## A.9: Compositional analysis of boron carbide thin films by resonant soft x-ray reflectivity

Boron carbide is an important x-ray optical element in both hard and soft x-ray regions. It is also an important barrier material to minimize the inter diffusion in multilayers (MLs). Boron carbide which has a very high melting and sublimation point is one of the suitable candidates for free electron laser applications. It is used as capping layer on top of the ML structure to protect ML structure from oxidation. Boron carbide is also a promising material for the next generation photo lithography applications at 6.x nm (the value of x still has to be determined by industry) wavelength. The compositional changes in the boron carbide causes significant changes in its optical constants in the vicinity of B K-edge and limits maximum achievable throughput from boron carbide based MLs. The optical band gap of boron carbide and the properties of boron carbide/Si diodes can be varied by simply changing composition of boron carbide. In many practical applications boron carbide thin films with thickness ranging from a fraction of nanometer to several nanometers have been used. It is thus important to study the thickness dependent compositional changes in boron carbide thin films.

In general ion and electron beam techniques are used to determine concentration profiles of thin films. Electron beam techniques like x-ray photo electron spectroscopy and Auger electron spectroscopy are surface sensitive and depth information is obtained by etching out the material. These techniques are destructive in nature and consequently repetitive measurements on specimen cannot be possible. Reflectivity measurements at shorter wavelengths are used to derive layer thicknesses, surface and interface roughness of thin films and MLs. However, the availability of synchrotron sources with high brilliance and tunable energy provide the opportunity for researchers to explore additional properties apart from structure using reflectivity technique. In the vicinity of the absorption edges optical index is strongly depends on the composition of layers. The reflectivity measured in the vicinity of absorption edges has opened up possibility to derive composition of thin films in nondestructive way. The angular dependence inherent to reflectivity measurements provides the depth resolution down to nm with penetration depths over hundreds of nanometers. Soft x-ray reflectivity measurements preformed in the vicinity of the B K-edge are used to estimate the composition of boron carbide thin films quantitatively. The optical constants of a multi-element layer can be written as

$$\delta = 2.7007 \times 10^{-4} \lambda^2 \rho \frac{\sum_j X_j \left( f^o_{NR,j} + f'_R(\lambda) \right)}{\sum_j X_j \mu_j}$$

$$\beta = 2.7007 \times 10^{-4} \lambda^2 \rho \frac{\sum_j X_j f''_R(\lambda)}{\sum_j X_j \mu_j}$$

where $\lambda$ is the incident wavelength [nm], $\rho$ is the density [g/cm$^3$], $X_j$ is the atomic fraction of $j$ atoms, and $\mu_j$ is the atomic weight of $j$ atoms [g/mol]. $f^o_{NR}$ is the non-resonant atomic scattering factor (ASF), $f_R'$ and $f_R''$ are the dispersion and absorption corrections to the ASF arise from the bounded electrons in an atom, respectively.

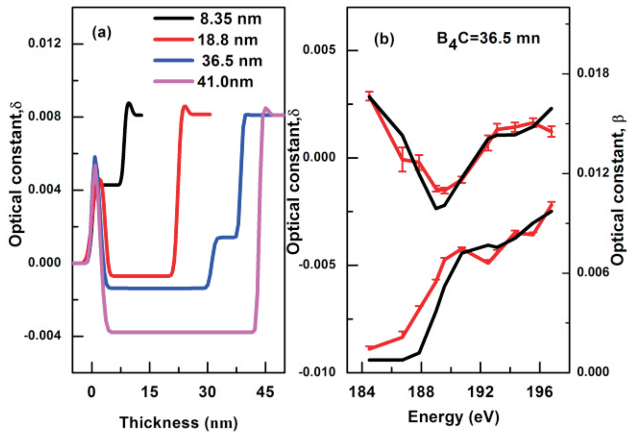


*Fig. A.9.1: (a) Showing the optical constant, δ profile obtained from the fitting of RSXR data at an energy of E=189.6 eV. (b) Showing the (color line) derived optical constant profile of born carbide film of thickness 36.5 nm in the vicinity of B K-edge (black line) model composition consisting of different atomic % (at.%) B, C and O.*

The optical index profile of boron carbide thin films of different thicknesses at an energy of E=189.6 eV are shown in Figure A.9.1(a).Optical index value increases with decreasing the film thickness. The increase in optical index value suggested that the decrease in the B atomic content in the film with decrease in thickness. A composition which gives the best fit to the experimentally derived optical constant profile shown in Figure A.9.1(b) is 63 at.% B, 32 at.% C, and 5 at.% O. In case of sample of thickness 8.35 nm, a composition which gives the best fit to the experimental data is 23 at.% B, 62 at.% C, and 15 at.% O. The atomic percentage of boron decreases with decrease in the film thickness. Such compositional changes have adverse effect on optical, electronic and oxidation properties of boron carbide. For more details, please refer to *P.N. Rao et al., Surface and coatings technology 334, 536(2018).*

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