Supplementary Material:

1. Examples of calculations

This supporting material presents the results of calculations by taking an example of partially decomposed B_4C thin films sandwich with Si. The case simulation study of multicomponent system is realized in practical B_4C films also, due to presence of unknown amount of decomposition/impurity during synthesis of films and/or generally films may get contaminated to different level basically with oxygen while exposed to ambient conditions.

1.1 **Sensitivity to low contrast interface**

In order to study microstructural parameters at low contrast Si/B_4C interface system by simulation, three different ideal thin film structures are chosen with varying spatial position of B_4C layer in Si as shown in Fig. I (a). The position of B_4C layer (30 Å) is at top, middle and bottom of Si in Samples S1, S2 and S3, respectively. A thin layer (10Å) of W is kept just above the Si substrate in all three samples to provide contrast between underlying substrate and overlying Si/B_4C layers as well to isolate substrate effect in calculated R-SoXR profiles. For simulation, we choose energy 194.1 eV near B K-edge of B_4C where the optical constants of B_4C exhibit strong variation as marked by vertical dotted lines in inset. Fig. I(b) shows simulated R-SoXR spectra from three different samples. As the spatial position of the B_4C layer varies in Si the entire R-SoXR profile get modulated due to strong scattering from Si/B_4C interface. Two dotted lines in Fig. I(b) represent guide to show how interference oscillations modulated in S1, S2 and S3. The modulation in amplitude of oscillation in S2 is significantly different as expected due to two interfaces via Si-on-B_4C and B_4C-on-Si compared to S1 and S2 where only one interface is present i.e. B_4C-on-Si in S1 and Si-on-B_4C in S2. The simulated spectra clearly demonstrate R-SoXR is highly sensitivity to spatial variation of the low contrast interface even if the ideal electron density contrast at Si/B_4C interface is very poor, $\Delta\rho/\rho$ =~0.05%.

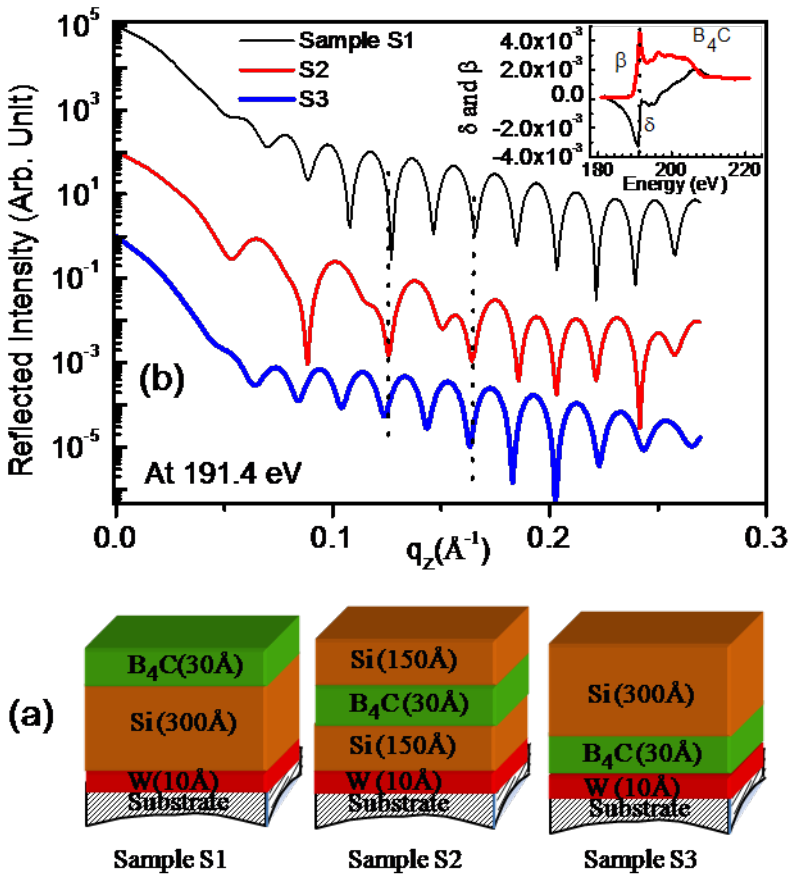

Figure I

(a) Represents the schematic layer structure of three different ideal (zero roughness) samples with varying spatial position of B_4C layer in Si. The position of B_4C is at top, middle and bottom of Si in Samples S1, S2 and S3, respectively. (b) Simulated R-SoXR spectra at B K-edge of B_4C (191.4 eV) demonstrating sensitivity to low contrast Si/B_4C interface. Two dotted lines represent guide to show how interference oscillations modulated for S1, S2 and S3. Inset shows measured optical constants (δ and β) of B_4C near B K-edge, the vertical dotted line represents the energy at which the simulated spectra are presented.

1.2 Sensitivity to atomic composition

Here we demonstrate the sensitivity of R-SoXR to the variation in atomic percent through simulations on ideal sample S1 where B_4C layer is at top of Si. Fig. II (c) shows a schematic diagram where different percent of B_2O_3 are uniformly distributed in top B_4C layer. In Fig. II (a), simulations are performed at two selected energies (194 and 194.3 eV) near B K-edge of B_2O_3 such that at these energies B_2O_3 exhibits a strong variation in optical constants as shown by two vertical lines in inset. As the content of B_2O_3 varies in B_4C, the simulated

spectral features vary significantly at these energies. Even by mixing 5 % of B_2O_3 brings significant change in optical properties of the B_4C layer which is sufficient to be observed through scattered profile (*e.g.* at 194 eV, δ changes from -4.53 $\times 10^{-4}$ to -8.33 $\times 10^{-4}$ and β changes from 2.62 $\times 10^{-3}$ to 3.41 $\times 10^{-3}$). However, in Fig. II (b), near B K-edge of elementary boron, simulated profiles undergo negligible changes by incorporation of different at. % of B_2O_3. Thus low sensitivity to B_2O_3 at these energies (189.8 and 190.7 eV) is expected due to nearly flat optical behavior of B_2O_3 which are marked by two vertical dashed lines in inset.

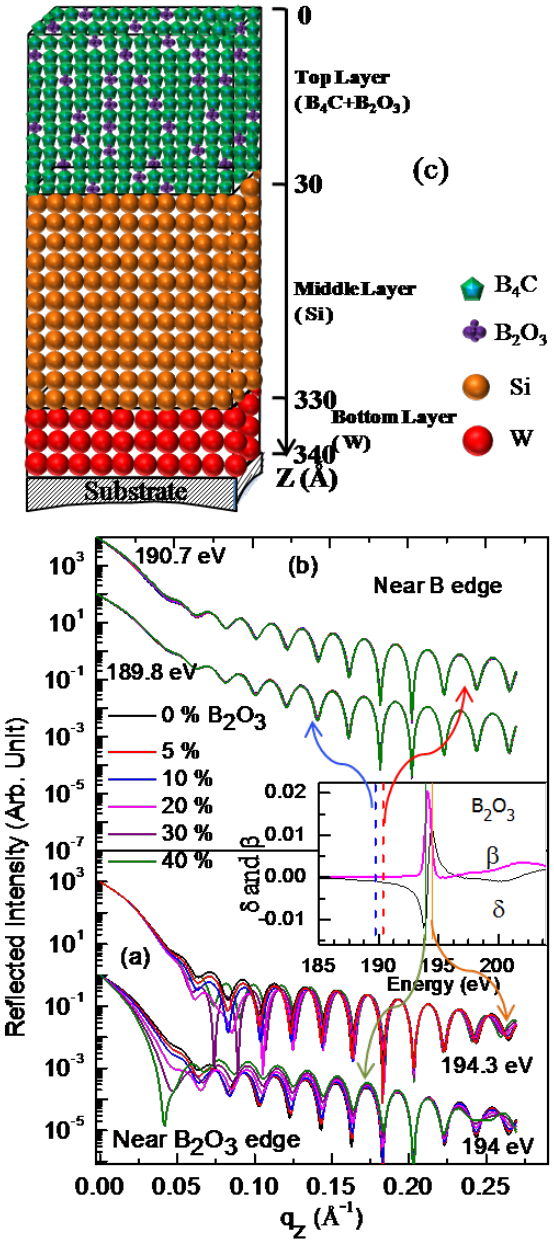

Figure II

Simulated R-SoXR profiles at different photon energies near different absorption edges for an ideal (zero roughness) thin film structures. (c) Schematic diagram of layer structure used in simulation where top B_4C layer is mixed with different atomic percent of B_2O_3. (a) Simulated profiles at two different selected energies near B K-edge of B_2O_3. The data at different energies are vertically shifted for clarity. (b) Simulated profiles at two different selected energies near B K-edge of elementary boron. Inset shows measured optical constants of B_2O_3 near B K-edge.

Similar to the sensitivity of R-SoXR to variation of content of B_2O_3 in B_4C layer near B K-edge of B_2O_3 that of elementary boron can be probe near B K-edge of elementary boron as demonstrated in Fig. III. Fig. III (b) shows a schematic diagram of ideal sample S1 where different percent of boron are uniformly distributed in top B_4C layer. In Fig. III (a), simulations are performed at two selected energies (189.8 and 190.7 eV) near B K-edge of elementary boron such that at these energies boron exhibits a strong variation in optical constants as shown by two vertical dotted lines in inset. As the content of B varies in B_4C, the simulated spectral features vary significantly at these energies. Even by mixing 5 % of B brings significant change in optical properties of the B_4C layer which is sufficient to be observed through scattered profile (*e.g.* at 189.8 eV, δ changes from -2.59 $\times 10^{-3}$ to -3.59 $\times 10^{-3}$ and β changes from 6.95 $\times 10^{-4}$ to 1.34 $\times 10^{-3}$). Thus, sensitive of the simulated resonant reflectivity profile to the variations of few at. % provides information to probe atomic compositions in the experimentally grown films by tuning energy to the respective absorption edges.

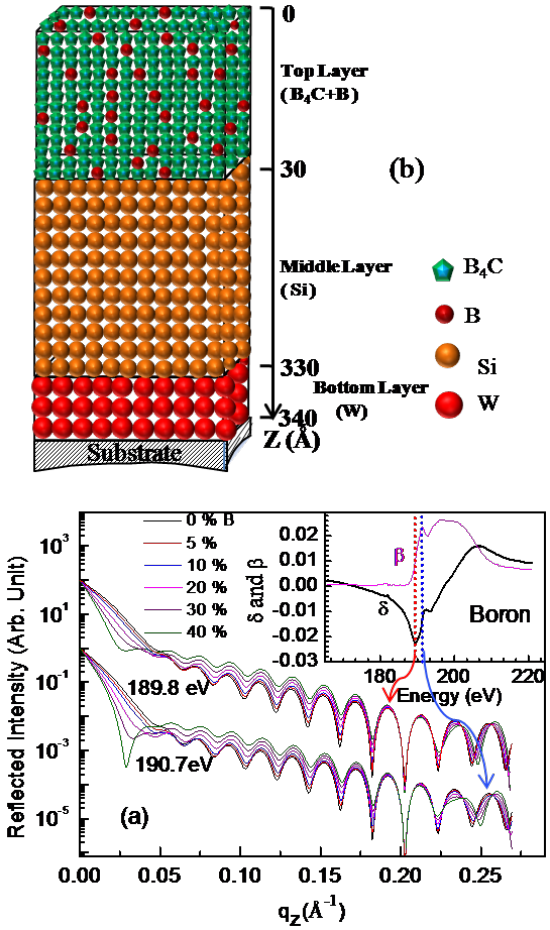

Figure III

(a) Simulated R-SoXR profiles at selected two different photon energies near B K-edge of elementary boron for an ideal (zero roughness) thin film structures. (b) Schematic diagram of layer structure used in simulation where top B_4C layer is mixed with different atomic percent of B. Simulated data at different energies are vertically shifted for clarity. Inset shows, measured optical constants of B near B K-edge.