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Mohammed Modi, Shruti Gupta, Praveen Yadav, Rajkumar Gupta, Aniruddha Bose, et al.. Study of interface reaction in a B₄C/Cr mirror at elevated temperature using soft X-ray reflectivity. *Journal of Synchrotron Radiation*, 2022, 29 (4), pp.978-984. 10.1107/S1600577522004738 . hal-03722588

HAL Id: hal-03722588

<https://hal.science/hal-03722588>

Submitted on 19 Oct 2022

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Study of interface reaction in B₄C/Cr mirror at elevated temperature using soft x-ray reflectivity

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B₄C is a prominent material for high brilliance synchrotron optics as it remains stable up to very high temperature. The present study reveals about a significant change taking place at 550°C in the buried interface region formed between the Cr adhesive layer and the native oxide layer present on the silicon substrate.

An in situ annealing study is carried out at Indus-1 reflectivity beamline from room temperature to 550°C (in step of 100°C) on a mirror like boron carbide thin film of 400 Å thickness deposited with an adhesive layer of 20 Å Cr on a silicon substrate. The corresponding changes in the film structure are recorded using angle dependent soft x-ray reflectivity measurements carried out in the region of the boron K edge after each annealing temperature. The analyses performed using the Parratt recursive formalism reveal that the top boron carbide layer remains intact but interface reaction takes place in the buried Cr-SiO₂ region. After 300°C temperature the Cr layer diffuses towards the substrate. At higher temperatures of 500°C and 550°C the Cr reacts with the native oxide layer and tends to form a low density compound of chromium oxysilicide (CrSiO_x). Depth profiling

of Si and Cr distributions as obtained from SIMS measurements corroborate the layer model obtained from the soft x-ray reflectivity analyses. Details of the interface reaction taking place near the substrate region of boron carbide/Cr sample are discussed.

1. Introduction

Artificial Bragg reflector¹ commonly known as multilayer mirror has revolutionized the field of x-ray optics particularly for low energy x-ray region (below 2000 eV) where natural crystals are not available or otherwise have limitations. In order to make a good multilayer optics its constituent layer materials should have good chemical and morphological stability besides of having good refractive index contrast and low absorption in the targeted x-ray energy region. In this quest, different material combinations have been studied and very good reflectivity performances have been achieved. Such multilayer optics have been deployed in various synchrotron beamlines^{2,3}. Many multilayers based on low Z and high Z materials combinations are being used and among those Mo/Si is one of the most popular multilayers for its high reflectivity performance in 100-200 Å wavelength range. Multilayers based on pure elements are prone to degrade early as large difference in their atomic sizes (low Z and high Z atoms) which leads to form a rough interface and thereby generates a large volume for intermixing at the interfaces. Recent development of X-ray Free Electron Laser (XFEL) sources^{4,5,6} generating ultra-short x-ray pulses have posed new challenges for x-ray optics: the need for more stable material combinations for x-ray mirrors. Particularly, x-ray pulses of very high intensity induce radiation damage in optical components and therefore numerous research works are being carried out to find out a high stability and high reflecting material combination for multilayer optics. Multilayers of compound materials are also proposed to obtain stable performances⁷ in extreme environment.

Boron carbide poses favourable thermal properties, a high melting point (~2700°C) and good thermal stability. It is a preferred material for XFEL optical applications. B₄C coated Kirkpatrick-Baez (KB) mirrors are used at Atomic, Molecular and Optical (AMO) science beamline at Linac Coherent Light Source (LCLS) at the SLAC National Accelerator Center⁸. B₄C is used as a spacer material and also as a diffusion barrier^{9,10} in multilayer optics both in soft and hard x-ray regime as it gives smooth and stable interfaces. Jiang et al¹¹ have studied W/B₄C, La/B₄C and Mo/B₄C multilayers to analyse B₄C interface behaviour with different metal species and found that the metal-on-B₄C interface is about 2-3 Å thick, and that of the B₄C-on-metal is >4 Å which seems reasonable for many applications.

Regarding B₄C performance in extreme conditions, it was reported that at AMO beamline the mirror of KB optics developed a blemish on mirror surface after about 9 months of use, as caused by intense XFEL pulse⁸. Aquila et al¹² found very high single shot damage threshold for B₄C. They have analysed single shot damage threshold fluence of 500 Å coated B₄C and ruthenium mirrors on silicon substrate using 7 and 12 keV photons. The Ru showed a cracking and ablation above the damage threshold however damage in B₄C was localized to the interface region between B₄C and the Si substrate. Contrary to other studies Morawe et al¹³ have reported a major reduction in thickness and composition of B₄C(195 Å)/Cr(21 Å)/Si stack after annealing in air at 300°C after 500 minutes annealing. After 700 minutes annealing in air at 300°C, the B₄C layer splits in two parts as top C layer of 100 Å and beneath it a 30 Å B₄C layer. In transmission electron microscopy measurement, Aquila et al¹² showed a sign of interface reaction in B₄C/Si interface, with no change in B₄C principal layer region. It is therefore desirable to investigate interface properties of B₄C layer at elevated temperatures by applying non-destructive techniques to understand interface reactions if happening at elevated temperatures and also to further establish stability issue of B₄C coating. To the best of our knowledge the interface studies on B₄C thin films using a non-destructive technique is rather scarce.

In the present study a mirror like sample of 400 Å thick boron carbide deposited on a Si substrate with 20 Å adhesive layer of chromium is studied to find out stability of boron carbide principal layer and related modifications at the interfaces at elevated temperatures up to 550°C at Indus-1 reflectivity beamline. It is found that the principal boron carbide layer remains intact however the interface region near the Cr adhesive layer and the native oxide layer on the Si substrate undergoes a significant change as Cr diffuses towards the substrate and tends to form a low density compound of chromium oxysilicide.

2. Experimental

2.1. Sample Preparation

A 400 Å thick boron carbide mirror like sample was deposited on a silicon substrate with 20 Å adhesive chromium layer using Pulsed DC Sputtering system. Prior to deposition, the substrate was ultrasonically cleaned. A commercially available 4 inches diameter B₄C target of 99.99% purity was used for deposition and argon gas of 99.99999% purity was used as a sputtering media. Before the deposition process, the base pressure in the chamber of 5×10^{-7} mbar was obtained. With Ar at 40 sccm (standard cubic centimeter per minute) flow rate,

the pressure of $\sim 3 \times 10^{-3}$ mbar was maintained in the chamber. Film thickness and deposition rate was monitored using a quartz crystal thickness monitor.

2.2. Characterizations

For the structural characterization of the thin film, grazing incident x-ray reflectivity (GIXRR) measurement was performed using a Bruker D-8 system consisting of a θ - 2θ goniometer and a Copper K_α hard x-ray source (1.54 Å). The angular step size for theta was kept as 0.005° to observe small variation in the interference fringes.

Angle dependent soft x-ray reflectivity (SXR) measurements and in situ annealing experiments have been carried out using Reflectivity beamline (BL-04)¹⁴ at Indus-1 synchrotron radiation facility. The Reflectivity beamline main optical components are a grazing incidence toroidal grating monochromator and toroidal mirrors for pre- and post-focusing optics. The beamline is designed to cover 10-300 eV photon energy range. Different harmonic suppression edge filters are installed in the beamline to reduce higher harmonic contamination¹⁵. Further details of the beamline can be found in Ref. [14].

The experimental station in this beamline is a high vacuum reflectometer¹⁶. The goniometer assembly of reflectometer station comprises of two rotary stages and one linear stage. The two rotary stages can be moved in coupled and uncoupled mode to carry out different modes of reflectivity i.e. detector scan, rocking curve scan, θ - 2θ scan etc. The linear stage is employed to bring the sample in and out of the direct beam, to facilitate the direct beam monitoring. Silicon XUV photodiode is used to monitor reflected beam intensity. To perform in situ annealing experiments, a sample heater made of boron nitride is mounted on the sample stage with custom designed housing.

Energy dependent SXR measurements in near vicinity of boron K edge (188 eV) was carried out using soft x-ray reflectivity beamline (BL-03)¹⁷ of Indus-2 synchrotron source. The beamline is equipped with a varied line spacing plane grating monochromator (VLS-PGM) which operates in constant deviation angle geometry. The beamline provides photons in the energy range of 100-1500 eV with moderate resolving power of 1000-6000 using three gratings with line densities of 150, 400 and 1200 l/mm. The beamline operating in ultra-high vacuum environment is separated from the experimental station working in $\sim 10^{-7}$ mbar using a custom designed differential pumping system. The reflectivity measurements were performed in s-polarization geometry with the goniometer working in a vertical dispersion geometry. The reflected beam from the sample is measured using a Si

photodiode detector (International Radiation Detectors Inc., USA) with 100% internal quantum efficiency.

To improve the spectral purity of the monochromatic light coming from the VLS-PGM, a three mirror based higher order suppressor (HOS) was used. The three mirrors have a stripe coating of four different materials i.e. carbon, chromium, silicon and nickel. In order to efficiently suppress the higher harmonics in 60-225 eV range a stripe of carbon coating is used. During the operation of the HOS the three mirrors can be set in the beam path with similar coatings on respective mirrors. The HOS setup improves the spectral purity and reduces the harmonic components below 0.1%.

ToF-SIMS measurements were performed using Cs^+ ion gun operating at 1 keV (TOFSIMS-5, IONTOF) to sputter the sample. However, the analysis was carried using Bi^+ ions operating at 30 keV, 4.7 pA. The analysis area was $100\text{ }\mu\text{m} \times 100\text{ }\mu\text{m}$ inside the sputter crater of $300\text{ }\mu\text{m} \times 300\text{ }\mu\text{m}$.

The Parratt recursive formalism¹⁸ was used for the analysis of the measured reflectivity data. The surface roughness effect was taken into account using Névot-Croce model¹⁹. The fitting of the experimental data is carried out using a Labview based SRxrr tool²⁰. This tool has many unique features as it considers higher-harmonic effect, polarization factor, beam divergence, and background noise. This tool calculates reflectivity and transmission both as a function of angle and photon energy/ wavelength.

3. Results and discussions

GIXRR

Figure 1 shows the measured and fitted GIXRR curves of 400 Å thick boron carbide thin film. In order to obtain a best fit of the GIXRR data, various models were tried but the best fit was obtained using a four-layer model which is shown in the inset of the Figure 1. The model consists of a native oxide layer on the Si substrate, a thin Cr layer as used for improving the film adhesion, a principal boron carbide layer and a top surface layer arising due to interaction of the surface with the ambient. The values of thickness, roughness and real part of refractive index (δ) of native oxide layer, Cr layer, principal boron carbide layer and top surface layer as obtained from the best fit of as deposited sample are mentioned in the Table 1. Electron density profile (EDP)²¹ of the sample as obtained from the GIXRR analyses is plotted in the Figure 2, which represents density variation across the depth of the

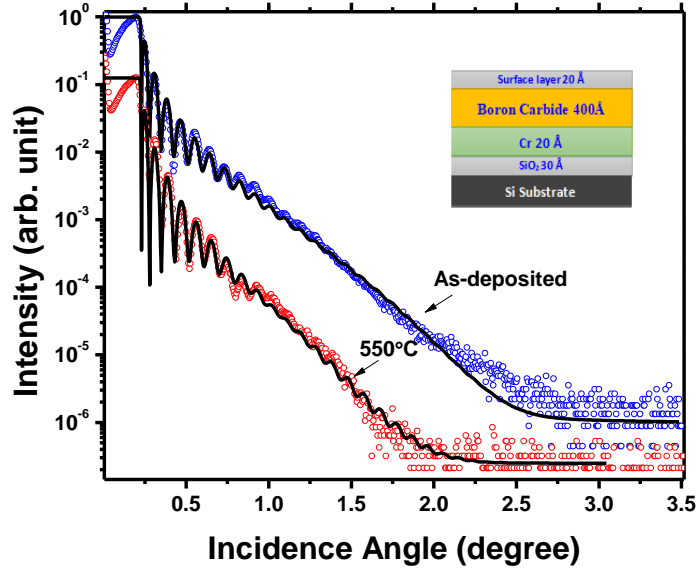


Figure 1: Measured (open circles) and fitted (continuous line) GIXRR curves of as-deposited and 550°C annealed boron carbide/Cr bilayer samples are shown. The layer model used to obtain best fit is also shown. For the sake of clarity, the curves are vertically shifted.

Table 1: GIXRR fit parameters of boron carbide/Cr as-deposited sample

Layer	Thickness Å	Roughness Å	delta
Surface layer	26	11.0	6.110×10^{-6}
Boron Carbide	431	8.0	7.063×10^{-6}
Cr	15.7	5.7	2.303×10^{-5}
SiO ₂	40.0	4.6	7.453×10^{-6}
Si Substrate	-	5.0	7.577×10^{-6}

sample. It is evident from the EDP that the boron carbide thin film is uniform across the depth except near the air/film region where it forms a low density surface layer due to reaction with the ambient. Near the film/substrate region a peak in the EDP corresponds to thin Cr layer which was deposited for improving the adhesion with silicon substrate. Thickness of the Cr layer is found to be 15.7Å which is slightly less than the targeted thickness value of 20Å. A tiny dip at the film/substrate region as indicated by an arrow is corresponding to the native oxide layer. Since the delta value of bulk SiO₂ is 7.122×10^{-6} which is slightly less than the delta value of bulk Si (7.577×10^{-6}), this difference gives rise to a dip in the density profile. In the present case of as-deposited sample this dip is not prominent because the fit value of SiO₂ delta is found slightly higher by ~4.4% (7.453×10^{-6}).

⁶). For the as prepared sample the density of the boron carbide layer is found to be 2.33 g/cm³ which is 91.7% of the bulk density (2.54 g/cm³).

In order to analyze the behaviour of the interfaces in the boron carbide/Cr bilayer at elevated temperatures, the same sample was annealed up to 550°C in step of 100°C for 2

Table 4: GIXRR fit parameters of boron carbide/Cr after 550°C annealing

Layer	Thickness Å	Roughness Å	delta
Surface layer	21.6	11.0	5.410×10^{-6}
Boron Carbide	428.0	7.0	7.103×10^{-6}
Cr	10.7	8.7	2.303×10^{-5}
SiO ₂	30	7.5	7.253×10^{-6}
Si Substrate	-	5.0	7.577×10^{-6}

hours at each temperature. The annealing experiments were carried out in reflectometer station at Indus-1 reflectivity beamline in $\sim 1 \times 10^{-6}$ mbar vacuum. After each annealing experiment an angle dependent SXR data were recorded in situ as discussed in the next section. The in-vacuum heater assembly mounted on the goniometer supports temperature up to 550°C. Thereafter the sample was taken out and further characterized using GIXRR measurement.

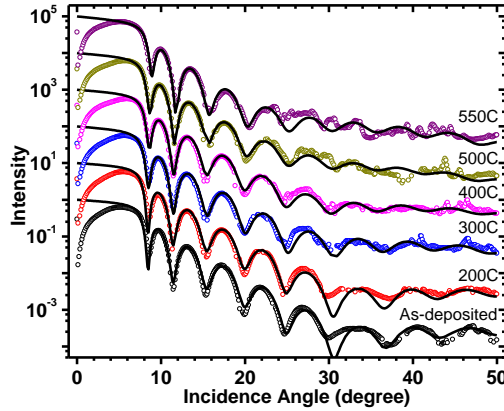


Figure 3: Measured (open circles) and fitted (continuous line) soft x-ray reflectivity curves of as-deposited and annealed samples using 155 eV incident photon energy (80\AA).

Figure 2: Electron density profile of as-deposited and 550°C annealed boron carbide/Cr bilayer samples as obtained from the GIXRR fit.

The measured and best fitted GIXRR curves of 550°C annealed sample are shown in Figure 1. The parameters of the best fitted curve of the annealed sample are mentioned in Table 2. After the 550°C annealing the boron carbide layer thickness slightly decreased from 431 \AA to 428 \AA ($\sim 0.6\%$ drop) whereas its density is increased in similar ratio from 2.33 g/cm^3 (91.7% of bulk value) to 2.35 g/cm^3 (92.5% of bulk value). The roughness of the principal boron carbide layer does not change much, it reduced from 8.0\AA to 7.0\AA . After the annealing, the electron density profile as shown in the Figure2 indicates that a major change is taken place near the Cr film region. The effective electron density of Cr layer is reduced from $1.97\text{ e}^-/\text{\AA}^3$ (as-deposited) to $1.4\text{ e}^-/\text{\AA}^3$ (550°C annealed sample). After the annealing at 550°C , thickness and density of the boron carbide layer have not changed much. The EDP suggest a major change in the Cr layer region which is likely be due to interaction between the Cr layer with the native silicon oxide layer. The GIXRR technique is less sensitive to find out any changes taking place in the SiO_2 layer because of poor refractive index contrast between Si and SiO_2 . Therefore to get more insight about the changes taking place in the SiO_2 layer due to its interaction with the Cr layer, the in situ SXR data taken during the annealing experiments are analyzed as discussed in the next section.

Soft x-ray reflectivity

Angle dependent SXR data measured after each annealing temperature is shown in Figure 3. The boron carbide/Cr bilayer shows distinct interference fringes up to 50° glancing angle.

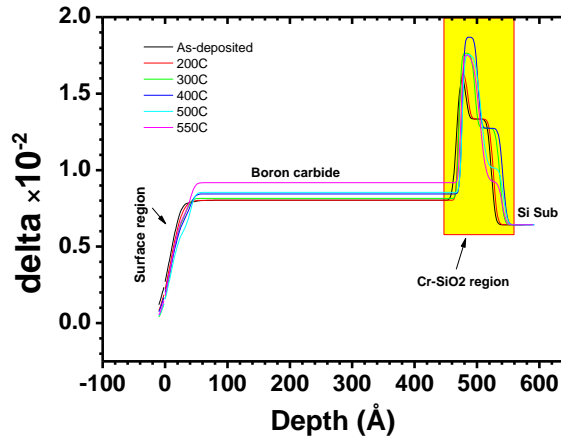


Figure 4: Optical density profile obtained from the best fit of SXR data taken after each annealing temperature. Region in box is zoomed out and shown in Figure 6.

The fringe pattern has a good contrast up to 550°C annealing temperature. These SXR data are analyzed using the same structural model as used for GIXRR analyses. For as-deposited sample the structural parameters obtained from the GIXRR analyses are used and kept fixed while the SXR fitting and only the δ (refraction) and β (absorption) parameters are varied to obtain a best fit. For high temperature, the structural parameters (thickness, roughness) are also considered as fitting variables in order to account any changes happening in the the film structure at the elevated temperatures. For the SXR data of 550°C, again structural parameters as obtained from the GIXRR analyses of 550°C annealed sample are used and only δ , β are varied. After a rigorous SXR data fitting the final optical density profile (delta profile) of the boron carbide/Cr bilayer for each temperature are obtained and plotted in the Figure 4. Contrary to the EDP profile obtained from the GIXRR data (Figure 2) the SXR analyses suggest a clear change taking place near the Cr-SiO₂ region upon annealing along with some minor change in the principal film region. Optical density of the boron carbide layer is increased by ~14% whereas its layer thickness is marginally decreased by 2 Å (< 0.5%) on annealing from room temperature to 550°C. Both GIXRR and SXR analyses confirms a 2-3 Å decrease in the principal boron carbide layer thickness after the annealing. The SXR analyses show a gradual increase in the delta values of the boron carbide layer from 8.02×10^{-3} (for as-deposited sample) to 9.17×10^{-3} (550°C annealed sample). The delta value of stoichiometric bulk boron carbide is 1.02×10^{-2} , which is found ~20% lower for as-deposited sample and ~10% lower for 550°C annealed sample. This indicates that upon the annealing the deposited boron carbide thin film is becoming more stoichiometric. The

change in stoichiometry of the principal layer is further confirmed from the energy dependent SXR data measured near the boron K edge region in which an edge shift of ~ 1.0 eV towards higher energy is observed after the annealing at 550°C (see Figure 5a).

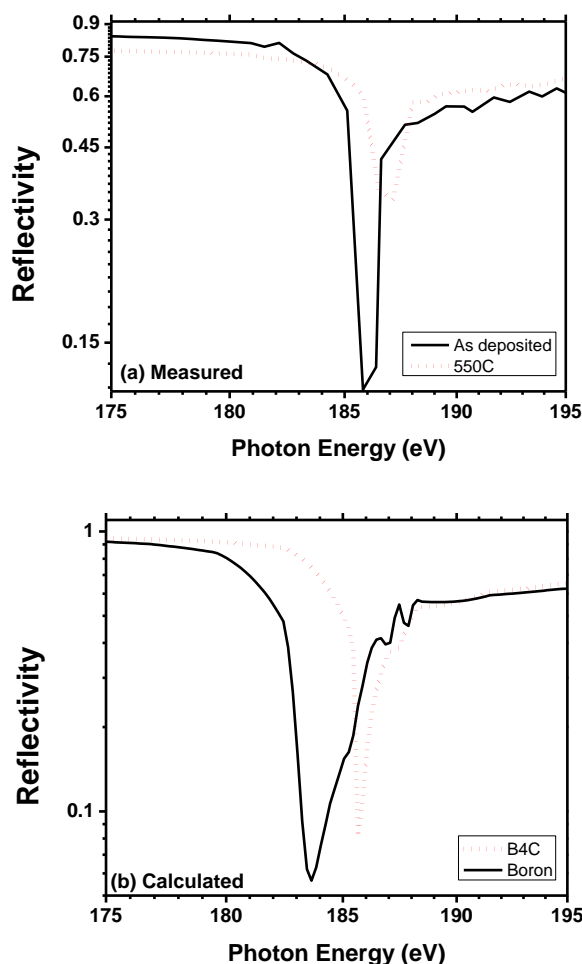


Figure 5: (a) Measured energy dependent soft x-ray reflectivity of boron carbide /Cr bilayer at 1.5° grazing incidence angle for as-deposited and 550°C annealed sample. (b) Calculated reflectivity of stoichiometric B_4C and boron is compared .

The energy dependent SXR data as measured before and after the annealing at fixed 1.5° glancing incidence angle are shown in Figure 5a. A prominent dip in reflectivity spectra of pristine sample is observed at 186 eV whereas for annealed sample it is shifted near 187 eV. In case of pristine sample the dip is strong indicating the film is boron-rich as higher boron content causes increased absorption near its K edge region that in turn lowers the reflectivity value. The calculated curve of boron is compared with that of B_4C in Figure 5b where it is obvious that the dip is prominent in boron case and it shifts towards higher

energy for boron carbide. In literature the reported K edge value of bulk boron is 188 eV²² whereas for stoichiometric B₄C the reported value of edge lies in 189-191.6 eV range^{23,24}. In x-ray absorption measurement performed on boron rich carbide film (B₁₁C), Jimenez et al²³ observed the boron K edge at 187 eV. In present case of 400 Å thick boron carbide film the position shifts of ~1.0 eV towards higher energy upon annealing at 550°C indicates

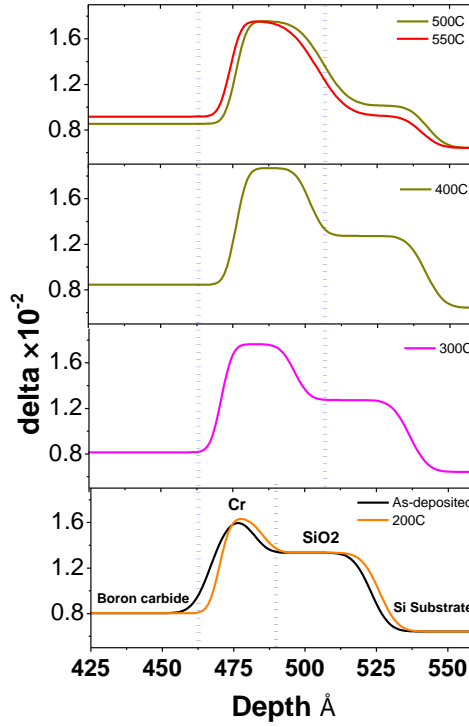


Figure 6: Optical density profile of Cr-SiO₂ region is plotted for each annealing temperature.

about increase in stoichiometric nature of pulsed DC sputtering grown boron carbide thin film.

Coming back to Figure 4 where the Cr-SiO₂ region shows an interesting change upon annealing, this region is zoomed out in the Figure 6 and curves are plotted separately for each annealing temperature. At 200°C, the Cr-SiO₂ region does not change much, however at 300°C annealing the thickness of Cr region increases from 15Å to 25Å whereas the SiO₂ region thickness remains unchanged at 40Å. Increase in Cr region thickness suggests a possible swelling of Cr layer due to oxidation as it interacts with nearby native oxide layer. Since the density of bulk Cr is 7.19 g/cm³ and bulk Cr₂O₃ is 5.22 g/cm³, oxidation of Cr atoms causes a decrease in film density and that in turn increases the film thickness. At higher temperatures (>400°C) probability of Cr interaction with Si and oxygen atoms to

form a oxysilicide phase increases as indicated from decrease in delta value of Cr region for 500°C and 550°C temperature with respect to that of 400°C temperature value. For 80 Å probing wavelength the delta value of bulk Cr is 2.84×10^{-2} and bulk CrSi_2 is 0.61×10^{-2} . Kuznetsova et al²⁵ have reported the formation of CrSi_2 at the interface of 300 Å thick Cr film on silicon substrate after the rapid thermal annealing at $>400^\circ\text{C}$ temperature. Furthermore, the delta value of SiO_2 region decreases from 1.33×10^{-2} to 9.23×10^{-3} and it is tending towards Si delta value of 6.42×10^{-3} . This indicates that the native oxide layer is shrinking upon annealing.

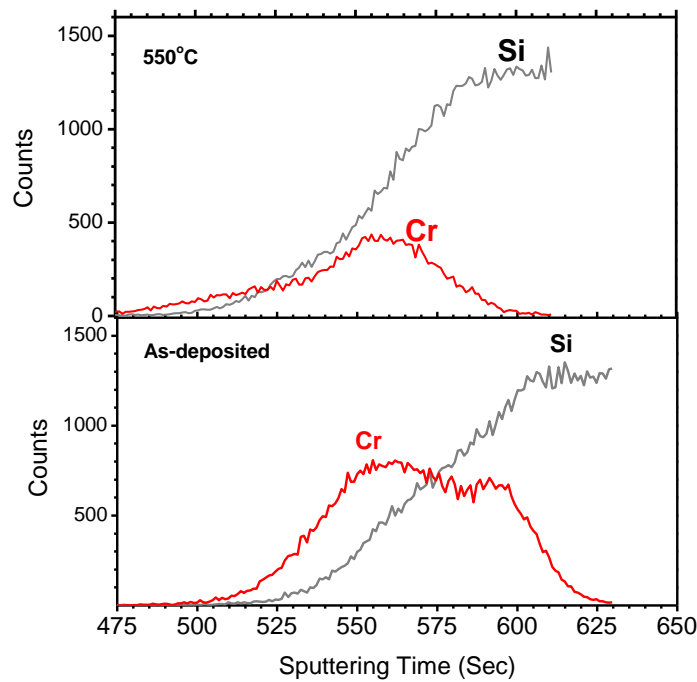


Figure 7: Cr and Si distributions in the bilayer sample as obtained as a function of sputtering time from SIMS measurement . In the figure only Cr-SiO₂ region is shown.

To corroborate the interface model deduced from the SXR analyses a SIMS measurements were carried out on as-deposited and 550°C annealed sample. The SIMS data confirms no change in boron carbide principal layer upon the annealing. The SIMS profile of Cr-SiO₂ region is plotted in the Figure 7 where the distributions of Cr and Si atoms are shown as a function of sputtering time. In the as-deposited sample the Cr signal starts after 500 sec and Si starts after 525 sec. The Si signal rises steadily and reaches to constant level once it enters in substrate region. Therefore the steadily rising reason of Si belongs to native oxide layer and then the flat region belongs to the Si substrate. The distribution of Cr shows its spread in wide region where some Cr lies before the native oxide layer and some Cr inside

the native oxide region. After the annealing the SIMS data indicate that the Cr atoms diffuse inside the native oxide layer as it is found in the SXR analyses also. The major portion of Cr lies inside the native oxide region where it is likely to form a oxysilicide phase as no independent Cr layer exist after the 550°C annealing as per the SIMS measurement. The SIMS data corroborate the SXR model indicating diffusion of Cr towards the native oxide region. Contrary to the SXR model the SIMS measurement shows a shrinkage in Cr region upon the annealing. This could be due to variation in sputtering yields of Cr and CrSiO_x. Beside this contradiction, both SIMS and SXR analyses clearly indicate an interface reaction in Cr-SiO₂ region in boron carbide mirror like sample where Cr diffuses towards substrate upon the annealing at 550°C temperature. The GIXRR analysis was able to indicate about reduction in film density in Cr region after 550°C annealing whose details could be unfolded with soft x-ray reflectivity.

4. Conclusions

A mirror like sample of 400 Å thick boron carbide thin film is deposited with 20 Å Cr adhesive layer on a silicon substrate and it is studied for interface reaction by performing in situ annealing experiments. The sample is annealed in situ from room temperature to 550°C in step of 100°C for 2 hours at each temperature. GIXRR, SXR and SIMS data revealed that the boron carbide layer is stable and its structural properties does not affect upon the annealing. However a significant change is observed at the Cr/Substrate interface region due to reaction of Cr layer with the native oxide layer present on the silicone substrate. The GIXRR measurement indicated a reduction in Cr density upon the annealing whose details could be unfolded with the SXR analyses. SXR analyses showed a diffusion of Cr towards the Si substrate and formation of low density compound of chromium oxysilicide due to reaction of Cr with Si at the elevated temperature. SXR could reveal subtle details about evolution of buried interfaces beneath the 400 Å thick boron carbide layer whose results are corroborated by SIMS measurement.

The SXR analyses give a clear insight about interface reaction at the buried Cr/ SiO₂ interface in a non-destructive manner. Such buried interface lying underneath a thick film of 400 Å is very difficult to analyze by other means as other techniques primarily depends on sequential sputtering and subsequent measurement of sputtered species. X-ray photo electron spectroscopy, and secondary ion mass spectroscopy have such limitation and also poses certain artifacts coming from sputtering process and also scaling (convert sputtering

time to depth) is difficult because of large variation in sputtering yield among different elements.

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