Study of optical response near the absorption edge using vacuum ultra violet/soft X-ray reflectivity beamline on Indus-1

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Abstract. Fine structure features of energy dependent atomic scattering factor near the atomic absorption edge, is used for characterization of low Z containing hard-condensed matter thin films. Near the atomic absorption edge, reflectivity provides increased sensitivity to composition of the interface, due to tunable contrast of optical constants. This is illustrated through the characterization of molybdenum silicon X-ray multilayer and boron carbide (B$_4$C) thin film.

1. Introduction
X-ray reflectivity (XRR) is an important, nondestructive tool to probe interfaces in thin film structures [1-4]. The large dynamic range and high momentum scattering vector ($q_z$-range), allows the use of Fourier transform methods to study the micro-structural parameters such as thickness, interface roughness and interface diffusion. Electrons are responsible for the interaction of X-ray with materials. X-rays actually probe effective electron density, which is directly related to the refractive index [2]. X-ray reflectivity shows a resonant behavior near the atomic absorption edges [5, 6] because of strong variation of atomic scattering factor. Anomalous terms of atomic scattering factor become significant near the absorption edges [7]. The effect is more pronounce in the soft X-ray region ($E<1.0$ keV) compared to hard X-ray region($E>1.0$ keV) [8]. The elemental specificity of resonant X-ray reflectivity can be achieved by tuning the energy of X-rays to the absorption edge of the element being investigated.

X-ray technique based on resonance phenomena has become popular with the availability of continuously tunable X-rays from synchrotron source. X-ray absorption based techniques use the imaginary part of the atomic scattering factor. The real part of atomic scattering factor is used in scattering/reflectivity based techniques. In the hard X-ray region, resonant (anomalous) scattering/reflectivity is used to study ion distribution at bio-membranes [9], spectroscopic structures of ion adsorbed at oxide-water interfaces [10], monolayer-level change of oxidation state at buried...
interface [11], chemical depth profile of passive oxide [12], location of the resonant atom at air/water interface [13], doping layers at heterostructure interface [14], phase problem in crystallography [19] and magnetic material [20]. In the soft X-ray region, resonant scattering/reflectivity is used in soft matter films to study heterogeneous chemical structure at nano scale [15-17]. In hard condensed matter soft X-ray scattering/reflectivity is used to measure the depth dependence of magnetization across the interface between ferro and anti ferro magnet [21], orbital and magnetic ordering [22], enhanced magnetic diffraction [23] and exchange coupling [24]. This and earlier report by us [18], reveals that soft X-ray resonant reflectivity opens the possibility to study low-Z thin films structures of hard condensed matter.

Recursive method given by Parratt [2], based on dynamic theory, can be used for the calculation of reflectivity from multilayer system. Taking the boundary condition of tangential component of electric field as continuous, the recursion relation for reflected amplitude between j and j+1 layer can be written as

\[
    r_{j,j+1} = b_j^2 \left( \frac{r_{j+1,j+2} + f_{j,j+1}}{1 + r_{j+1,j+2}f_{j,j+1}} \right)
\]

where \( b_j = \exp \left( -i q_{j,z} t_j \right) \) is the amplitude factor for half the perpendicular distance \( t_j \) (the thickness of \( j \)-th layer). \( q_{j,z} \) is the normal component of wave vector transfer in the \( j \)-th layer and is given by

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

\( \lambda \) is the wavelength of incident X-ray at the angle of incidence \( \theta \) and \( n_j \) is the refractive index of the \( j \)-th layer. For s-polarized radiation, where the electric field vector is perpendicular to the plane of incidence, the Fresnel reflection coefficient, \( f_{j,j+1} \), between j and j+1 layer is given by

\[
    f_{j,j+1} = \frac{E_{j}^{R}}{E_{j}} = \frac{q_{j,z} - q_{j+1,z}}{q_{j,z} + q_{j+1,z}}
\]

where, \( E_j \) and \( E_j^{R} \) are the amplitude of electric vector of incident and reflected waves on the interfaces j and j+1. For a multilayer system with N number of layers on an infinite thick substrate, the recursion relation starts from the bottom layer, with the assumption that \( r_{N,N+1} = 0 \), as there is no reflection from the bottom surface of the substrate. If \( I^{R} \) and \( I_o \) are reflected and incident intensity, then the final reflectivity can be written as

\[
    R = \frac{I^{R}}{I_o} = |r_{1,2}|^2
\]

The reflected amplitude in eq. (1) is for the ideal case of perfectly smooth and abrupt interfaces. But in the real system, the interfaces are not perfectly smooth and have some finite width due to roughness, inter diffusion and chemical reactivity etc. The imperfect interfaces can be dealt either by statistical approach or multiple layer model, with the incorporation of inter- layers between the two-
layer systems. In the statistical approach, if a continuous refractive index profile is assumed between layers $j$ and $j+1$, with error function for imperfection at the interfaces, then Eq. (1) is to be multiplied with the factor $\exp\left(-q_{j,j+1}^2\sigma_j^2/2\right)$, where $\sigma_j$ is the root mean square deviation of interface with respect to a smooth interface. In case when a compound is formed at the interfaces, the multiple layers model gives a better model fitting than the statistical approach. For Mo/Si multilayer system, the multiple layer model based on four layer system gives better experimental fit than the statistical model due to formation of interlayer at the interfaces between Mo and Si [26]. For experimental data fitting, the initial gauss values are layer thickness, optical constants and rms roughness. These parameters are varied and fitted to the measured data using a non-linear least square fitting procedure.

The optical properties of materials can be described by the response of electrons in an oscillatory electric field $E$. The atom can be represented by a massive nucleus surrounded by electrons held at discrete binding energies. In bound multi-electron atom system, the various electrons are bound to the nucleus by a restoring force, and respond to the incident field. The response depends on the resonant frequencies $\omega_s$ of the bound electrons. In Eq. (2), the refractive index $n_j$ of the material with bound multi-electron system in $j$th layer can be written in terms of forward atomic scattering factor as $f_j^0$ as [27]

$$n_j(\omega) = 1 - \frac{\lambda^2 r_e N_{\omega(j)} f_j^0(\omega)}{2\pi}$$

with

$$f_j^0(\omega) = \sum_s \frac{g_{s(j)} \omega^2}{\omega_s^2 - \omega^2 + i\gamma_\omega}$$

where $r_e=2.82\times10^{-13}$ cm is the classical electron radius, $N_s$ is the number density of atoms in the material. $Z$ is the atomic number, $g_s$ is the oscillator strength, and $\gamma$ is the damping constant. In terms of real and imaginary part Eq. (6) can be written as [7]

$$f_j^0 = f_{0(j)} + \Delta f_j^r - i\Delta f_j^i$$

where $f_0$ is the scattering factor for Thomson scattering (number of free electrons associated with a given atom that are active in the scattering process). $\Delta f^r$ and $\Delta f^i$ are the dispersion and absorption parts of energy-dependent correction terms to atomic scattering factor, respectively. These are also referred to as resonant (or anomalous) terms of atomic scattering factor. The tightly bound inner electrons mostly give rise to anomalous terms [28].

Far from the absorption edge, electron with binding energy less than incident photon energy scatter according to Thomson free electron model [27] and phase of polarization lags by $180^\circ$ to the applied field. Bound electrons with energy grater than incident photon energy, contribute to in-phase polarization. This contribution is negligible compared to Thomson free electron scattering. Near to the absorption edge, the in-phase polarization component becomes significant due to quantum mechanical exchange of oscillator strengths between various core levels, and cannot be neglected. At the energy just below the atomic absorption edge, electron undergoes virtual transition in modified electric field of the atom. The electron is not able to move out of the local environment of the atom and contributes to in-phase polarization with incident field of the photon. However just above the absorption edge energy, the electron moves out of the local environment of the atom, leading to real transition of the electron. In case, the in-plane polarization component is sufficient to overcome the out of phase polarization component, real part of atomic scattering factor $(f_0 + \Delta f^r)$ undergoes sign reversal. Most favorable materials for sign reversal of real part of atomic scattering factors are third-period
elements in the periodic table, around L_{II,III} edges. Other possibilities are M_{IV, V} edges of the fourth period elements and K-edges of the second period elements.

Benfatto et al [29] have given the theory of resonant atomic scattering factor based on a multiple scattering approach. Henke et al [30] have given a comprehensive tabulation of atomic scattering factor (calculated and experimental for some of elements) for all the elements Z=1-92 in the energy region 50 to 30000 eV. Figure 1 shows the variation of (\(f_0+\Delta f\)) and \(\Delta f\) as function of photon energy for silicon using Henke et al [30] database. The real part \(f_0+\Delta f\) approaches a value equal to the atomic number Z (number of electrons per atom) for photon energies much above at the K absorption edge. This is because at higher energies, all the electrons behave as free electrons. Free electron is loss-free and all the energy received by the electron is reradiated. Formally, losses are introduced in the imaginary part \(\Delta f\). The imaginary part \(\Delta f\) decreases with energy, except when it encounters an absorption edge. Close to the absorption edge \(f_0+\Delta f\) and \(\Delta f\) change rapidly with energy (anomalous dispersion). There is a sharp jump in \(\Delta f\) from below the edge (in energy) while \(f_0+\Delta f\) dips to a large negative value through the edge. The atomic like assumption is clearly a poor approximation in the vicinity of absorption edge and can be effected by chemical environment. The calculations of Henke et al. may not sufficient to establish the details of the dispersion at the edges. The atomic scattering factor of a compound can be calculated using scattering factor of individual atoms weighted with density [31]. At the absorption edges, change in \(f_0+\Delta f\) and \(\Delta f\) can be significantly large with small change in composition of the materials. This could be used for the analysis of composition of buried interface through contrast in optical constant.

Comparing Eqn (5) and Eqn (7), the real and imaginary part of refractive index can be written in term of real and imaginary part of atomic scattering factor as

$$n_j = 1 - \delta_j + i\beta_j = 1 - \frac{\lambda^2 r_e N_{a(j)}}{2\pi} \left( f_{0(j)} + \Delta f_j' + i\Delta f_j'' \right)$$

with

$$\delta_j = \frac{\lambda^2 r_e N_{a(j)}}{2\pi} f_{0(j)}$$

$$\beta_j = \frac{\lambda^2 r_e N_{a(j)}}{2\pi} \Delta f_j'$$

where \(\delta_j\) (dispersion) and \(\beta_j\) (absorption) are optical constant material of the \(j^{th}\) layer. The real part of the complex energy dependent refractive index is less than unity for energies above the valence-electron plasma frequency (commonly 10-20 eV) [27]. The important consequence of this is the phenomena of total external reflection (in the limit of \(\beta=0\)) at material / vacuum interface below the critical angle \(\theta_c \approx \sqrt{2\delta}\). The real part of refractive index (1-\(\delta\)) exceeds unity near some X-ray absorption edges due to sign reversal of real part of atomic scattering factor. In such an “anomalous” region, total external reflection does not occur at any angle.
3. Experimental

Mo/Si multilayers (MLs) and B$_4$C thin films are deposited using an ultra high vacuum electron beam evaporation system (pressure of $\sim 2 \times 10^{-9}$ mbar). A deposition rate of $\sim 0.6$ nm/min for Mo and Si, and of $\sim 1$ nm/min for B$_4$C is maintained using a quartz crystal microbalance. The Mo (2.7 nm)/Si (6.3 nm) MLs are fabricated on float glass substrate with 5 layer pairs. B$_4$C thin film of 80 nm is deposited on float glass. The surface roughness of float glass used is 0.5 nm. Hard X-ray reflectivity measurements are carried out on the X-ray reflectometer with a Cu target (E=8047 eV). The depth graded X-ray photoelectron spectroscopy (XPS) study is carried out using photoelectron spectroscopy workstation coupled to a toroidal grating monochromator (TGM) beam line on Indus-I SR source. This workstation is equipped with an OMICRON 180° hemispherical analyzer (model EA 125) along with a twin anodes (Al $K_{\alpha}$ and Mg $K_{\alpha}$) X-ray source. The details of experimental condition are given elsewhere [32].

Angle-dependent soft X-ray reflectivity measurements were carried out using extreme-ultraviolet/soft X-ray reflectometry beamline on Indus-I synchrotron radiation (SR) source. Due to numerous atomic resonances lying in this wavelength region, it is also possible to do experiments of elemental

| Parameters                  | 10-300 eV |
|-----------------------------|-----------|
| Energy range                | 10-300 eV |
| Monochromator Type          | TGM       |
| Grating 1 (300 eV-103 eV)   | 1800 groove/mm |
| Grating 2 (103 eV-35 eV)    | 600 groove/mm |
| Grating 3 (35 eV-10 eV)     | 200 groove/mm |
| Resolving power $E/\Delta E$| 200-500   |
| Photon flux                 | $\sim 10^{11}$ photons/sec. |
| Mirror M1, M2               | Toroidal gold coated |
| Beam size at experimental station | $\sim 1$ mm x $1$ mm |

Figure 2 Optical constants for Mo, Si, MoSi$_2$, Mo$_2$Si$_3$ and Mo$_3$Si calculated as function of photon energy near the Si L-absorption edge.
Figure 3 Simulated soft x-ray reflectivity pattern of [Mo (2.7 nm)/Si (6.3 nm)]₅ ML structure at selected photon energies at Si L-edge.

identification. The reflectometer system is designed and developed indigenously, for a reflectometry beamline on Indus-1 synchrotron source [33]. The beamline provides a monochromatic photon in the wavelength range of 10-300 eV, using a toroidal grating monochromator. The resolving power of beamline i.e. E/ΔE is in the range of 200 –500. Different parameters of beamline are given in Table 1. The reflectometer chamber connected to this beamline is a big cylindrical shell of volume ~1200 liters. A θ-2θ goniometer is installed inside the chamber and is fabricated using two rotary stages of diameter 160 mm. The rotary motion of these stages is accomplished by using the stepping motors operated in micro stepping mode. The angular resolution of the reflectometer is 0.005 degree. Spring-loaded sample holder is designed for mounting the sample at a fixed reference level so that surface of the sample can be maintained at a level of goniometer rotation axis. A linear translation stage is used for mounting the sample holder that in turn is mounted on the sample rotation axis. This feature enables the measurement of direct beam intensity as sample can be retracted from the beam path. Detector arm of 200 mm length is used where a silicon photodiode detector is mounted. A versatile data acquisition and control system is developed for online monitoring and controlling various movements and signals. Using LABVIEW programming language, control software is developed. Features of various scan modes i.e. θ-2θ scan, detector scans, rocking curve scans offset scans are incorporated. Due to presence of goniometer, stepping motors, electrical wire etc inside the chamber, the base pressure limits in the range of 5×10⁻⁷ mbar. To withstand the vacuum requirement of beamline i.e. 1×10⁻⁶ mbar, a differential pumping system is constructed that allows the reflectometer to operate at ~ 1×10⁻⁶ mbar vacuum. In present configuration, the dynamic range of five orders is obtained. The present measurements are performed in the s-polarized geometry. Various research studies are pursued using this reflectometry beamline recently, for example surface deformation in the hydrogenated silicon nitride film on soft X-ray/VUV illumination [34], gas phase photo-ionization experiments [35] and optical constant measurements of different materials [36].

4. Results and discussions

4.1. Mo/Si multilayer system
The optical constants depend on the electron distribution in the materials through the atomic scattering factor as given in Eqn (9) and Eqn (10). Figure 2 shows the optical constants calculated in the energy range from 94 to 113 eV for Mo, Si and different silicide compositions, using the Henke et al [30] atomic scattering database. For the silicide phases, we have taken tabulated densities of MoSi$_2$, Mo$_5$Si$_3$, and Mo$_3$Si which are 6.24, 8.24 and 8.968 gm/cm$^3$, respectively [37]. The optical constants are calculated using weighted averages of atomic scattering factors. In the vicinity of Si L-edges (L$_{II}$=100.47 eV and L$_{III}$=99.9 eV), the optical constants of Si and its different silicide compositions change rapidly as a function of photon energy. In general, the fine structures of the optical constants near absorption edges depend on the composition of the phases. It is also clear from figure 3 that the three different silicide phases (MoSi$_2$, Mo$_5$Si$_3$ and Mo$_3$Si) of varying Si content display markedly different optical constants at the edge. The optical contrast is sufficiently large to enable observation of changes in reflectivity patterns from buried interfaces.

Figure 3 shows the effect of energy-dependent optical constants on angle dependent reflectivity $R(q_z = 4\pi \sin \theta / \lambda )$ near the Si L-edge through simulations for an ideal (without roughness) Mo/Si ML structure with varying interlayer thicknesses ($t_i$=0.5, 1 and 1.5 nm), and changing interlayer compositions. We have used Mo (2.7 nm)/Si (6.3 nm) with the number of layer pairs, $N=5$ for the simulation. The reflectivity pattern clearly distinguishes three different compositions even when the interlayer thickness is in sub-nanometer range. The refraction changes the angle of propagation of the radiation entering the ML and thus changes the angular position of Bragg peak for different compositions.

Before the soft X-ray reflectivity measurements, the micro structural parameters (such as thickness $t$ and roughness $\sigma$ etc) are obtained using hard X-ray reflectivity measurements at Cu K$_\alpha$ energy (E=8047eV). The micro structural parameter obtained from best-fit results for Mo/Si ML used in the present study are: $t_{Mo} = 2.4 \pm 0.1$ nm with $\sigma = 0.6$ nm; Si-on-Mo interlayer, $t_{So-on-Mo} = 0.8 \pm 0.1$nm with $\sigma = 0.5$ nm; $t_{Si} = 4.7 \pm 0.1$ nm with $\sigma = 0.5$ nm; Mo-on-Si interlayer, $t_{Mo-on-Si} = 1.0 \pm 0.1$ nm with $\sigma = 0.45$ nm. The asymmetry in the interlayer is due to difference in heat of sublimation of Mo and Si. This affects diffusion of Si in Si-on-Mo and Mo-on-Si case differently. The initial intermixing would be thermally activated process by the negative thermodynamic heat of mixing, because any process involving condensation from the vapor will release latent heat. The latent heat of sublimation [38] of Mo and Si is 664.5 and 450.1 KJ g-atom$^{-1}$ respectively. The thermal conductivity of Mo is higher than Si. So, the heat produced on the Si surface by the Mo ad atoms will be large and diffuse slowly due to lower thermal conductivity compared to that depositing Si on Mo surface. This may lead to a higher local temperature in Mo on Si case and hence more probability of surface diffusion for silicon. When the interlayer thickness reaches 10±0.5Å, it becomes a barrier for further surface diffusion of Si. Similarly in Si-on-Mo case, the local rise in temperature may be lower. Since Si is the dominant diffusant in Mo/Si system, therefore after arrival of Si on Mo surface, Si has to diffuse through bulk diffusion in
the Mo layer. Since the coefficient of bulk diffusion for Si is very low in low temperature range [39] and local rise in temperature is low. There is less probability of bulk diffusion and hence a thin interlayer of thickness 8±0.5 Å is formed at Si-on-Mo interfaces. When the interlayer thickness reaches 8±0.5 Å, it becomes a barrier for further bulk diffusion of Si. The best-fit result reveals the formation of a native oxide of 1.2 nm thickness with roughness of 0.5 nm on the Si layer at the top of the ML structure. The experimental data are fitted with three possible silicide phases at the interfaces. Hard X-ray reflectivity far from absorption edge is not sensitive to the composition of phases formed at buried interface. This is due to the small difference in optical constants for different interlayer composition. We have used the fine structure feature of atomic scattering factor near the Si L-edge to determine the composition of interlayer formed at buried interface. Figure 4 shows the soft X-ray reflectivity spectra measured near the Si L-edge at the selected photon energies along with the fitted curves. The experimental data are fitted for three different compositions i.e. MoSi$_2$, Mo$_5$Si$_3$, and Mo$_3$Si. For the fitting, the micro structural parameters obtained from hard X-ray reflectivity (given above) are used, and the optical constants (δ and β) are taken from figure 2 as the initial guess. The measured reflectivity profile shows an overall trend similar to that of the simulations (figure 3). For two different photon energies, good agreement between measured and best-fit curves is obtained for the MoSi$_2$ composition. The amplitude of the intensity modulation is smaller at E=100.8 eV than at E=100 eV, which is due to the increase in the effective electron density, which in turn depends on the real part of the atomic scattering factor f$_0$+δf. The best-fit results are tabulated in Table 2. At E=100 eV and 100.8
Table 2  The best-fit results of soft X-ray reflectivity measurements on Mo/Si ML with MoSi$_2$ composition at interfaces obtained by tuning at selected photon energies near Si L- absorption edge. In square brackets are the tabulated values of $\delta$ and $\beta$ from Henke et al [30].

| Energy (eV) | $\delta_{\text{Si}}$ | $\beta_{\text{Si}}$ | $\delta_{\text{Mo}}$ | $\beta_{\text{Mo}}$ | $\delta_{\text{MoSi}_2}$ | $\beta_{\text{MoSi}_2}$ |
|------------|----------------------|----------------------|----------------------|----------------------|----------------------|----------------------|
| 100.8      | -0.012 1             | 0.015 9              | 0.058 5              | 0.004 8              | 0.007 9              | 0.017 6              |
| [-0.014]   | [0.0167]             | [0.0589]             | [0.005]              | [0.0089]             | [0.0184]             |
| 100        | -0.015 5             | 0.007 4              | 0.060 5              | 0.005 1              | 0.008               | 0.0092               |
| [-0.0163]  | [0.0066]             | [0.0603]             | [0.005]              | [0.0071]             | [0.0085]             |

eV, both $\delta$ and $\beta$ values for Si and MoSi$_2$ differ significantly from those of Henke et al [30] given in Table 2 within square brackets. At the absorption edge, these discrepancies in optical constants may be due to rapid variation and/or extreme sensitivity to slight error in energy calibration or resolution. For Mo, both $\delta$ and $\beta$ values agree well with the values of Henke et al (within experimental error) for the two different energies. The fitted curves for Mo$_5$Si$_3$ and Mo$_3$Si deviate significantly from the measured data. Thus, we conclude that interlayer formed at Mo/Si interface has a composition MoSi$_2$.

The observed results obtained from soft X-ray resonant reflectivity are correlated with depth profile XPS measurements using Al K$_\alpha$ source. The survey scans of the Mo/Si ML sample indicated the presence of adsorbed oxygen and carbon only on the top surface. The narrow scans of Mo 3d spectrum for different sputtering times are shown in figure 5 along with the fitted curves. To calibrate the chemical shift at the interface, XPS spectra of Mo thin films were measured and are shown at top of figure 5. The fitted Mo 3d spectrum corresponding to virgin sample show no signal from Mo, since Si is the top surface. After 15 minutes sputtering, peaks at binding energy 227.5 eV and 230.7 eV are observed. These peaks are assigned to Mo 3d$_{5/2}$ and Mo 3d$_{3/2}$ of MoSi$_2$, respectively. During fitting all possible Mo-Si compounds are taken into account. Thus, it can be seen from the analysis of figure 5, that MoSi$_2$ is the majority compound at the Mo/Si interfaces. As the sputtering time increases, the Mo contribution from pure Mo (B.E. 227.9 eV and 231.02 eV for Mo 3d$_{5/2}$ and Mo 3d$_{3/2}$, respectively given at top of figure 5) and from the silicide MoSi$_2$ increases. At the first interface (Si-on-Mo), the maximum contribution of Mo is from MoSi$_2$. The shift in the Mo 3d$_{5/2}$ and Mo 3d$_{3/2}$ peaks are ~0.4 ±0.04 eV, with respect to pure Mo, towards lower binding energy. As the sputtering time increases (35 minutes), the Mo contribution from pure Mo increases and that of MoSi$_2$ decreases. Similarly, we have seen, at the second interface (Mo-on-Si), shift in the Mo 3d$_{5/2}$ and Mo 3d$_{3/2}$ peaks are ~0.4 ±0.04 eV, with respect to pure Mo, towards lower binding energy [32]. The Mo 3d peaks shift by ~0.4 ±0.04 eV towards lower binding energy with respect to pure Mo, suggesting the formation of the MoSi$_2$ phase [40] at both the interfaces. This result agrees well with the phase composition obtained using nondestructive soft X-ray resonant reflectivity. Our results of MoSi$_2$ composition at interfaces of Mo/Si ML system agree well with previously reported results using transmission electron microscopy [39].
4.2 B₄C thin film

Figure 6 shows optical constant (δ and β) in the energy range from 165 to 205 eV for B₄C using the Henke et al [30] atomic scattering database. In the vicinity of boron K-absorption edge (E=187.7 eV), the optical constant of B₄C change rapidly as a function of photon energy. The dispersion term of optical constant (δ) becomes negative near the K-edge, because of sign reversal of real part of forward atomic scattering factor (f₀+Δf) at the absorption edge. The reflectivity from a particular interface can be selectively tuned using the fine structure features of energy dependent optical constants at the absorption edge of constituent element.

Before the soft X-ray measurements, micro structural parameters of B₄C thin film were determined using hard X-ray reflectivity at Cu Kα energy (E=8047 eV). The best-fit results reveals thickness and rms surface roughness of B₄C film are 80.5 nm and 1.2 nm, respectively. Figure 7 shows, soft X-ray reflectivity spectra as a function of scattering vector (qₓ) of 80.5 nm thin B₄C film, at photon energies near the boron K-absorption edge. For the fitting, the micro structural parameters (such as thickness, density and roughness) obtained from hard XRR (given above) were used, and the optical constant (δ and β) are taken from figure 6 as the starting guess. The best-fit results are tabulated in Table 3. The amplitude of the intensity modulation is larger for 173 eV due to the relatively well-matched Fresnel reflection co-efficient of vacuum/B₄C and B₄C/substrate interfaces. As the photon energy increases, for 180 eV the amplitude modulation decreases. For 185.3 eV, there is no observable intensity modulation. At this energy, δ≈0 and β≈0 for B₄C (Table 3), which is close to the refractive index for vacuum (δ=0 and β=0). Therefore, at this energy B₄C becomes almost invisible and only reflection takes place from substrate. For 187.5 eV, again the amplitude of intensity modulation re-appears due to reflection from vacuum/B₄C and B₄C/substrate interfaces. As the energy increases further, the absorption in the layer increases significantly (for 188.5 eV, 192 eV and 200 eV) and intensity modulation is observed at higher qₓ values. The steep fall of reflected intensity at the critical angle is observed for 173 eV and 180 eV due to total external reflection phenomena and low absorption in the layer at these energies. In the anomalous range where real part of refractive index (1-δ) is positive (for 187.5 eV and 188.5 eV), total external reflection does not occur and hence no critical angle is observed. For the energy 192 eV and 200 eV the absorption in the layer becomes significant and hence the reflected intensity at the critical angle shows a gradual fall.
Table 3: The best-fit results of soft X-ray reflectivity measurements of B$_4$C thin films near boron K absorption edge.

| Energy (eV) | $\delta_{\text{B}_4\text{C}}$ (expt.) | $\delta_{\text{B}_4\text{C}}$ (Henke) | $\beta_{\text{B}_4\text{C}}$ (expt.) | $\beta_{\text{B}_4\text{C}}$ (Henke) |
|------------|-----------------|-----------------|-----------------|-----------------|
| 173        | 0.0059          | 0.00611         | 0.0009          | 0.00082         |
| 180        | 0.0039          | 0.00414         | 0.0005          | 0.00057         |
| 185.3      | 0.00001         | 0.00085         | 0.0003          | 0.00052         |
| 187.5      | -0.0082         | -0.00675        | 0.0007          | 0.00051         |
| 188.5      | -0.0059         | -0.00381        | 0.0082          | 0.00921         |
| 192        | 0.0014          | 0.00226         | 0.0095          | 0.00869         |
| 200        | 0.0046          | 0.00505         | 0.0081          | 0.00766         |

The optical constants obtained from best-fit angle dependent soft X-ray reflectivity measurements are shown in Table 3 along with tabulated values from Henke et al [30]. Far from absorption edge (for 173 eV, 180 eV and 200 eV), our values of optical constants agree well with Henke et al. within the experimental error. At the absorption edge, our values of optical constants are significantly different from Henke et al. At the absorption edge, these discrepancies in optical constants are due to rapid variation and/or extreme sensitivity to slight error in energy calibration or resolution and/or uncertainty in the tabulated values of Henke et al.

5. Conclusion

We present the utility of fine structure feature of the atomic scattering factor near the absorption edge for probing thin films and buried interfaces at sub-nanometer scale of low-Z materials. The atomic scattering factor undergoes sign reversal due to strong anomalous effect near absorption edges of some of the materials. It is sensitive to the composition of the constituent elements. The selected interface can be probed by tuning the incident photon energy near the atomic absorption edge of constituent element. The results reveal that the MoSi$_2$ composition is formed at both the interfaces, which agrees well with results obtained using depth graded XPS measurements. In another study, the optical constants of B$_4$C obtained from angle dependent reflectivity measurements shows anomalous behavior near the boron K-absorption edge.) We demonstrate composition specificity of soft X-ray reflectivity by tuning photon energy near the absorption edge through the characterization of B$_4$C thin film.

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