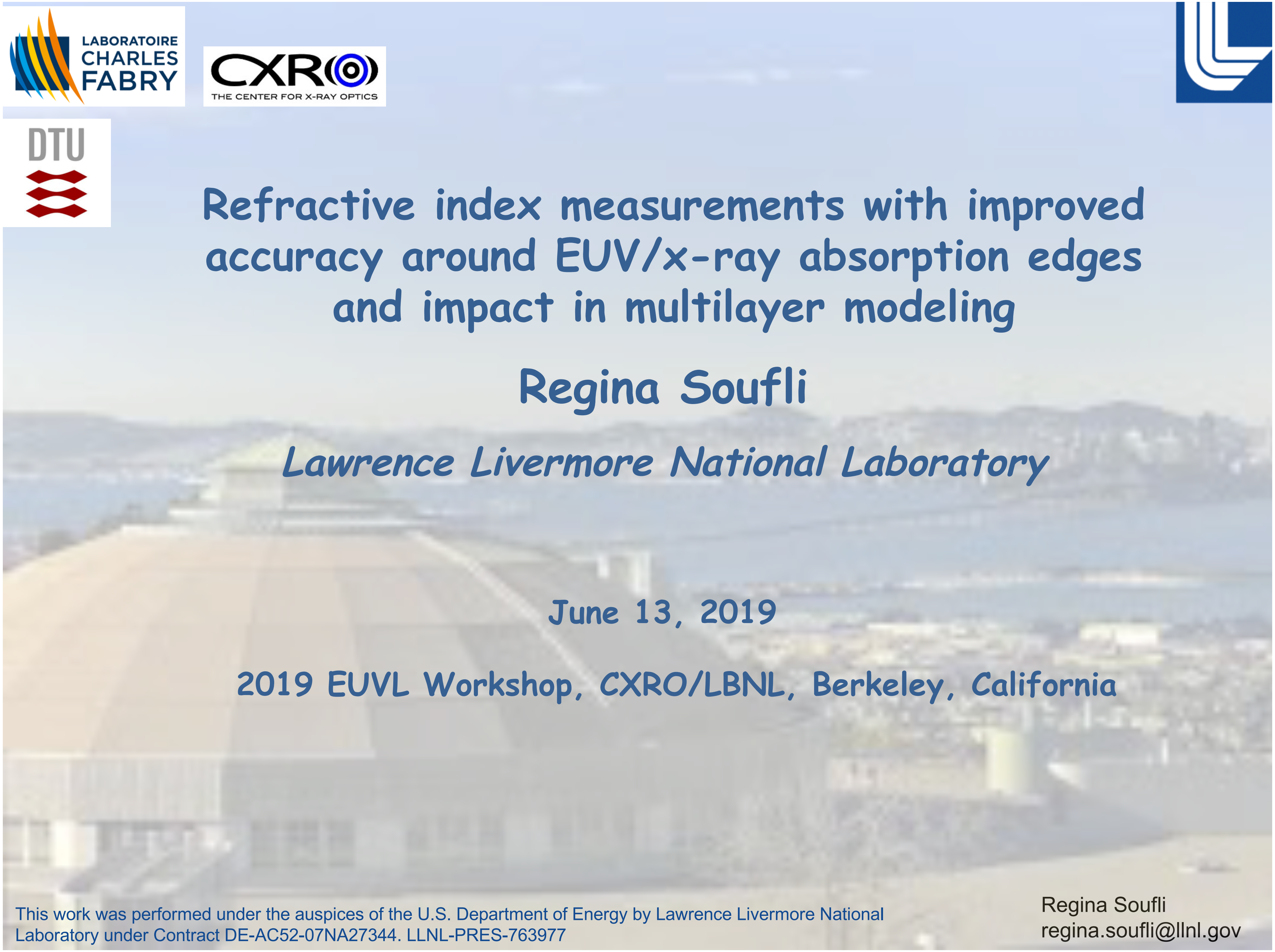


Refractive index measurements with improved accuracy around EUV/x-ray absorption edges and impact in multilayer modeling

Regina Soufli

Lawrence Livermore National Laboratory

June 13, 2019

2019 EUVL Workshop, CXRO/LBNL, Berkeley, California

This work was performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract DE-AC52-07NA27344. LLNL-PRES-763977

Regina Soufli
regina.soufli@llnl.gov

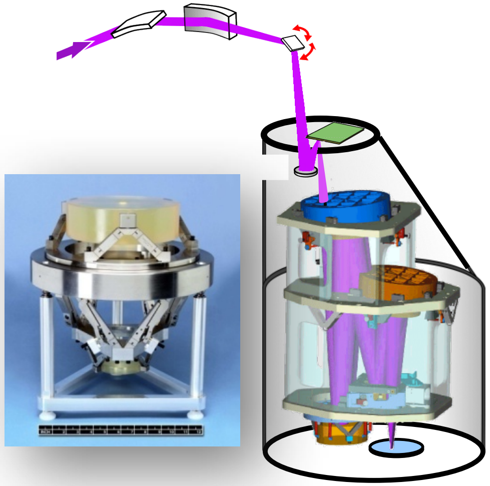
Technical contributors and sponsors

- R. Soufli, C. Burcklen (*LLNL*)
- F. Delmotte, C. Burcklen, E. Meltchakov, J. Rebellato (*LCF / IOGS*)
- E. M. Gullikson, F. Salmassi, J. Meyer-Ilse (*CXRO / LBNL*)
- N. Brejnholt, S. Massahi, D. Girou, F. Christensen (*DTU – Space*)

Regina Soufli
regina.soufli@llnl.gov

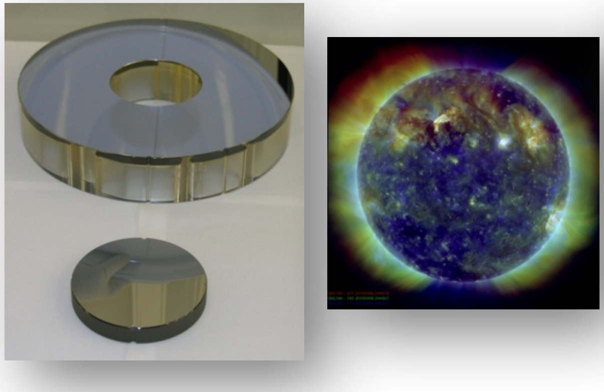
Our group at LLNL has developed short-wavelength optics for various applications

EUV Lithography:
ETS1, ETS2, MET2, MET5

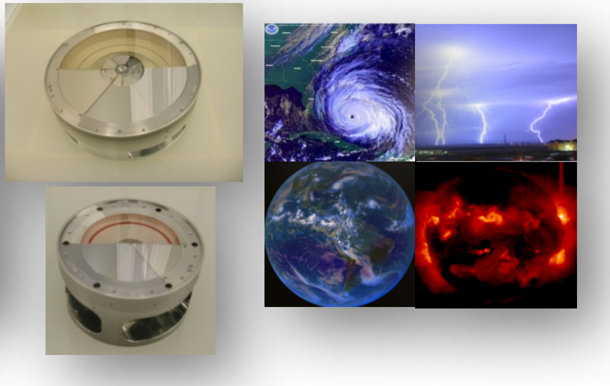


EUV solar physics, laser sources
Corrosion-resistant multilayers

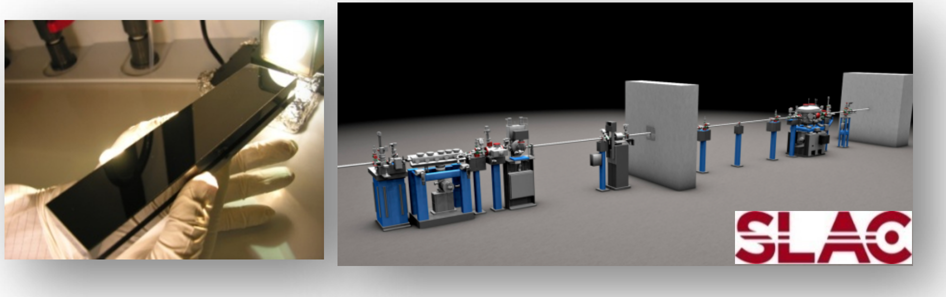
Solar Dynamics Observatory



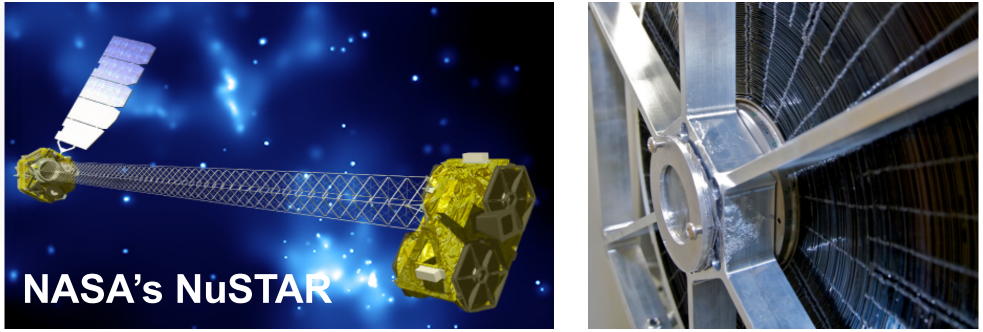
GOES space weather satellites



X-ray optics for the LCLS free-electron laser

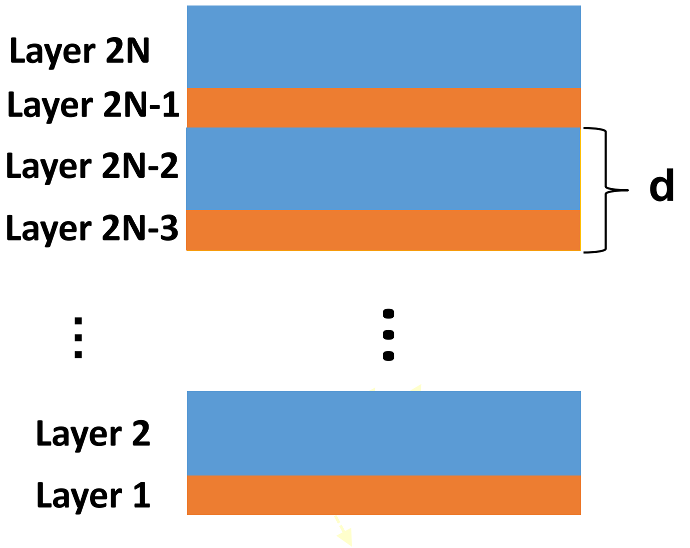


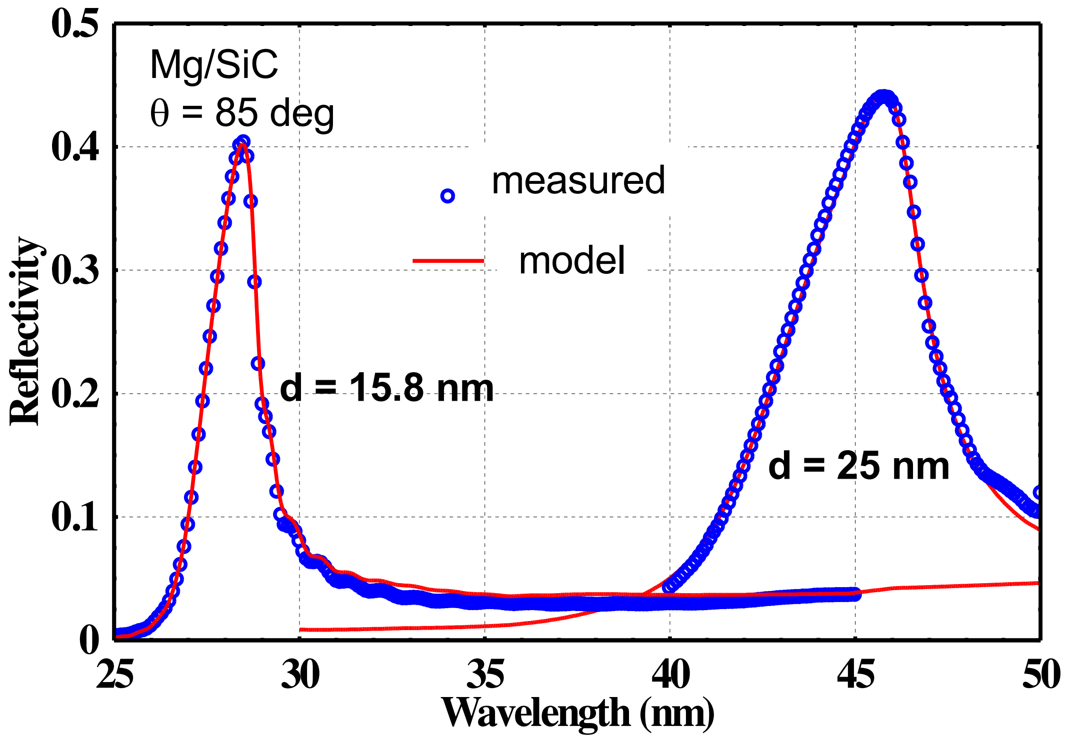
Hard x-ray /gamma-ray astrophysics, radiation detection, target diagnostics



Regina Soufli
regina.soufli@llnl.gov

EUV/x-ray component design and modeling requires accurate refractive index values





Multilayer model includes

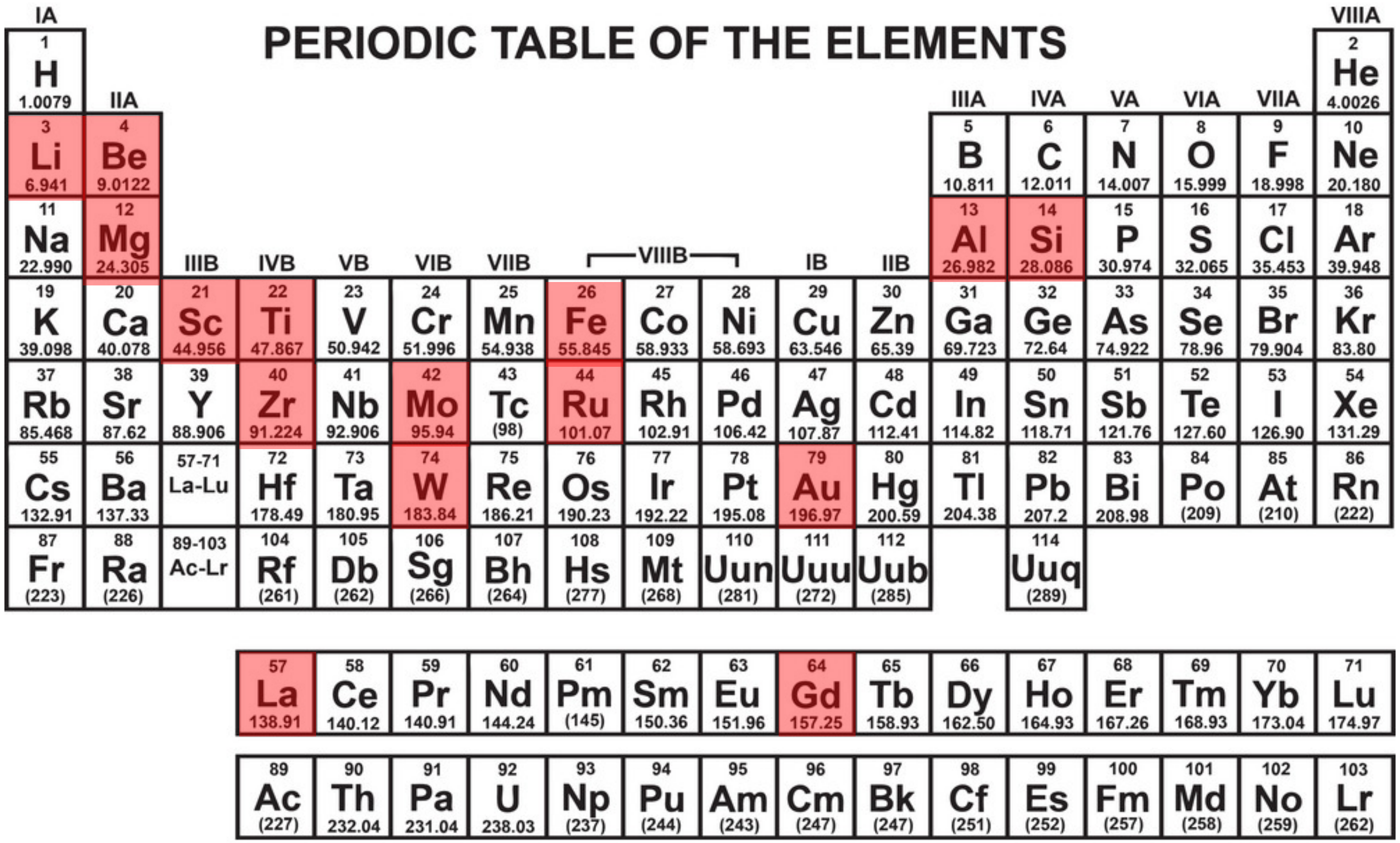
- Layer stacking configuration
- Layer thicknesses
- Layer refractive index
- Interface roughness
- Interdiffusion or interfacial layers

Fresnel thin film interference equations

Regina Soufli
regina.soufli@llnl.gov

Tabulated values of the refractive index at short wavelengths

B. Henke. E. Gullikson, J. Davis, Atomic Data Nucl. Data Tables 54, 181-342 (1993).
http://henke.lbl.gov/optical_constants/ (CXRO / LBNL)



PERIODIC TABLE OF THE ELEMENTS

IA	IIA	IIIB	IVB	VB	VIB	VIIB	VIIIB			IB	IIB	IIIA	IVA	VA	VIA	VIIA	VIIIA
1 H 1.0079																	2 He 4.0026
🟥 3 Li 6.941	🟥 4 Be 9.0122											5 B 10.811	6 C 12.011	7 N 14.007	8 O 15.999	9 F 18.998	10 Ne 20.180
11 Na 22.990	🟥 12 Mg 24.305											🟥 13 Al 26.982	🟥 14 Si 28.086	15 P 30.974	16 S 32.065	17 Cl 35.453	18 Ar 39.948
19 K 39.098	20 Ca 40.078	🟥 21 Sc 44.956	🟥 22 Ti 47.867	23 V 50.942	24 Cr 51.996	25 Mn 54.938	🟥 26 Fe 55.845	27 Co 58.933	28 Ni 58.693	29 Cu 63.546	30 Zn 65.39	31 Ga 69.723	32 Ge 72.64	33 As 74.922	34 Se 78.96	35 Br 79.904	36 Kr 83.80
37 Rb 85.468	38 Sr 87.62	39 Y 88.906	🟥 40 Zr 91.224	41 Nb 92.906	🟥 42 Mo 95.94	43 Tc (98)	🟥 44 Ru 101.07	45 Rh 102.91	46 Pd 106.42	47 Ag 107.87	48 Cd 112.41	49 In 114.82	50 Sn 118.71	51 Sb 121.76	52 Te 127.60	53 I 126.90	54 Xe 131.29
55 Cs 132.91	56 Ba 137.33	57-71 La-Lu	72 Hf 178.49	73 Ta 180.95	🟥 74 W 183.84	75 Re 186.21	76 Os 190.23	77 Ir 192.22	78 Pt 195.08	🟥 79 Au 196.97	80 Hg 200.59	81 Tl 204.38	82 Pb 207.2	83 Bi 208.98	84 Po (209)	85 At (210)	86 Rn (222)
87 Fr (223)	88 Ra (226)	89-103 Ac-Lr	104 Rf (261)	105 Db (262)	106 Sg (266)	107 Bh (264)	108 Hs (277)	109 Mt (268)	110 Uun (281)	111 Uuu (272)	112 Uub (285)		114 Uuq (289)				
			🟥 57 La 138.91	58 Ce 140.12	59 Pr 140.91	60 Nd 144.24	61 Pm (145)	62 Sm 150.36	63 Eu 151.96	🟥 64 Gd 157.25	65 Tb 158.93	66 Dy 162.50	67 Ho 164.93	68 Er 167.26	69 Tm 168.93	70 Yb 173.04	71 Lu 174.97
			89 Ac (227)	90 Th 232.04	91 Pa 231.04	92 U 238.03	93 Np (237)	94 Pu (244)	95 Am (243)	96 Cm (247)	97 Bk (247)	98 Cf (251)	99 Es (252)	100 Fm (257)	101 Md (258)	102 No (259)	103 Lr (262)

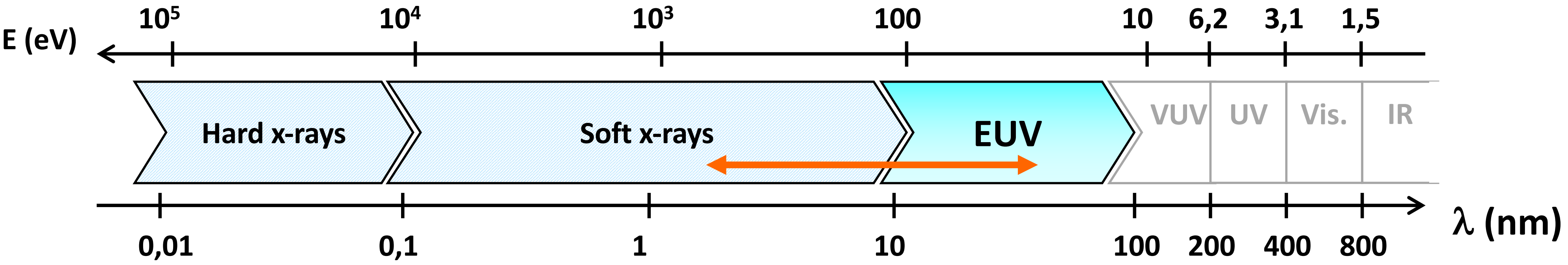
- Elements updated with experimental data

- Compound materials (**oxides, carbides, silicides, nitrides**) also need dedicated measurements

Atomic-like approximation is not valid near electronic absorption edges – dedicated measurements are needed

Regina Soufli
regina.soufli@llnl.gov

Refractive index measurements at short wavelengths are very difficult!



Complex refractive index: n $= 1 - \delta + i\beta$ with $\delta, \beta \leq 10^{-1}$ (optical constants)

Challenges in determination of n

- ☐ Absorption length ≈ 10 $\lambda \Rightarrow$ high **absorption**
- ☐ Need bright, monochromatic, well-characterized **light source** facility
- ☐ Sensitivity to **contamination**, surface oxidation
- ☐ Presence of absorption edge **fine structure**

Transmittance: β = measured, δ = K-K relation

- ☐ Need freestanding thin films 10 – 100 nm thick
- ☐ Need compilation of absorption (β) data in entire spectrum to calculate δ from K-K relation

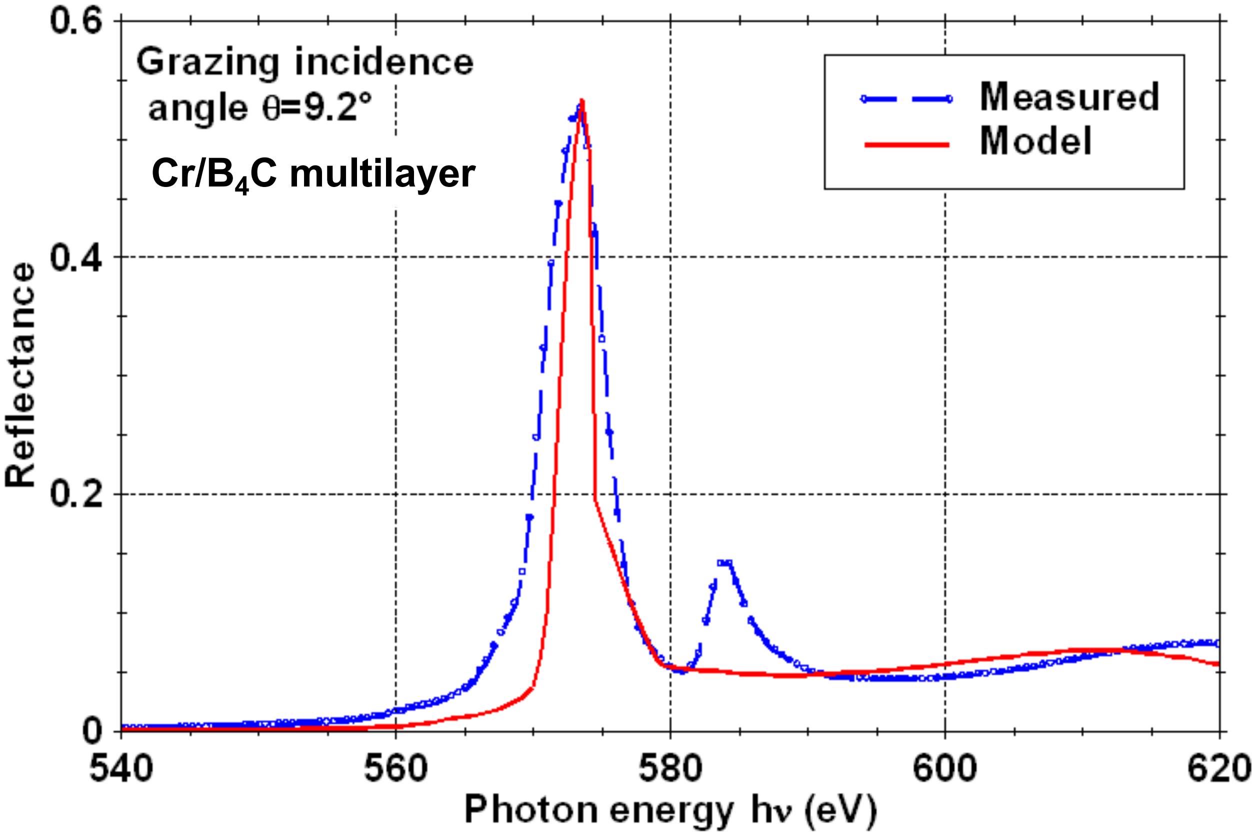
Reflectance: δ and β = measured

- ☐ Sensitivity to surface roughness, contamination
- ☐ Difficult to measure large energy bands in small step sizes

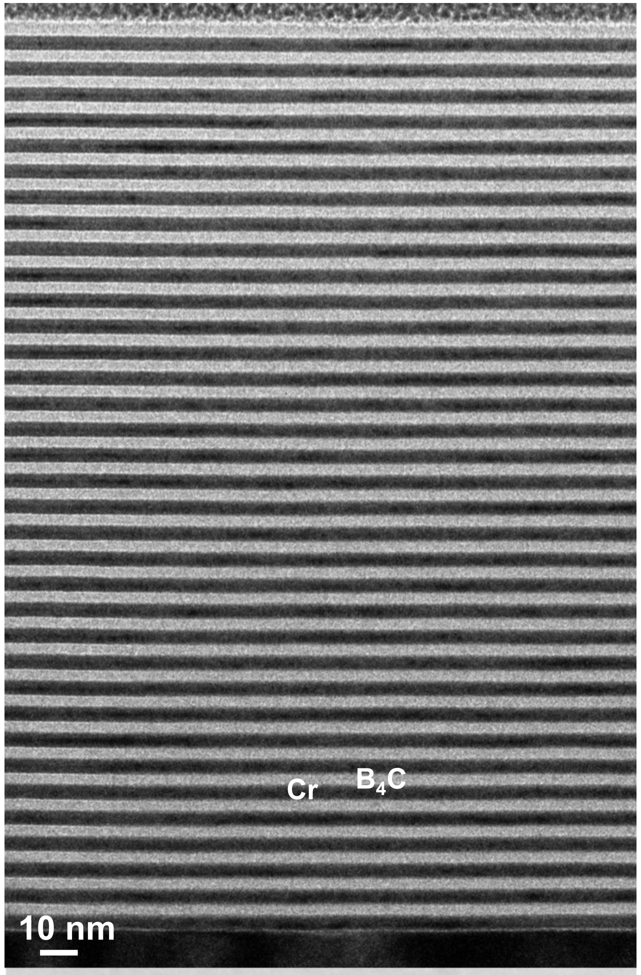
Regina Soufli
regina.soufli@llnl.gov

Example: tabulated refractive index of Cr is incorrect near the $L_{2,3}$ edge

Measured at ALS beamline 6.3.2.



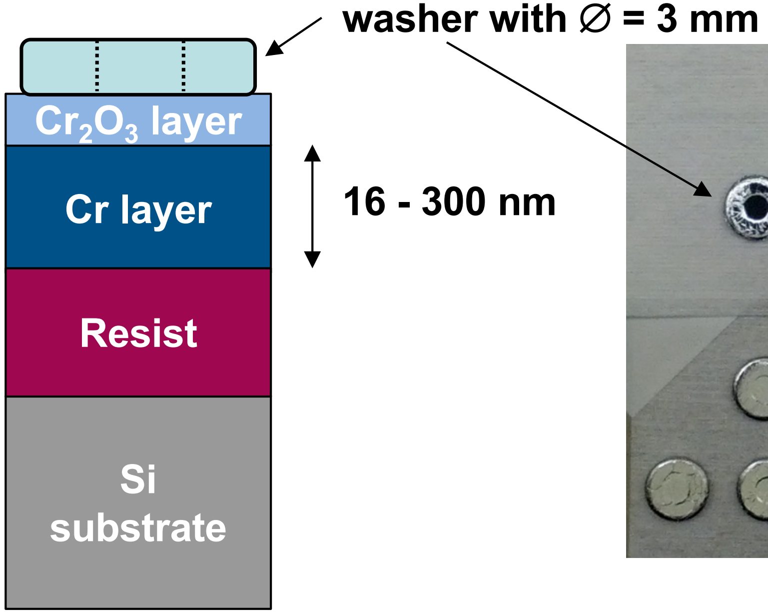
C. Burcklen, R. Soufli, D. Dennetiere, F. Polack, B. Capitanio, E. Gullikson, E. Meltchakov, M. Thomasset, A. Jérome, S. de Rossi, and F. Delmotte, J. Appl. Phys. ***119*** *125307 (2016).*

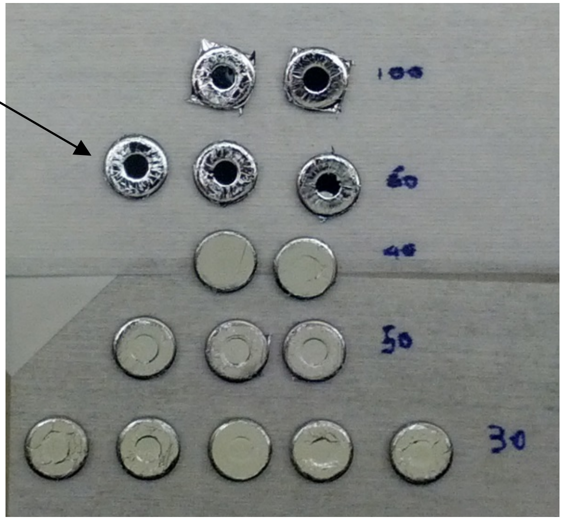


Cross-sectional TEM image of Cr/B4C multilayer

Regina Soufli
regina.soufli@llnl.gov

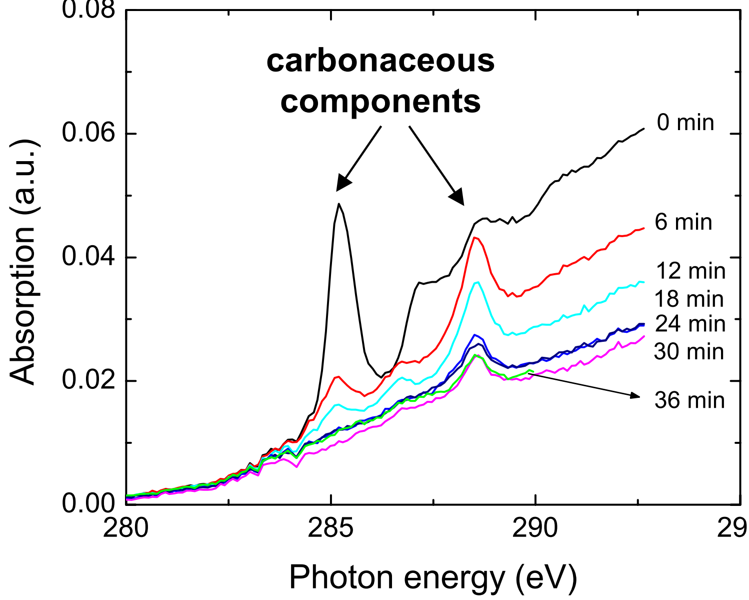
Freestanding Cr thin films

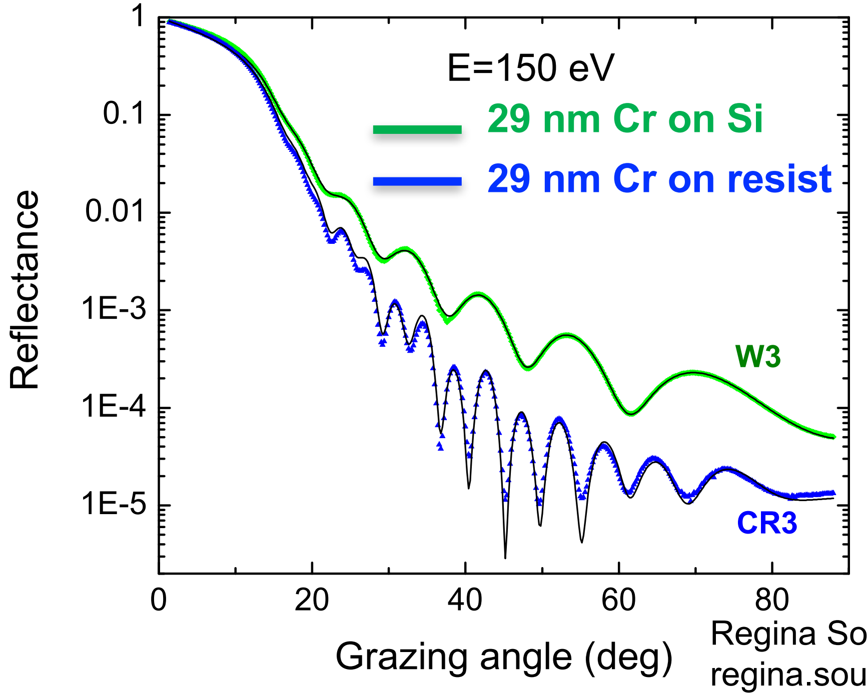




- Freestanding Cr thin film prepared at CXRO / LBNL
- RBS analysis: ρ **= 7.19 g/cm3**
- Cr thin films have ~ 1 nm surface oxide, **stable for 3 years**
- Thickness measured by reflectance at 8.05 keV and 150 eV

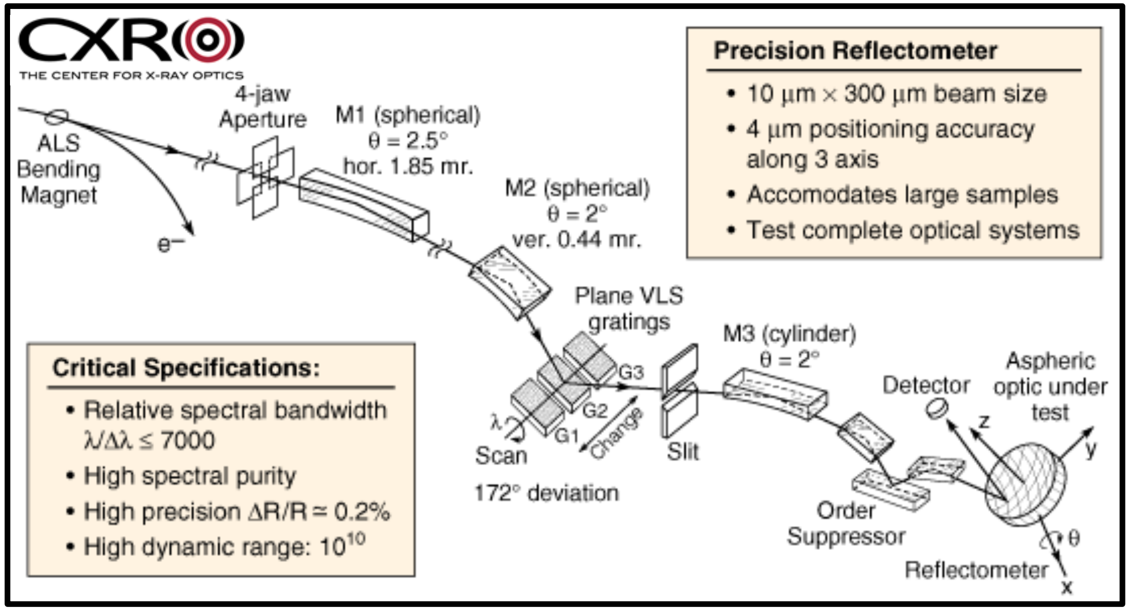
Removal of resist residues by UV-ozone lamp exposure





Regina Soufli
regina.soufli@llnl.gov

ALS beamline 6.3.2 is a precisely calibrated facility for refractive index measurements

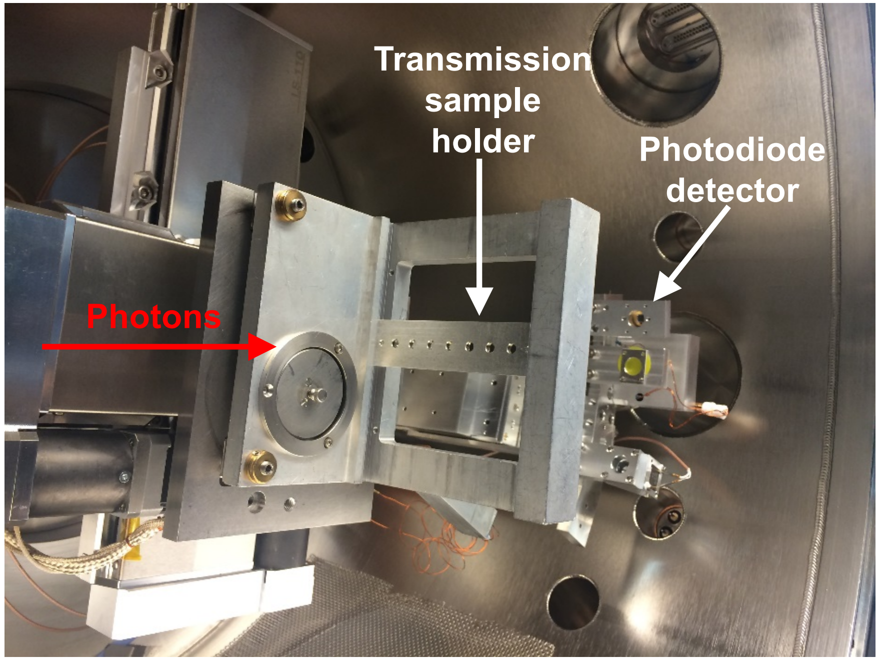


Precision Reflectometer

- 10 µm × 300 µm beam size
- 4 µm positioning accuracy along 3 axis
- Accomodates large samples
- Test complete optical systems

Critical Specifications:

- Relative spectral bandwidth $\lambda/\Delta\lambda \leq 7000$
- High spectral purity
- High precision $\Delta R/R \simeq 0.2\%$
- High dynamic range: 10^{10}



ALS Calibration and Standards beamline 6.3.2

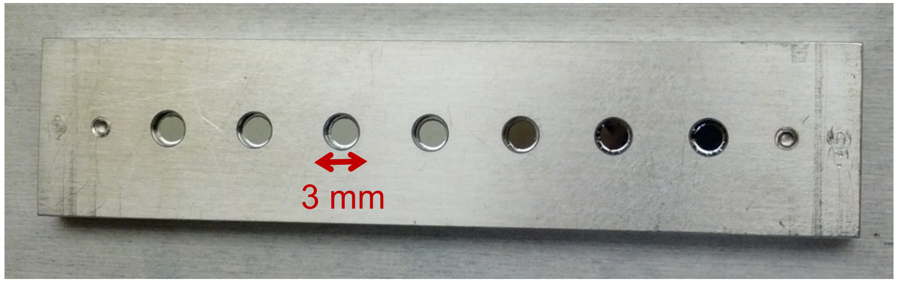
λ = 1 - 90 nm

PI = Eric Gullikson

Regina Soufli
regina.soufli@llnl.gov

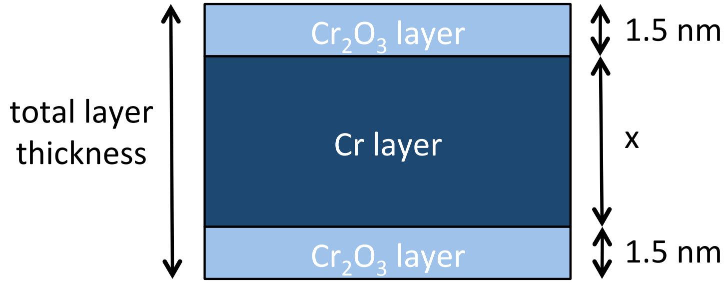
Cr photoabsorption measurements

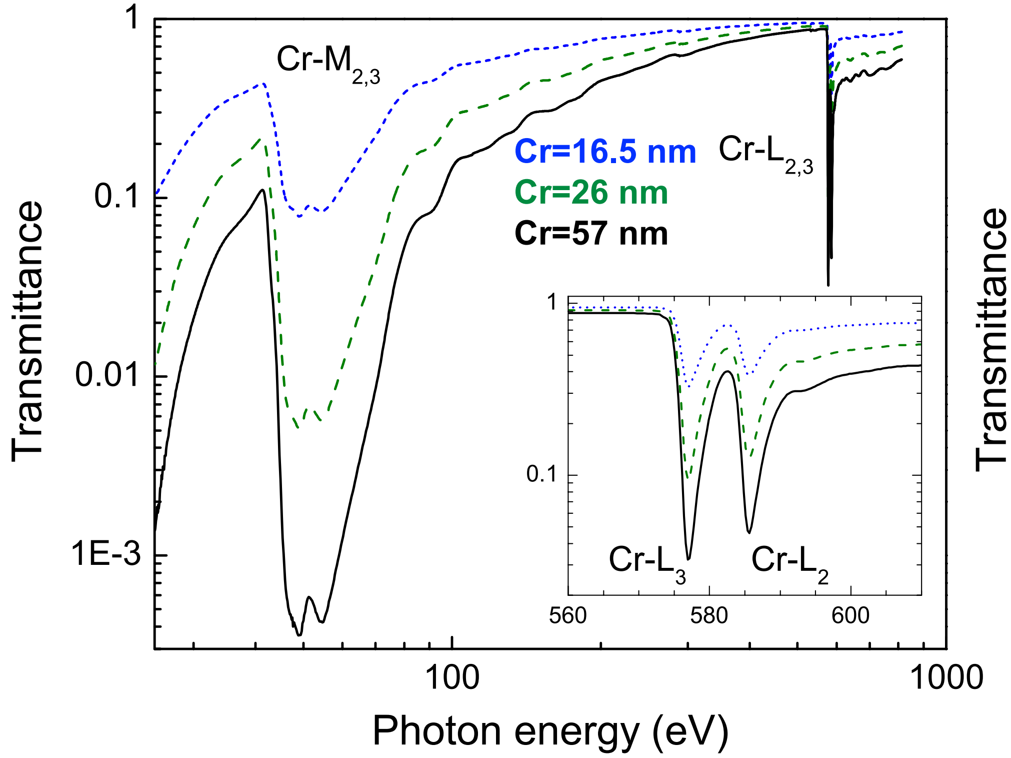
Transmittance measurements at ALS beamline 6.3.2 from 25 eV to 813 eV

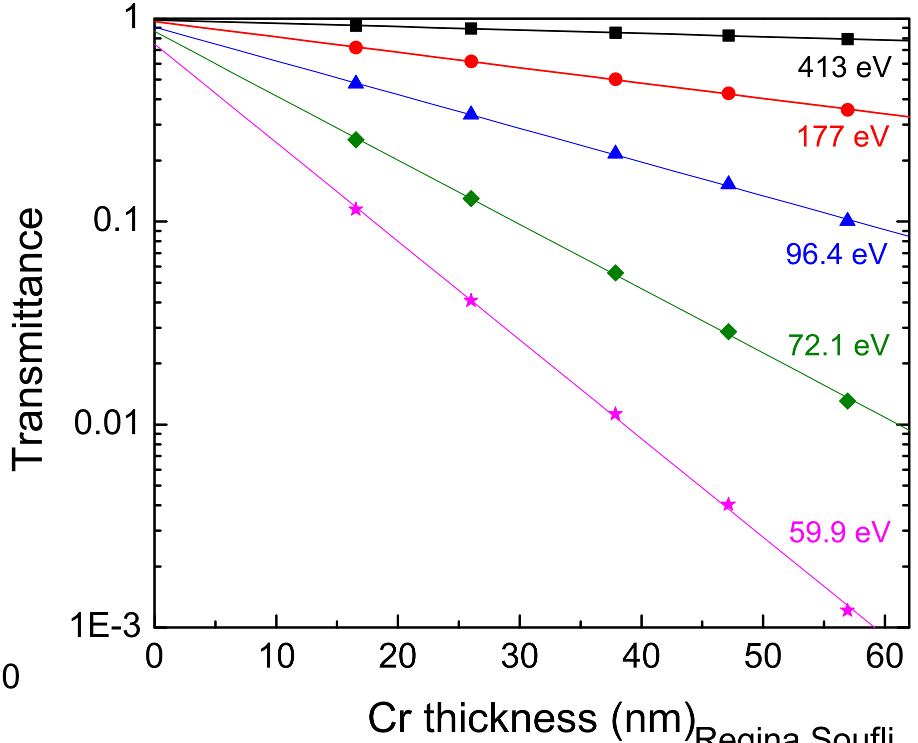


Transmittance (*T*) vs Cr thickness (*x*)

$$T(E,x) = T_0(E)e^{-x\,\alpha(E)}$$



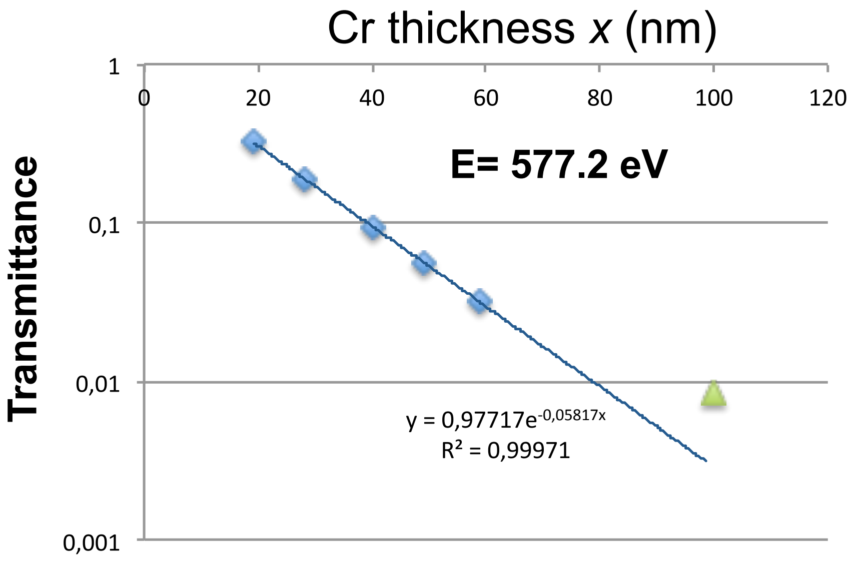


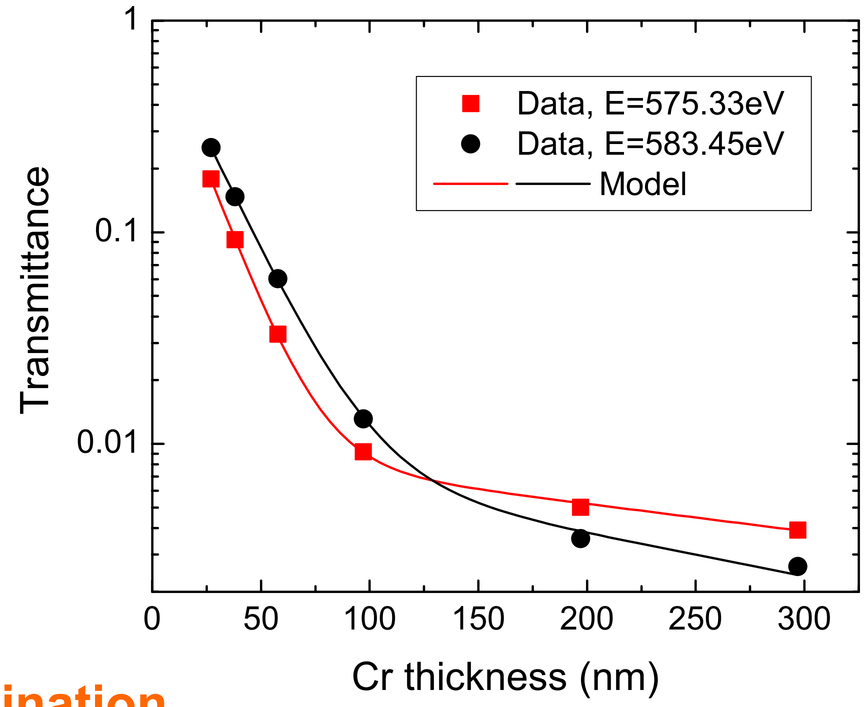


Regina Soufli
regina.soufli@llnl.gov

The effect of 1% spectral contamination at high energies

We have developed a method to remove spectral contamination from the data.





$$I_0(E) = I(E) + I_{SC}(E)$$

spectral contamination

$$T(E,x) = \underbrace{\kappa\, T_{0(E)}\, e^{-x\,\alpha(E)}}_{I(E)} + \overbrace{(1-\kappa)\, T_{SC}(E)\, e^{-x\,\alpha_{SC}(E)}}^{\text{spectral contamination}}$$

significant when $\alpha >> \alpha_{sc}$ and x=large

Energy (eV)	κ	T_0 (=T_{sc})	α (nm^{-1})	α_{sc} (nm^{-1})
575.33	0.990	0.946	0.06321	0.00298
583.45	0.989	0.954	0.05026	0.00503

Regina Soufli
regina.soufli@llnl.gov

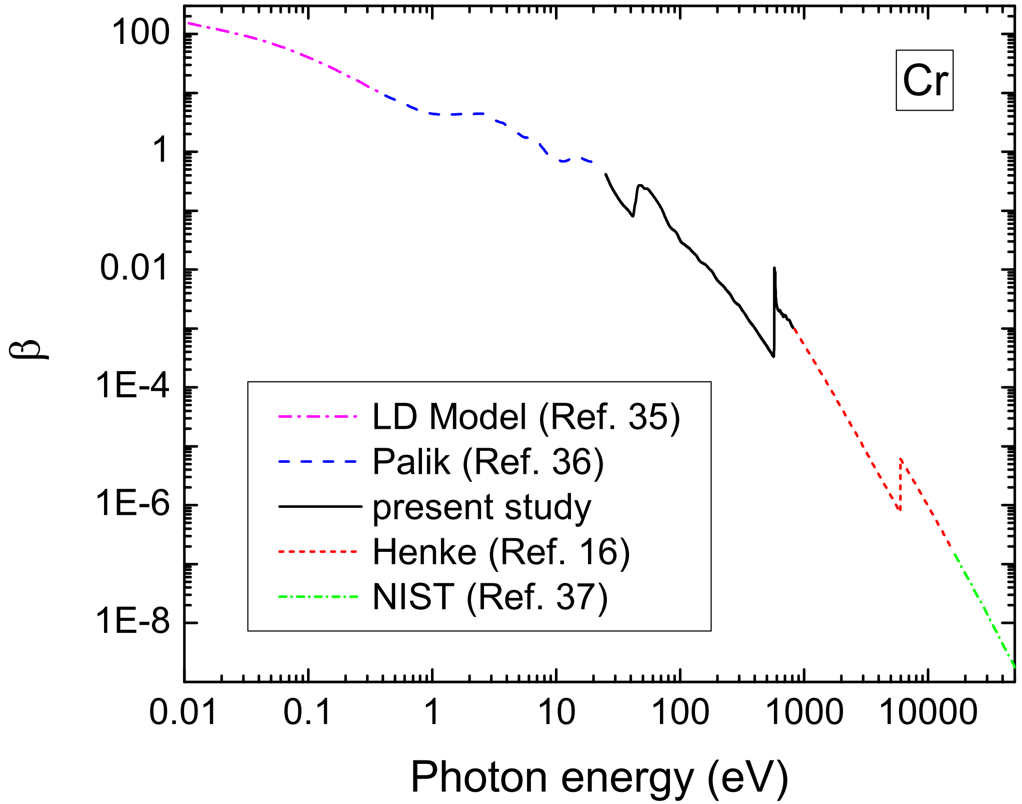
Compilation of Cr absorption data

Complex refractive index n = 1 – δ + i β

✓ **Absorption coefficient**

$$\beta(E) = \frac{\lambda}{4\pi}\alpha(E)$$

✓ **Dispersive part (1-δ)**



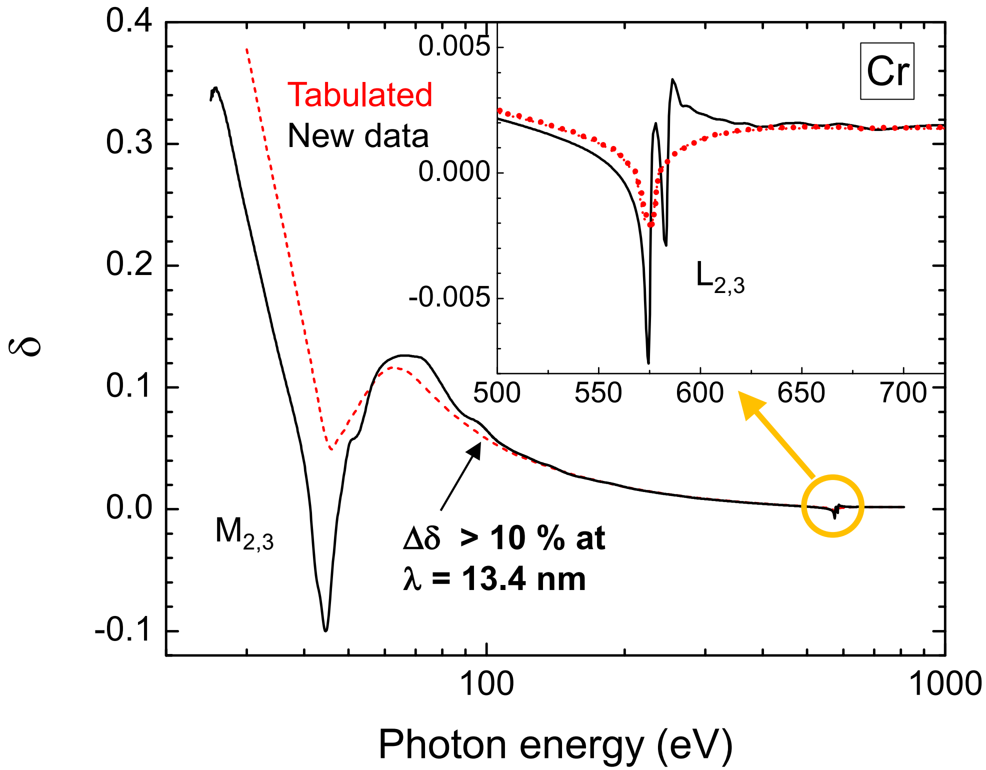
Calculation via Kramers-Kronig relation

$$\delta(E) = -\frac{\pi}{2}\,\mathrm{P}\int_0^\infty \frac{E'\beta(E')}{E'^2 - E^2}\,dE'$$

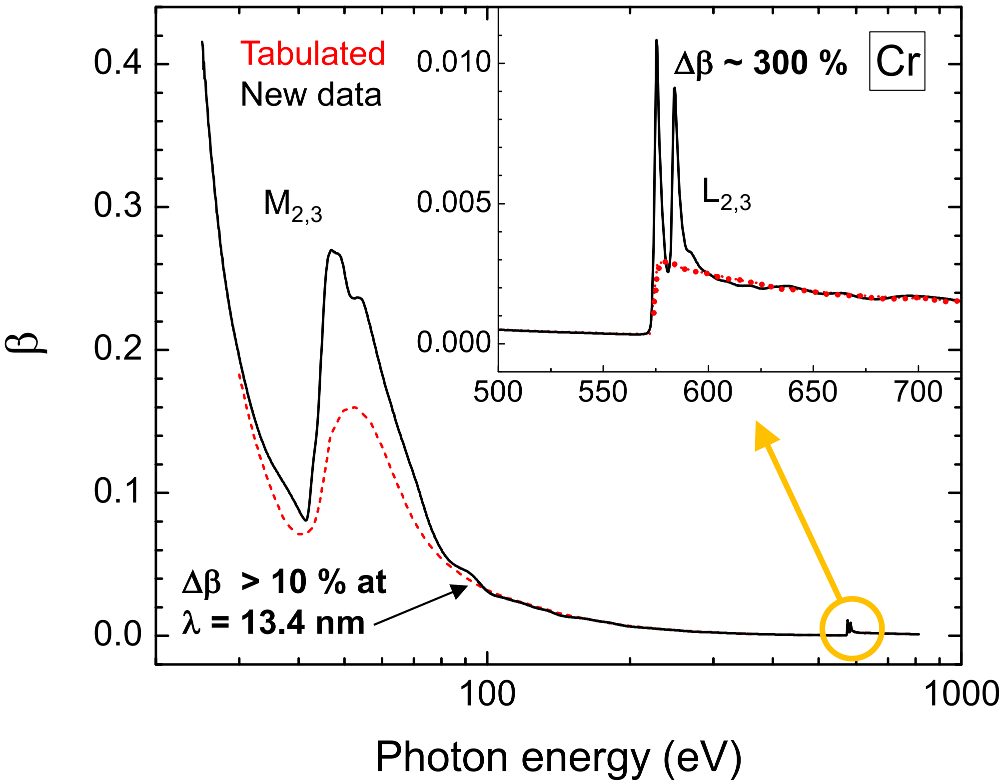
- **LD** = Lorentz-Drude model. A. D. Rakić, et al., "Optical properties of metallic films for vertical-cavity optoelectronic devices," Appl. Opt. 37, 5271-5283 (1998).
- **Palik** = *Handbook of Optical Constants of Solids*, edited by E. D. Palik, (Academic Press, Boston, 1998) pp. 374-385.
- **Henke** = B. Henke , E. Gullikson , and J. Davis , “X-ray interactions: photoabsorption, scattering, transmission, and reflection at E=50-30000 eV, Z=1-92,”At. Data Nucl. Data Tables 54, 181-342 (1993)
- **NIST** = Chantler, et al.(2005), “X-Ray Form Factor, Attenuation and Scattering Tables (version 2.1)”, NIST

Large differences with tabulated values revealed near the Cr $L_{2,3}$ and $M_{2,3}$ edges

$$n = 1 - \delta + i\beta$$



Δδ > 10 % at λ = 13.4 nm



Δβ ~ 300 %

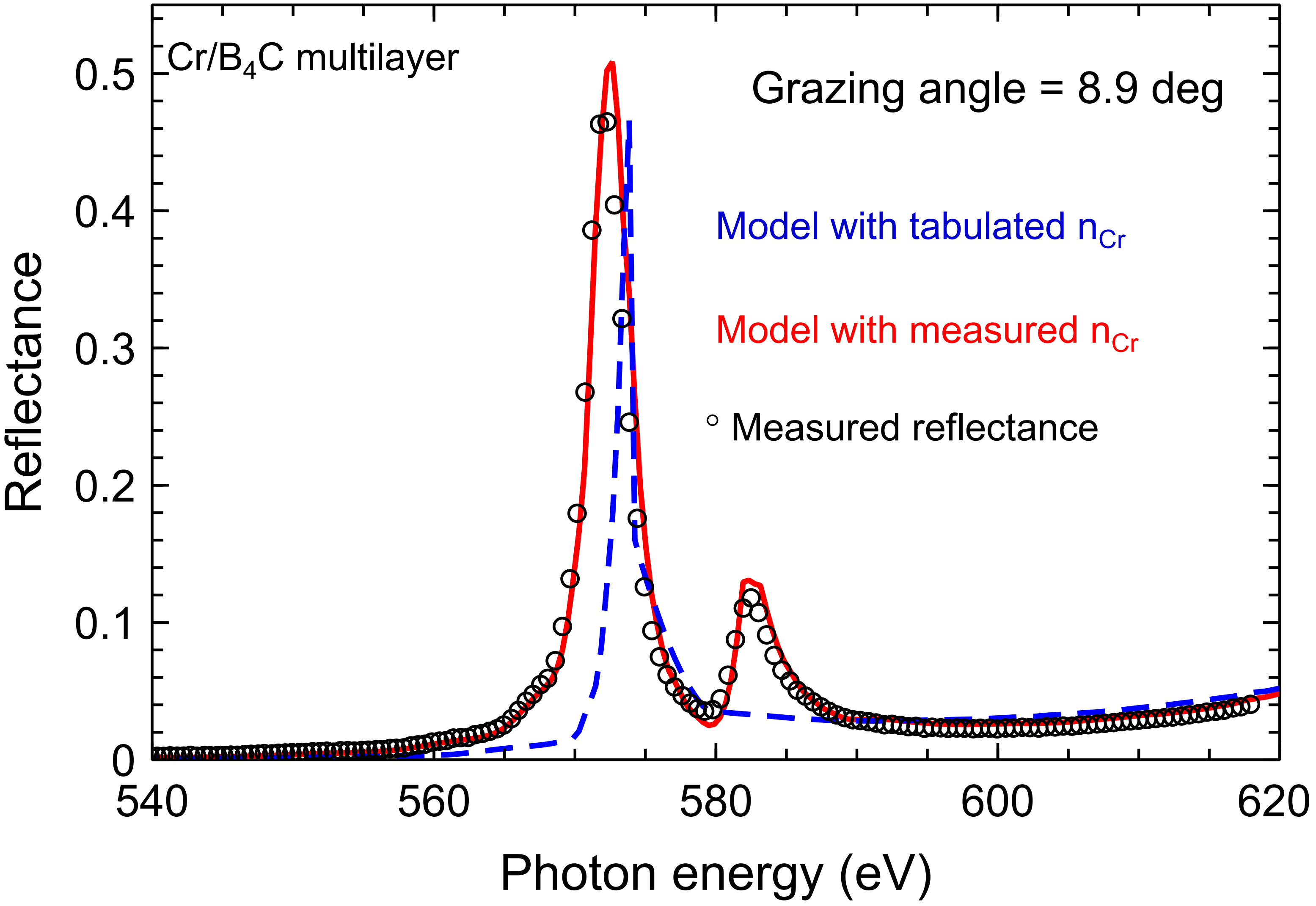
Δβ > 10 % at λ = 13.4 nm

New compilation of Cr refractive index (δ, β) values is now available for use

F. Delmotte, J. Meyer-Ilse, F. Salmassi, R. Soufli, C. Burcklen, J. Rebellato, A. Jérome, I. Vickridge, E. Briand, and E. Gullikson, J. App. Phys 124, 035107 (2018).

Regina Soufli
regina.soufli@llnl.gov

New Cr refractive index is validated by measured Cr/B_4C reflectance

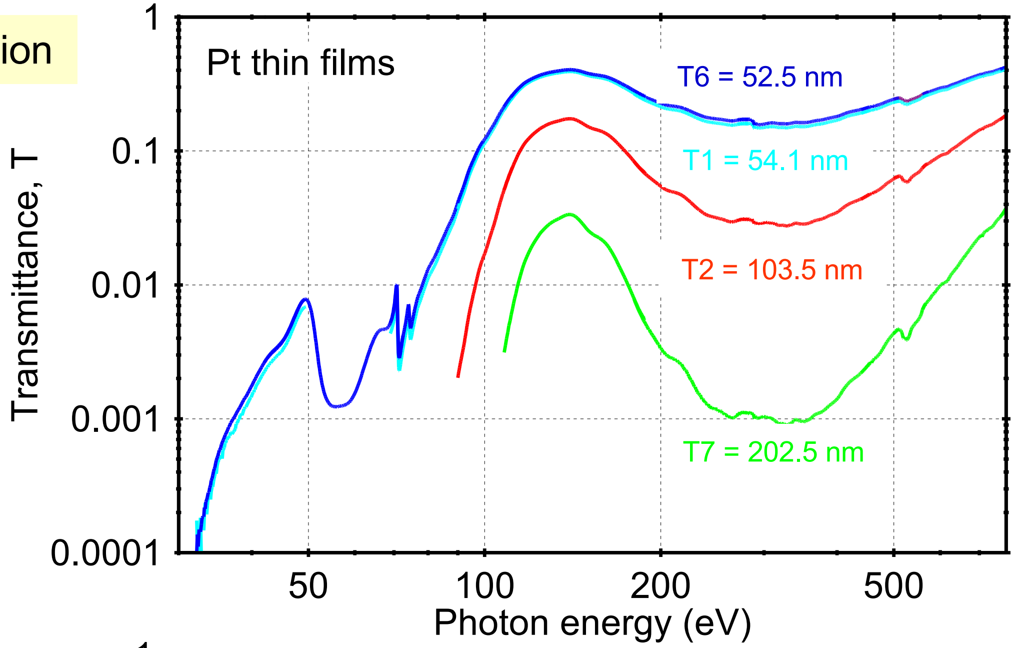


Regina Soufli
regina.soufli@llnl.gov

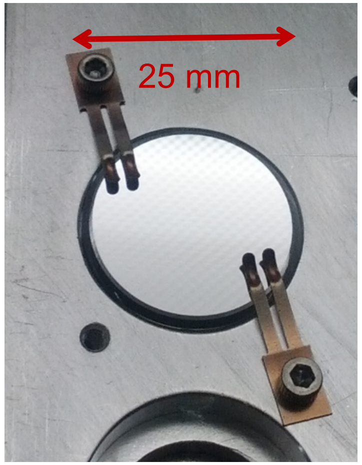
We studied Pt in the vicinity of N- and O-shell absorption edges

Transmittance method: β measured, δ from K-K relation

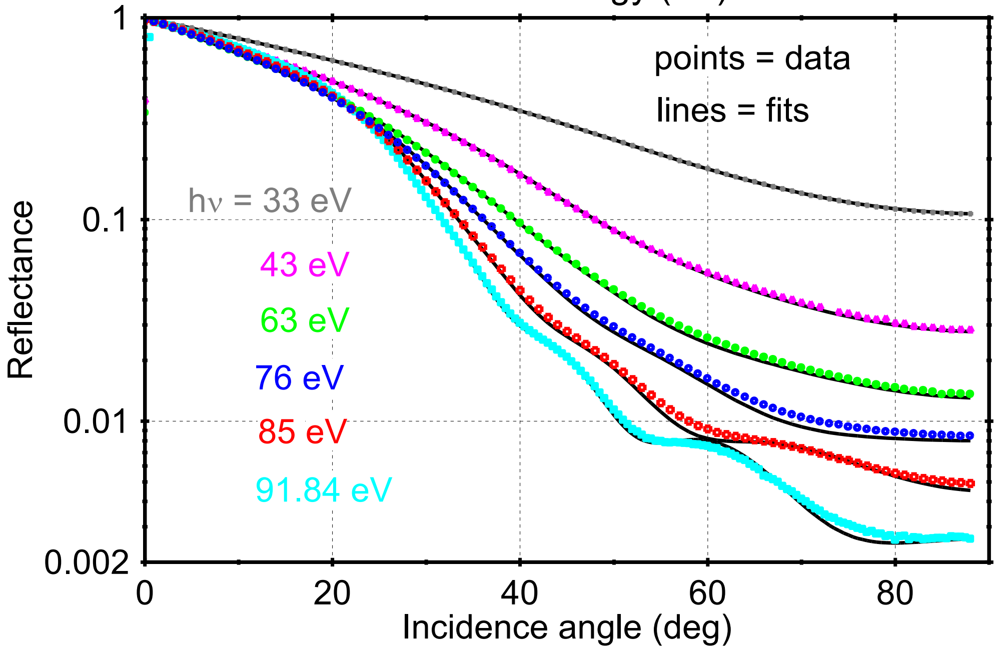
- Pt films deposited at DTU-Space
- Removed and mounted at CXRO/LBNL
- Pt thickness and density measured by reflectance at 8.05 keV and 83 – 188 eV



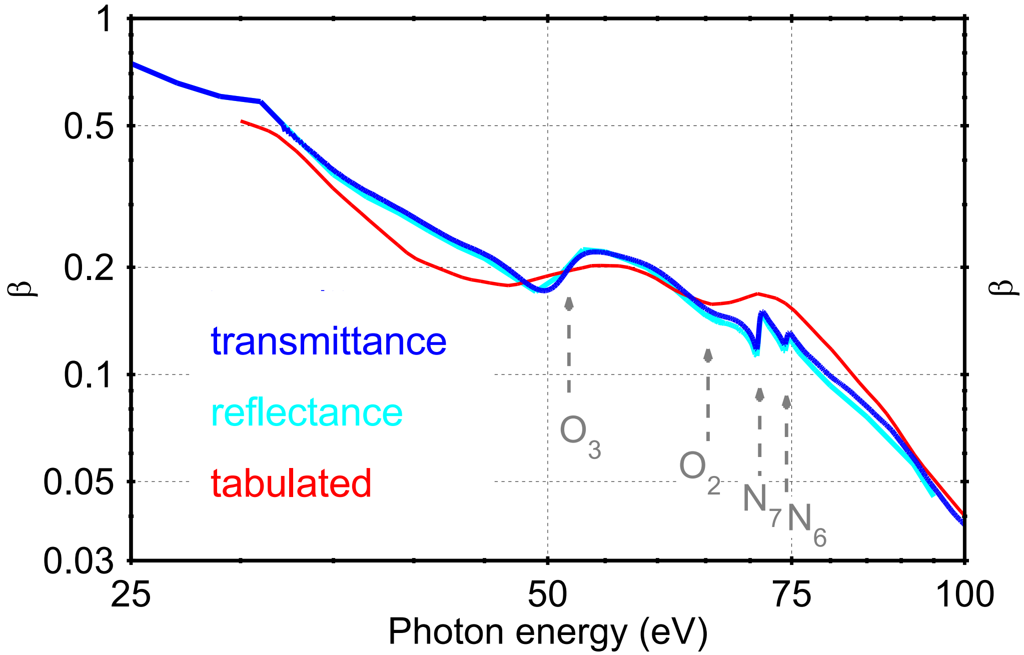
Reflectance method: δ and β from measurement

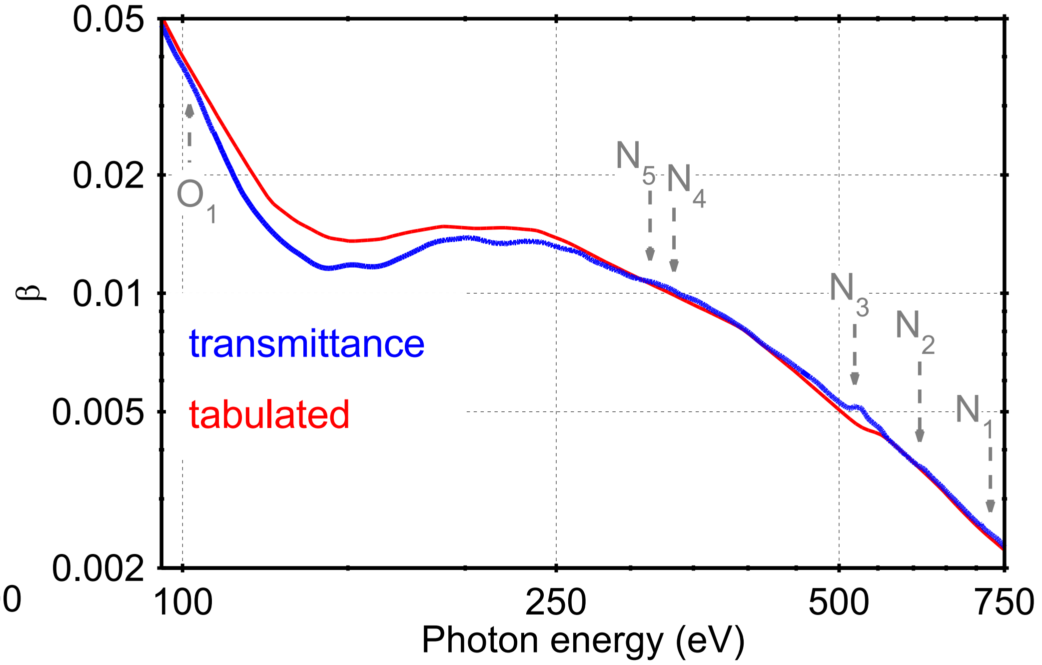


- Pt coating deposited at CXRO
- Pt thickness = 31.4 nm, density = 21.45 g/cm^3 measured by reflectance at 8.05 keV and 78 - 92 eV



Measured Pt absorption near O- and N- edges

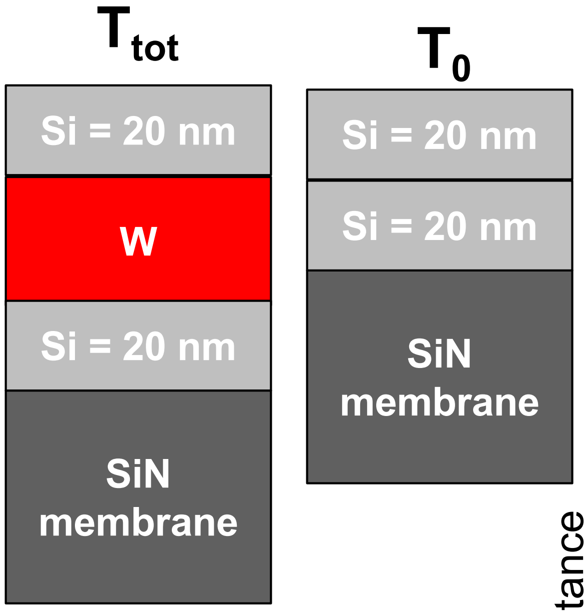




New compilation of Pt refractive index (δ, β) values is now available for use

R. Soufli, F. Delmotte, J. Meyer-Ilse, F. Salmassi, N. Brejnholt, S. Massahi, D. Girou, F. Christensen, E. M. Gullikson, "Optical constants of magnetron sputtered Pt thin films with improved accuracy in the N- and O- electronic shell absorption regions", J. Appl. Phys. ***125****, 085106 (2019).*

Transmittance measurements on encapsulated W films to protect from oxidation



T_{tot}

Si = 20 nm

W

Si = 20 nm

SiN membrane

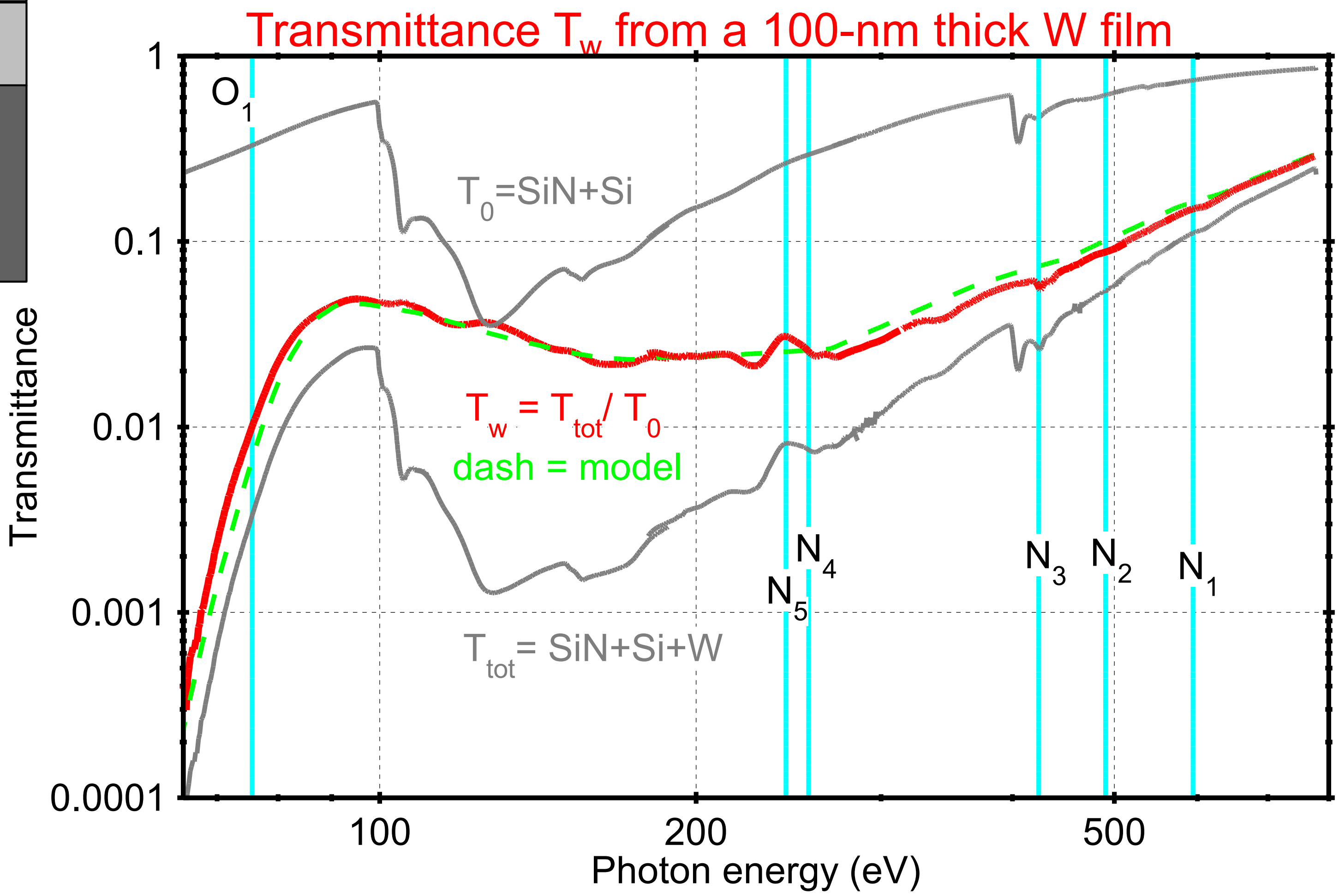
T_0

Si = 20 nm

Si = 20 nm

SiN membrane

- W degrades with oxidation
- Encapsulate W between two Si layers, deposit on SiN membrane (T_{tot})
- Deposit Si+SiN sample (T_0)
- Samples deposited at CXRO

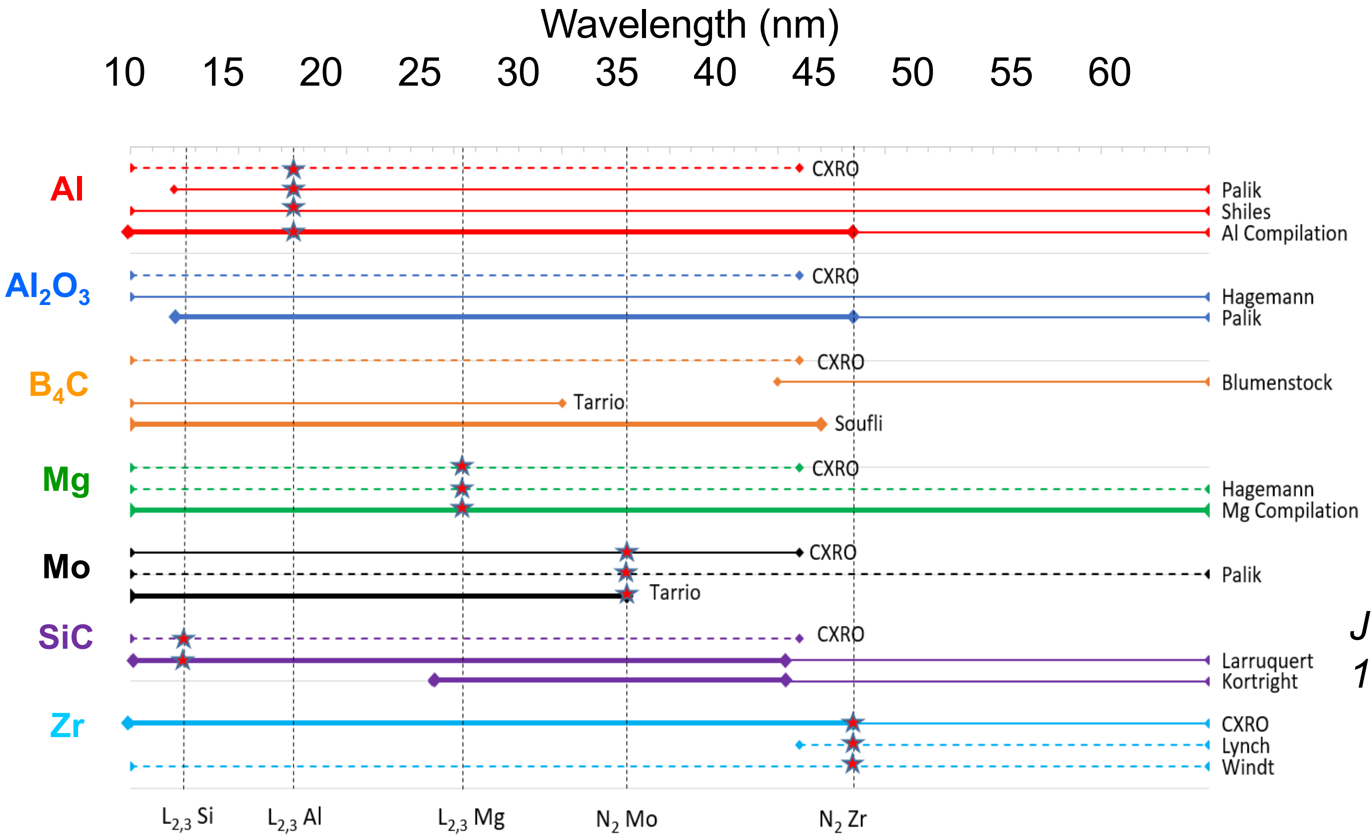


Transmittance T_w from a 100-nm thick W film

Regina Soufli
regina.soufli@llnl.gov

Conclusions

- Refractive index is not accurately known in EUV / x-ray
- We have optimized methodologies to measure Cr, Pt and W with improved accuracy near M- N- and O- edges.
- More materials need measurements – accurate refractive index values will enable the design of EUV components with maximized performance



J. Rebellato et al, SPIE 10691, 106911U (2018).

Regina Soufli
regina.soufli@llnl.gov