

Grazing incidence X-Ray Fluorescence Analysis and X-Ray Reflectivity

Giancarlo Pepponi Fondazione Bruno Kessler MNF – Micro Nano Facility pepponi@fbk.eu

> MAUD school 2018 Caen, France





$= \underbrace{\mathsf{XRF}}_{\mathsf{FONDAZIONE}} \mathsf{XRF} \to \mathsf{GIXRF}$

A. H. Compton, The total Reflection of X-Rays, Phil. Mag., 45, 1121; 1923 *φ*=20 Crystal Mirror Ionization S₂ 31 chamber Sli P C λ 0.708 from glass λ 0.708 from speculum λ 1.537 from glass λ 1.537 from speculum P С

GIXRF and XRR- MAUD school 2018 - Giancarlo Pepponi

Pictures from the

December 12, 1927

Nobel Lecture,





Index of refraction – decrement - delta

FONDAZIONE BRUNO KESSLER



Critical angle for total reflection

FONDAZIONE BRUNO KESSLER

> Si 10¹ Ge Au 10⁻¹ critical angle / deg critical angle / rad 10⁰ 10⁻² 10⁻¹ 10⁻³ 5000 10000 15000 20000 0 photon energy / eV



Beer-Lambert's Law:



$$\hat{n} = \frac{\cos \phi_1}{\cos \phi_2} = 1 - \delta_2 - i\beta_2$$

$$\beta = \frac{\lambda \mu}{4\pi}$$

Linear absorption coefficient:

 $\mu = \tau_{photoelectric} + \sigma_{elastic} + \sigma_{inelastic}$

Snell's law – x-ray region – with absorption



$$\hat{n} = 1 - \delta - i\beta$$
 $\beta = \frac{\lambda\mu}{4\pi}$

medium 1 is vacuum

FONDAZIONE BRUNO KESSLER

$$\hat{n} = \frac{\cos \phi_1}{\cos \phi_2} = 1 - \delta_2 - i\beta_2$$

 β is typically 2 orders of magnitude smaller than δ

Total external reflection

$$\cos\phi_c = 1 - \delta$$

$$\phi_c \approx \sqrt{2\delta}$$
$$\cos x_{(x_0=0)} = 1 - \frac{x^2}{2} + o(x^4)$$

GIXRF and XRR- MAUD school 2018 - Giancarlo Pepponi





$$\frac{d\sigma_{el}}{d\Omega} = \frac{d\sigma_T}{d\Omega} \left| F(x, Z) \right|^2 \qquad x = \frac{\sin \frac{\sigma}{2}}{\lambda}$$

$$f = f^{0}(x, Z) + f'(E, Z) + if''(E, Z)$$

$$F(x, Z) = 4\pi \int_{0}^{\infty} r^{2} \rho(r, Z) \frac{\sin(4\pi xr)}{4\pi xr} dr$$

'anomalous' energy dependent terms



photoelectric absorption

corrections for photoabsorption (Kramers-Kronig dispersion) relativistic effects, nuclear scattering

ρ

EXAMPLE 7 Atomic form factor (forward direction)

forward scattering factors (x = theta = q = 0)

$$\begin{split} f &= f(0,Z,E) = f_1 + i f_2 & \text{photoabsorption} \\ f_2 &\equiv f'' & \mu_a = 2 r_0 \lambda f_2 \end{split}$$

$$f_1 \equiv f^0(x=0) + f'$$

f1 and f2 are directly related to the index of refraction (reflection, refraction, XRR) 1

$$n = 1 - \frac{1}{2\pi} N r_0 \lambda^2 (f_1 + i f_2)$$
$$n = 1 - \delta - i\beta$$

$$\delta = \frac{1}{2\pi} N r_0 \lambda^2 f_1$$

$$\beta = \frac{1}{2\pi} N r_0 \lambda^2 f_2$$



Propagating electromagnetic field

$$\nabla^2 \mathbf{E} - \frac{\epsilon \mu}{c^2} \ddot{\mathbf{E}} = 0 \qquad \nabla^2 \mathbf{H} - \frac{\epsilon \mu}{c^2} \ddot{\mathbf{H}} = 0$$

$$\mathbf{E} = \mathbf{E}_0 e^{-i(\mathbf{k} \cdot \mathbf{r} - \omega t)}$$

Photon Energy
$$E=h
u$$
 $\omega=2\pi
u$

Energy of the electromagnetic field, number of photons

$$egin{aligned} \mathbf{S} &= \mathbf{E} imes \mathbf{H} \ I_0 \doteq < \mathbf{S} > \propto \left| \mathbf{E}_0
ight|^2 \ \mathcal{R} &= rac{\left| \mathbf{R}
ight|^2}{\left| \mathbf{E}_0
ight|^2} \end{aligned}$$

Propagation of an Electromagnetic Wave

Electric Field

Vectors

Figure 1

Magneti Field

Vectors

Discharging Spark or Oscillating Molecular Dipole

$$\mathbf{E}_{1} (\mathbf{r}, t) = \mathbf{E}_{0} e^{i(\omega t - \mathbf{k}_{1} \cdot \mathbf{r})}$$
$$\mathbf{E}_{1}^{R} (\mathbf{r}, t) = \mathbf{R} e^{i(\omega t - \mathbf{k}_{1}^{R} \cdot \mathbf{r})}$$
$$\mathbf{E}_{2} (\mathbf{r}, t) = \mathbf{T} e^{i(\omega t - \mathbf{k}_{2} \cdot \mathbf{r})}$$







 $\hat{n} = 1 - \delta - i\beta$

 \mathcal{R}^{\perp}

Electric vector perpendicular to the plane of incidence (s, TE, polarisation) In German senkrecht = perpendicular

$$\mathcal{R}^{\perp} = \frac{\left|R^{\perp}\right|^{2}}{\left|E_{0}^{\perp}\right|^{2}} = \frac{a_{0}^{2}\left(\sin\phi_{1} - a_{0}\right)^{2} + \beta^{2}}{a_{0}^{2}\left(\sin\phi_{1} + a_{0}\right)^{2} + \beta^{2}}$$

Approximations (ignore quadratic terms):

 $\hat{n}^2 \simeq 1 - 2\delta - 2\beta$

Same formalism as for XRR X-Ray Reflectivity

$$\phi_2 = \arctan(a_0)$$

$$a_0 = \sqrt{\frac{1}{2}\sqrt{(\phi_1^2 - 2\delta)^2 + 4\beta^2}} - (\phi_1^2 - 2\delta)$$

$$\mathcal{R}^{\parallel} = \frac{\left|R^{\parallel}\right|^{2}}{\left|E_{0}^{\parallel}\right|^{2}} = \frac{\left(\sin\phi_{1} - 2\delta\sin\phi_{1} - a_{0}\right)^{2} + \left(2\beta\sin\phi_{1} - b_{0}\right)^{2}}{\left(\sin\phi_{1} - 2\delta\sin\phi_{1} + a_{0}\right)^{2} + \left(2\beta\sin\phi_{1} + b_{0}\right)^{2}}$$

FONDAZIONE BRUNO KESSLER Reflectivity







Reflectivity =-< FONDAZIONE BRUNO KESSLER



18



incident energy = 20000.0 eV

FONDAZIONE BRUNO KESSLER Reflectivity

1.0



 $\hat{\epsilon} = 1 - \alpha - i \gamma$ ~ Complex dielectric constant

$$n = \sqrt{\epsilon} \implies 1 - \alpha - i\gamma = (1 - \delta - i\beta)^2$$

$$\alpha = 2\delta - \delta^2 + \beta^2$$
$$\gamma = 2(1 - \delta)\beta$$

$$\mathcal{R}^{\perp} = \frac{4a^2 (\sin \phi - a)^2 + \gamma^2}{4a^2 (\sin \phi + a)^2 + \gamma^2} \qquad \phi_2^{\perp} = \arcsin \frac{a}{\sqrt{\cos^2 \phi + a^2}}$$

$$a = \sqrt{\frac{1}{2}} \left\{ \sin^2 \phi_1 - \alpha + \sqrt{\left(\sin^2 \phi_1 - \alpha\right)^2 + \gamma^2} \right\}$$

B.L. Henke, Phys. Rev. A, 6, 1, (1972) M.-R. Lefévère, M. Montel, Opt. Acta 20, 97 (1973)

Fresnel – approximated vs exact - angle of refraction





Fresnel – approximated vs exact - transmission

 $\mathcal{A}^{ extsf{difference}} = rac{\mathcal{A}^{approximated} - \mathcal{A}^{exact}}{\mathcal{A}^{approximated}}$



FONDAZIONE BRUNO KESSLER



L. Parratt, Physical Review, 95(2), 359–369, 1954

$$a_{n-1}E_{n-1} + a_{n-1}^{-1}E_{n-1}^{R} = a_{n}^{-1}E_{n} + a_{n}E_{n}^{R}, \qquad (5)$$

$$(a_{n-1}E_{n-1} - a_{n-1}^{-1}E_{n-1}^{R})f_{n-1}k_{1} = (a_{n}^{-1}E_{n} - a_{n}E_{n}^{R})f_{n}k_{1}, \quad (6)$$

where the amplitude factor a_n for half the perpendicular depth d_n is, from Eq. (2),

$$a_n = \exp\left(-ik_1 f_n \frac{d_n}{2}\right) = \exp\left(-\frac{\pi}{\lambda} f_n d_n\right).$$
(7)

In the optical range:

F. Abeles, Le Journal de Physique et le Radium, "La théorie générale des couches minces", 11, 307–310 (1950) Recursive transfer matrix method, used also for XRR



 $R_{n-1, n} = a_{n-1}^{4} \left[\frac{R_{n, n+1} + F_{n-1, n}}{R_{n, n+1} F_{n-1, n} + 1} \right],$

$$LK_{n, n+1}F_{n-1, n}$$

$$R_{n, n+1} = a_n^2 (E_n^R / E_n)$$

$$F_{n-1, n} = \frac{f_{n-1} - f_n}{f_{n-1} + f_n}.$$

$$|\vec{\mathbf{E}}(z,\phi_i,E_0)|^2$$

$$|\mathbf{M}(z,\phi_i,E_0)|^2$$

$$|\mathbf{M}(z,\phi_i,E_0)|^2$$

$$|\mathbf{H}(z,\phi_i,E_0)|^2$$

$$|\mathbf{H}(z,\phi_i,E_0)|^2$$

$$|\mathbf{H}(z,\phi_i,E_0)|^2$$

$$|\mathbf{H}(z,\phi_i,E_0)|^2$$

$$|\mathbf{H}(z,\phi_i,E_0)|^2$$

EDITIONE MULTIPLE Layers

where

and



PHYSICAL REVIEW B

VOLUME 44, NUMBER 2

1 JULY 1991-II

Glancing-incidence x-ray fluorescence of layered materials

D. K. G. de Boer

Philips Research Laboratories, P.O. Box 80000, 5600JA Eindhoven, The Netherlands





$$-\frac{\partial P_{jz}}{\partial z} = \frac{1}{2Z_0} \frac{4\pi}{\lambda} N'_{jz} N''_{jz} \left\{ |E_j^t|^2 \exp\left[-\frac{4\pi N''_{jz} z}{\lambda}\right] + |E_j^r|^2 \exp\left[\frac{4\pi N''_{jz} z}{\lambda}\right] \right\}$$

$$I_{aj} = \frac{\lambda}{hc} C_{aj} \frac{\tau_{a\lambda}}{\mu_{j\lambda}/\rho_j} J_{a\lambda} w_a g_a \exp\left[-\sum_{n=1}^{j-1} \frac{\mu_{na} d_n}{\sin \psi_d} + |E_j^r|^2 \exp\left[\frac{4\pi N''_{jz} z}{\lambda}\right] + \left[E_j^{t*} E_j^r \exp\left[\frac{4\pi i N'_{jz} z}{\lambda}\right] + \left[E_j^{t*} E_j^r \exp\left[\frac{4\pi i N'_{jz} z}{\lambda}\right] + \exp\left[\frac{4\pi i N'_{jz} z}{\lambda}\right] + \exp\left[-\frac{4\pi i N'_{jz} z}{\lambda}\right] + \exp\left[-\frac{4\pi i N'_{jz} z}{\lambda}\right]$$

Total reflection, OK, but practically?

FONDAZIONE BRUNO KESSLER



The interference of incident and reflected beam causes a standing wave field above the reflectors surface.





Intensity distribution as a function of incident angle and depth

Total reflection, OK, but practically?

TXRF – analysis of surface contamination analysis of materials deposited on flat reflecting surface

BRUNO KESSLER



- GIXRF get "positional-structural" (as well as chemical) information through the angular dependence of fluorescence in the grazing incidence region: above-below surface film-like, particle-like particle size layered samples
- XSW standing wave field created by interference of incident and Bragg reflected field but also the study of crystalline like "super-structures" (e.g. Langmuir-Blodgett films)



Quantitative analysis

Empirical methods

PROS No physical model needed

CONS Need of SPECIFIC standard samples One calibration per experimental condition

APPLICATION Good for monitoring very similar samples First principles / fundamental parameters - deterministic

- Monte Carlo

PROS

NON SPECIFIC standard samples used to evaluate model parameters One calibration per experimental condition

CONS Need a physical model to simulate results

APPLICATION Good if samples keep changing



First principles / fundamental parameters

- deterministic
- Monte Carlo

PROS

NON SPECIFIC standard samples used to evaluate model parameters One calibration per experimental condition

CONS Need a physical model to simulate results

APPLICATION Good if samples keep changing Describe/model

- source
- detector (efficiency)
- sample

Interactions:

- scattering
- photoelectric absorption
- fluorescence/auger

Fundamental Parameters



First principles / fundamental parameters

- deterministic
- Monte Carlo

PROS

NON SPECIFIC standard samples used to evaluate model parameters One calibration per experimental condition

CONS

Need a physical model to simulate results

APPLICATION Good if samples keep changing Peak intensity Extraction Intensity simulation/comparison/fitting

Spectrum (spectra) simulation/comparison/fitting

Fundamental parameters

LONDMEIGHE	
PR PR 1 2 8 2 45 1 4 20 40 40 40 40 40 40 40 40 40 40 40 40 40	
RRUNO KESSU	

10	1) ite
main								~ Luc
Tables (24)								
* xraydata_auger_total								
xraydata_auger_transitions	60	- 27						
 xraydata_brennan_cowa 								Col: 1 Row: 1
 xraydata_compton_proni xraudata_coster_krooin_l 	1000			1440 and 1				
 xraydata coster kronig r 			0 0 H	2 🤴				
» xraydata_ebel_a_rho								
* xraydata_ebel_elastic	Full Vier	w Rem	view Script Out	put				
 xraydata_ebel_inelastic 		7	lodmus	name	A	density	row in PT	col in PT
 xraydata_ebel_tau_range xraydata_ebel_tau_shell 			1 H	hydrogen	1.00794	8.40-05	1	1
* sraydata element	1 1 1		2 144	heliom	4.002602	0.000166	18	1
 IE2 Columns (7) 	40		3.11	Inhium	A 641	0.534		
9 Indexes (0)	3		1 84	handliven	0.013103	1 848	-	
System indexes (0)	4.		4 04	oerymon	9.012192	1.040		6
 araufata eodi97 f1F2 	5		5.8	boron	10.811	2.37	13	2
 xraydata fluo yield 	6		6 C	carbon	12.0107	2	34	2
xraydata_general_shell_def	7		7 N	nitrogen	14.0067	0.001165	15	2
xraydata_henke_f1f2	8		8 0	oxygen	15,9994	0.001332	16	2
 xraydata_hubbell_f0 	9		9 F	fluorine	18.998403	0.00158	17	2
 Arayoata nubbeu nr araufata orbital 	10		10 Ne	neon	20.1797	0.000839	18	2
 xravdata shell data 								
> xraydata shell def	Query O	ĸ						
* xraydata_transition_data	Row(s) n	eturned:	109					
» xravdata transition def								

https://data-minalab.fbk.eu/txrf/xraydata/

42 KN2

42 KN3

19965.27

19965.27

0.00722

0.01403

						h	ome x
	-	.					
Х	-Ra	iy Lin	les/Tr	ansi	tions		
Se	earch						
All	l lines o	f element:	Мо				
Al	l lines w	ith energy	above (eV):	16000			
Al	l lines w	ith energy	below (eV):				
S	earch		_				
R	earch esults	for "ele	ment = N	lo and 1	16000 <	Energy	/eV <
s Re z	earch esults symbol	for "ele	ment = N A density	lo and 1	1 6000 < r col_in_PT	Energy	/eV <
S R Z 42	earch esults symbol Mo	for "ele	ment = N A density 95.96 10.22	Io and 1	L6000 < [col_in_PT 5	Energy	/eV <
S R 2 42	earch esults symbol Mo	for "ele name molybdenum	ment = N A density 95.96 10.22	fo and 1 row_in_PT 6	L6000 < r col_in_PT 5	Energy	/eV <
R Z 42 X-1	earch esults symbol Mo Ray line	for "ele name molybdenum s (transitio	ment = N A density 95.96 10.22 ns) list	Io and 1 row_in_P1 6	L6000 < [col_in_PT 5	Energy	/eV <
S R 42 X-1 Z	earch esults symbol Mo Ray line transitio	for "ele name molybdenum s (transitio	ment = N A density 95.96 10.22 ns) list V probability	Io and 1 7 row_in_PT 6	L6000 < r col_in_PT 5	Energy	/eV <
R (Z 42 X-1 Z 42	earch symbol Mo Ray line transitio KL2	for "ele name molybdenum s (transitio on energy_e 17374.29	ment = N A density 95.96 10.22 ns) list V probability 0.28821	Io and 1 7 row_in_PT 6	L6000 < r col_in_PT 5	Energy	/eV <
R (4 Z 42 X-1 Z 42 42	earch symbol Mo Ray line transitio KL2 KL3	for "ele name molybdenum s (transitio on energy_e 17374.29 17479.372	ment = N A density 95.96 10.22 ns) list V probability 0.28821 0.54964	Io and 1 7 row_in_PT 6	L6000 < r col_in_PT 5	Energy	/eV <
R (2 42 X-1 2 42 42 42 42	earch symbol Mo Ray line transitio KL2 KL3 KM2	for "ele name molybdenum s (transitio n energy_e 17374.29 17479.372 19590.25	ment = N A density 95.96 10.22 ns) list V probability 0.28821 0.54964 0.04774	10 and 1 7 row_in_P1 6	L6000 < r col_in_PT 5	Energy	/eV <

- Standard Atomic Weight: IUPAC recommended values
- Elemental densities: J. H. Hubbell and S. M. Seltzer
- Electron binding energies, Edge Jump, X-Ray lines, Transition probabilities, Fluorescence yield, Cascade effect: xraylib, T. Schoonjans et al.

introduction element view x-ray lines absorption ed chemical com references

- Atomic energy level widths: J. L. Campbell, T. Papp
- Fluorescence yield, Coster-Kronig probabilities: M. O. Krause
- Atomic scattering factors (150eV-30000eV): B. L. Henke et al.
- Atomic scattering factors (30000eV 300000 eV): S. Brennan et al.
- Phoelectric (shell-specific and total), elastic and inelastic scattering cross sections: H.Ebel et al.

Fundamental parameters

FONDAZIONE BRUNO KESSLER

Materials Layers Sample **Contamination/dopant** Profile) Simulation **Nanoparticles** Experimental Experimental Data Fitting **Parameters** Set-up (primary beam, detector) Geometrical Configuration **Experimental Data**

Fundamental parameters



In XRF:

Cross sections are tabulated in cm²/g For single elements



To define a material in XRF you must provide: Weight fractions and density

In XRD: you just need the phase parameters



Example : doped silicon surface



GIXRF quantitative analysis





GIXRF quantitative analysis

FONDAZIONE BRUNO KESSLER



FONDAZIONE BRUNO KESSLER





GIXRF vs XRR ?

GIXRF and XRR- MAUD school 2018 - Giancarlo Pepponi



XRR

reveals elemental surface concentrations:

- material composition
 - in depth elemental information

sensitive to electron density and its changes:

- material density
 - film thickness
 - optical constants
 - roughness



GIXRF - ambiguity problem - As doping profile

FONDAZIONE BRUNO KESSLER







GIXRF fit result looks very good, almost no difference between calculation and measurement ... but the result for the depth distribution is unrealistic -> GIXRF is ambiguous

GIXRF - ambiguity problem – Hf thin film

sample D07(nominal 2nm) and calculated 1.65nm HfSiOx on Si-substrate sample D07(nominal 2nm) and calculated 1.9nm HfSiOx on Si-substrate normalized fluorescence [a.u.] normalized fluorescence [a.u.] 0.8 0.8 0.6 0.6 0.4 0.4 measured Si measured Si calculated Si calculated Si 0.2 0.2 measured Hf measured Hf calculated Hf calculated Hf 0 n 2 3 2 -2 3 0 angle of incidence [mrad] angle of incidence [mrad]

GIXRF measurement data fitted to calculated values. This comparison shows the ambiguity of GIXRF concerning density and thickness. For the left side a layer-density of 6.7 g/m3 was used, while on the right 6.1 g/m3 was used

GIXRF can only determine surface mass concentration! Ambiguity thickness vs. density (XRR probably better)

RRUNO KESSLER

GIXRF - XRR combined





Si wafers implanted with 1E15 atoms/cm² of Arsenic by beamline ion implantation with different implantation energies:

- As1 0.5keV
- As3 2keV
- As4 3keV

^{_}_{0.8} Combined evaluation of grazing incidence X-ray fluorescence and X-ray reflectivity data for improved profiling of ultra-shallow depth distributions[☆]

D. Ingerle^{a,*}, F. Meirer^b, G. Pepponi^c, E. Demenev^c, D. Giubertoni^c, P. Wobrauschek^a, C. Streli^a



Multiply reflectivity and transmission by a damping factor

- P. Croce and L. Nevot, Rev. Phys. Appl. 11, 113 (1976)
- L. Nevot, P. Croce, Revue de physique appliquée, 15, 761 (1980)
 - $Q_{j,j+1} = 1$ smooth surface
 - $Q_{j,j+1} = e^{-2\sigma_j^2 k_j^2}$ Debye-Waller factor
 - $Q_{j,j+1} = e^{-2\sigma_j^2 k_j k_{j+1}}$ Nevot-Croce factor

factors multiplying the Fresnel coefficient

All good for XRR but what about Fluorescence???

interface layers with changing index of refractionerror function , linear

Can we model it as particles?

GIXRF and XRR- MAUD school 2018 – Giancarlo Pepponi



0.5nm

1nm

10⁰

20nm Ge on Si - roughness - rough substrate (4nm r.m.s.)

0.5nm

1nm

ENDAZIONE ERUNO KESSLER 10° _____ 20nm Ge on Si - roughness - smooth substrate

10

E Solution – buried layers and interfaces

Definition of depth resolution: - different at different depths

FONDAZIONE BRUNO KESSLER

Sample 10nm In2O3 / 4nmAg / 10nm In2O3



CIII silicon 100

Depth resolution – junction depth

FONDAZIONE BRUNO KESSLER





Fluorescence intensity ERNEAZIONE cascade effect – secondary fluorescence



GIXRF - secondary fluorescence

FONDAZIONE BRUNO KESSLER

J. Appl. Phys. **75**, 2026 (1994); http://dx.doi.org/10.1063/1.356303 (3 pages)

Molecular beam epitaxial growth of single domain ZnSe on Ge

L. K. Li, Y. Wang, M. Jurkovic, and W. I. Wang



Geometric corrections



Conway, John T., Nuclear Instruments and Methods in Physics Research Section A: Accelerators, Spectrometers, Detectors and Associated Equipment 614.1 (2010): 17-27.

GIXRF and XRR- MAUD school 2018 - Giancarlo Pepponi

EDIVERSENT

$$I_{abs} = I(z) T(\phi_1) \sin \phi_1 \frac{\tau_s}{\sin \phi_2} dz$$







"the principle of microscopic reversibility predicts that the results of absorption- and emission-type experiments should be identical were they performed with the same wavelength radiation."

- higher lateral resolution Disadvantage:
 - reduced sensitivity



Thank you for your attention!

For any further question or doubt: pepponi@fbk.eu