Spatially and Chemically Resolved Atomic Profile of Low Contrast Interface Structure using Resonant X-ray Scattering

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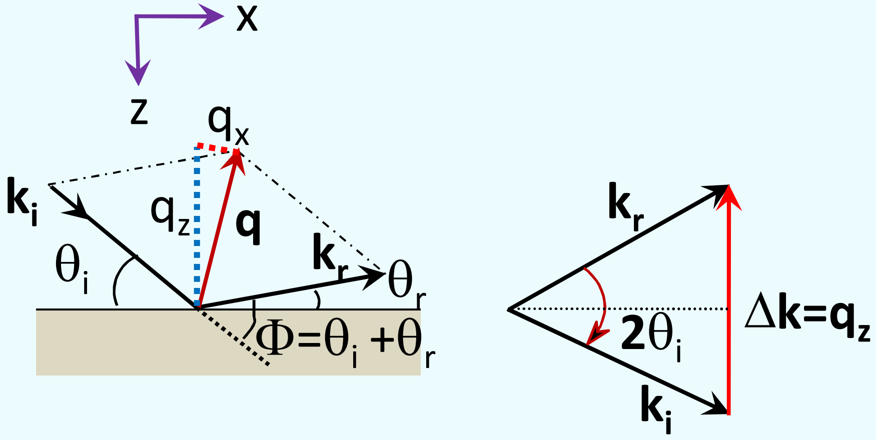
❖*Outline*

- **An Overview: X-ray Scattering**
- **Novelty of Resonant X-ray Scattering**
- **Case Studies: Low Contrast Interface Structures**
  - *Partially Decomposed BN Thin Films
  - *B_4C Marker Layer in Si
  - *Buried Interfaces in Mo/Si Multilayer
- **Conclusion**

X-ray Scattering

Scattering Geometry:



Momentum Transfer Vector

$$\mathbf{q} = \Delta\,\mathbf{k} = \mathbf{k}_f - \mathbf{k}_i$$

Where,

$$q_x = k\,(\cos\theta_r - \cos\theta_i)$$

$$q_z = k\,(\sin\theta_r + \sin\theta_i)$$

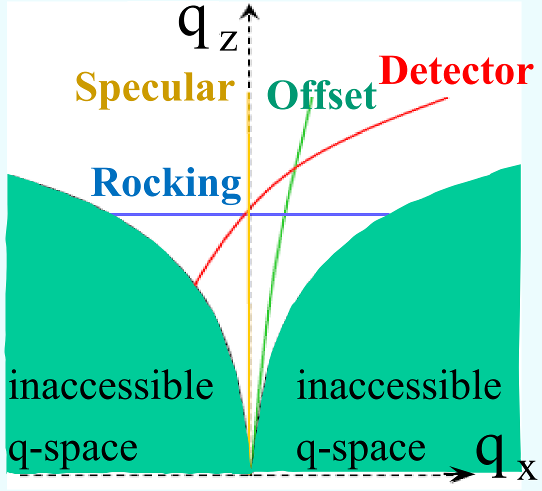
Different scans:

Specular ($\theta_i = \theta_r$)

Rocking ($\theta_i + \theta_r$ =fixed)

Offset ($\theta_i - \theta_r = \pm\delta\theta$)

Detector(θ_i fixed, θ_r changes)

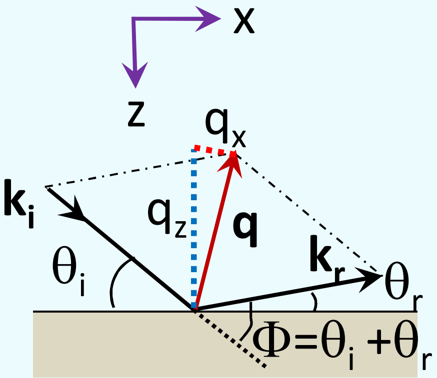


X-ray Scattering (Special Case)

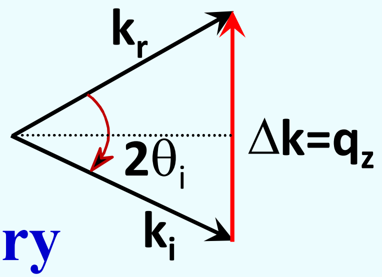
Specular Reflectivity: ($\theta_i = \theta_r$)

In this case, $q_x = 0$ and

$$\boxed{q_z = \frac{4\pi \sin\theta_i}{\lambda}}$$



Scattering geometry



Fresnel Reflectivity in q-Space:

$$R(q_z)=\frac{16\pi^2}{q_z^4}\left|\int_{-\infty}^{+\infty}\frac{d\rho(z)}{dz}\exp(-iq_z z)dz\right|^2$$

Phase factor

Electron density gradient

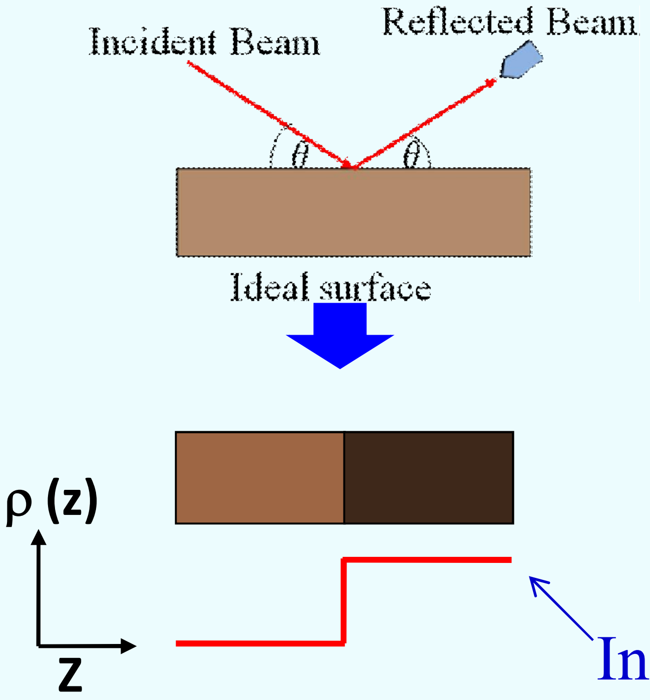
Measured reflectivity

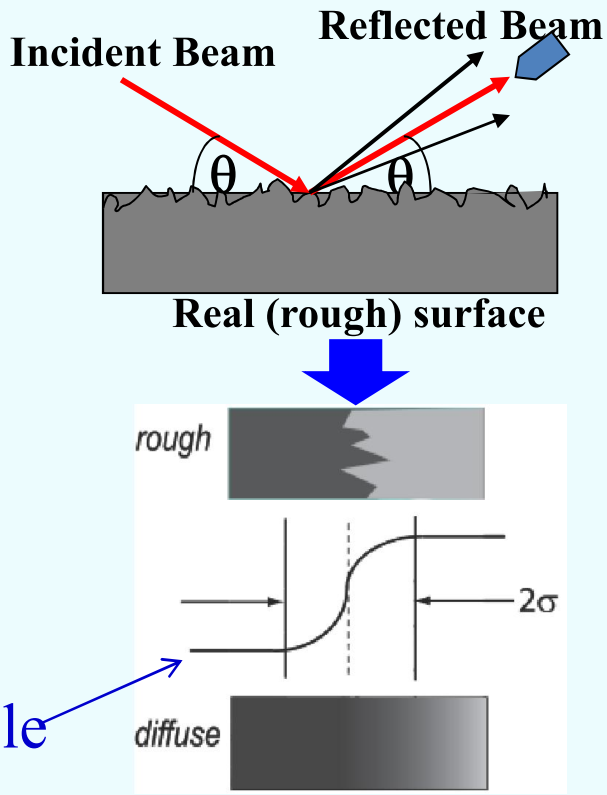
- Intensity ✓
- ✗ Phase (well known phase problem)

Required modeling of electron density profile to obtain real space information.

X-ray Reflectivity-Imperfections

Modelling of Imperfections at Interface:





Interface density profile

$$R^{\mathrm{Real}} = R^{ideal} \exp\left(-q_z^2 \sigma^2\right) \longrightarrow$$

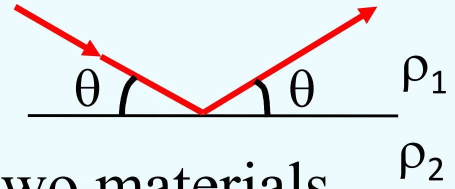
Debye-Waller factor

XRR is a unique non-destructive way for structural analysis of surface/interface on atomic scale in nano-scaled thin film MLs.

Physics issue

Difficulty of XRR for low contrast and atomic composition

Fresnel eflectivity: $\boxed{R \propto (\rho_2 - \rho_1)^2 = (\Delta\rho)^2}$

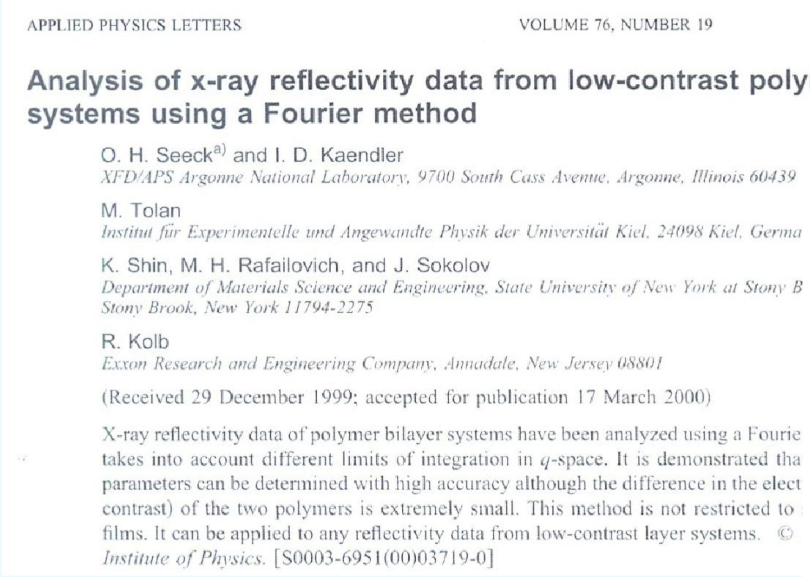


$\Delta\rho \longrightarrow$ electron density difference between two materials

If $\Delta\rho \to 0$, conventional XRR is not sensitive !

XRR: ~~Direct Atomic Composition~~

Theoretically, <u>even if 5% contrast</u> at interface has no change in conventional hard x-ray reflectivity profile.



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Analysis of x-ray reflectivity data from low-contrast polymer bilayer systems using a Fourier method

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X-ray reflectivity data of polymer bilayer systems have been analyzed using a Fourie takes into account different limits of integration in q-space. It is demonstrated tha parameters can be determined with high accuracy although the difference in the elect contrast) of the two polymers is extremely small. This method is not restricted to films. It can be applied to any reflectivity data from low-contrast layer systems. © *Institute of Physics.* [S0003-6951(00)03719-0]

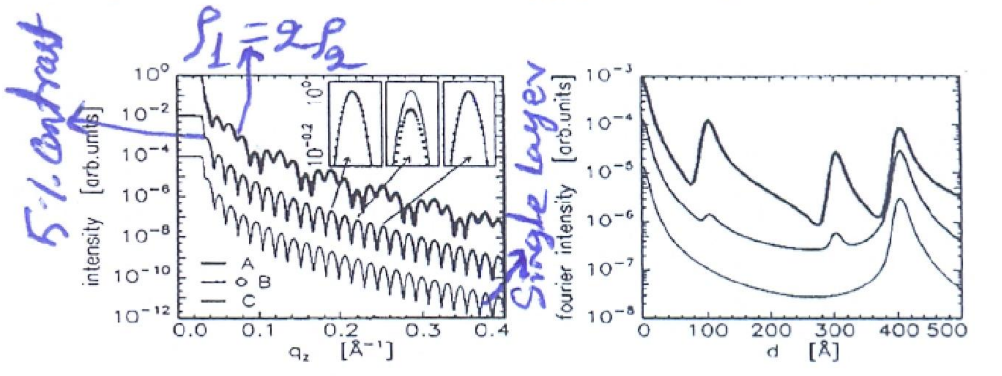


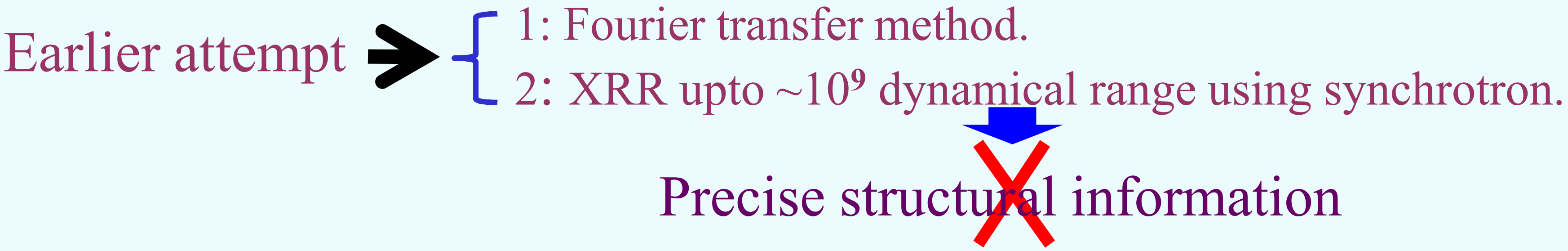
FIG. 1. Calculated RFs (left) and FTs (right). (A) bilayer on silicon with maximum contrast ($\rho_1 = 2\rho_2$) and $d_1 = 100$ Å and $d_2 = 300$ Å. (B) bilayer with 5% contrast, $d_1 = 100$ Å, and $d_2 = 300$ Å. (C) monolayer, $d_1 = 400$ Å. All σ_j are 5 Å, the q_z limits are $q_{z,\mathrm{low}} = 0.065$ Å^{-1} and $q_{z,\mathrm{up}} = 0.8$ Å^{-1}. For clarity, the RFs are only shown up to 0.4 Å^{-1}. The insets show that curve (B) still exhibits a tiny modulation.

Difficulty of XRR for low contrast and atomic composition

Low Contrast System:

1: Native oxide: e.g. Si/SiO_2 ($\Delta\rho$=0.675-0.67=**0.005** e/Å^3)

2: C/Si ($\Delta\rho$=**0.007** e/Å^3); B/BN= ($\Delta\rho$=**0.004** e/Å^3)



Earlier attempt ➔

1: Fourier transfer method.

2: XRR upto ~10^9 dynamical range using synchrotron.

Precise structural information

Remains an open question !

Possible solution

Resonant Scattering: For low contrast, chemical analysis ?

Atomic scattering factor:

$$f(\bar{q},E) = \underbrace{f_0(\bar{q})}_{\text{free electrons}} + \underbrace{f_1(E)}_{\text{bound electrons}} + \underbrace{if_2(E)}_{\text{absorption}}$$

Non-Resonant

Resonant Part

Fresnel reflectivity: $R \propto (\delta_2-\delta_1)^2 + (\beta_2-\beta_1)^2$ $\boxed{=(\Delta\delta)^2+(\Delta\beta)^2}$

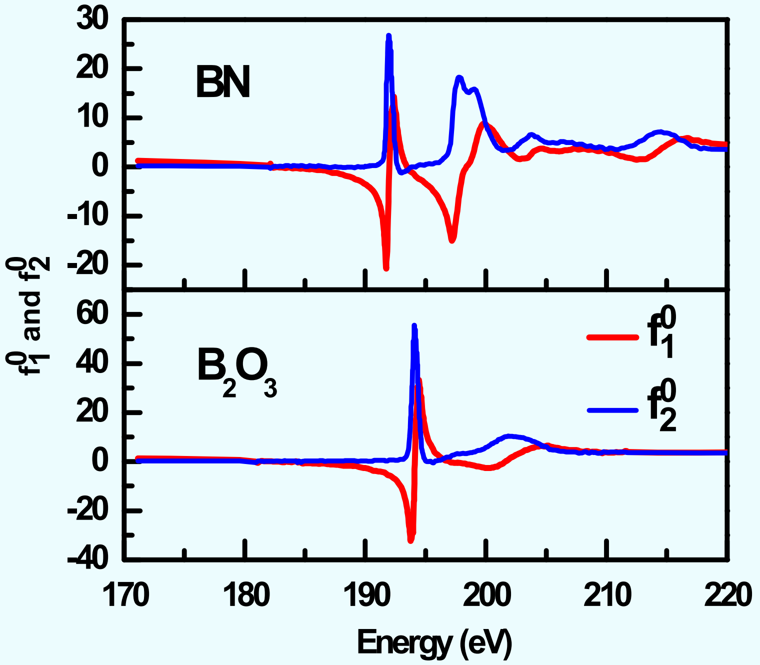
Scattering Contrast

where $n(\omega)=1-\delta(\omega)+i\beta(\omega)=\frac{r_e\lambda^2N_a}{2\pi}\left(f^0(\omega)\right)$

with $f^0(\omega)=\sum_{s=1}^{Z}\frac{g_s\omega^2}{\omega^2-\omega_s^2+i\gamma\omega}=f_1^0(\omega)+if_2^0(\omega)$

g_s is No. of electrons in particular energy level.

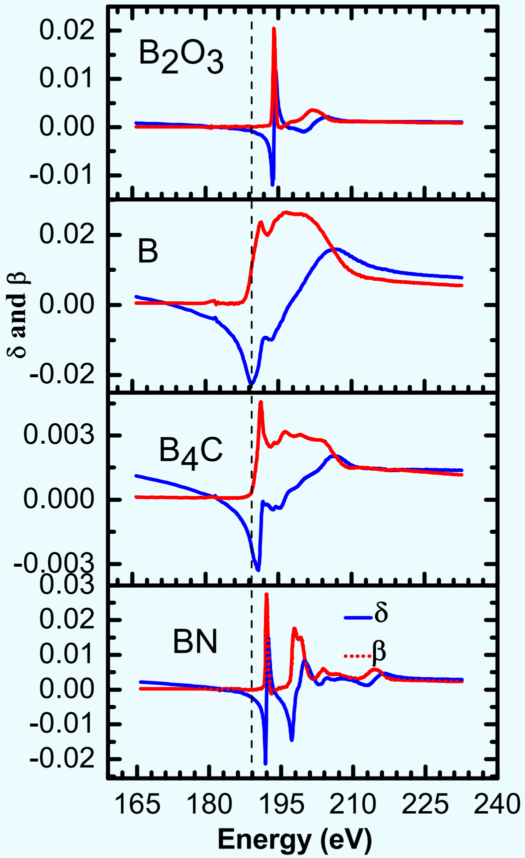
ω_s is natural frequency.

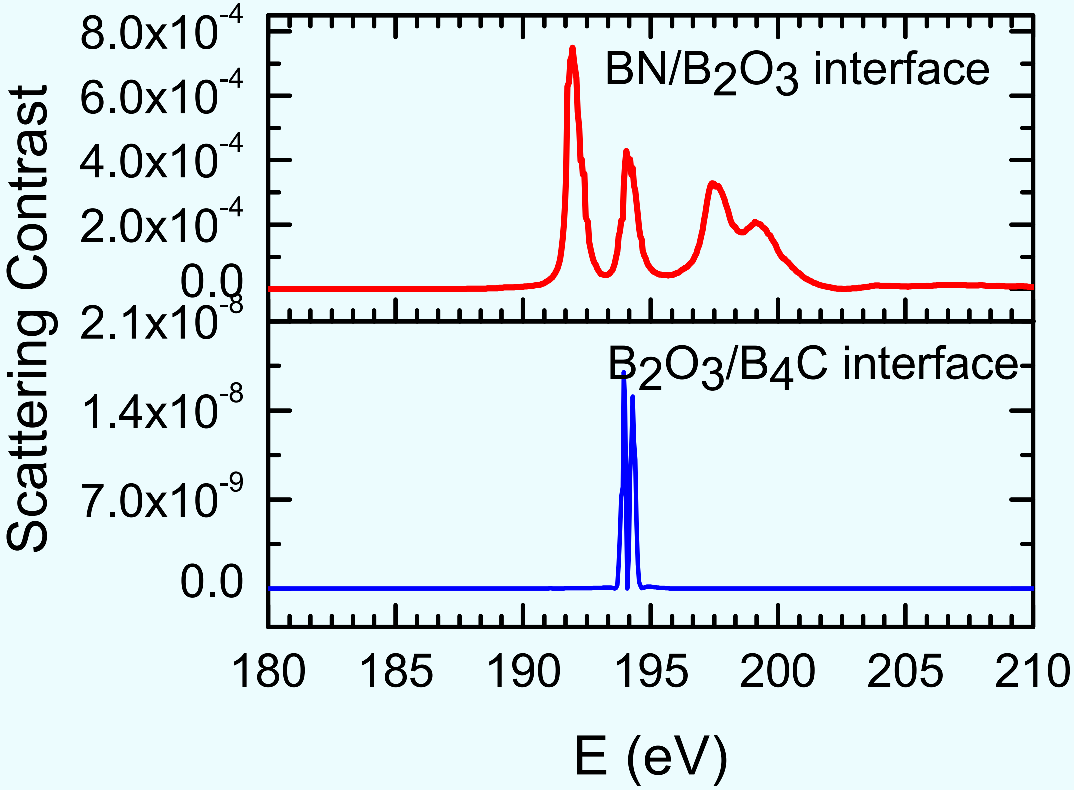


- ❖Strong variation of $f^0(\omega)$ near edge.
- ❖Interaction at resonant energies is a finger print of chemical elements.

Possible solution

Resonant Scattering: For low contrast, chemical analysis ?





By tuning incident photon energy near edge (resonant x-ray scattering):

(a) Element specificity

(b) contrast variation

Possibility for chemical analysis

To probe low contrast

M. Nayak et. al, Appl. Phys. Lett. 89, 181920 (2006); J. Appl. Phys. 107, 023529 (2010).

Soft X-ray reflectometer on Indus-1 SR Source

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

R.V. Nandedkar, K nha, M.H. Modi,
M. Nayak, *Curren*

Thin Film and X-ray Multilayer Growth Facilities

Ion assisted e-beam evaporation setup

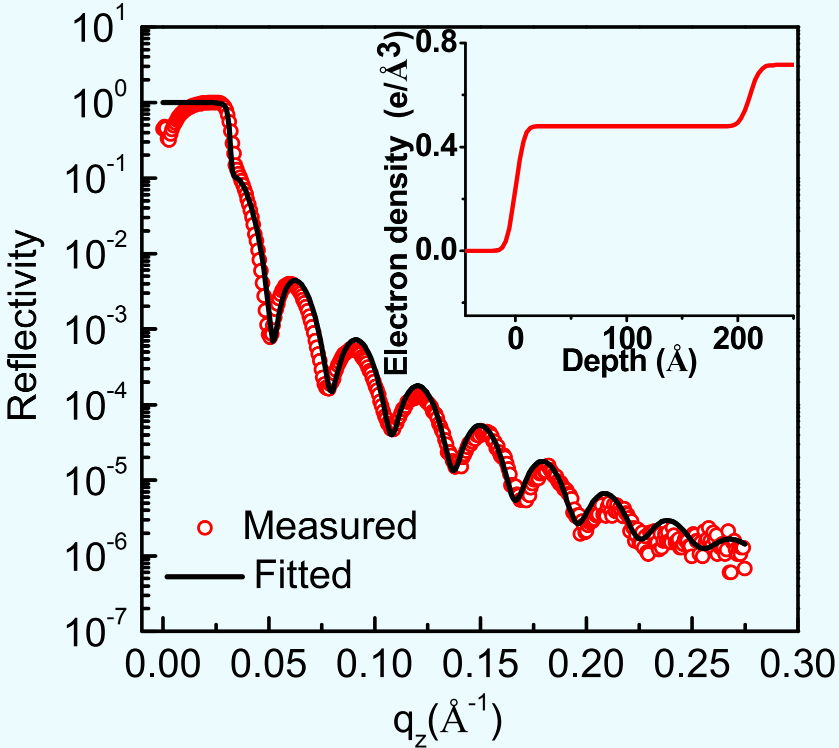
Ion beam sputtering setup

DC/ RF sputtering system

M. Nayak *et. al*, Asian J. Phys., 19, 1-14, (2010).
M. Nayak, *et. al*, Asian J. Phys., 16, 395 (2007).

RXRR: probing partial decomposed BN thin film

Hard XRR results of BN film:



Measured and fitted spectra of BN at Cu K_α.

✓Well-fitted with single layer model.

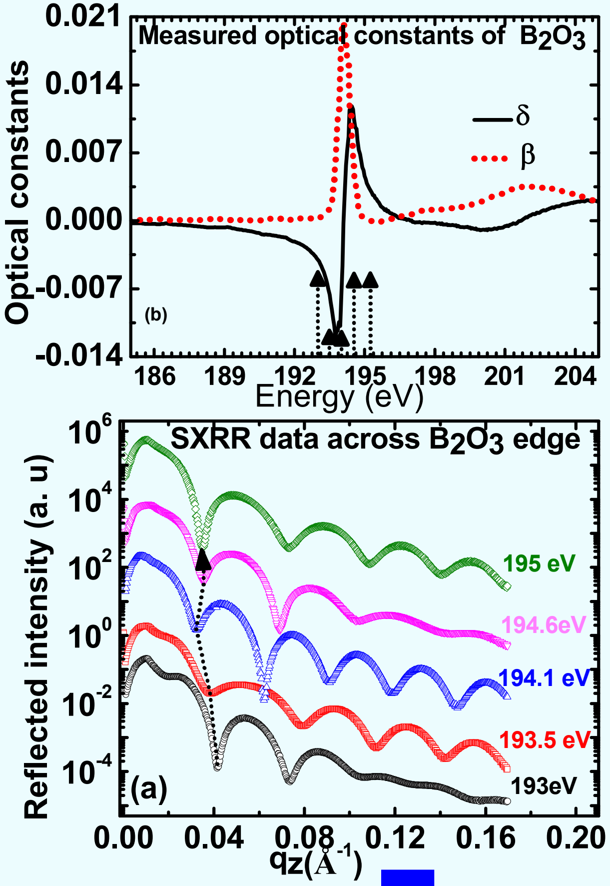
✓Best-fit data revealed No signature of compositional changes or layer formation. However, elementary B and oxide is expected due to decomposition of some BN during deposition.

But, **conventional XRR is not sensitive.**

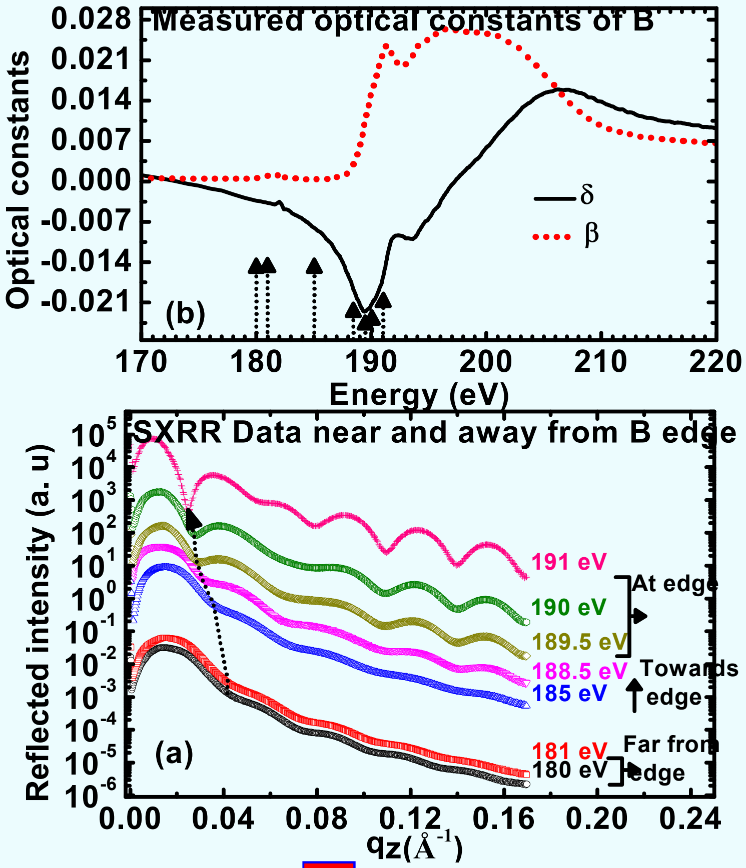
Can resonant x-ray reflectivity (RXRR) able to address the aforesaid difficulty ?

Fitted Results			
Layer	Thickness (Å)	Roughness (Å)	Mass density
BN	217	6	$1.64 gm/cm^3$
Sub.	∞	4	…

RXRR: probing partial decomposed BN thin film



✓Evidence of chemical changes in films



❖**Near B_2O_3 edge** (~194.1 eV), B_2O_3 has sharp optical variation, whereas BN and B exhibit nearly a flat optical behavior.

❖ Strong variations of RXRR profiles near B_2O_3 edge confirm presence of B_2O_3 in the film.

❖**Near B K –edge** (~189.5 eV), B has sharp optical variation, whereas BN and Boron oxide exhibit a flat optical behavior.

❖ Strong variations of RXRR profiles near B edge confirm presence of elementary B in the film.

M. Nayak , G. S. Lodha, J. of At., Molecular and Opt. Phys. (**Review Article**), 2011, Art. ID 649153, pages 23 (2011)

RXRR: probing partial decomposed BN thin film

Simulations: Sensitive to atomic composition

In Fig (b)

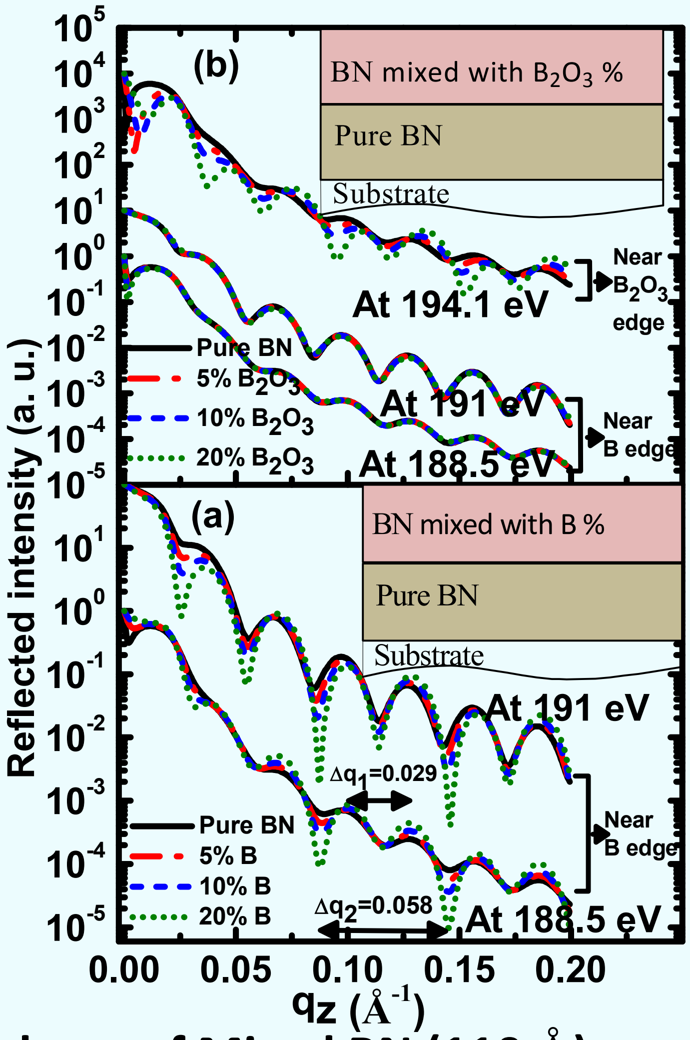
(1): Adding atomic % of B_2O_3, brings changes in amplitudes and shape of the envelope **only near B_2O_3 edge** (194.1 eV).

(2) Adding B_2O_3 near B –edge (188.5 and 191 eV), no changes in the profile.

In Fig (a)

(1) Adding atomic % of B, brings changes in amplitudes and shape of the envelope **only near B edge** (188.5 and 191 eV).

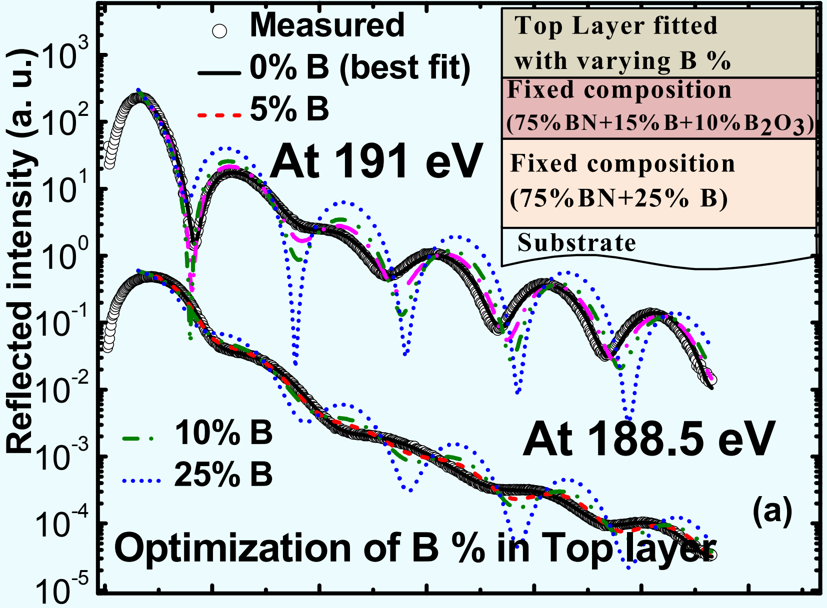
Thus, chemical analysis can be possible using x-ray scattered intensities at the ***respective absorption edges*** of constituent materials of the sample.



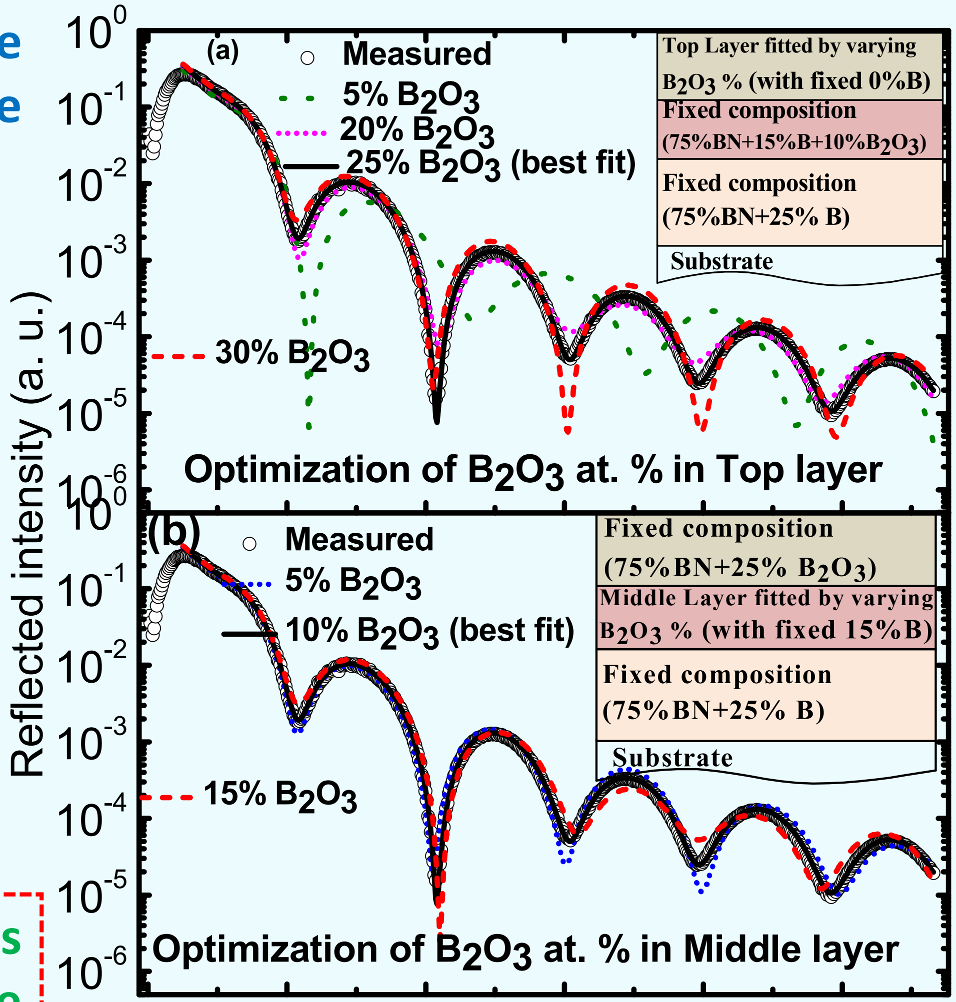
Bi-layer of Mixed BN (110 Å)-on-Pure BN (110Å). (a) Mixed with B and (b) mixed with B_2O_3

RXRR: probing partial decomposed BN thin film

Simultaneously RXRR fitting procedure at respective edges for quantitative chemical analysis:



Near B edge



Near B_2O_3 edge

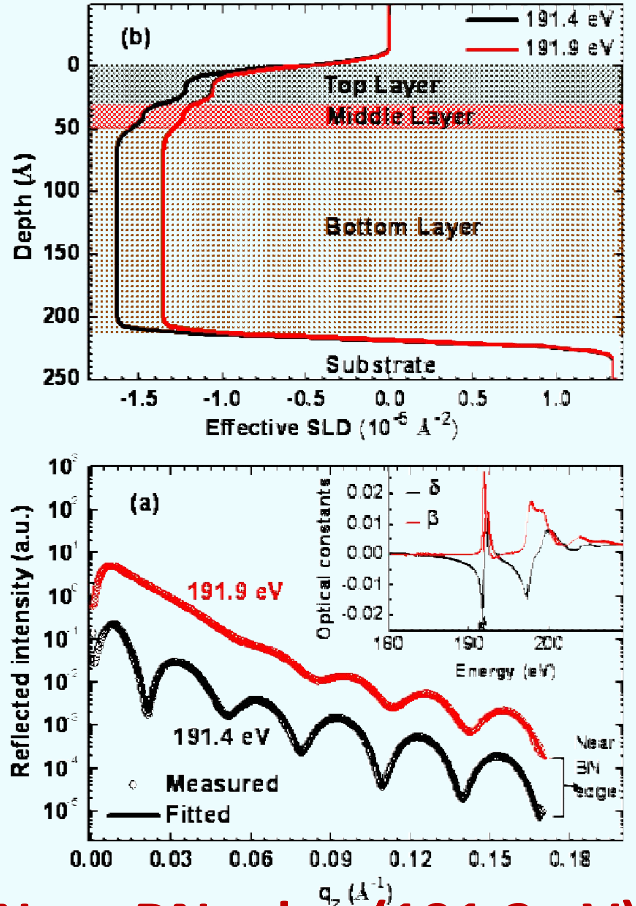
If the composition of each layer varies even 5% than the best-fit value, the calculated profile differs significantly from the measured curve.

M. Nayak and G. S. Lodha: J. Appl. Cryst. 46, 1569 (2013)

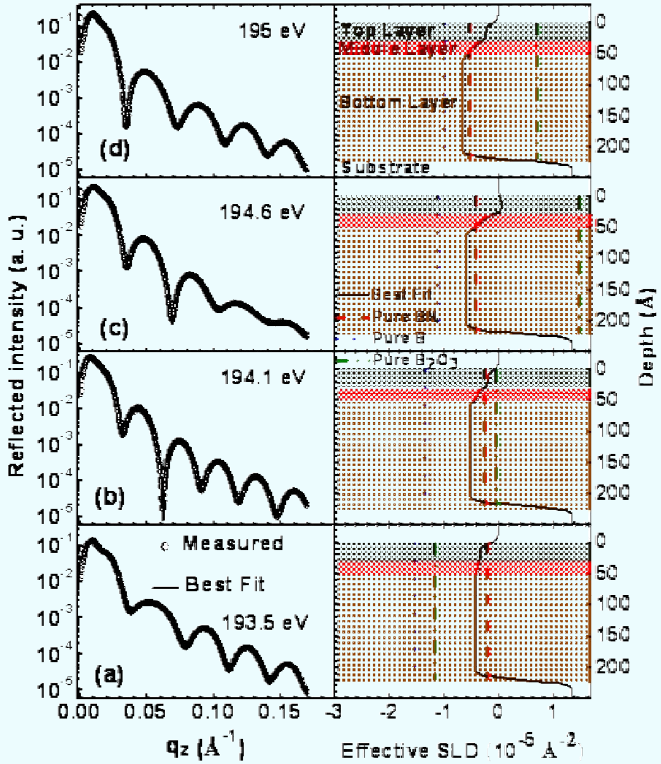
Research using Indus SR

RXRR: probing partial decomposed BN thin film

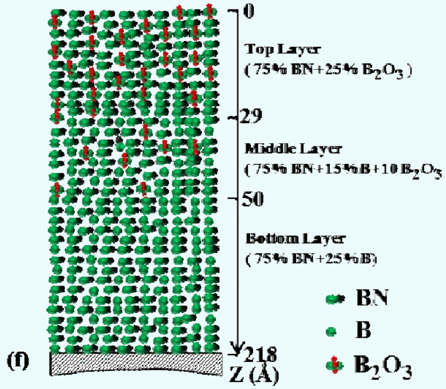
Best fit data near respective edges:

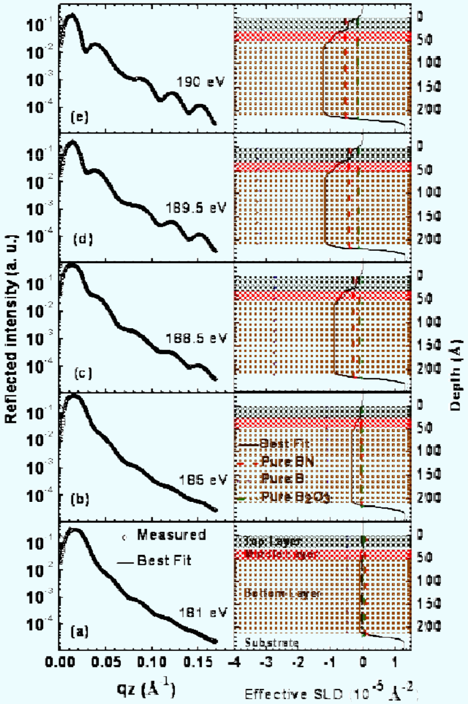


Near BN edge (191.3 eV)



Near B_2O_3 edge





Near B edge

Best fit Results:

Top Layer (29 Å):75% BN+25% B_2O_3

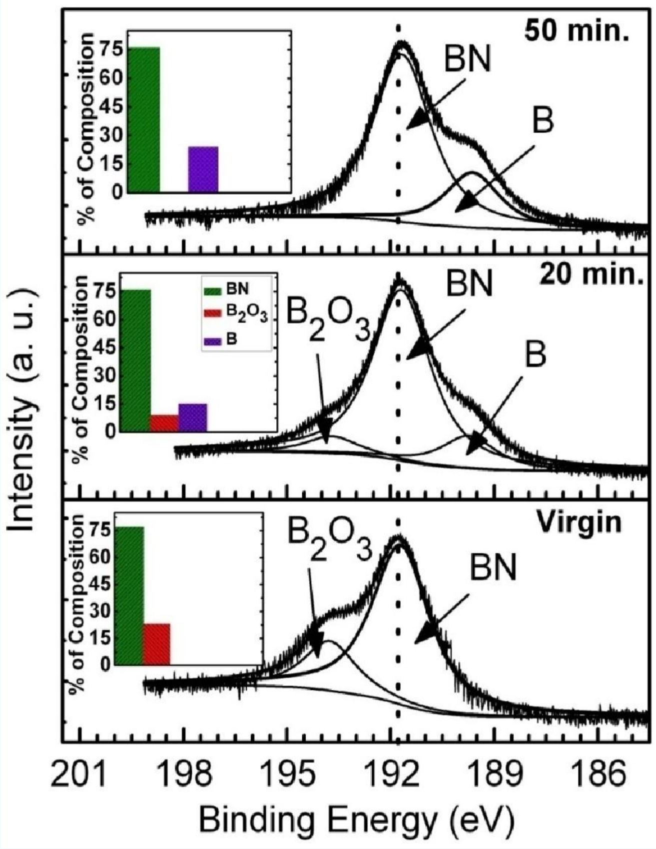
Middle Layer (21 Å nm):75% BN+15% B+10% B_2O_3

Bottom Layer (168 Å):75% BN+25% B

M. Nayak and G. S. Lodha, J. Appl. Phys. .114, 023505 (2013).

RXRR: probing partial decomposed BN thin film

Depth profile XPS:



XPS narrow scan of B 1s peak of partially decomposed BN film with different sputtering time.

- **Top layer:** 76 % of BN and ~24 % of B2O3
- **Middle (after 20 min.):** 77 % of BN, ~9 % of B2O3 and ~14 % of B.
- **Bottom (after 50 min.):** 77 % of BN and ~23 % of B.

B.E. and (FWHM):

B: 189.6 (1.9)

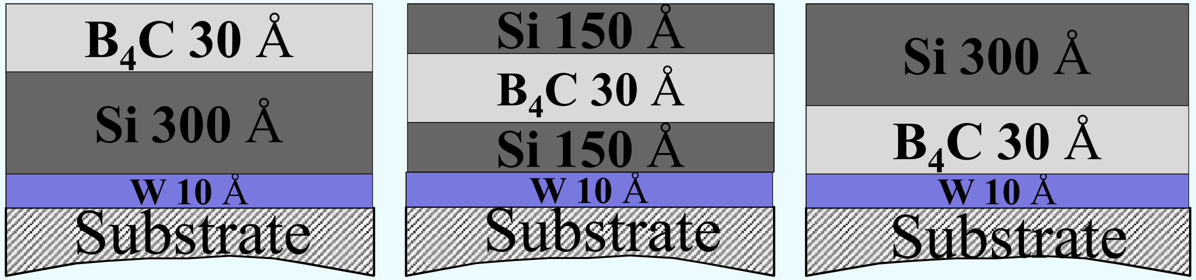
B-N: 191.7 (1.9)

B2O3: 193.8 (1.8)

XPS result agrees well with SXRR for chemical composition.

RXRR: B_4C marker layer in Si film

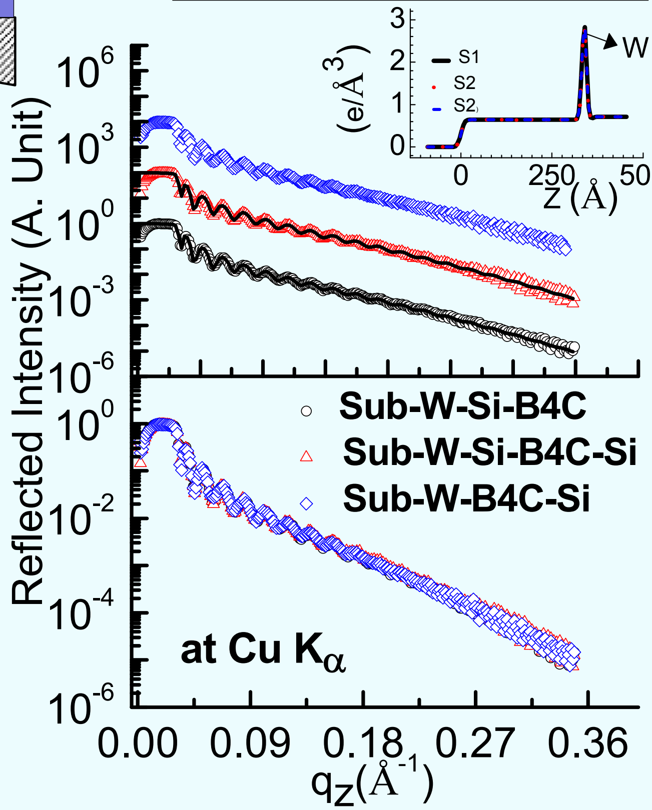
Conventional hard X-ray reflectivity (Before resonant Reflectivity):



Sample 1 **Sample 2** **Sample 3**

Note:
ρ(Si)=0.71453 e/Å^3
ρ(B4C)=0.71489 e/Å^3
Δρ/ρ=~0.05%

Fitted hard XRR Results			
Layer	**Thickness (Å)**	**Roughness (Å)**	**Mass density**
Si/B_4C	**333**	**~8**	**95% of Bulk**
W	**10**	**5**	**94% of Bulk**



- Well-fitted with taking Si+B_4C as single layer.
- **No sensitivity to Si/B_4C interface**
- Best-fit data **revealed No signature of compositional changes or layer formation if any** (because of low-contrast difficulty and no-element specificity of hard XRR)

Can resonant reflectivity able to address the aforesaid difficulty ?

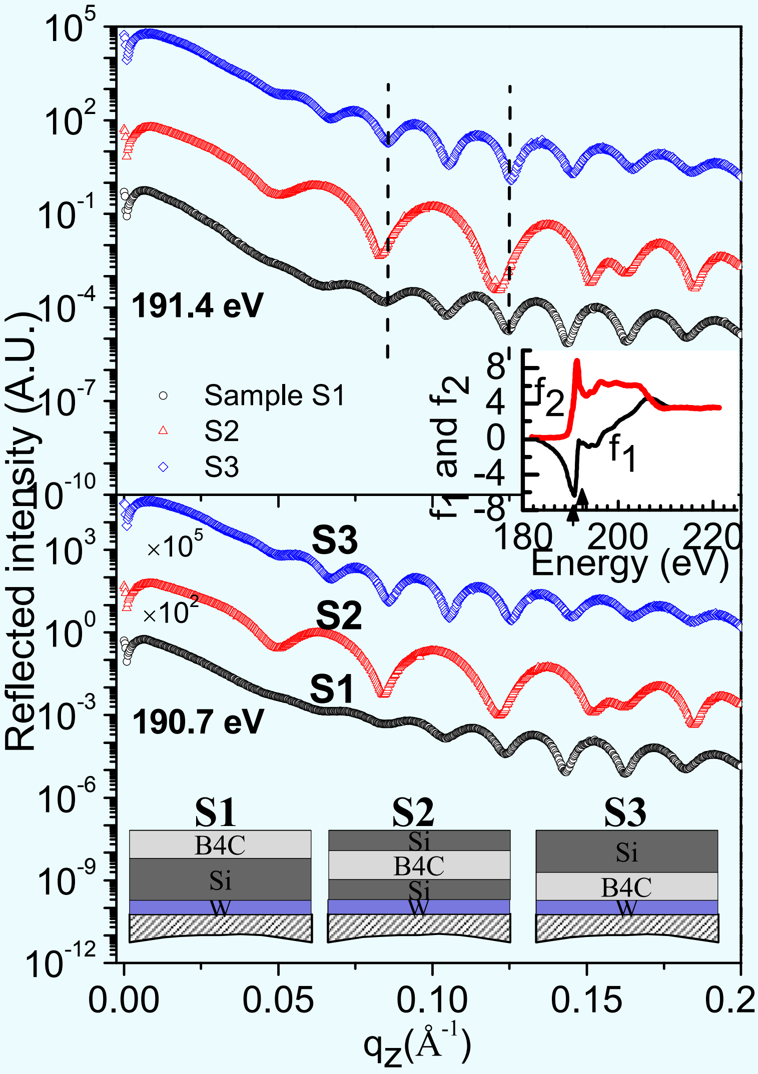
RXRR: B_4C marker layer in Si film

Structural Sensitivity of RXRR to low contrast thin film system:

- ❖**Near B4C K –edge** (~191.4 eV), B_4C has sharp optical variation.

- ❖ Different samples (S1, S2 and S3) exhibit different RXRR profiles near B_4C edge.

- ❖ **Strong Variations of RXRR profiles (Period, shape and amplitude of oscillations) confirm sensitivity to Si/B_4C (low contrast structure) interface.**

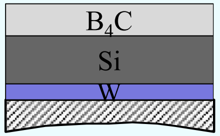


Measured using Indus SR

RXRR: B_4C marker layer in Si film

Sample 1:

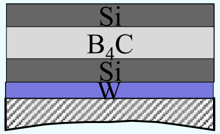
❖ Strong variations of RXRR profiles near B_2O_3 edge (~194.3 eV) confirms **presence of B_2O_3** in the sample S1. No variation near of RXRR near B edge (~189.5eV) confirms there is **no boron** in S1.



Similarly:

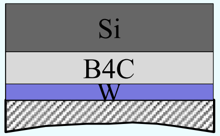
Sample 2:

❖ Variations of RXRR profiles near B edge confirms **presence of elementary B** in the film. No variation of RXRR profile near B_2O_3 edge confirms **no B_2O_3** in S2.

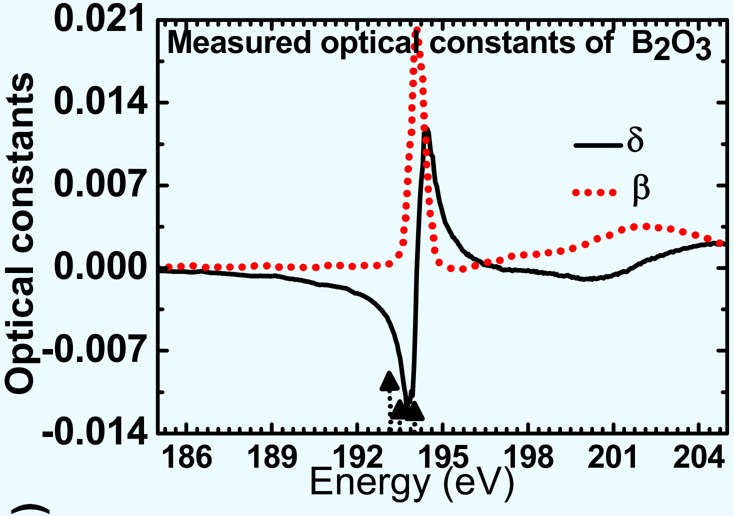


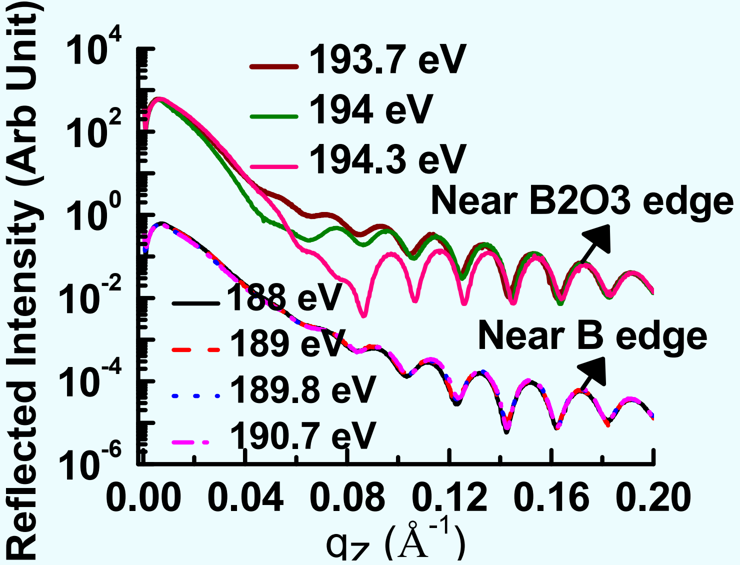
Sample 3:

❖Similarly in sample 3, **B is present but not B2O3**.



✓Evidence of chemical changes in films



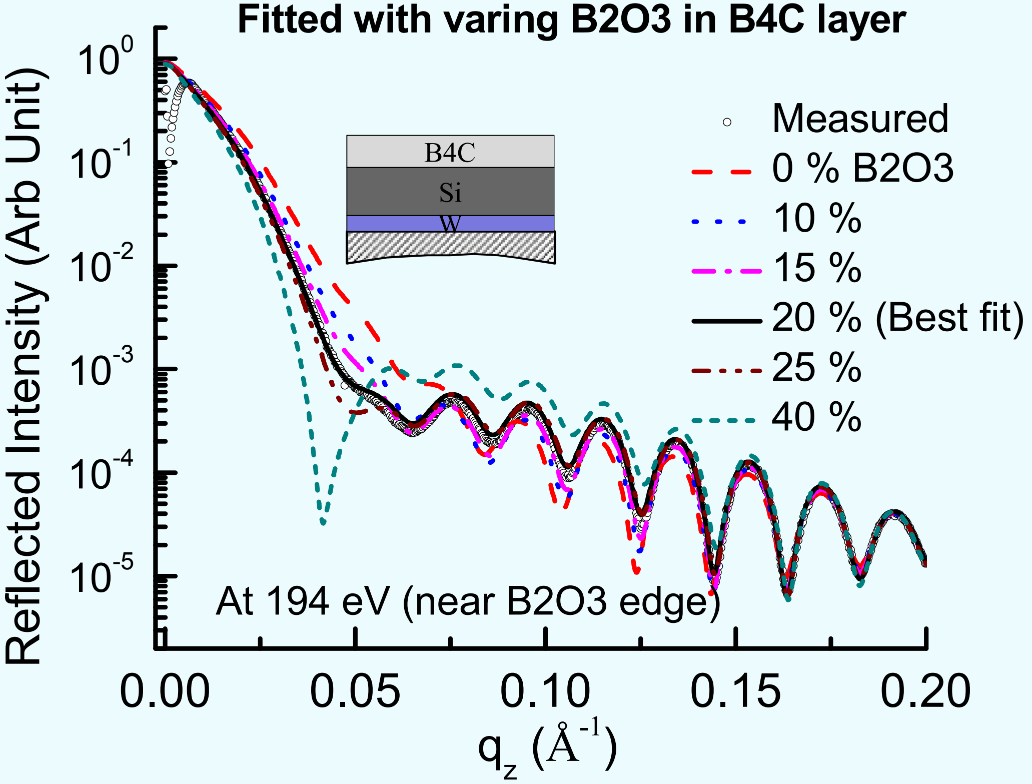


RXRR: B_4C marker layer in Si film

RXRR fitting at respective edges for quantitative structural and chemical analysis:

Best-fit RXRR Results:

Fitted SXRR Results (**For Sample 1**)			
Layer	t (Å)	σ (Å)	Composition
B_4C	31	8	80% B_4C+20% B_2O_3
Si	302	9	
W	10	6	
Sub	∞	5	



If the composition of B_4C layer varies even 5% than the best-fit value, the calculated profile differs significantly from the measured curve.

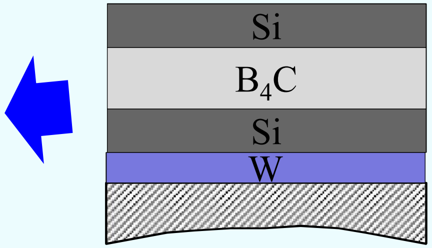
RXRR: B_4C marker layer in Si film

RXRR fitting at respective edges for quantitative structural and chemical analysis:

Similarly:

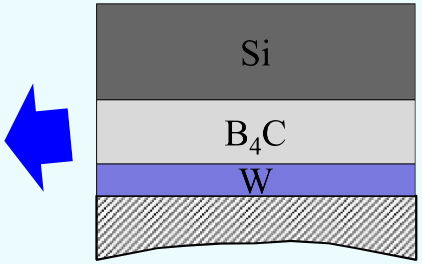
Best-fit RXRR Results:

Fitted RXRR Results (For Sample 2)			
Layer	t (Å)	σ (Å)	Composition
Si	151	7	
B_4C	31	5	80%B_4C+20%B
Si	151	7	
W	10	6	
Sub	∞	5	



Similarly for Sample 3:

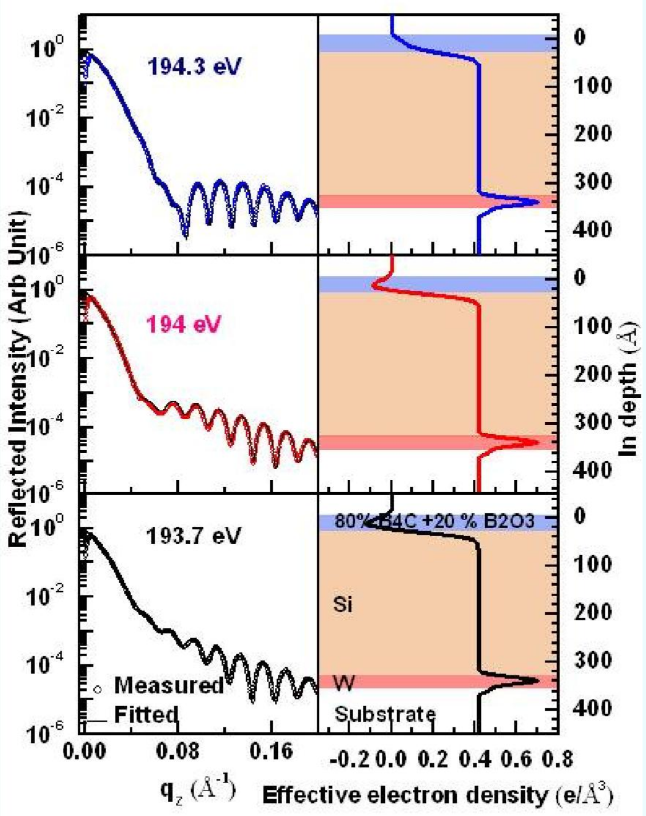
Fitted RXRR Results (For Sample 3)			
Layer	t (Å)	σ (Å)	Composition
Si	302	9	
B_4C	31	6	80%B_4C+20%B
W	10	6	
Sub	∞	5	



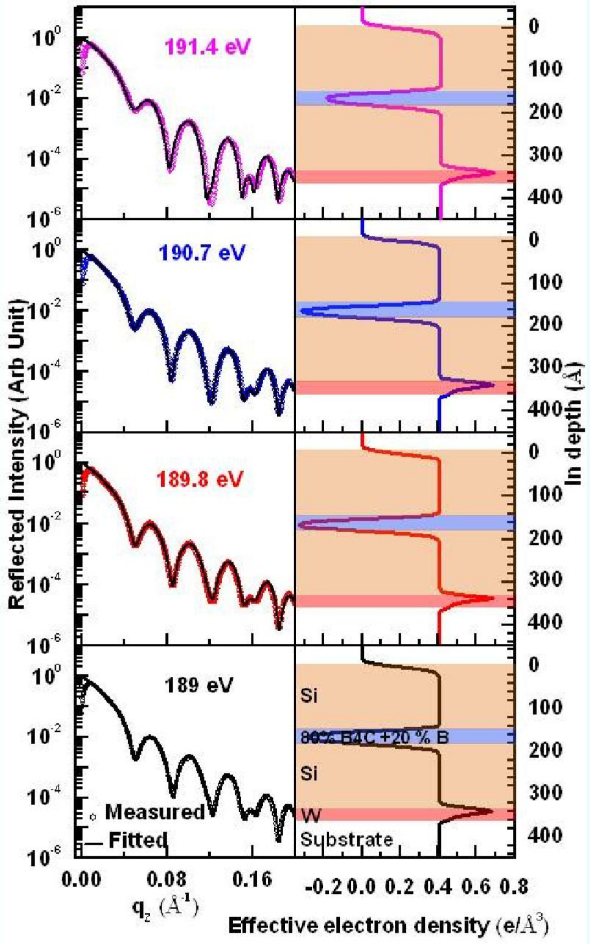
M. Nayak, P. C. Pradhan and G. S. Lodha (To be Communicated)

RXRR: B_4C marker layer in Si film

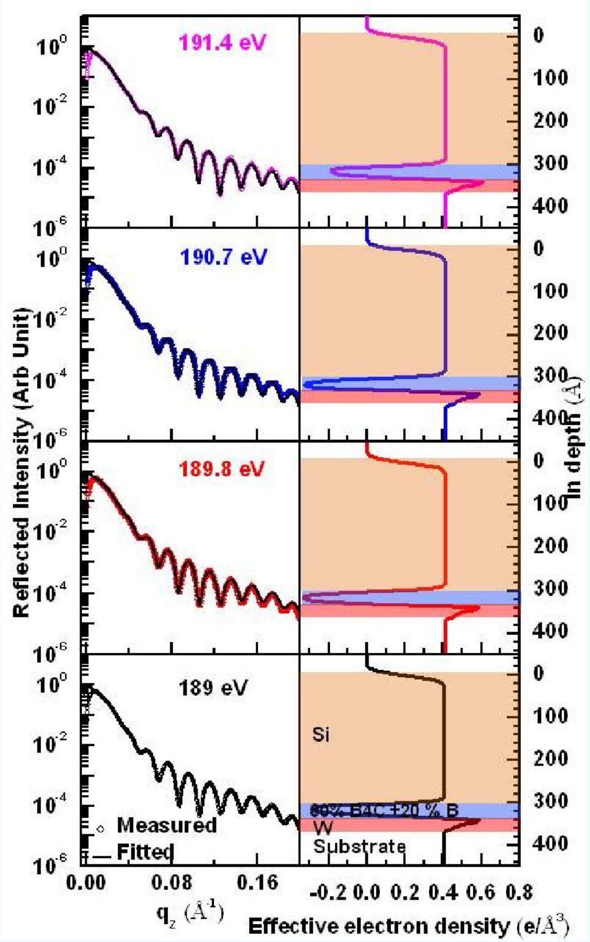
Best fit data near respective edges:



Near B2O3-edge (For Sample 1)



Near B-edge (For Sample 2)

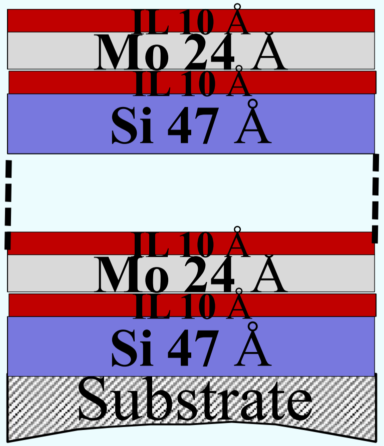


Near B-edge (For Sample 3)

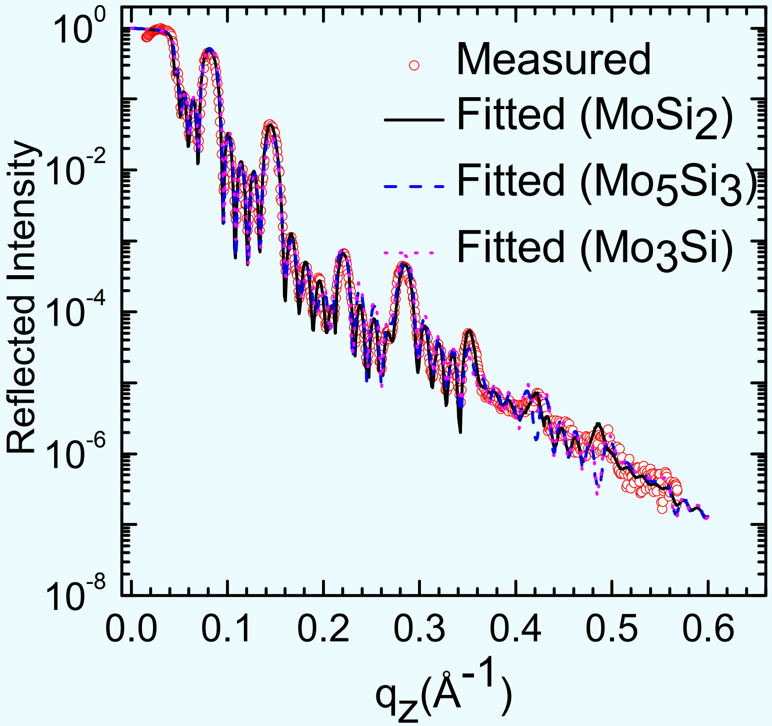
Thus, chemical analysis can be possible using x-ray scattered intensities at the *respective absorption edges* of constituent materials of the sample.

RXRR: Probing Multilayer Interfaces

Hard XRR before RXRR:



Mo/Si ML (N=5 and d=90 Å). IL denotes interlayer



Hard XRR data of at Cu K_α

Best fit results:

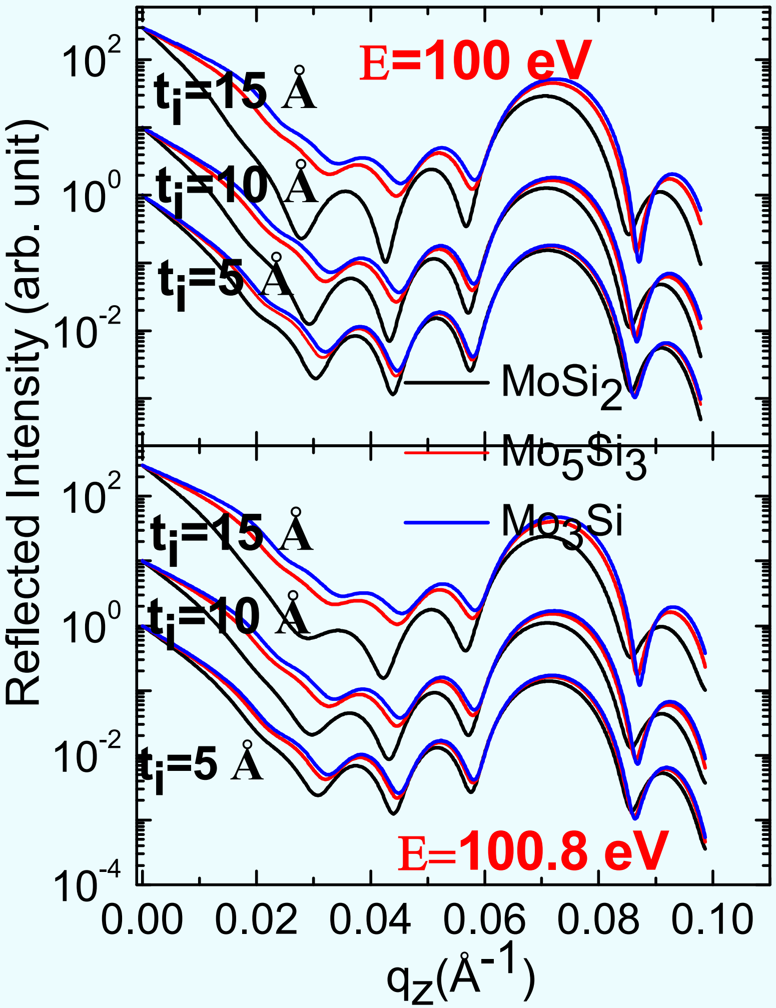
Layer	Thickness (Å)	roughness (Å)	δ ×10^{-6}	β ×10^{-7}
Si	47	5	6.4	1.4
Interlayer	10	5	19.1	11.6
Mo	24	6	27.6	16.3
Interlayer	1	4.5	19.1	11.6

No sensitive to interlayer composition

RXRR: Probing Multilayer Interfaces

Simulated SXRR profiles for different composition and thickness:

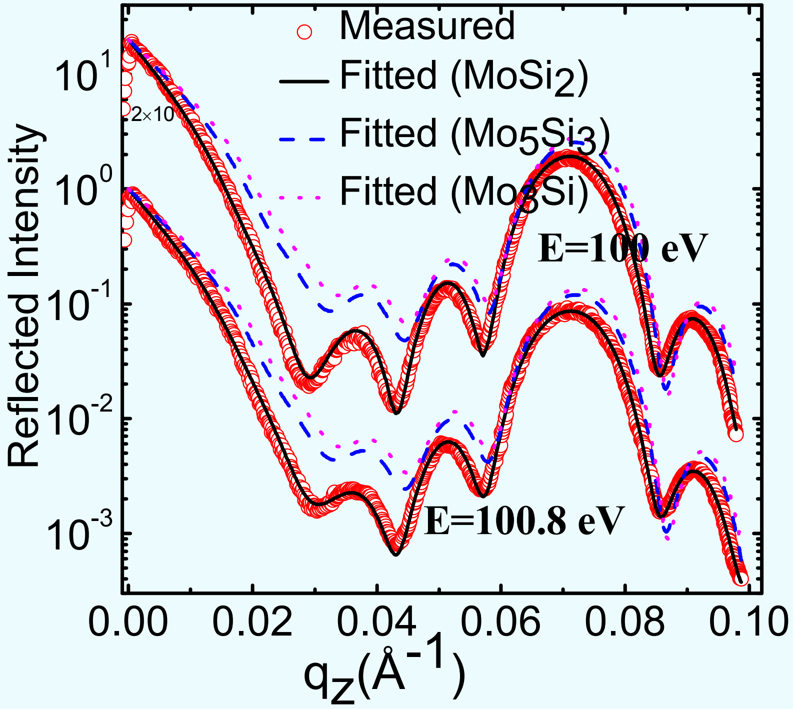
- Demonstrated sensitivity to interlayer composition.



$[Mo/Si]_5$ ideal ML with d=90 Å and Γ=0.3

RXRR: Probing Multilayer Interfaces

Sensitive using RXRR:



RXRR Measurements using Indus -1 SR.

- ➢SXRR best fit results reveal $MoSi_2$ composition at interface.

The technique is applicable in-general to any thin film ML system.

M. Nayak et al. Appl. Phys. Lett. 89, 181920 (2006).

RXRR: For low contrast & chemical analysis !

Summary on resonant x-ray reflectivity:

- A possibility for **chemical selective micro-structural analysis** of nano-scaled thin film and ML systems **using resonant x-ray reflectivity**.

- **Composition profile** is determined from free surface to buried interfaces in a **low contrast (<0.05%)** system.

- The t**echnique is applicable in-general to any systems** with the absorption edges such that at-an-energy only one shows unique features in order to enhance contrast and rest are rather flat.

- So, the spatial distributions of individual element/compound presents in the film are quantified from RXRR measurements at their respective edges.

RXRR: probing partial decomposed BN thin film

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Thank You