EDS on the Nanoscale in TEM/STEM and SEM



Bruker Nano Analytics, Berlin, Germany Webinar, June 14, 2017



Presenters



Dr. Meiken Falke

Global Product Manager TEM Bruker Nano Analytics, Berlin, Germany

Mats Eriksson

Electron microscopy department manager Hitachi High-Tech Europe, Sweden

Dr. Igor Németh

Application Scientist, EDS Bruker Nano Analytics, Berlin, Germany





- Technology and options provided
- Examples of nanoanalysis approaches in TEM/STEM
- Approaches for nanoanalysis in (T)SEM (Flatquad detector)

• High sensitivity EDS combined with Cold Field Emission in SEM

Spatial Resolution: Cs- Correction and Brightness

SEM: bulk



S/B Signal to background ratio

- σ_a atoms cross section
- d_p probe diameter
- *d_d delocalisation from inelastic scattering*
- I_p probe current (typ. 500 pA)
- ϵ detection efficiency
- t acquisition time
- *ρ* number of atoms per unit area

S/TEM: thin specimen, small probe



$$S/B = Sa/\sqrt{Sb}$$

$$= \sigma_a / (d_p^2 + d_d^2) * \sqrt{I_p \varepsilon t / (\sigma_b \rho_b e)}$$

O. Krivanek, Chapter in P. Hawkes "Advances in Imaging and Electron Physics"

Detector quantum efficiency



Detector quantum efficiency





O-rings, Au-spacers, ..., reaction species sticking to walls Webinar, L. Allard

Reaction Cell Windows

Gas, liquid, + heat ... cells: Window materials:

- graphene,
- Si3N4 / alpha SiNx
 - thickness,
 - support (grid): Si, polymer film, SiC (heating)
 - Al film (light tight))
- Reaction species sticking to cell walls
- > All affect transmission (efficiency) curve

calculate transmission depending on thickness here: <u>http://henke.lbl.gov/optical_constants/filter2.html</u> suggests materials too, but e.g. 30nm Al cover and window support not included





In situ: Reaction Cell and Detector Windows





EDXS Elemental mapping in liquids



Sarah Haigh group: Lewis et al Chem Comm (2014) 50, 70, 10019-22

EDS for Life Science at 0.1sr Yeast Cell: Element Mapping of immunolabels and light and heavy elements



30 mm², 0.12 sr (Standard EDS); Conventional STEM



EDS for Life Science at 0.1sr Yeast Cell: Element Mapping of immunolabels and light and heavy elements



30 mm², 0.12 sr (Standard EDS); Conventional STEM









$$I_{x} = N_{A} \sigma_{A} \omega_{A} (\Omega/4\pi) \varepsilon N_{e} = n_{A} t \sigma_{A} \omega_{A} (\Omega/4\pi) \varepsilon N_{e}$$

Cliff and $\underline{I_A} = \underline{I_A}$ $- - k_{AB} C_B$ k_{AR} can be determined experimentally or theoretically Lorimer: number of X-ray photons in a characteristic peak of species A I_{x} Ν number of atoms per unit volume number of atoms per unit area times thickness nt ionization cross section (Casnati et al., 1982, Bote et al., 2009) σ fluorescence yield (Hubbell et al., 1994, Krause, 1979) ω $\Omega/4\pi$ solid angle / geometrical collection efficiency detection quantum efficiency 3 number of incident electrons N_e

+ absorption



TEM EDS Quantification; R. Egerton 1994, line intensity for a particular element line / transition

Zeta-Factor

I_x

$$= N_{\rm A} \sigma_{\rm A} \omega_{\rm A} (\Omega/4\pi) \varepsilon N_{\rm e} = n_{\rm A} t \sigma_{\rm A} \omega_{\rm A} (\Omega/4\pi) \varepsilon N_{\rm e}$$

Cliff and $\frac{I_A}{I_B} = \frac{C_A}{k_{AB} C_B}$ k_{AB} can be determined experimentally or theoretically

 I_x number of X-ray photons in a characteristic peak of species A

- N number of atoms per unit volume
- *n t* number of atoms per unit area times thickness
- σionization cross section (Casnati et al., 1982, Bote et al., 2009)ωfluorescence yield (Hubbell et al., 1994, Krause, 1979) $\Omega/4\pi$ solid angle / geometrical collection efficiencyεdetection quantum efficiency
- $N_{\rm e}$ number of incident electrons
- + absorption

The CL-method is a ratio method by $\frac{C_A}{C_B} = k_{AB} \frac{I_A}{I_B}$ Graham Cliff and Gordon Lorimer: M. Watanabe J. of Micr. 2005: $\rho_A t = \zeta_A \frac{I_A}{C_A D_C}$ For a standard with known thickness t **C** can be determined: D_e (total electron dose) must be known for all measurements. A_A Then, for a sample $C_{A_{L}} C_{B_{L}} \rho$ and t are unknown. N equations with N unknown variables. $\rho t = \frac{\zeta_A I_A + \zeta_B I_B}{D_{\rho}}$ A_B $C_A + C_B = 1$ $C_1 + C_2 + \dots = 1$ $C_A = \frac{\zeta_A I_A}{\zeta_A I_A + \zeta_R I_P}$ absorption corr. $> \rho t > iteration$

TEM EDS Quantification Zeta-factor Method vs Cliff Lorimer



G. Kothleitner, et al., Microsc. Microanal. 20, 678-686, 2014

For testing we used Si_3N_4 a single layer (30nm) as the sample a double layer (60nm) as the standard

N at%

STEM probe current: 344pA ٠

Si3N4_expected 42,86 57,14

Zeta vs CL

•

Standard:

Si3N4_60nm_st. 42,86 57,14 CL: Si3N4_30nm 43,84 56,16 Zeta: Si3N4_30nmZeta 41,96 58,04 30

Si at%

TEM EDS Quantification

• Further tests with Al₂O₃, TiO₂, GaP (G. Kothleitner, W. Grogger, K. Volz)

- Very sensitive to
 - probe current and
 - thickness variations



30nm



60nm

TEM EDS Quantification in Esprit 2.1 Zeta Method: Set up using Si₃N₄ 60nm



RESULIS - SISIN4_344PA_00INIM			
Options		Standards	Results
automatic element identification, quantification with Cliff-Lc		1	
	Name Si3N4_344pA_60nm		
Minimum concentration 0,00 %	Description		
Fast quantification	Real time [s]: 336,760		
Elements Standards	Life time [s]: 332,679		
	Specification in O Mass-% Atomic-% Stoich-%		
H He Li Be B C N O F Ne	Element Concentration [%] Error [%]		
Na Mg Al Si P S Cl Ar	Nitrogon		
K Ca Sc Ti V Cr Mn Fe Co Ni Cu Zn Ga Ge As Se Br Kr			
RD SF Y ZF ND MO IC RU RN PO AG CO IN SN SD IE I XE	g Oxygen		
Fr Ra Ac	5 Silicon 42,86		
The Dr. H. No. Dr. Am Cra Bla Cf. Fa Fra Md Na. La	te Chlorine		
In Pa O NP PU AMOMBK CI ES PM Mu No Lr	ge Cothon		
Autosoarch			
Autosearch			
Element overview list			
Compound Fix % Dec. Diff. Fact.			
C 4 0.00			
0			
Cl 2 0,00			
O Calib fit			
• P/B - ZAF • Zeta factor method			
O Phi(Rho,Z) O Cliff-Lorimer	Sum of concentrations (9/1) 100 0004		
\Box Use standards	Sum of concentrations [7]. 100,000		
O P/B film	Thickness [nm] 50		
Layer thickn. [µm]	Add as tandard		
Substrate (mean. AN) 0	Density [g/cm] 1,7228 Adda reference		
Additional settings 200,0 keV, 0° 👻	Beam current [pA] 344		
· · · · · · · · · · · · · · · · · · ·			
Load Save Add to projec Apply		ок	Cancel

6/21/2017

TEM EDS Quantification in Esprit 2.1 Zeta Method: Set up using Si₃N₄ 60nm



		VALID	TERONO, EE	TETER SCHAT		
RESULTS - SI3N4 344PA 60NM		Confirm	assignment ar	d certification v	alues	
Options		Commit	assignment a		alues.	
automatic element identification, quantification with Cliff-Lc		Standar	rd: Si3N4_	_344pA_30nm		
Minimum concentration 0.00 %	Name Si3N4_344pA_60nm	Descrip	tion:			
Fast quantification	Description Real time [s]: 336,760	Assign	Element	Mass concentration	Error	Currently assign
Elements Standards	Life time [s]: 332,679		Nitrogen	39.94		
	Specification in O Mass-%		Silicon	60.06		
H He Li Be B C N O F Ne	Element Concentration [%] Error [%]		Silleon	00,00	70	
Na Mg AISIPS CIAr K Ca Sc Ti V Cr Mn Fe Co NiCu Zn Ga Ge As Se Br Kr	Nitrogen 57,14					
Rb Sr Y Zr Nb Mo Tc Ru Rh Pd Ag Cd In Sn Sb Te I Xe	e Oxygen					
CS BALA HT TA W RE OS IT PT AU HG IT PD BI PO AT RN Fr Ra Ac Co Dr Nd Desser Eu Cd Th Du Ha Er Ter Vh Lu	5 Silicon 42,86					
Th Pa U Np Pu Am Cm Bk Cf Es Fm Md No Lr	5 Chlorine					
	E Carbon					
Auto search Clear	00					
Element overview list	2/u2	Check va	lue of Zeta fac	tors:		
Compound Fix % Dec. Diff. Fact.	ō	Assign	Element	New factor	Old factor	
C 0,00		Image: A start of the start	Nitrogen	2662,74699	4 3,50274	
O			Silicon	491,94108	1,00000	
Calib fit						
Quantification model						
P/B - ZAF O Zeta factor method						
Phi(Rho,Z) Cliff-Lorimer	Sum of concentrations [%]: 100 00%					
O P/B film Layer density [g/cm ³]	Sum of concentrations [76].					
Layer thickn. [µm] 0	Thickness [nm] 60 Add asstan	d		OK	Back	
Substrate (mean. AN) 0	Density [g/cm ³] 1,72298 Add a refer					-
Additional settings 200,0 keV, 0°	Beam current [pA] 344					
Load Save Add to projec Apply						OK Cancel

6/21/2017

TEM EDS Quantification in Esprit 2.1 with 1-2 standards all other Zeta – factors can be obtained from theoretical C-L-factors





TEM EDS Quantification in Esprit 2.1 Zeta Method: Set up using Si_3N_4 60nm Zeta: 344pA, single layer Si_3N_4 d=?





6/21/2017

Quantified Linescan InAs Nanorods with P-rich layers: Deconvolution of P and Au, 0.12sr





Quantified Linescan extracted from HyperMap: NiSi(Pt)-NiSi₂-Junction on Si





Quantified Pt-content in the HyperMap, and in Linescan extracted from HyperMap: NiSi(Pt)-NiSi₂-Junction on Si, 0.12sr





NiSi(Pt)-NiSi₂-junction on Si, Map, explore other elements!







EDS for Catalysis, Quantification Pt-Pd Core Shell Particles



mass%, 30 mm², 0.12 sr (Standard EDS); Cs-corr. STEM





M. W. Chu, Phys. Rev. Lett. 104, 196101 (2010)

Simultaneous EDXS and EELS from a single Si atom, 30mm², SLEW, C-FEG STEM



Tracking movie of 1 Si atom on graphene as recorded during EDS spectrum acquisition



10 Carbon K 8 ED(X)S Si K 4 2 0 0 1 2 3 4 X-ray Energy (keV)

ADF image of a defect in monolayer graphene recorded *after* spectra were acquired. Arrow points to a tracked Si impurity atom.

EDXS and EELS data recorded simultaneously.

 $I_p = 190 \text{ pA}, 0.09 \text{ sr}, 224 \text{ sacquisition};$

Thereof ~10s beam close to the atom.

Nion UltraSTEM100, 60 keV Daresbury UK. Bruker SDD EDXS, Gatan Enfina EELS

70

60-

50-40-

30-

20-

10

100

Counts × 10^4

FFIS

150

200

250

e٧

T. C. Lovejoy et al., APL 100, 154101 (2012)

mp man when when we have

400

350

300

Single atom spectra





T. C. Lovejoy et al., APL 100, 154101 (2012)

Single atom spectra: Theory vs. experiment



$R = (n \cdot \sigma / A) (\omega \cdot \Omega / 4 \pi \cdot \varepsilon)$

- R: count rate, X-rays / s / atom
- A: scanned area
- N: beam current, electrons / s
- σ : cross section for particular atom and shell
- ω : fluorescence yield
- $\Omega/4\pi$: geometrical efficiency (solid angle)
- ε: quantum efficiency

	<u>theo</u>	~ 2x	<u>exp</u>
Si-K	7 cts/s		4 cts/s
C-K	2 cts/s		1 cts/s
Pt-M	28 cts/s		14 cts/s

T. C. Lovejoy et al., APL 100, 154101 (2012)

EDXS with 100 mm² windowless oval detector area; Nion UltraSTEM, Cs-corrected, high brightness source

EDXS at ~0.7 sr. This is the real solid angle for a flat vertical SDD.

Wrong calculation:

 $100 \text{mm}^2 / (10.5 \text{mm})^2 = 0.91 \text{sr}$

TOA: 13.4°





Identifying atoms by EDXS, one-by-one

100 mm² windowless SDD at 0.7 sr collection angle



*tracking area was ~2x larger for S, hence the lower counts.Cu is a system peak due to sample holder & polepiece caps.

R. M. Stroud et al., APL 108, 163101 (2016) open access

EDXS detects single atoms and concentrations ~0.01%



EDXS Mapping of Bi₆Ti_xFe_yMn_zO₁₈



TCD (Trinity College Dublin) Nion UltraSTEM200XE with Bruker 100 mm² X-flash SD detector, 200 kV. 432x225 pixels, 4.1 msec/pix => 400 sec for map.

No drift correction. Bi = green, Ti = blue.

courtesy Lynette Keeney, Clive Downing and Valeria Nicolosi. TCD, Ireland. See

"Direct atomic scale determination of magnetic ion partition in a room temperature multiferroic material" Scientific Reports **7**, Article number: 1737 (2017)

100 mm² windowless SDD at 0.7 sr collection angle

SEM: Four channel annular SDD: XFlash[®] 5060FQ, >1 sr collection angle





Flat QUAD detector in combination with a conventional XFlash detector at the Hitachi SU8000 series (Cold-Emission FE-SEM)





FLATQUAD in SEM

Semiconductor chip structure prepared with FIB in cross section





FLATQUAD in SEM

Semiconductor chip structure prepared with FIB in cross section





FLATQUAD in SEM

Semiconductor chip structure prepared with FIB in cross section





FLATQUAD in SEM

Semiconductor chip structure prepared with FIB in cross section





FLATQUAD in SEM

Semiconductor chip structure prepared with FIB in cross section







Extracted linescan from the map data Effective measurement time of lineprofiles: 8 s More Information



For more information, please contact us:

Meiken.falke@bruker.com

lgor.nemeth@bruker.com

info.bna@bruker.com

mats.eriksson@hht-eu.com



Innovation with Integrity

EDS on the nanoscale

Mats Eriksson Department manager electron microscopy Hitachi High-Technologies Europe





High sensitivity EDS combined with Cold Field Emission

Optical Properties of FE sources

Very high density of electrons with small energy spread from a small source makes a very fine beam spot for high resolution imaging

	Coherent beam Cold FE Gun	Schottky FE
Cathode	Cold cathode	Thermal cathode
Energy spread(⊿E)	0.2~0.3eV	0.6~0.8eV
Source size	< 5nm	< 30nm
Brightness	2×10 ⁹ A/cm ² sr	2 × 10 ⁸ A/cm ² sr
Flashing	Flash free	Flash free
Specimen current	Over 20nA	Over 100nA
Life time	Over 5 years	2 years





Hitachi 2017

FE sources overview

Schottky and Cold FE Tips





Small source size – fine beam Small energy spread: 0.2~0.3eV Higher brightness and resolution

Images courtesy of Mark J. Grimson, Texas Tech

Suitable scanning electron microscope



- Coherent beam cold field emission gun
- Easy to operate at low dose with high S/N
- Immersion lens providing high efficiency SE and BSE collection through the lens
- Fits FlatQuad geometry well as BSE can be captured simultaneously using the in-lens SE/BSE detectors
- Flexible imaging in transmission mode using BF and DF detectors with variable collection angles









Energy materials

Low kV analysis for surface sensitivity

LIB Electrode: Material vs.Topographic Information



Vacc: 0.2kV, Mag.: x30k SE-Top

Material type shown by surface potential (voltage contrast) Organic, inorganic and Carbon Black



Vacc: 0.2kV, Mag.: x30k SE + BSE Upper

Enhanced topography image using mixed SE and BSE



Science for a better tomorrow

Low kV analysis for surface sensitivity

LIB Electrode: Material vs.Topographic Information

EDS: Flat Quad 5060F Vacc: 2kV Mag.: 30kX Acquisition time: 4min.



60mm² large sensor and 1.1sr solid angle enabled fast and high spatial resolution

EDS mapping even at 2kV in 4 min.

C: Carbon black Co, Ni & O: Active material F, O: Organic materials



/ WD: 10mm

Low kV analysis for spatial resolution

Catalyst : FeNi-ZrO2



Sample courtesy : Prof. Kohsuke Mori, Osaka University







Nano Pillars

SU8200 Applications

Nano Pillar



The above nano-pillar images were taken with our SU8200 as examples for researchers interested in imaging photonics and related materials. The gold (Au) particles in this dotted pattern formed into pillars on this silicon plate after chemical etching. Furthermore, the surface was coated with silver (Ag) to improve the specimen properties. These 100nm diameter nano-pillars were imaged using our "bird's eye view" SEM function.

Sample courtesy: Prof. Masahiko Yoshino,

Department of Mechanical and Control Engineering, Tokyo Institute of Technology

HITACHI Inspire the Next

SU8200 Applications

Nano Pillar



The image on the left has been enlarged to 100,000x which enables the observation of the silver (Ag) coating particles on the surface of each pillar. The image on the right is a cross-sectional view after milling through the pillars with our IM4000 broad beam ion milling unit. The image was taken using the BSE signal at a magnification of 100,000x at 1.6kV accelerating voltage. The silver (Ag) coating on the surface of the gold (Au) is clearly observed using the BSE signal for improved compositional information.

Sample courtesy: Prof. Masahiko Yoshino,

Department of Mechanical and Control Engineering, Tokyo Institute of Technology



SU8200 Applications

Nano Pillar



Left are EDS maps taken with a large active area SDD EDS detector at a magnification of 200,000x. The silicon (Si) plate pattern structure, gold (Au) particles, and 10nm diameter silver (Ag) coating around the nano-pillars were clearly revealed in ~5 minutes.

Acc. voltage: 6kV Magnification: 200,000x Analysis time: 313 sec. EDS: Bruker FlatQUAD



Sample courtesy: Prof. Masahiko Yoshino,

Department of Mechanical and Control Engineering, Tokyo Institute of Technology





III-V Nanowires

Hitachi 2017

EDS on the nanoscale

InAs-InP Nanowires





Accelerating voltage : 20 kV Magnification : x200,000 Acquisition time : 300 sec.

Sample courtesy: Prof. Kimberly Dick Thelander, Dr. Sebastian Lehmann Department of Solid State Physics, Lund University, Sweden



Hitachi 2017

EDS on the nanoscale

InAs-InP Nanowires





EDS on the nanoscale

GaAs-AlAs-AlGaAs Nanowires



20 kV, x250,000, 326 sec.

Sample courtesy: Prof. Kimberly Dick Thelander, Dr. Sebastian Lehmann Department of Solid State Physics, Lund University, Sweden



Thank you for your attention !

