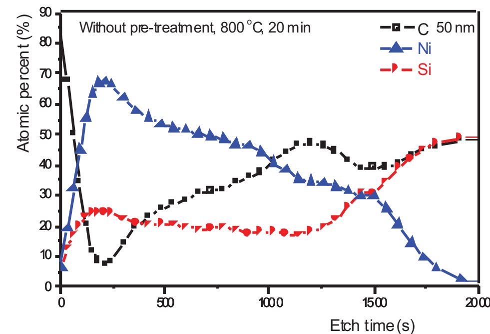
- High temperature applications
- High power devices
- High frequency devices



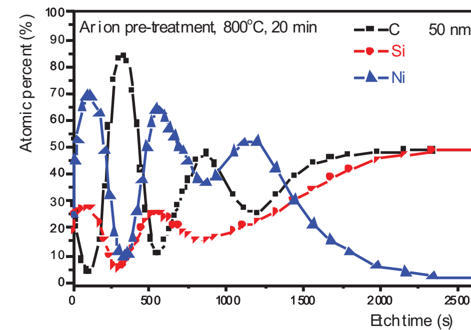
Cree's first power device combination pack.

Infineon's 600 V Schottky diode

Ni film on SiC: Phases after Heat Treatment



No pre-treatment or just chemical cleaning before Ni deposition



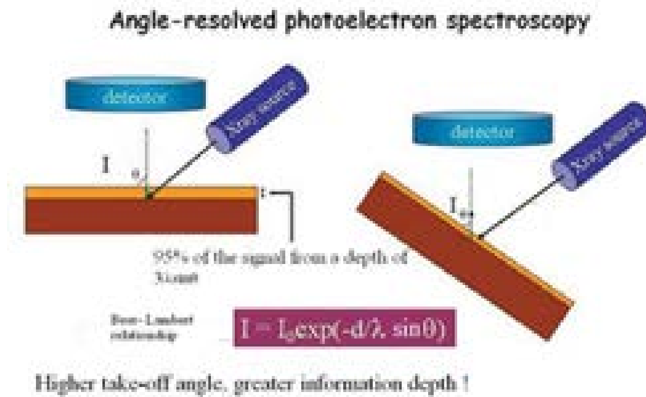
Argon ion etching before Ni deposition

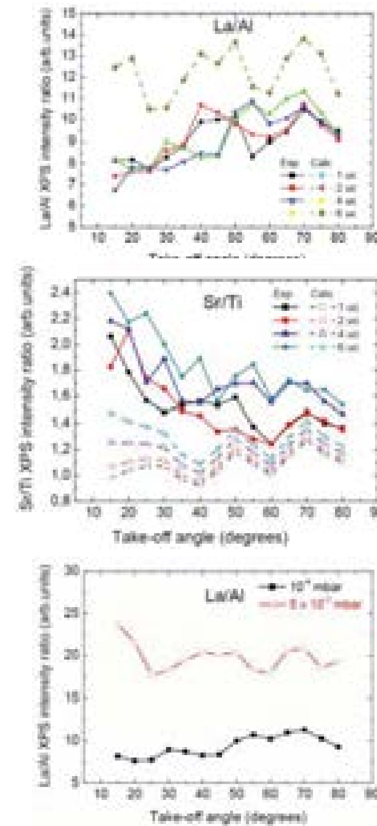
- C (graphitic) on top
- C inside whole reaction layer, clusters close to interface

- C (graphitic) on top
- Multi-layer structure

3. Cationic intermixing of $LaAlO_3/SrTiO_3$ interface

Angle-resolved XPS



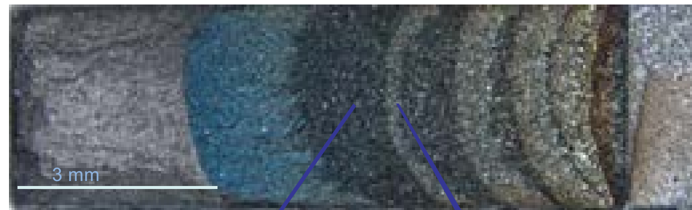


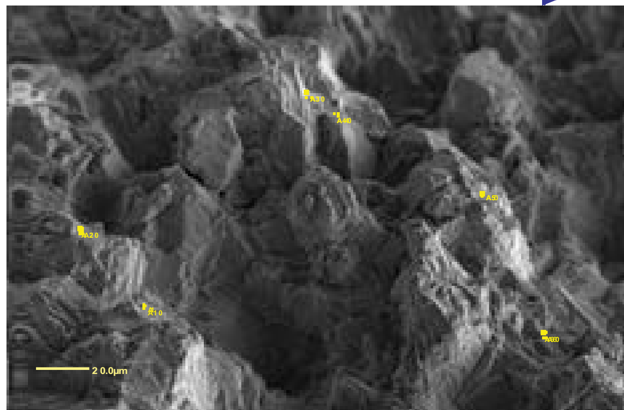
- La diffuses deeper than Al into the substrate,
- Sr diffuses more towards the surface than Ti
- Ratio of La/Al depends significantly on O_2 pressure

4. XPS and Auger evaluation of 718^+ Ni-base supperalloy

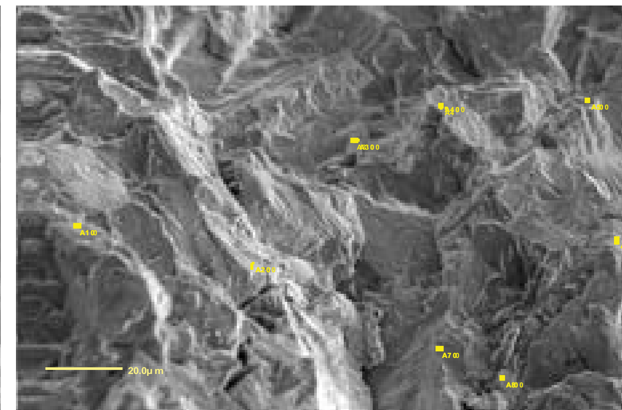
SEM Images of Fracture Surfaces for 718^{+} Ni Base Supperalloy

High temperature Hold-time fatigue test: 704°C, R=0.05 100s at P_{max}





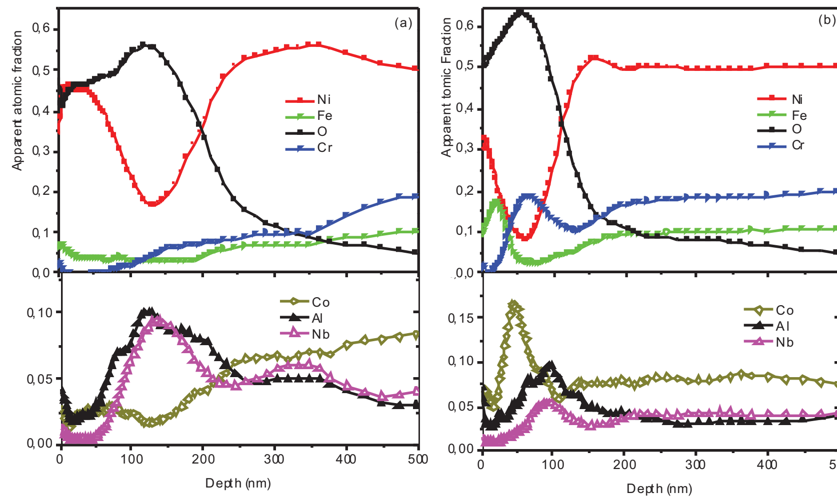
Hold time area: mainly intergranular



Cyclic area: mainly transgranular

Auger Evaluation of 718$^+$ Ni Base Supperalloy

Two types of oxide in both cyclic and hold time areas:



Typical AES depth profile.
(a)oxide type 1
(b)oxide type 2. The lower part in b) is from a cation profile disregarding O.

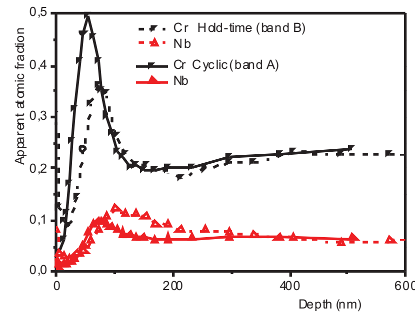
Type1:

- Thicker oxide
- Outer layer: Ni rich
- Inner layer: Nb, Al rich
- No obvious Cr oxide

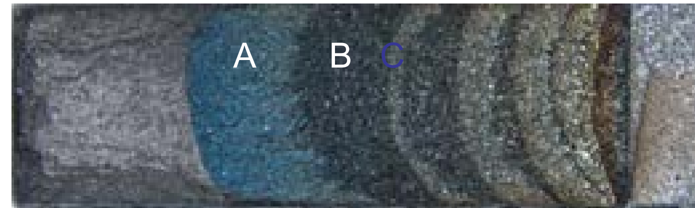
Type2:

- Thinner oxide
- Multiple layers
- Less (Nb, Al)-rich layer
- Clear Cr oxide

Auger Evaluation of 718^{+} Ni Base Supperalloy



Comparison of Cr and Nb cation profiles disregarding O under cyclic (band A) and hold-time (band B) loading



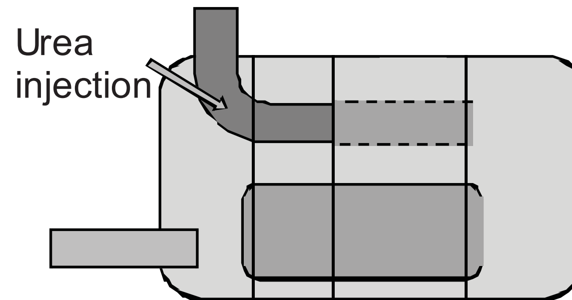
	area A (nm)		area B (nm)		area C (nm)	
AES	107 (1)*	75(2)*	230 (1)	165(2)	210(1)	120(2)
XPS	120		180		—	

(1): oxide type 1
(2): oxide type 2

- Proportions of two types of oxides differ
- Cyclic area: more type 2 oxide; thinner oxide
- Hold time area: larger area fraction of type 1 oxide; thicker oxide

5. High temperature corrosion in diesel exhaust gas after-treatment systems

Selective Catalytic Reduction, SCR



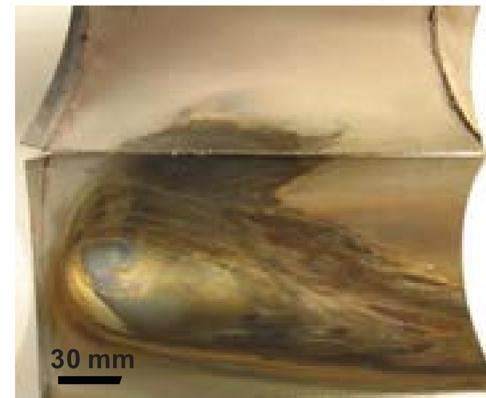
Reduction of NOx by NH_3 (ammonia) on a catalyst, resulting in H_2O and N_2.

Ammonia is difficult to handle. Instead urea(aq) is injected in the exhaust flow. Urea is decomposed and NOx emissions can then be reduced to H_2O and N_2.

Urea decomposition products sometimes cause corrosion

Bench test, ~1000h

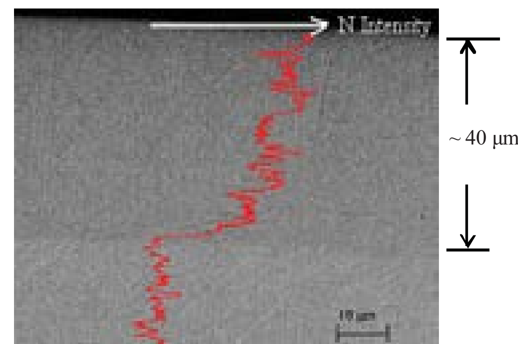
304L



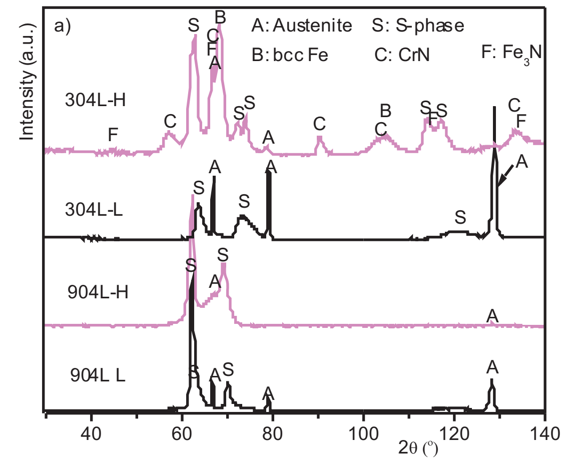
904L

Alloy	Fe	Cr	Ni	Mo	Cu
304L	Bal.	18.0	10.0	-	-
904L	Bal.	20.0	25.0	4.0	1.2

Plasma Nitriding



304L-H



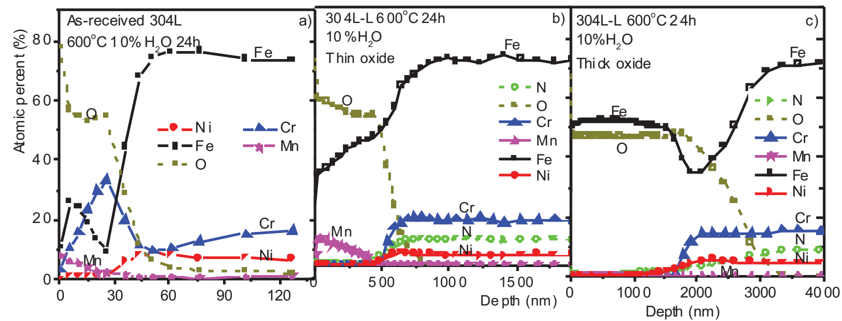
- Sharp interface
- Surface: 18-20 at% N estimated by XPS
- Formation of S-phase
- 304L-H: double peak for S-phase; bcc Fe; CrN; Fe_3N
- S-phase less stable in 304L than in 904L.

Oxide thickness (nm) for materials oxidized for 24h in 10% H_2O.

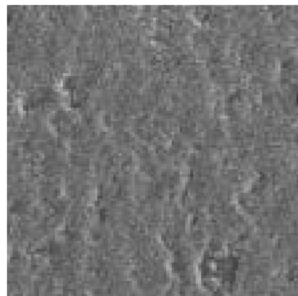
Alloy	304L							904L						
Nitriding	none	none	H	L	L	L	L	non e	none	H	L	L	L	L
Temp.(^{o}C)	450	600	450	450	500	550	600	450	600	450	450	500	550	600
XPS/AES	28	37	2200	2500	4500	470/ 4000	560/ 2600	32	50	250	150	210	135	110

- N is detrimental for oxidation properties.
- Compared to as received material, oxides 70-100 thicker for 304L; 2-5 times thicker for 904L.
- Areas of thin and thick oxides in 304 L.

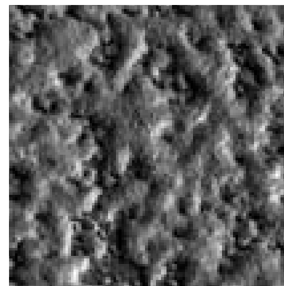
Oxidation of nitrided 304L



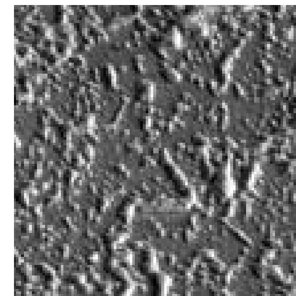
- Areas of thin and thick oxides formed at all temperatures.
- Area fraction of thick oxides decreased with increasing temperature.
- Main difference between the temperatures was the coverage of thick oxides.



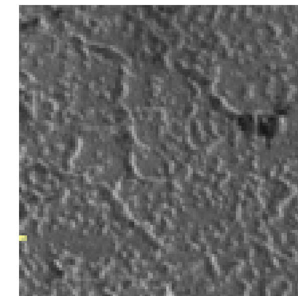
450°C



500°C

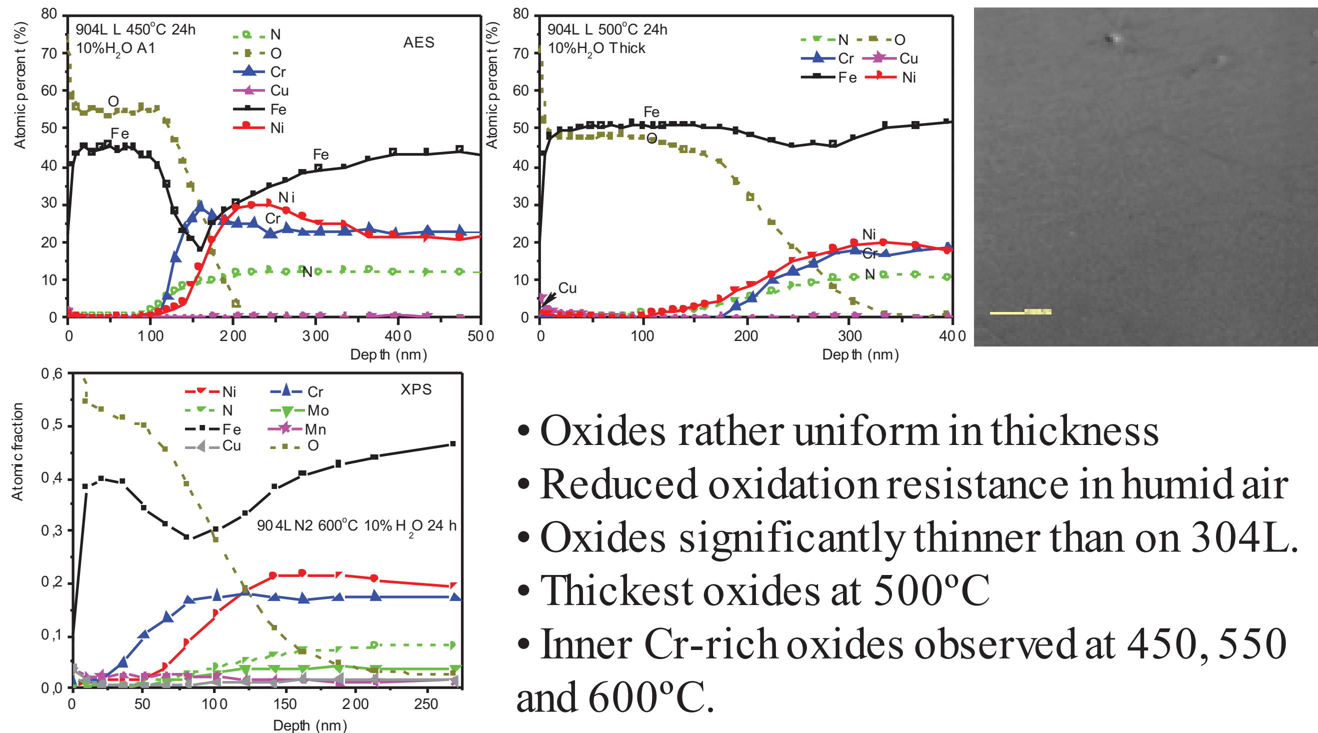


550°C



600°C

Oxidation of Nitrided 904L



- Oxides rather uniform in thickness
- Reduced oxidation resistance in humid air
- Oxides significantly thinner than on 304L.
- Thickest oxides at 500°C
- Inner Cr-rich oxides observed at 450, 550 and 600°C.

THANK YOU FOR YOUR ATTENTION!

谢谢大家!