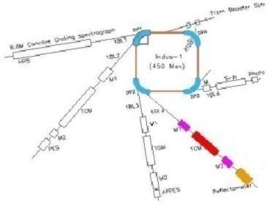

Applications of soft x-ray reflectivity beamline

for

Depth resolved structure and composition analysis of thin films

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Indore 452013 India.

Outline of the talk

- ⇨ Introduction
- ⇨ Beamline
- ⇨ Results
- ⇨ Summary

User base

IIT Delhi

IIT Mumbai

BARC Mumbai

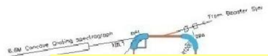
DAVV Indore

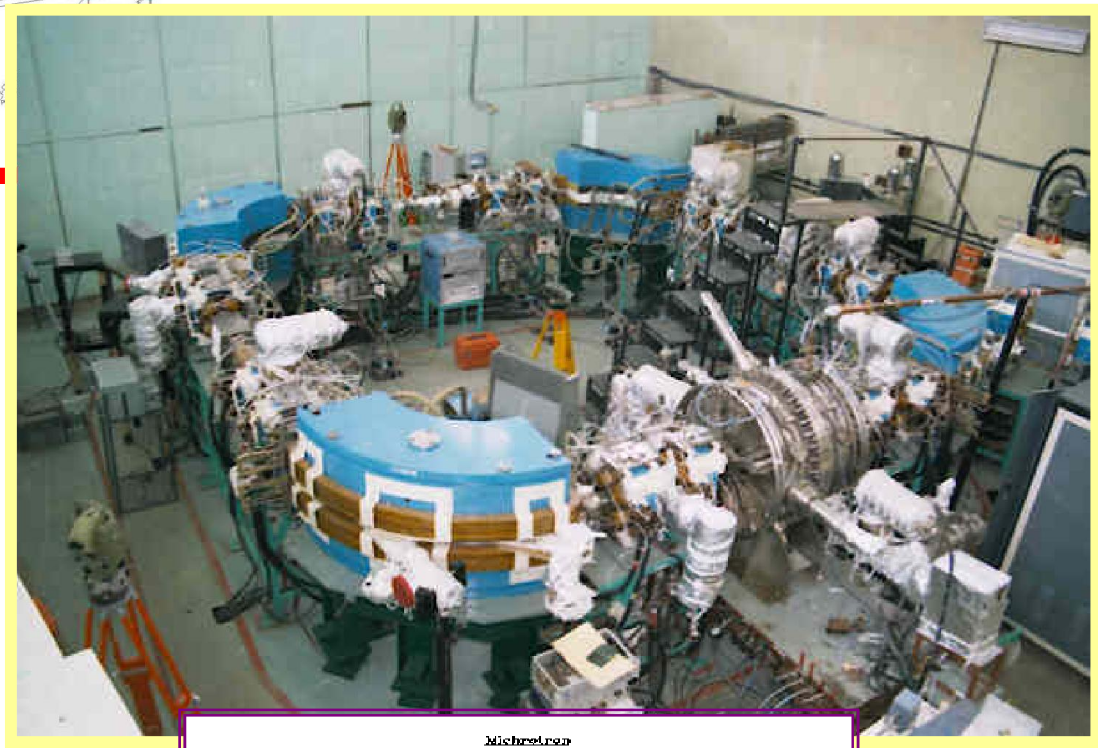
UGC-DAE-CSR

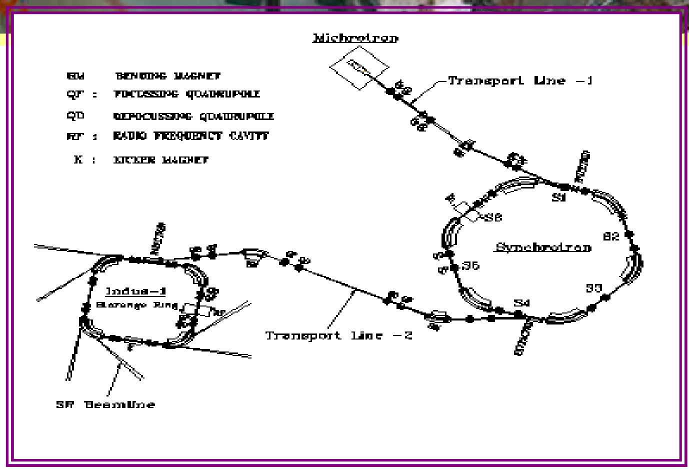
TIFR Mumbai

PRL Ahmedabad

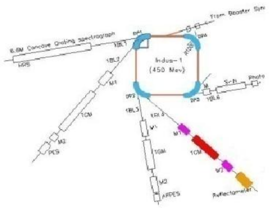
- **Developed by ISUD, RRCAT**
- **Publications: > 60**
- **PhDs: 7 completed**
  5 in progress



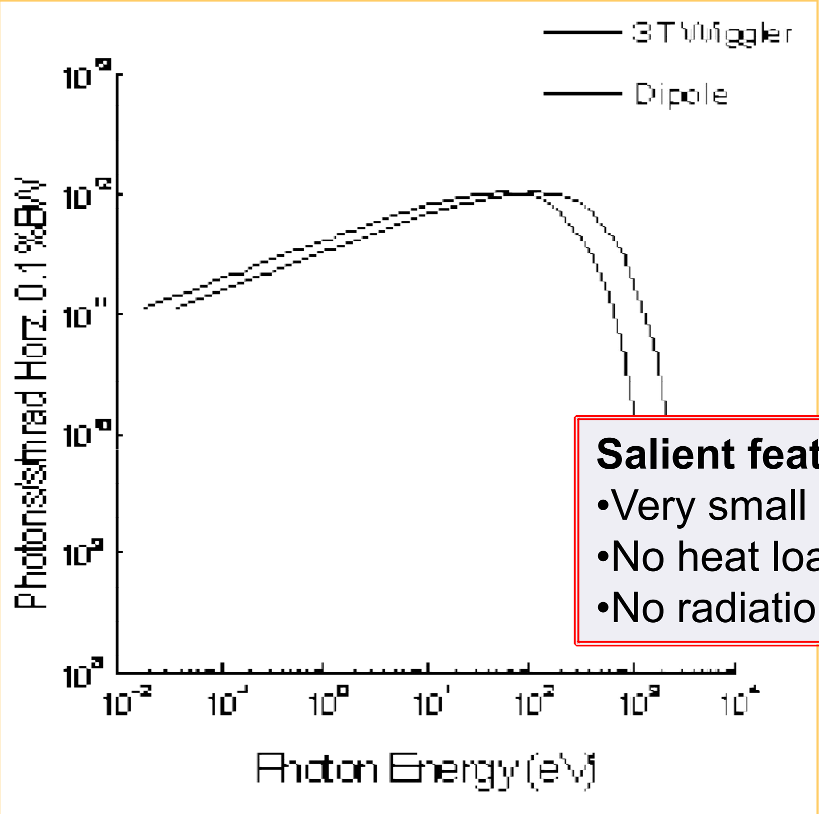


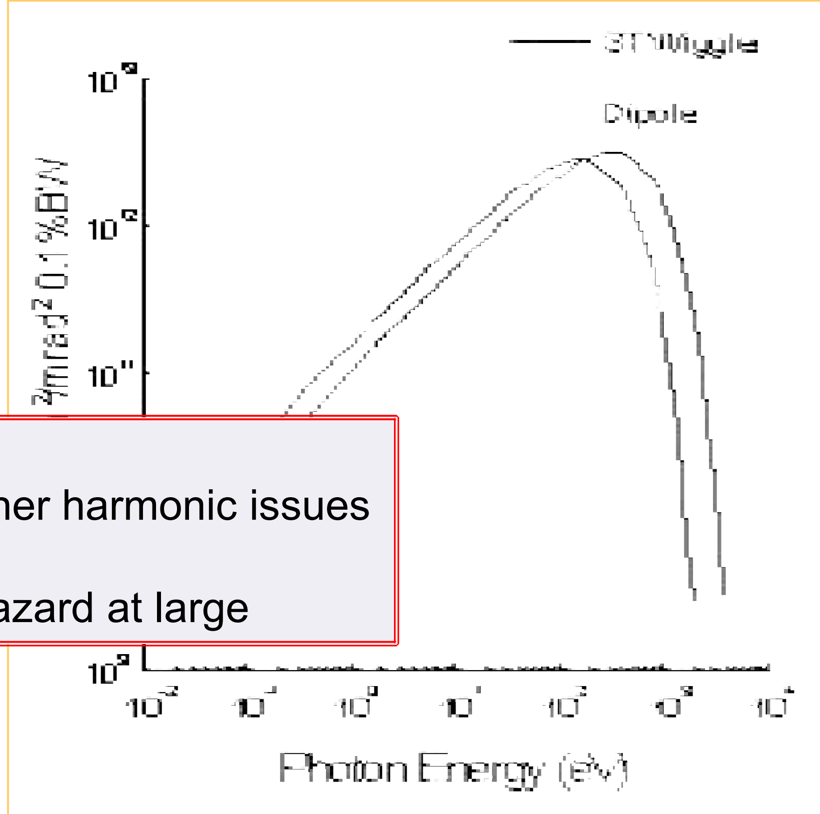


Electron Energy	*450 MeV*
Beam current	*100 mA*
Beam lifetime	*1.8 hrs*
Dipole bending field	*1.5 T*
Critical wavelength (energy)	*61.38$\AA$ (202 eV)*
Circumference	*18.96 m*
Typical tune point*	*1.55, 1.56*
Beam emittance* horizontal vertical (1% coupling)	*210 nm.rad* *2.1 nm.rad*
Photon flux (at critical wavelength)	*7.2 x 10^{11} photons/sec/mrad horiz./0.1%BW*
Brightness	*6.5 x 10^{11} photons/sec/mm^2/$mrad^2$/0.1%BW*



Indus-1 450 MeV synchrotron spectrum



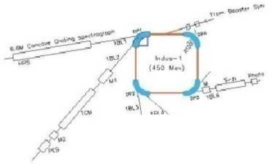


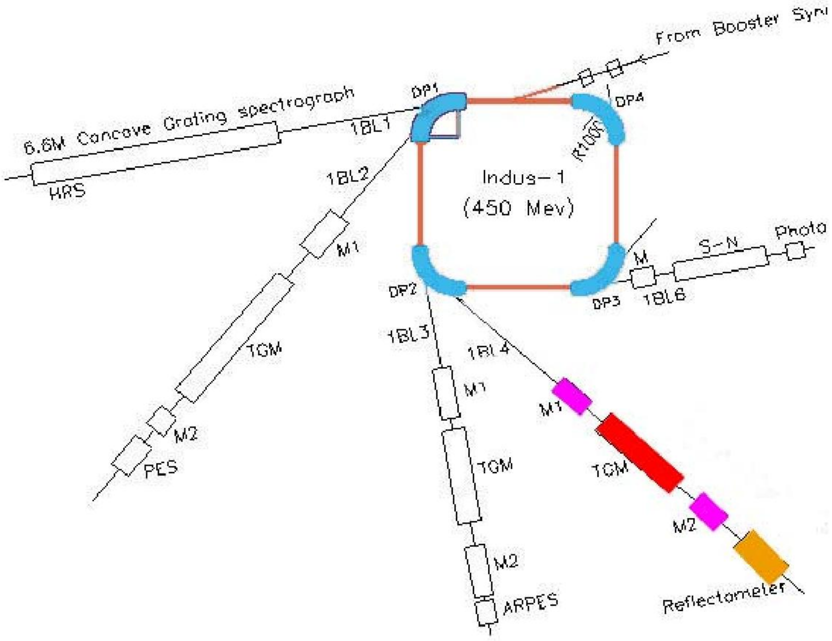
Salient feature

- Very small higher harmonic issues
- No heat load
- No radiation hazard at large

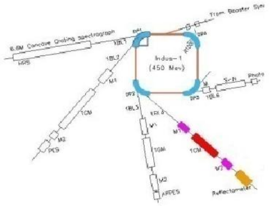
Electron Energy : 450 MeV
Peak flux ≈7.1x10^{11} ph/sec/mrad
Critical wavelength: 61Å
Beam Life time : 1.8 hours (design)

Current : 100 mA
Brightness ≈7.1x10^{11} ph/sec/mm^2/mrad^2
Magnetic Field : 1.5 Tesla
Bending radius : 1 meter

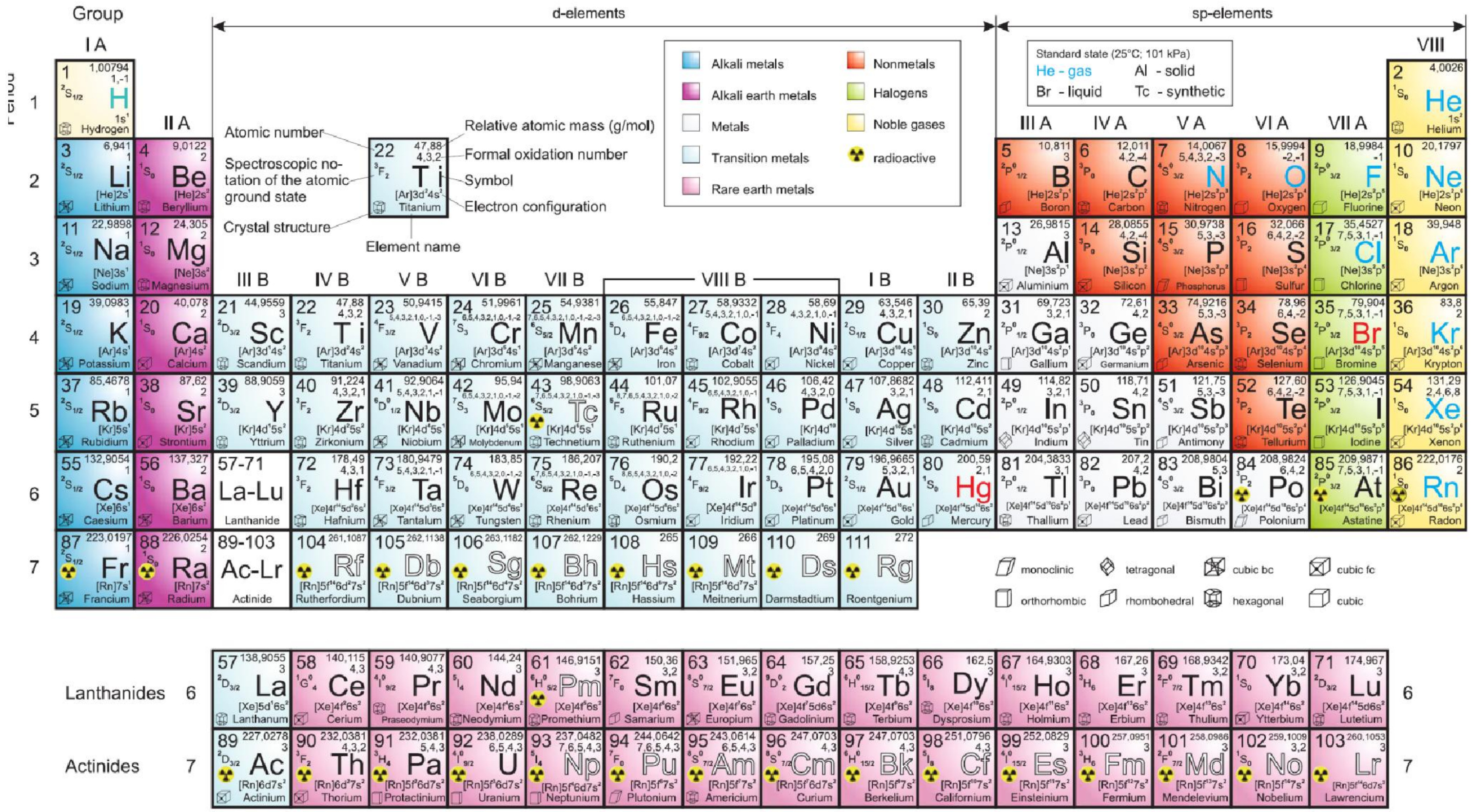




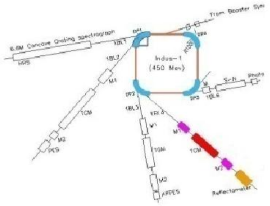
Beamline	Wavelength range	Monochromator
1. Reflectivity	40 1000 Å	TGM
2. Angle integrated PES	60 1600 Å	TGM
3. Angle resolved PES	40 1000 Å	TGM
4. Photophysics	500 – 2500 Å	Seya-Namoika
5. High resolution VUV	400 - 2500 Å	Off-plane Eagle



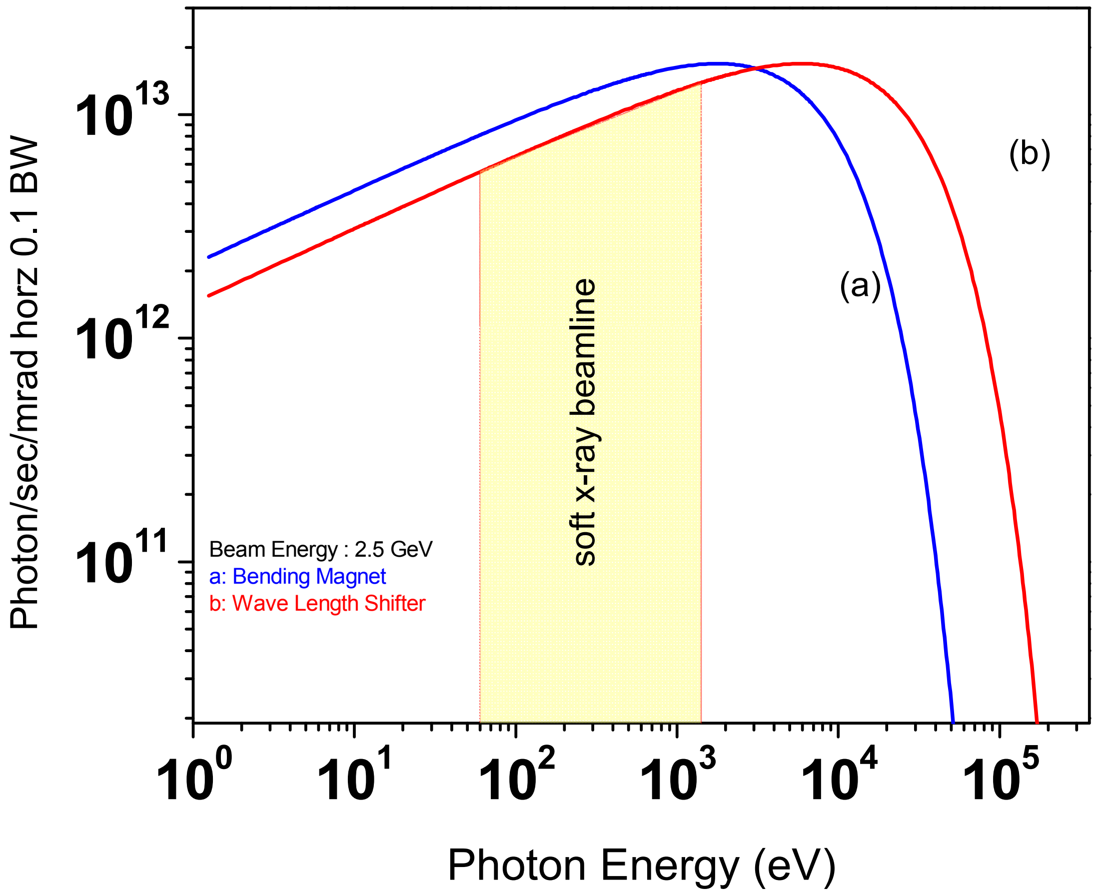
What can be probed using Indus SXR?



Indus-1: K edge upto C 280 eV and L edge upto S, Cl 250eV
Indus-2: K edge upto Al 1500eV and L edge upto As 1500eV

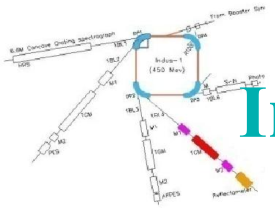


Indus-2: 2.5 GeV synchrotron spectrum



Indus-2 Parameter

Energy : 2.5 GeV
Current : 300mA
Field : 1.5 T (BM)
Curcumference: 172 m
Lifetime: 15 Hrs
λ_c =1.98 Å (6.23 KeV)



Indus-2: Soft X-ray Reflectivity Beamline (BL – 3)

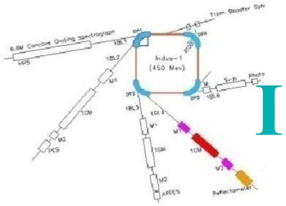
This beamline is planned to extend the soft x-ray activity of Indus-1 reflectivity beamline to much broader energy range, such that the absorption edges of most of the elements can be covered.

Applications

- **X-ray mirrors , filters, detectors**
- **Thin film/ Multilayers**
- **Soft matter films**
- **Polymers**
- **Photo induced damage**

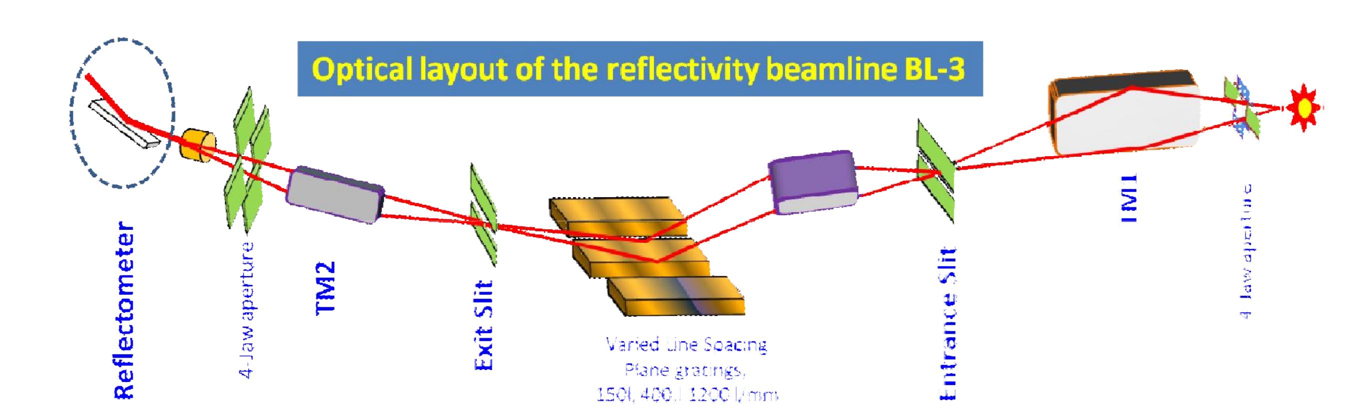
Specifications

- **Energy range** 100-1500 eV
- **Flux** 10^{9}-10^{11} ph/sec (@ 300mA 2.5 GeV)
- **Resolution** 2,000-6,000
- **Beam size** 0.5 mm(H) X 0.1 mm (V)
- **Monochromator** VLS-PGM 3 gratings



Indus-2: Soft X-ray Reflectivity Beamline (BL – 3)

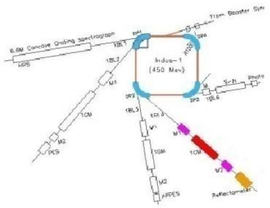
- ❑ Source : Bending magnet port No. 3
- ❑ σ_x= 0.203 mm, σ_y =0.272 mm
- ❑ σ'_x (H)= 0.323 mrad, σ'_y(V) = 0.062 mrad
- ❑ Acceptance: 3mrad V x 2mrad H



Parameters of the optical elements

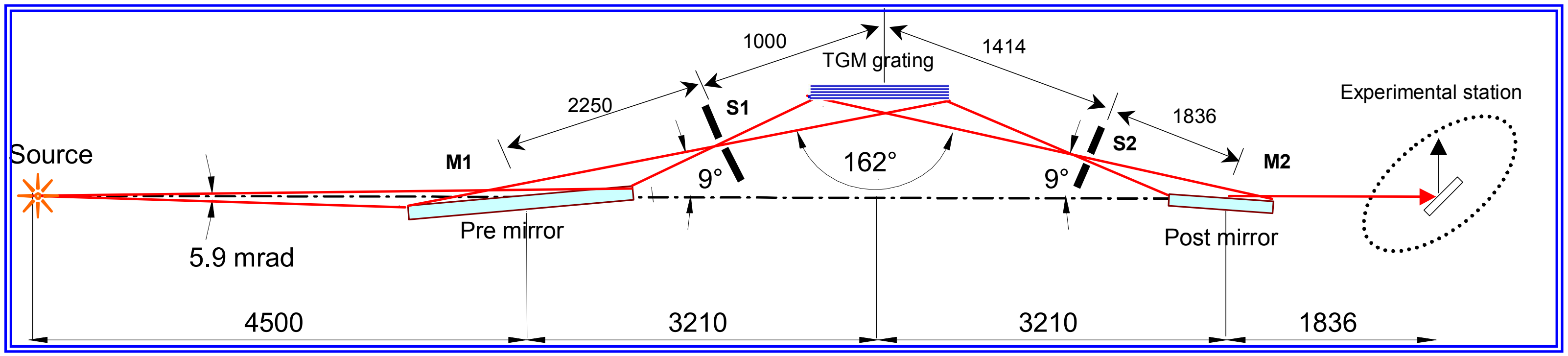
Optical Element	TM_1	SM	TM_2	G_1	G_2	G_3
Deflection	Horizontal	Vertical	Horizontal	Vertical	Vertical	Vertical
Size(mm^2)	900 ×50	300×20	250×20	200×20	200×20	200×20
Included angle (deg)	176	177	176	174.5	174.5	174.5
Groove density (lines/mm)	--	--	--	1200	400	150
Energy range (eV)	--	50-1500	--	400-1500	150-600	50-225

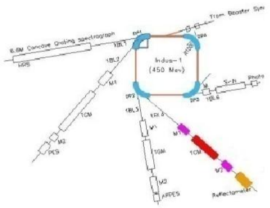
TM1: Pre focusing Toroidal mirror, **SM:** Spherical mirror, **TM2:** Post focusing Toroidal mirror



Indus-1Reflectivity beamline

Parameters	
Wavelength Range	*40-1000Å*
Monochromator	*TGM*
Resolving Power $\lambda/\Delta\lambda$	*200-500*
Photon flux	*$\sim 10^{11}$*
Beam spot	*1mm × 1mm*





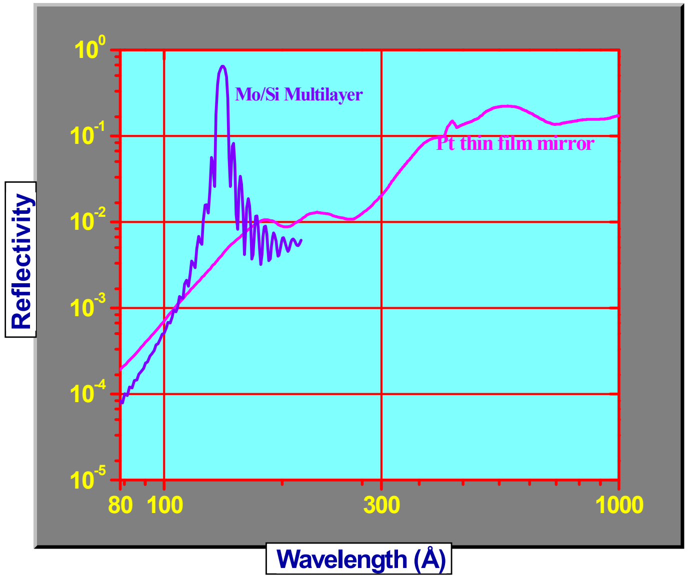
SXR measurement

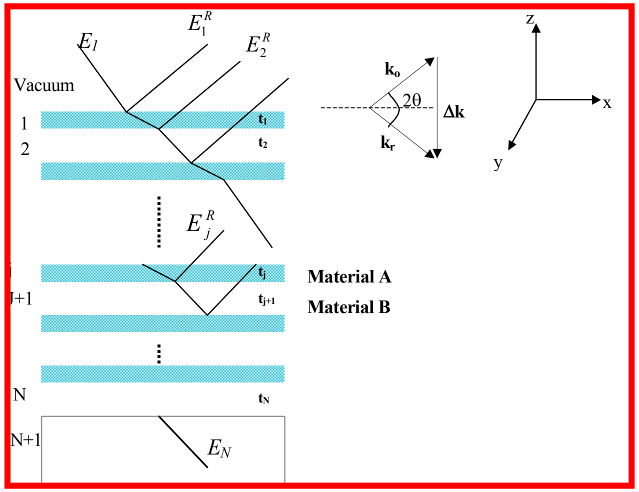
$$n = 1 - \delta + i\beta$$

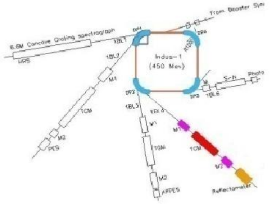
$\delta \sim 10^{-2} - 10^{-5}$

$\beta \sim 10^{-2} - 10^{-7}$

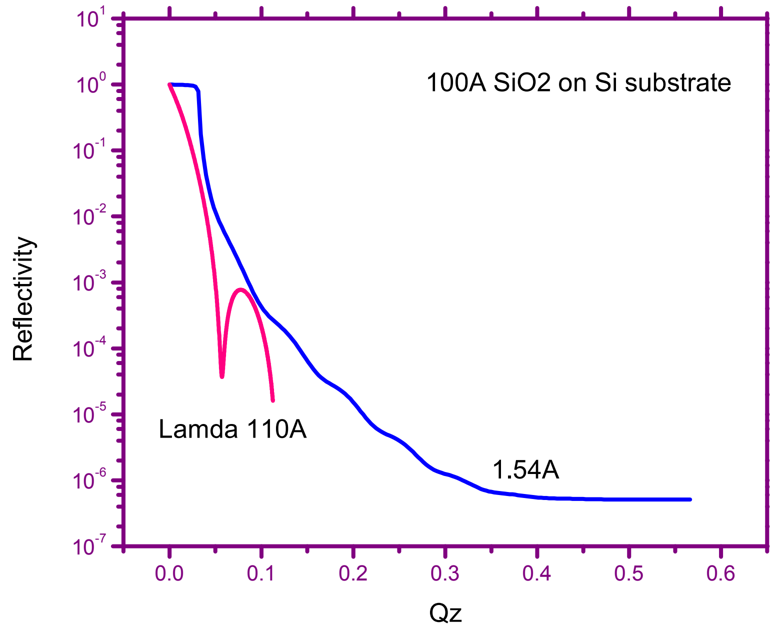
$$R = \left| \frac{n_1 - n_2}{n_1 + n_2} \right|^2$$



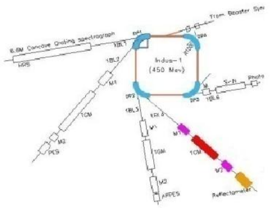




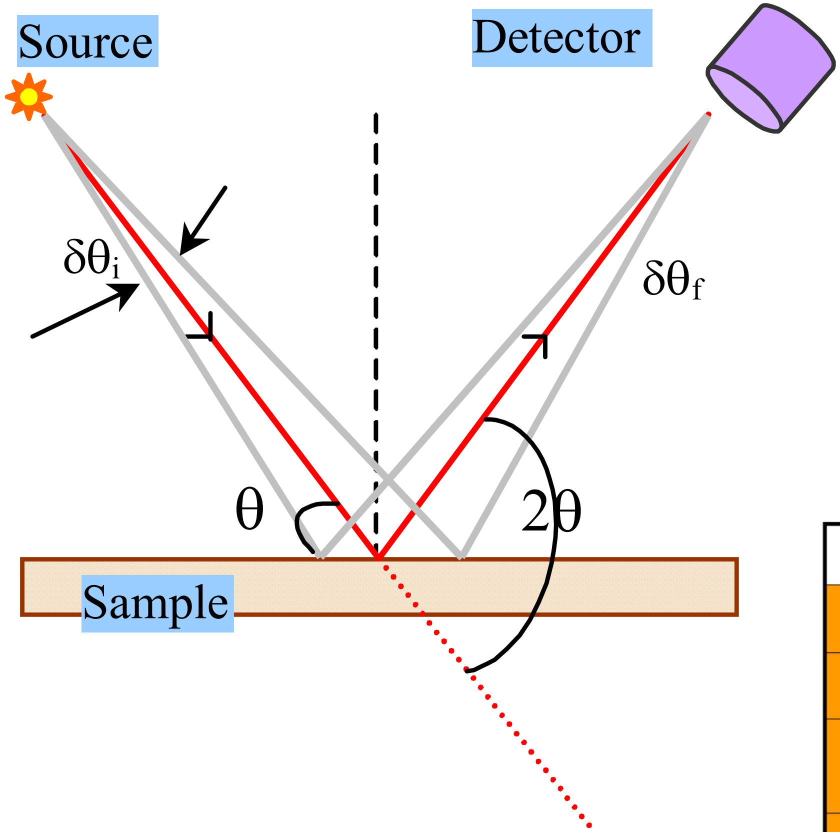
- Thicknesses at atomic scale
- Density distribution
- Interface quality
- Chemical compositions
- Low contrast thin films



➔ In soft x-ray region optical constants of various materials are not known (experimental data missing).!!!

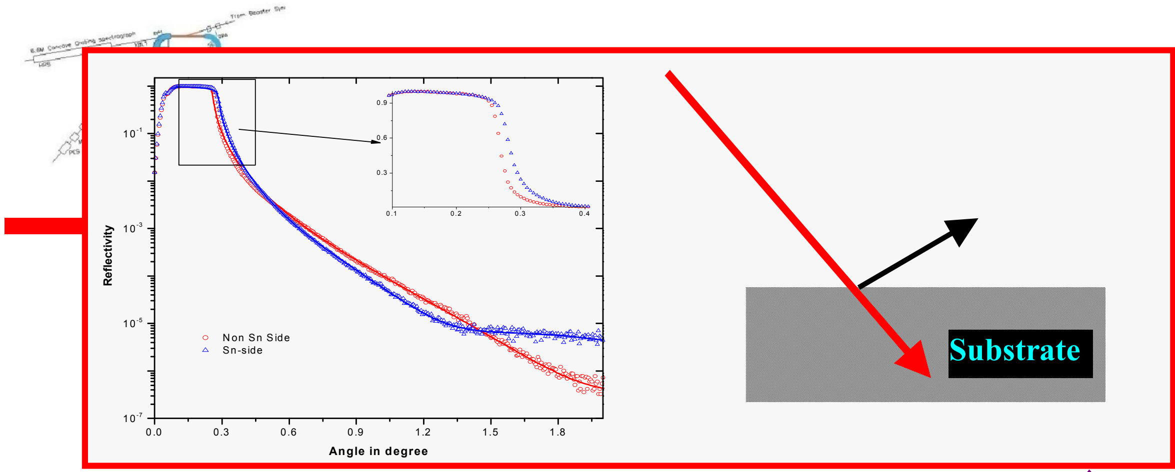


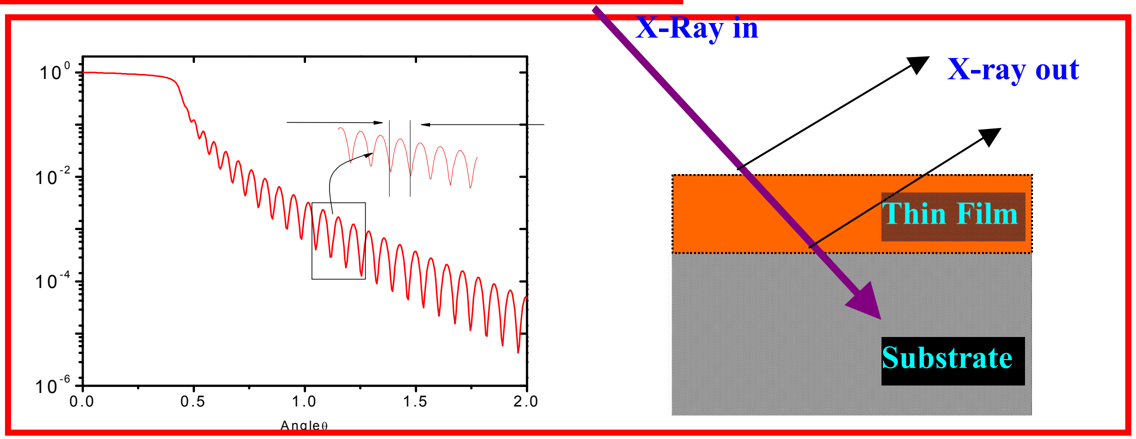
Reflectometer ?



- Basic Component
  - ***X-ray Source***
  - ***Beam Optics***
  - ***Goniometer***
  - ***Detector***

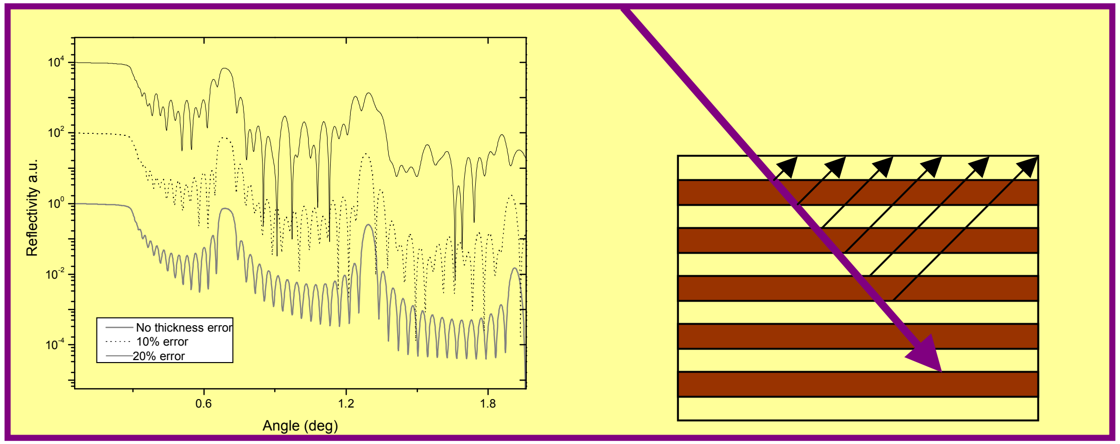
	Conventional	XRR
Geometry	Parafocusing	Parallel beam
Monochromator	Not required	Required
Primary Divergence	>1 deg, depends on slit setup	<0.1 deg
Beam Intensity	Low	High (>10^7 cps)
Range (2θ in deg)	>10 deg	~0
Beam attenuator	Not required	Required

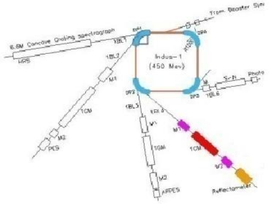




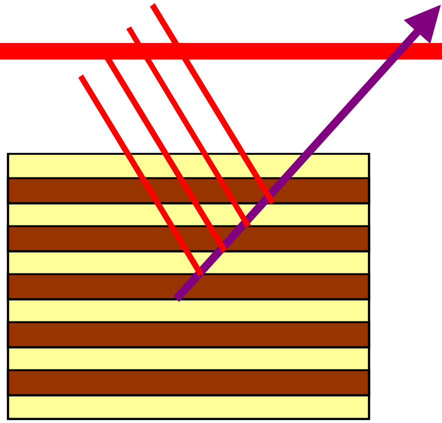
$$\frac{\Delta\rho}{\rho} = 2\left(\frac{\Delta\theta}{\theta_c}\right)$$

$$\frac{\Delta t}{t} = \left(\frac{\Delta\theta}{\theta}\right) \approx \frac{1}{m_{max}}$$

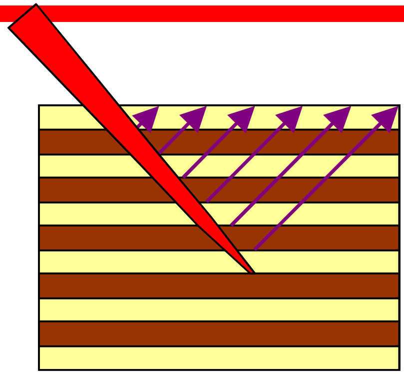




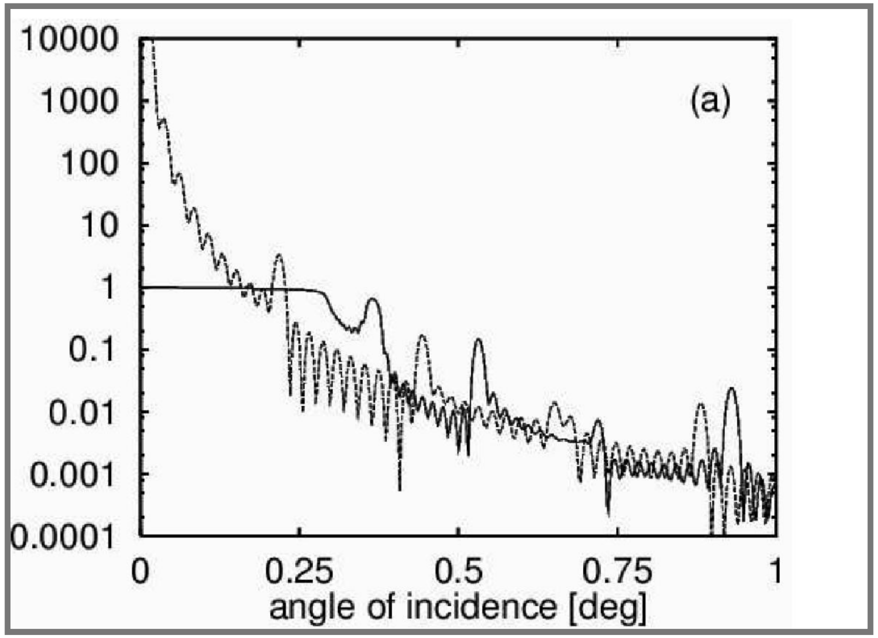
Analysis approach

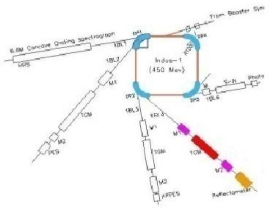


Kinematical



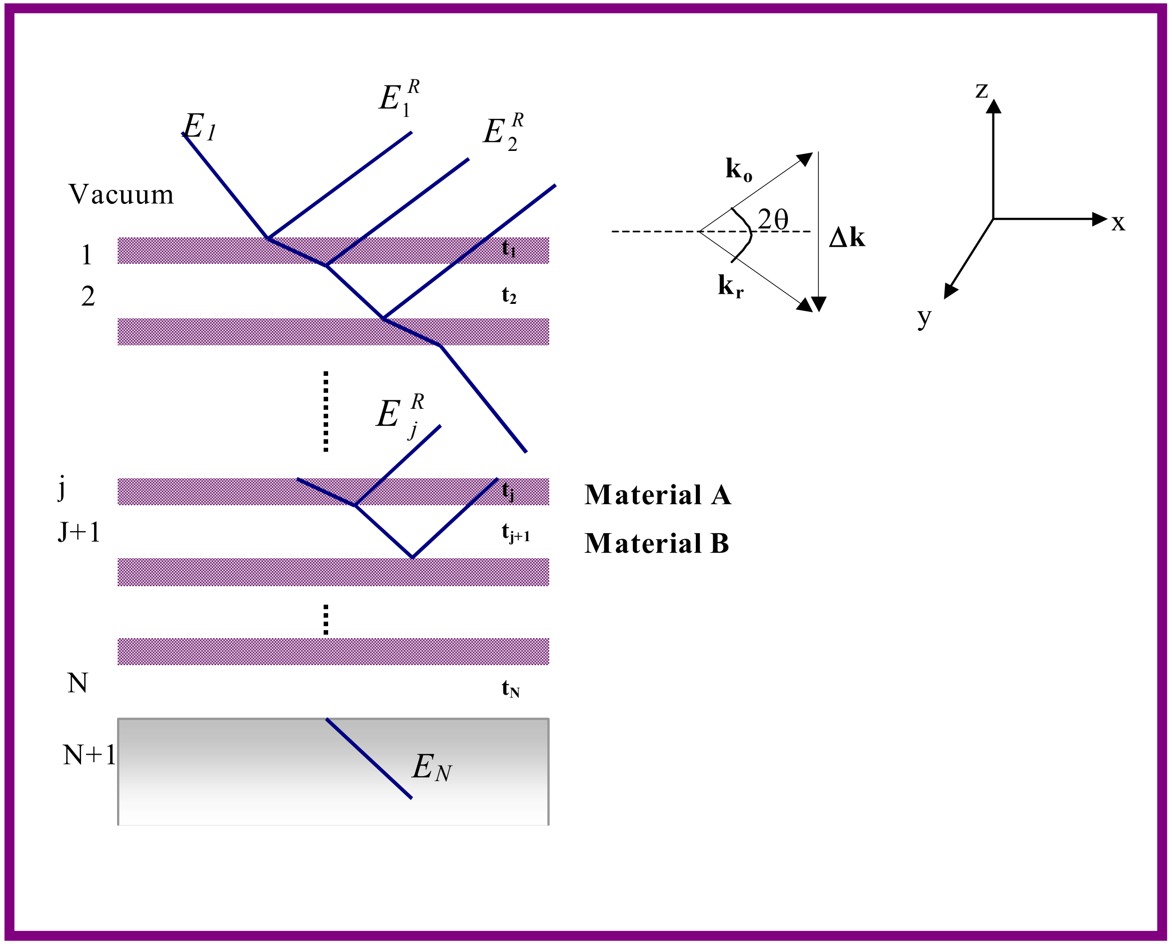
Dynamical





Wave vector transfer

$$q_{j,z} = \frac{2\pi}{\lambda}\left(n_j^2 - \cos^2\theta\right)^{1/2}$$



Fresenel coefficient

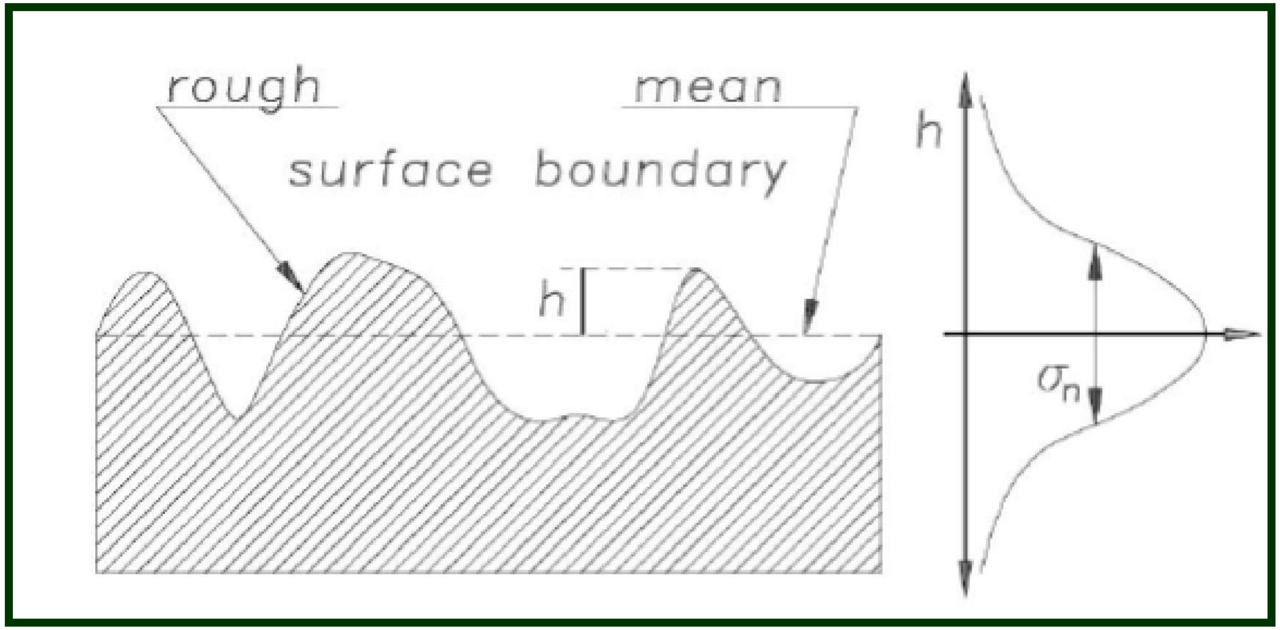
$$F_{j,j+1} = \frac{E_j^R}{E_j} = \frac{q_{j,z} - q_{j+1,z}}{q_{j,z} + q_{j+1,z}}$$

Reflected amplitude

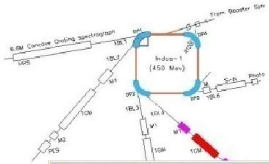
$$R_{j,j+1} = a_j^2 \frac{R_{j+1,j+2} + F_{j,j+1}}{1 + R_{j+1,j+2} * F_{j,j+1}}$$

Reflectivity

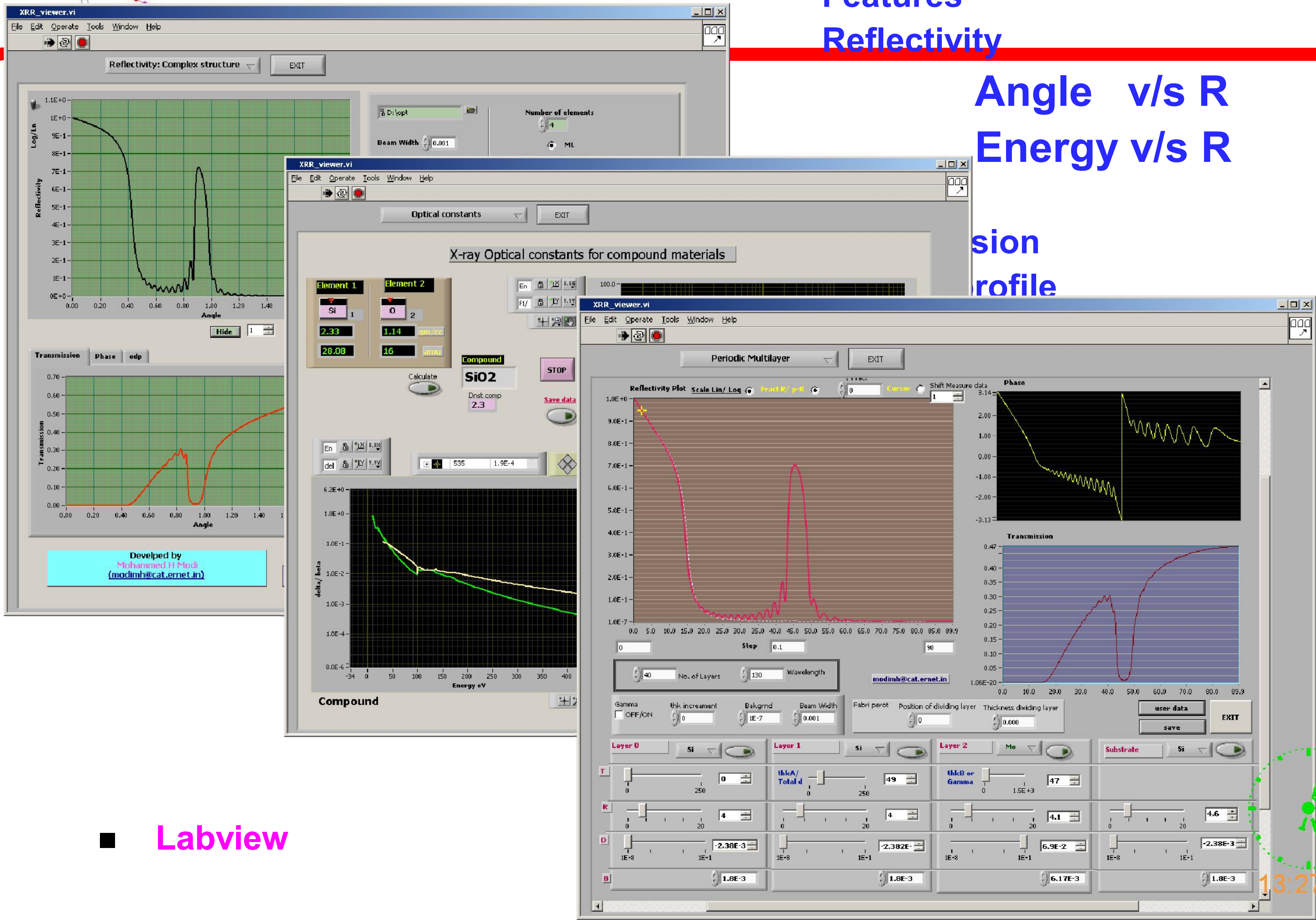
$$\left|R_{1,2}\right|^2 = \frac{I_R}{I_o} = \left|\frac{E_1^R}{E_1}\right|^2$$



$$\tilde{r}_{j,j+1} = r_{j,j+1}\exp\left(-2q_{j,z}q_{j+1,z}\sigma_j^2\right)$$



Software



Features

Reflectivity

Angle v/s R

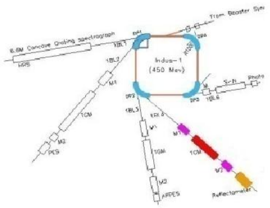
Energy v/s R

sion

rofile

- **Labview**

13:2



Silicon Nitride

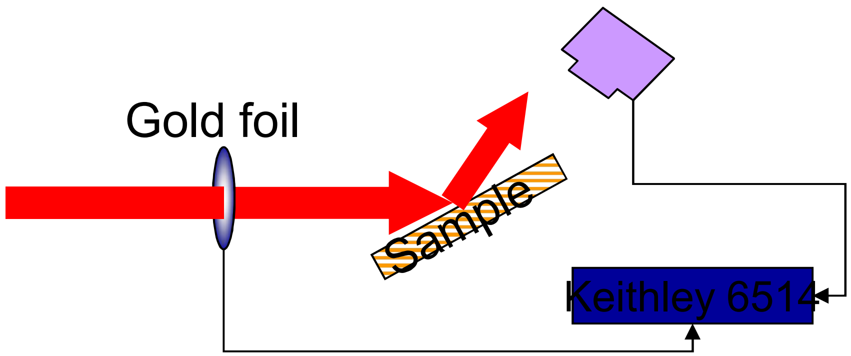
Silicon nitride films are commonly used in electronics, opto electronics, photonic devices

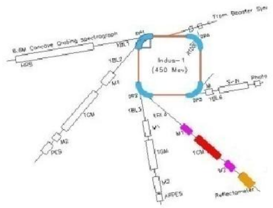
They have some novel physical properties

High melting point, high density,low mechanical stress, very good diffusion barrier.

They used as a x-ray mask in lithography applications.

Post deposition annealing of amorphos silicon nitride increases the internal quantum efficiency of underlying silicon solar cells





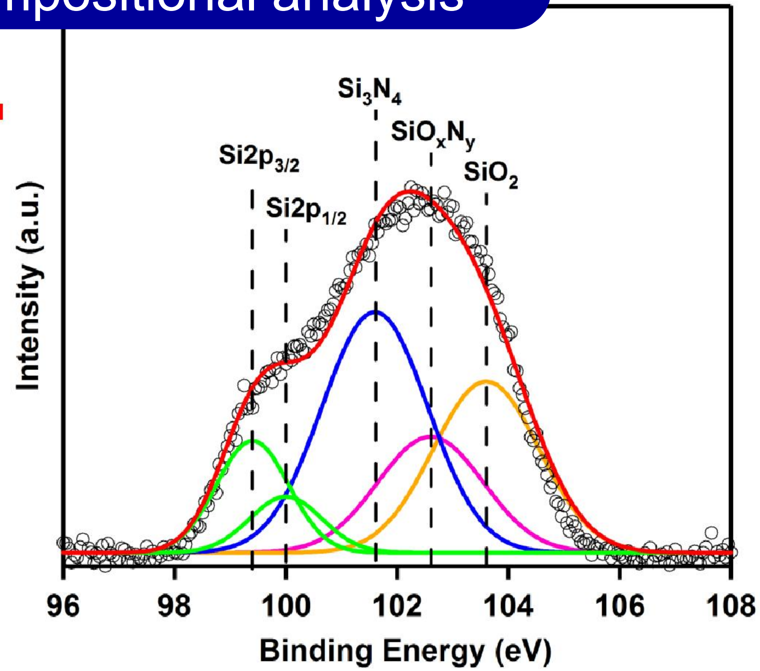
Growth kinetics and compositional analysis

Hg-sensitized Photo-CVD

D_P = 800 ± 5 mTorr ,
T_{Hg}= 100 °C , T_s= 200 °C
Reactant gases: SiH_4 (4 % argon diluted) & NH_3
Substrate: Si (100)

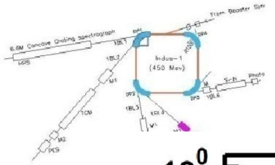
***R = SiH_4/NH_3**

R= 0.34

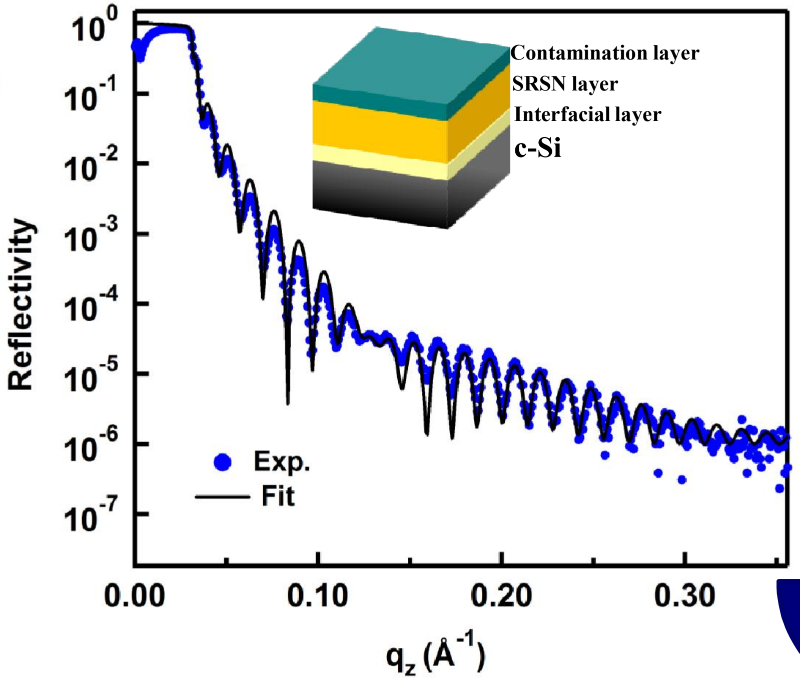


Si 2p core-level XPS spectra

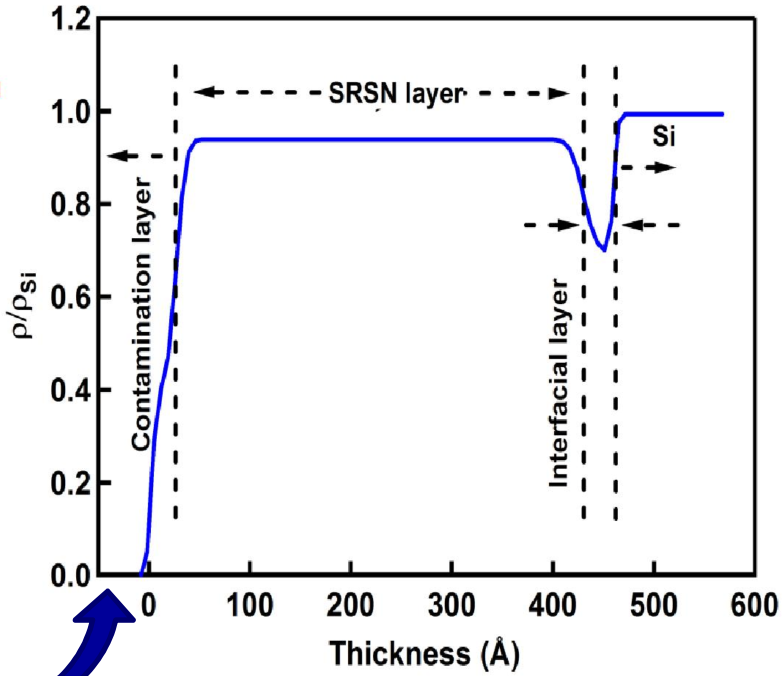
- Peaks centred at 99.4 & 100 ±0.1 eV are signature of elemental Si
- Presence of Si_3N_4 as dominant phase
- Oxidation of the film surface



Hard X-ray reflectivity



XRR curve as a function of wave vector transfer 'q_z (Å^{-1})'



Electron density profile (EDP) normalized to the Si substrate

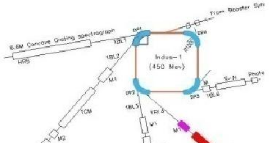
Thickness 't'(nm), Density 'ρ'(g/cm^3), Roughness 'σ'(nm)

Top layer : 2.5, 1.7 0.5
SRSN Middle layer : 40.5, 2.1, 0.3
Interfacial layer : 3.0, 1.6 0.8

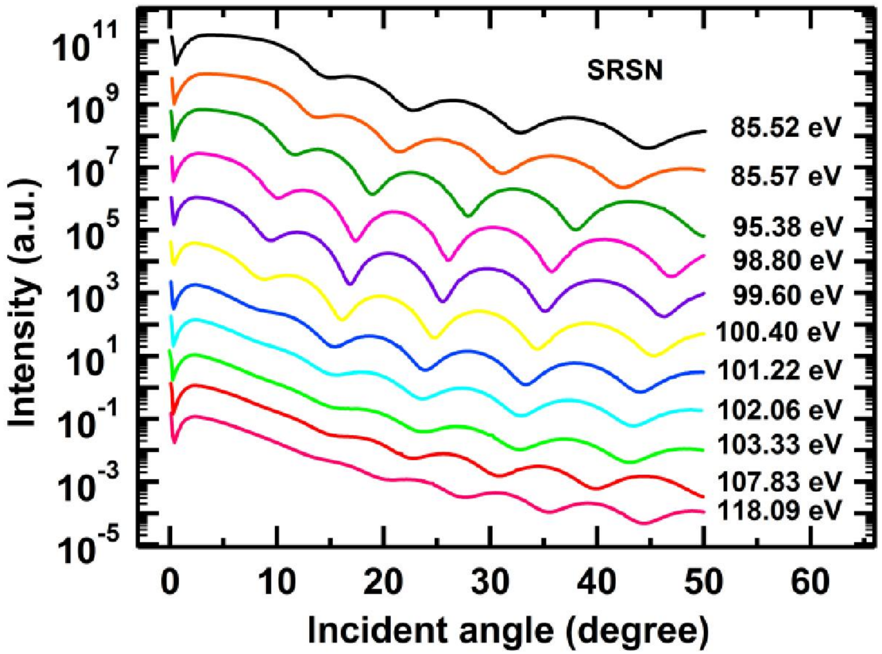
→ **Hydrogen incorporated void structure**

* **Density of Silicon oxide , Silicon nitride and Silicon are 2.20, 3.10 and 2.33 gm/cm^3 respectively**

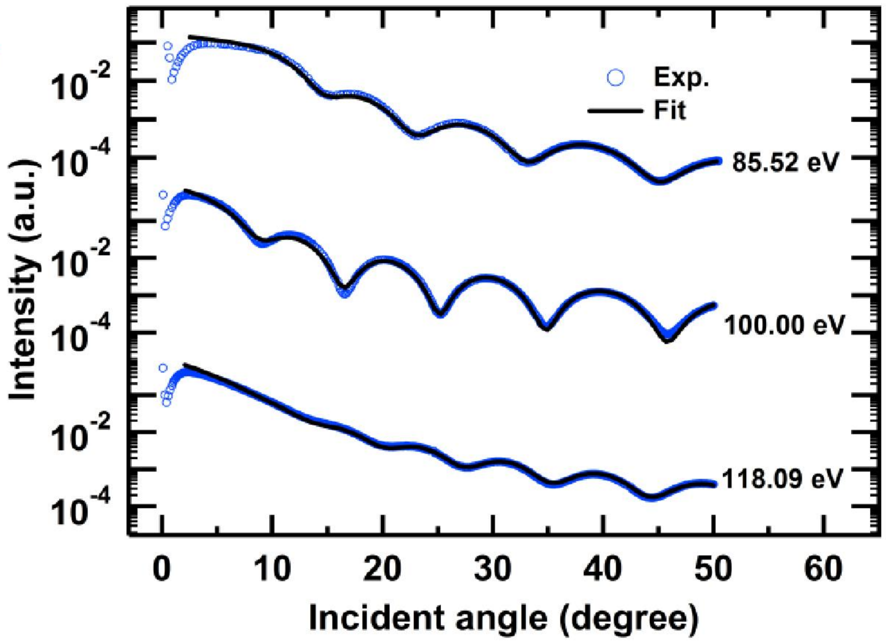
Appl. Phys. Lett. **97**, 151906 (**2010**)



Soft X-ray reflectivity



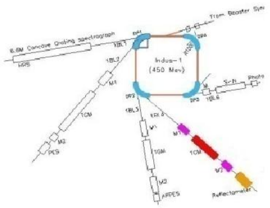
Reflectivity curves of SRSN film at different photon energy near Si $L_{2,3}$ absorption edge

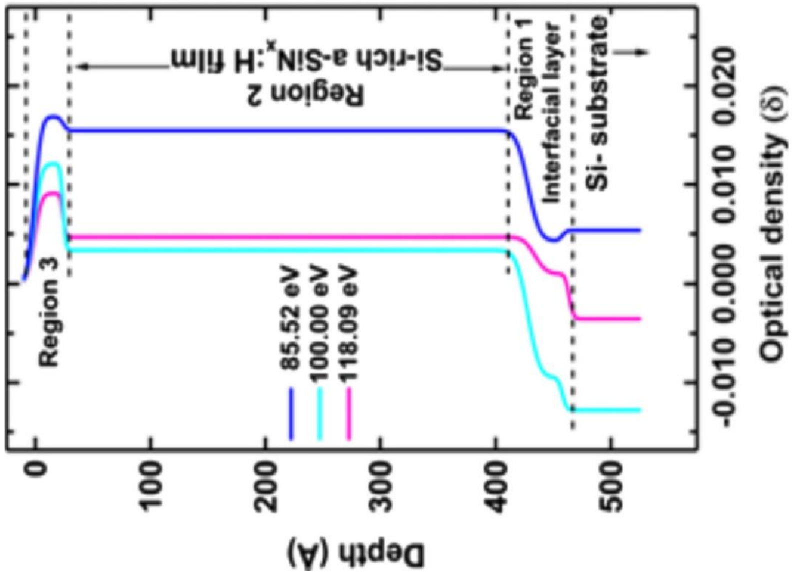


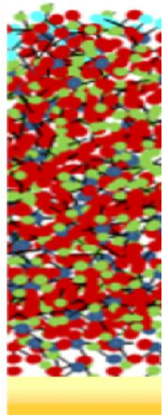
Reflectivity curves both experimental and fitted of SRSN film at selected photon energies

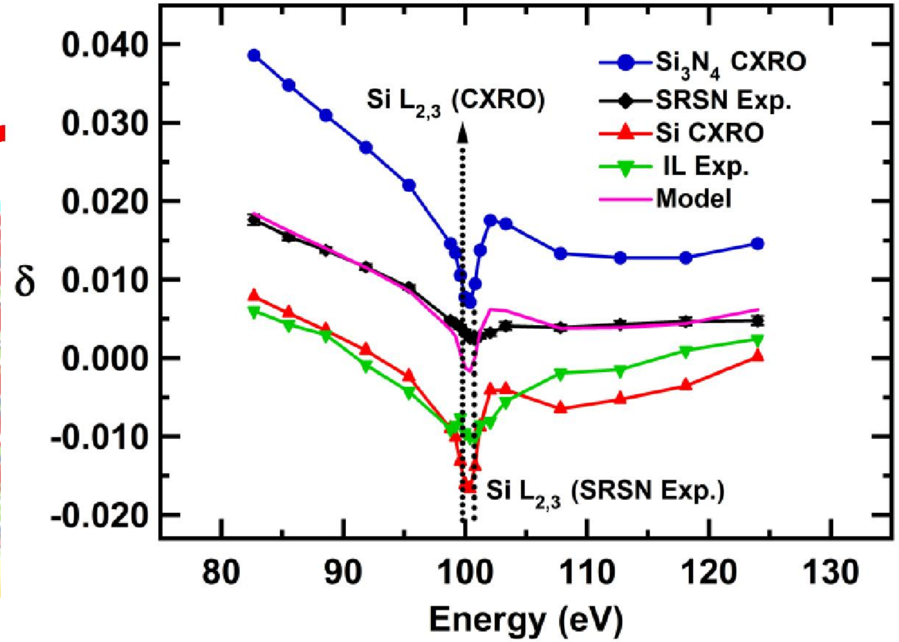
- Uniform modulations with Δq=0.14 nm^{-1}
- Clear contrast in reflectivity pattern due to enhancement in optical index contrast near absorption edge energy
- At each photon energy the reflected intensities are entirely different

Appl. Phys. Lett. **97**, 151906 (**2010**)









Model composition

[30% (H + voids) + 42 % (Si_3N_4) + 28% (Si)]
by volume

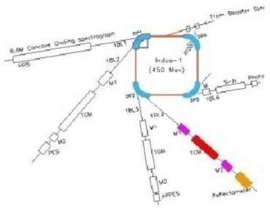
$Hg^*(^3p_1) + SiH_4 \longrightarrow Hg(^3s_1)$ + free radicals

Higher molecular species SiH_x (x = 0 - 3)

vertical growth profile of SRSN film. Red, light green, blue and sky blue balls are representative of Si, H, N and O atoms.

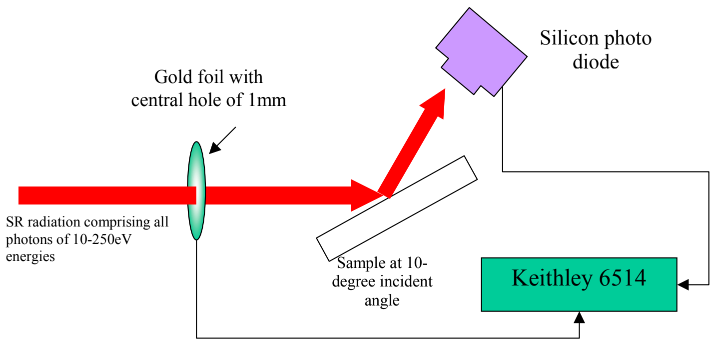
Appl. Phys. Lett. **97**, 151906 (**2010**)

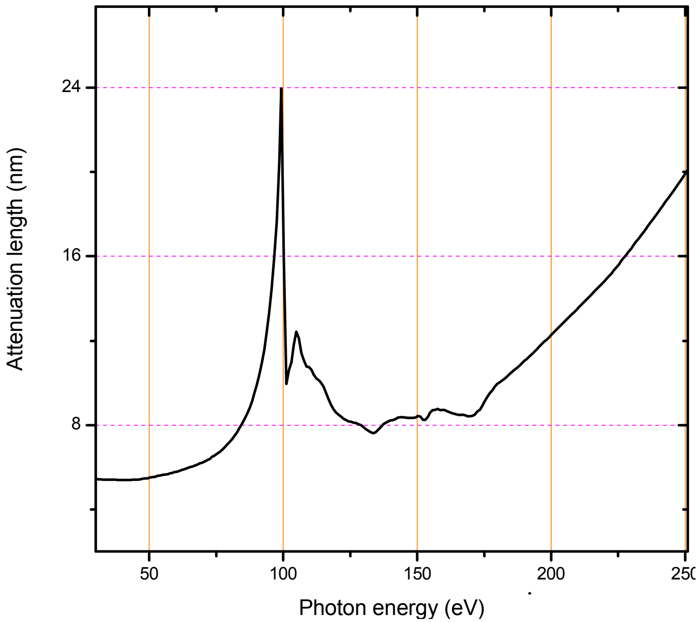
- For 10.5 and 12.4 nm wavelength porosity (δ≈0; β≈0) and hydrogen incorporation near silicon substrate will increase the value of optical index profile
- At 14.5 nm presence of porosity and hydrogen will decrease the value of optical index profile

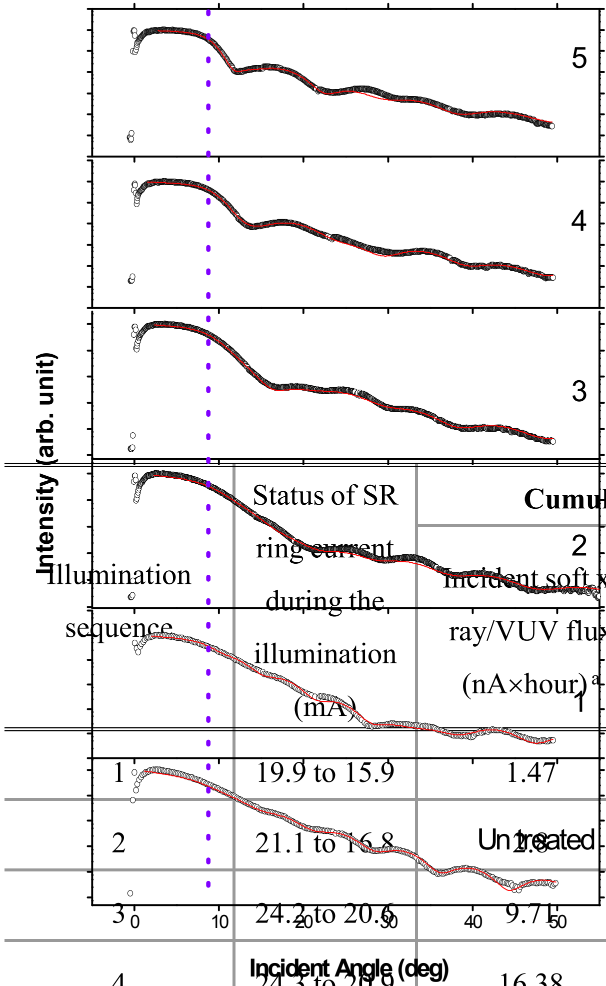


Silicon nitride : SR illumination effect

- SR Irradiation 10-300eV photons ,

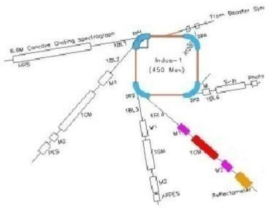






Illumination sequence	Status of SR ring current during the illumination (mA)	Cumulative Dose	
		Incident soft x-ray/VUV flux (nA×hour)[a]	Reflected flux (μA×hour)[b]
1	19.9 to 15.9	1.47	5.02
2	21.1 to 16.8	2.8	13.12
3	24.2 to 20.6	9.71	103.42
4	24.3 to 20.9	16.38	194.46
5	22.7 to 20.5	19.79	251.92

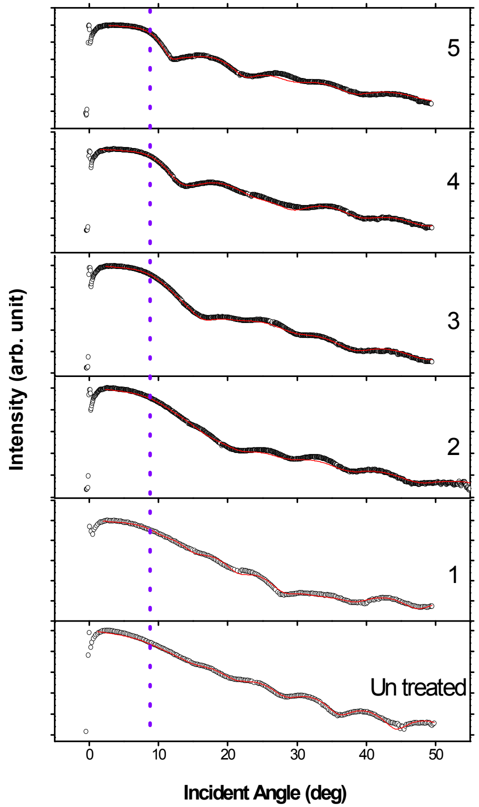
Physical Review B 74, 045326 (2006)

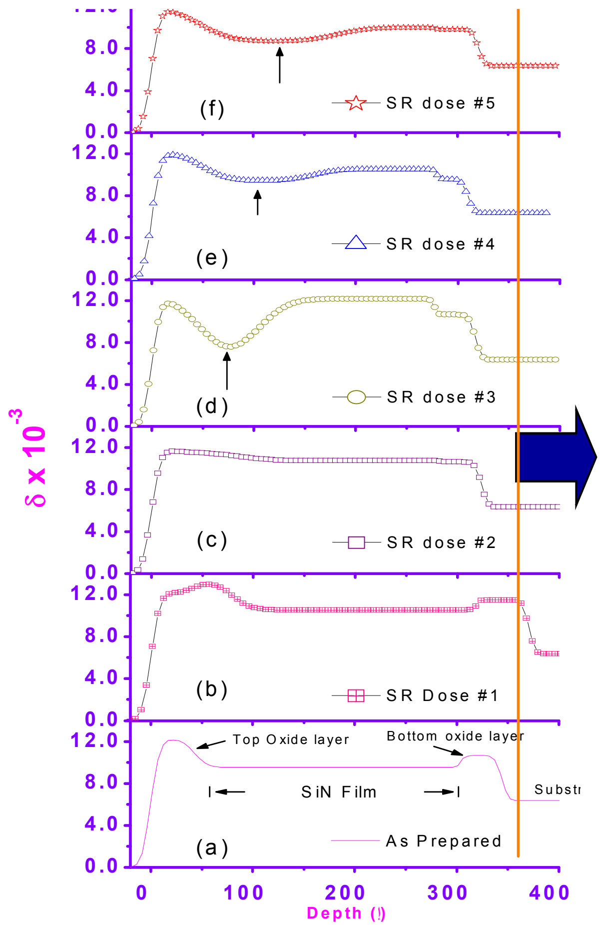


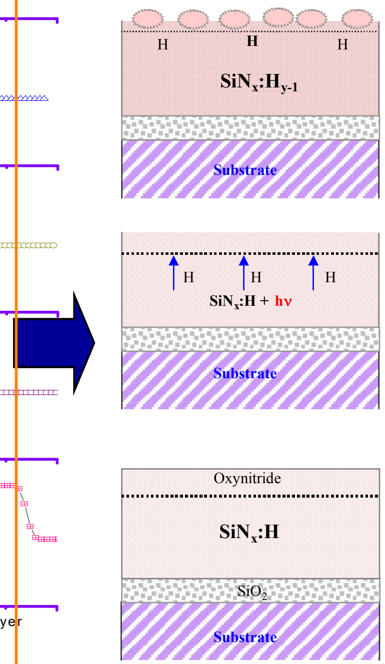
Silicon nitride : SR illumination effect

- SR Irradiation 10-300eV photons ,

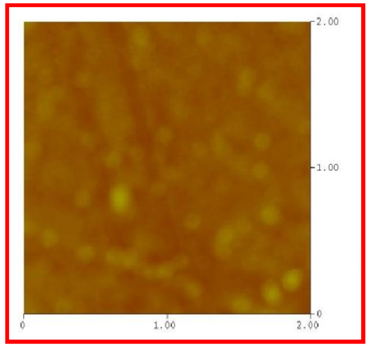
Insitu reflectivity



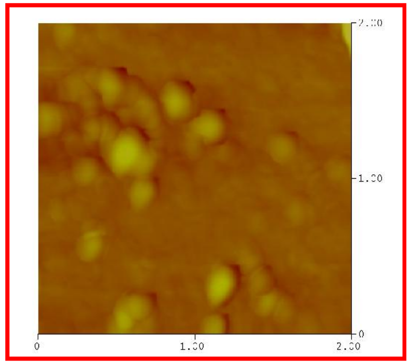




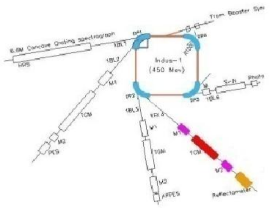
Virgin film



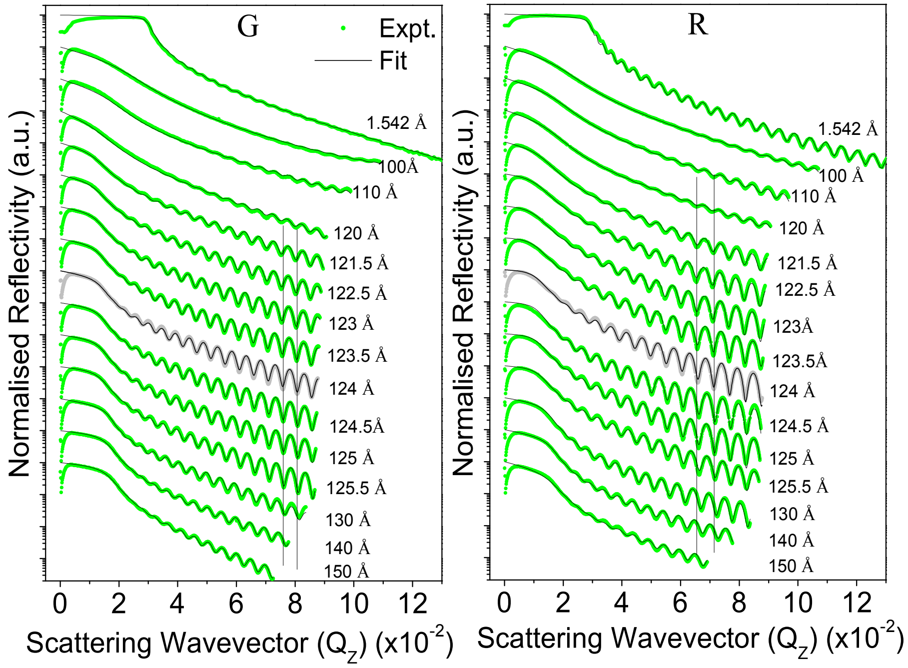
SR treated

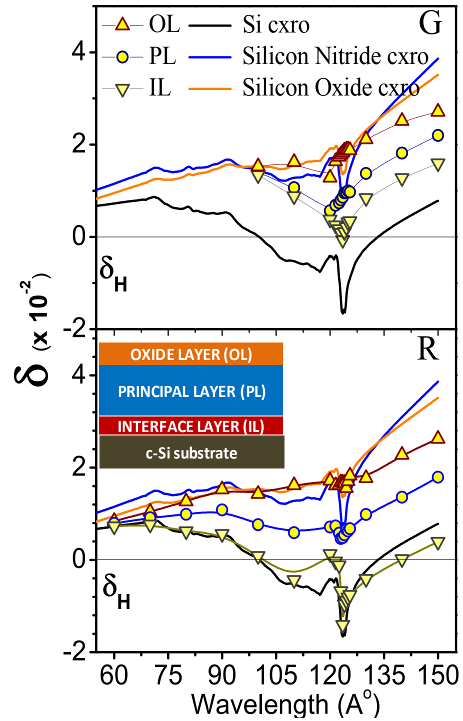


Physical Review B 74, 045326 (2006)



Difference in Composition of a-SiN_x:H Thin Films probed by Soft X-Ray Reflectivity





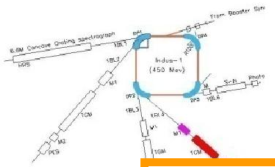
Qualitative percentage composition

Film	Si_3N_4 x%	Si (2.33) y%	H + Voids z%	ERDA H content
G-PL	58	1	41	32%
G-IL	40	20	40	
R-PL	45	15	40	37%
R-IL	0	60	40	

Applied Surf Sci. (2014) in press

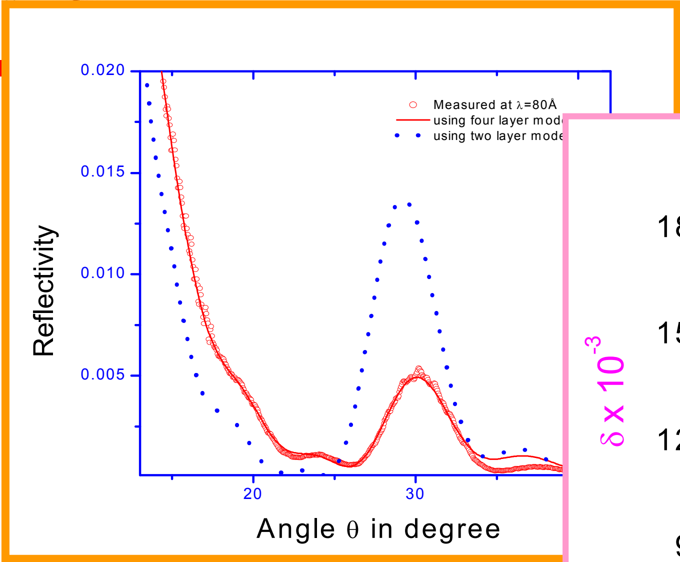
The Model parameters used to fit R-SoXR data.

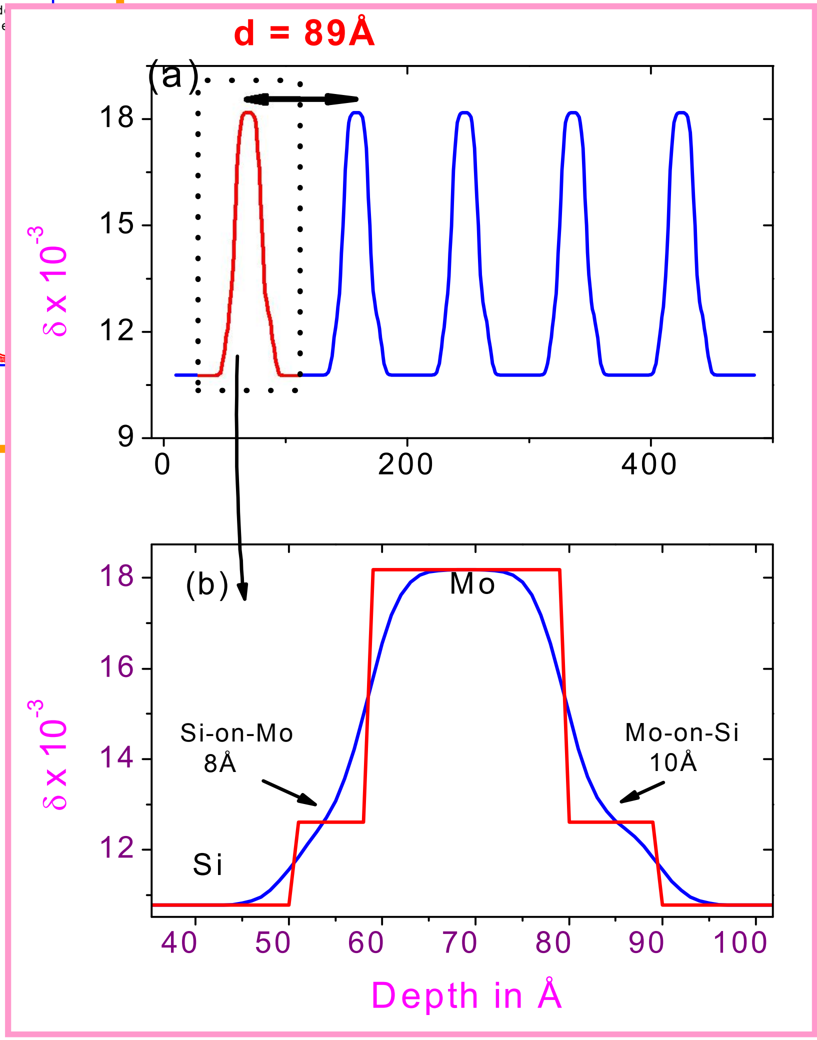
	G		R	
Layer	Thickness	Roughness	Thickness	Roughness
Top (OL)	51.17	5	50	5.8
Middle (PL)	1198.83	8	1110	8.4
Bottom(IL)	23.12	5	11	5
Substrate		5		8.3

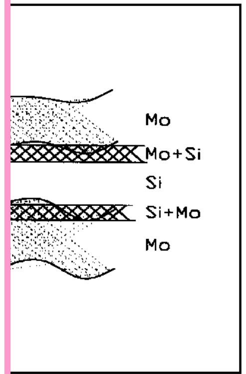


Mo/Si Multilayer

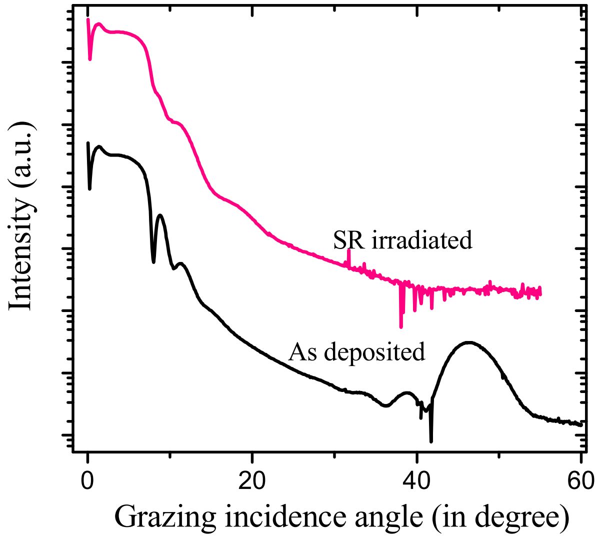
- e-beam deposited
- Period 89Å $(30\text{Å Mo}/ 59\text{Å Si})_5$
- Å







Soft Matter Thin Film

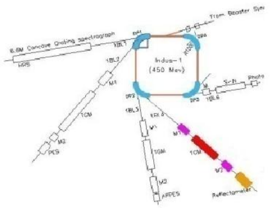


19-monolayered Cd-arachidate Langmuir-Blodgett multilayer on a float glass substrate

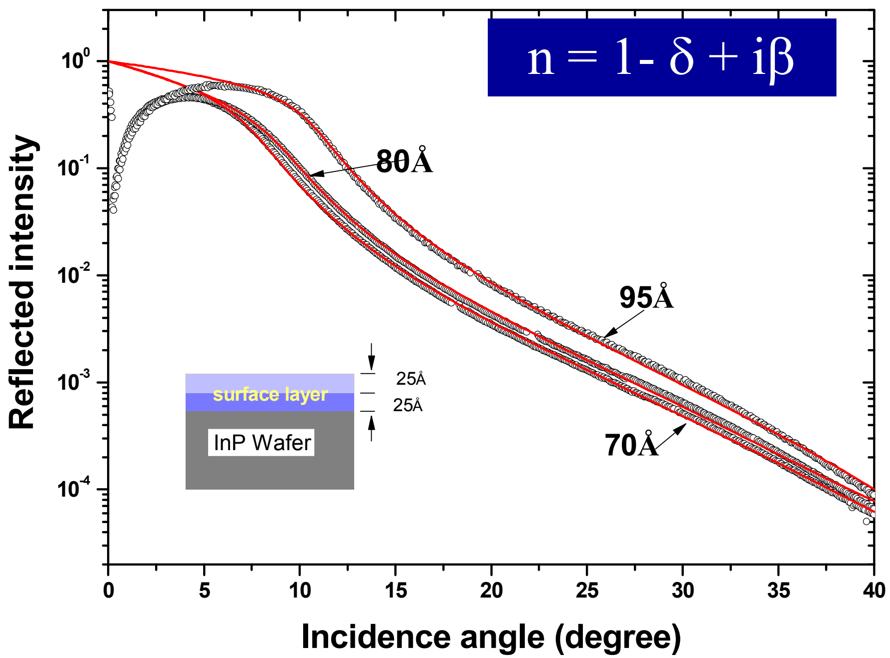
No.	Layer	Thickness (Å)
1	Cd	0.6
2	COO	2.7
3	$CH_3(CH_2)_{18}$	22.9
4	gap	3
5	$CH_3(CH_2)_{18}$	22.9
6	COO	2.7
7	Cd	0.6
Total thickness		55.4

No.	Bond	ΔH=K J/ mole
1	C–C	345.6
2	C–O	357.7
3	H–C	411
4	O–CO	459
5	C=O	789
6	O=O	493
7	H-H	432
8	Cd- O	258

AIP Conf. Proc. 1349, 701-702 (2011); doi: 10.1063/1.3606051



Optical properties



Refractive index is a response function of the material to the incident EM field.

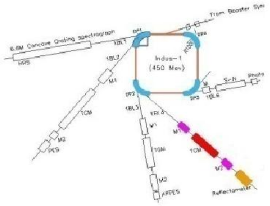
Its real and imaginary part are related to each other by Kramer-Kronig integrals

In XRR method both delta and beta are determined simultaneously by fitting the reflected profile at each energy

Thus determination of any one part from an experiment can help to determine the other

The error is basically introduced by finite range of integration as experimental data over infinite range is not possible

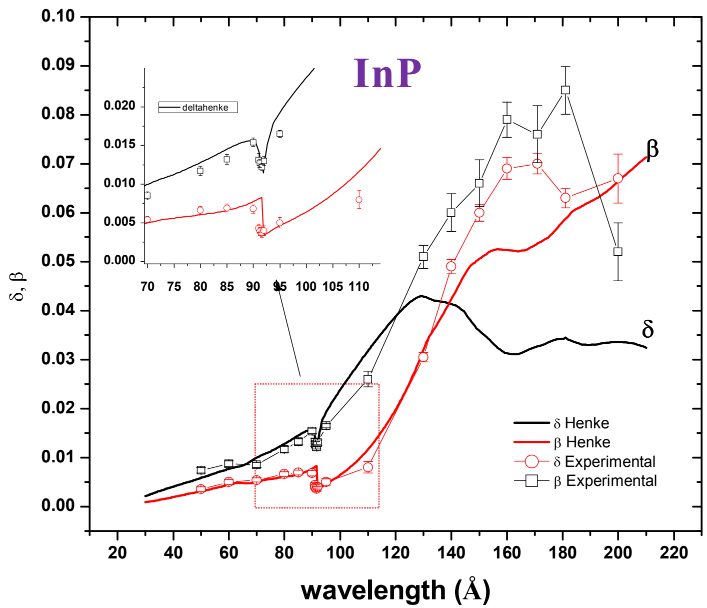
Applied Optics 49, 5378 (**2010**).



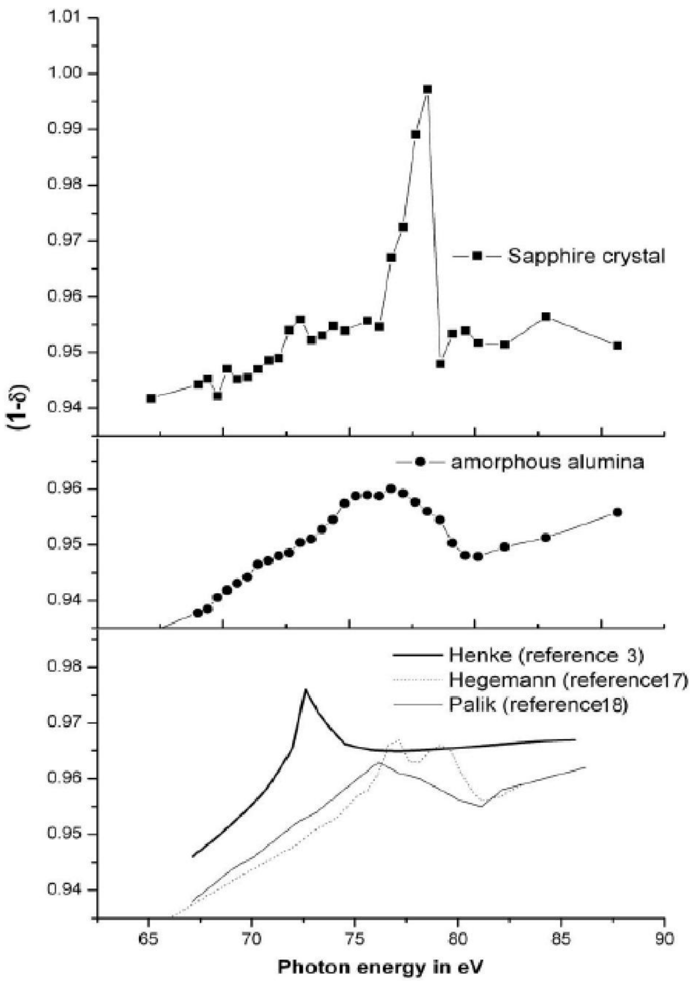
Soft x-ray optical properties of compound materials

Formation of chemical bond changes the binding energy and so the absorption edge.

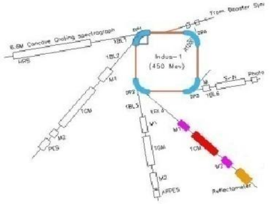
Optical constants of crystalline material further modified due to formation of conduction band



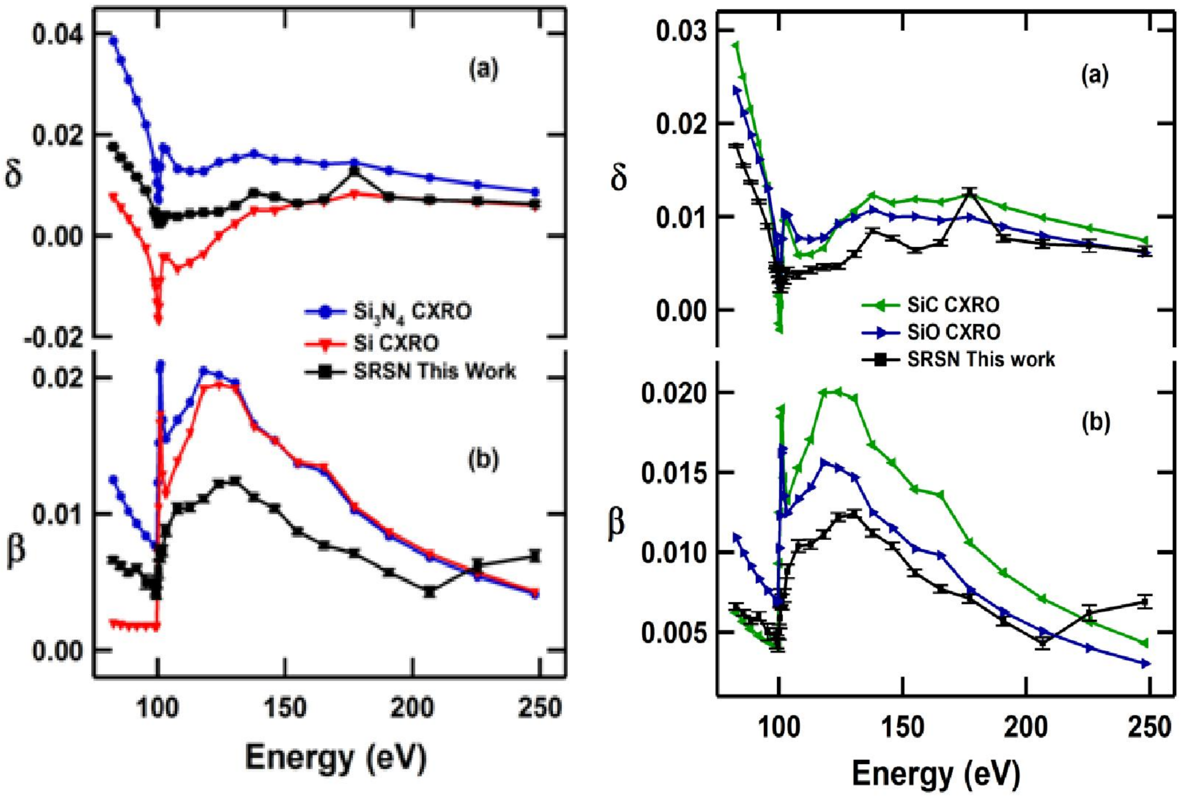
Optical constants of compound materials finally differ from Henke's tabulated value



Applied Optics 51, 7402 (2012).



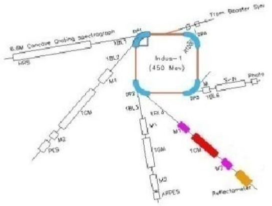
Si-rich a-SiN_x:H Thin Film : An Optical Response near Si $L_{2,3}$ -edge



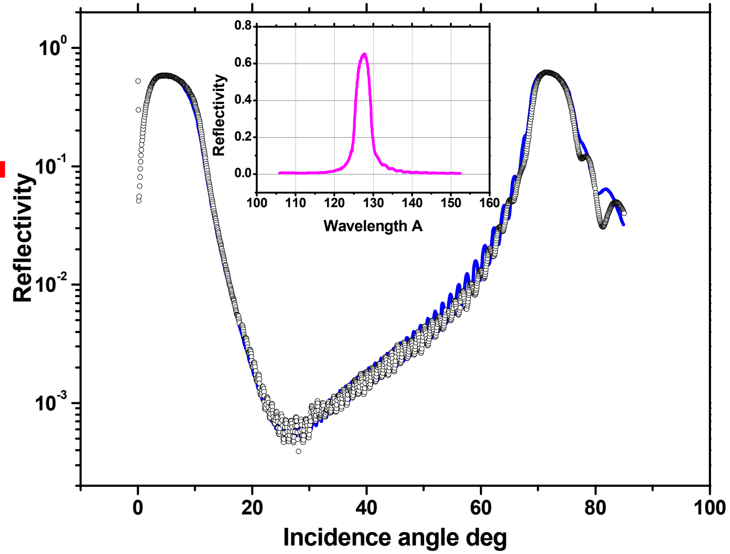
- Delta and Beta values are less than that of SiC and SiO
- SRSN: Potential material for EUV lithography

Comparison of optical index profile δ and β of SRSN film with Si, Si_3N_4, SiC and SiO near Si $L_{2,3}$ absorption edge

J. Phys. D: Appl. Phys. 44, 215501(**2011)**



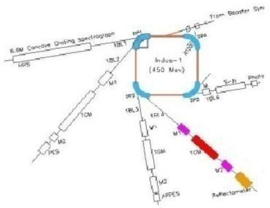
Mo/Si multilayer



- **Period 69Å,**
- **No. of Layer pairs N=65**
- **Reflectivity 63%**

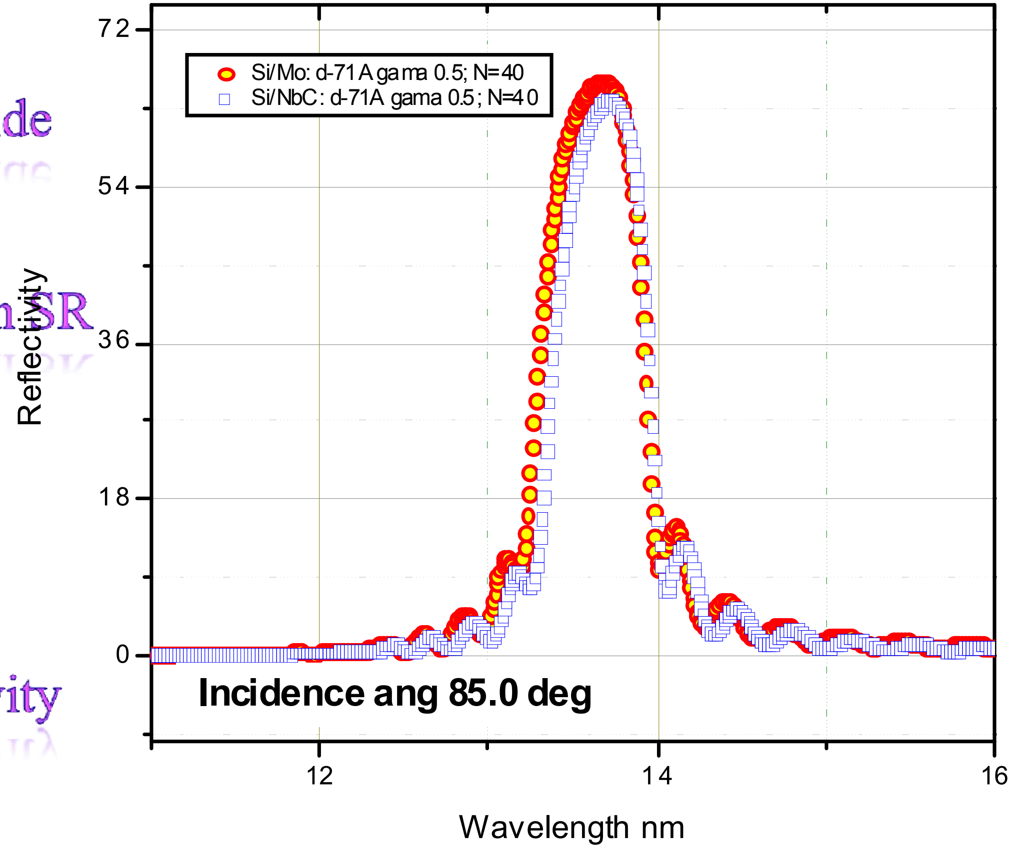
- *Achieved high normal incidence reflectivity comparable to those achieved in other world laboratories*
- *It shows our strength to make soft x-ray multilayer mirrors on large surfaces.*
- *It exhibits our capability to deposit several layer pairs with required thickness control of $\lambda/4$ precision.*
- *Reflectivity beamline has played an important role in achieving this goal*

Advances in Optical Technologies. Vol. 2012, Article ID 976868



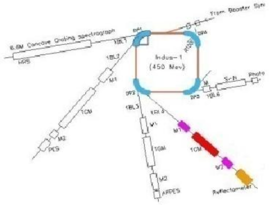
Mo/Si v/s NbC/Si

- Mo/Si poor thermal stability
- Structural degradation due to silicide formation
- Can not be used in third generation SR applications



- NbC/ Si gives equivalent reflectiivity performance
- Very high thermal stability
- No chemical reacation upto 700C

Optics Express 20, 15114 (**2012**)



Summary

- A new non destructive method using soft x-ray reflectivity has been proposed for qualitative compositional analysis.
- Reflectivity beamline has been used to contribute new dataset of optical constants of various materials in soft x-ray region.
- Various new materials has been proposed for better optical response in the soft x-ray region.
- Photo induced damage in SiN film is analyzed using soft x-ray reflectivity.
- NbC/Si multilayer shows comparable reflectivity as that of Mo/Si multilayer
- NbC/Si thermal stability is far better than that obtained with Mo/Si combination

Thanks for your kind attention