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► **To cite this version:**

Jingtao Zhu, Jiayi Zhang, Haochuan Li, Yuchun Tu, Jinwen Chen, et al.. Improving the soft X-ray reflectivity of Cr/Ti multilayers by co-deposition of B₄C. *Journal of Synchrotron Radiation*, 2020, 27 (6), pp.1614-1617. 10.1107/S1600577520011741 . hal-02995210

HAL Id: hal-02995210

<https://hal.science/hal-02995210>

Submitted on 9 Jan 2023

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Improving the soft x-ray reflectivity of Cr/Ti multilayers by deposition of B₄C

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Synopsis Systematic analysis on interfaces of Cr/Ti multilayer has been performed in this work. The near-normal incidence reflectivity increases from 4.48% to 15.75% at wavelength of 2.73nm using co-deposition of B₄C.

Abstract “Water window”, covering from 2.4 nm to 4.4 nm, is an important wavelength range especially essential to biology researches. Cr/Ti multilayers are one of the promising reflecting elements in this region because their near-normal incidence reflectivity is theoretically as high as 64% at 2.73 nm. However, due to multilayer imperfections, the reported reflectivity is lower than 3% for near-normal incidence. We intentionally incorporated boron and carbon into ultra-thin Cr/Ti soft x-ray multilayers by co-deposition of B₄C at the interfaces. The effect on the multilayer structure and composition has been investigated using x-ray reflectometry, x-ray photoelectron spectroscopy and cross-section electron microscopy. It is shown that B and C are mainly bonded to Ti atoms, forming a non-stoichiometric TiB_xC_y compound, which hinders the interface diffusion, suppresses the crystallization of layers and dramatically improves the interface quality of Cr/TiB_xC_y multilayers. As a result, the

near-normal incidence reflectivity in the soft x-ray range increases from 4.48% to 15.75% at wavelength of 2.73 nm.

Keywords: Synchrotron radiation; multilayer; interface; Cr/Ti

1. Introduction

Multilayer coatings for the soft x-ray region have drawn a great deal of attention due to their vital importance in high-resolution microscopes, deep-space telescopes and soft x-ray polarimetry.(Artyukov *et al.*, 2009, Windt *et al.*, 2004, Kitamoto *et al.*, 2010) In these applications, reflectivity is one of the most critical parameters of a multilayer. Cr/Ti multilayers are one of the suitable candidates in the “water window” wavelength range (2.4–4.4 nm) because the theoretical near-normal incidence reflectivity is as high as 64% at wavelengths just above the Ti 2p edge (2.73 nm). However, the reported reflectivity of real Cr/Ti multilayers at near-incidence angles is lower than 3%.(Ghafoor *et al.*, 2006) The large disparity between the theoretical and measured reflectivity is caused by several physical limitations, among which the most important is the interfacial imperfections, especially for ultra-short periods ($\Lambda \sim 1.4$ nm) used.

In recent years there has been a huge effort to develop techniques that can reduce the interface width of multilayers. One recent attempt involved the intentional incorporation of light-element impurities such as N into multilayers. It has been shown that the incorporation of N in Cr/Sc(Ghafoor *et al.*, 2008) or B₄C/La(Tsarfati *et al.*, 2010) multilayers can form nonstoichiometric nitride multilayers with reduced interdiffusion or reaction between the constituent layers and leads to major improvement of soft x-ray reflectivity. Another scheme is the introduction of B₄C, which have been found effective in Cr/Sc(Ghafoor *et al.*, 2017) and Cr/V(Huang *et al.*, 2016) system. Concerning Cr/Ti multilayers, B or C is a better choice than N because of a stronger absorption of N in the application wavelength range of Cr/Ti multilayers, which is at a slightly lower wavelength than the N K edge (3.02 nm). In this work, we intentionally incorporated B and C during deposition and investigated the microstructure and optical performance of the multilayers.

2. Fabrication

The Cr/Ti multilayers were deposited by DC magnetron sputtering system with B and C impurities incorporated by the deposition of ultra-thin B₄C at the interfaces of Cr/Ti multilayers. All the multilayers were deposited onto natively oxidized Si (001) wafer with a roughness of 0.3nm. The pressure of residual gas before deposition was 5.0×10^{-5} Pa and that of Ar sputtering gas was 0.13 Pa with a purity of 99.999%. Sub-nm thin layers were obtained by optimizing target-substrate distances and magnetron power. Target-substrate distances were all

8 cm. The magnetron power of B₄C, Cr and Ti were 40 W, 20 W and 40 W respectively. Experimental details can be found in the PhD thesis by Yunchun Tu (Tu, 2015).

3. Characterization for the interfaces of Cr/Ti multilayers

Firstly, we studied the effect at interfaces of different amounts of the incorporated B₄C. We deposited a series of Cr/Ti multilayers, which can be divided into four groups. All the multilayers were designed with period number N=50. B₄C was incorporated at both Cr-on-Ti and Ti-on-Cr interfaces for the first group, only at Cr-on-Ti interfaces for the second group, and only at Ti-on-Cr interfaces for the third group. The multilayers in those three groups were deposited with the same thicknesses of Cr layers and Ti layers ($d_{Ti}=d_{Cr}=0.7$ nm). Each of those three groups consisted of six multilayers with different amounts of B₄C, where one multilayer had no B₄C, and the nominal amounts (in thickness) of B₄C for the other five multilayers were 0.08, 0.13, 0.18, 0.22 and 0.27 nm, respectively. For comparison, the last group contained four pure Cr/Ti multilayers without B₄C. The period thicknesses of the four groups of multilayers ranged from 1.4 nm to 1.7 nm and their thickness ratio ($\Gamma=d_{Cr}/\Lambda$) was ~ 0.5 .

All the multilayers were characterized by low angle x-ray reflectometry (XRR). Measurements were performed on a Bede D1 diffractometer with a Cu x-ray source ($\lambda=0.154$ nm). Only the first order Bragg peak could be observed for each multilayer because of the ultra-short period. We present the peak reflectivity as a function of the grazing incident angle in Figure 1, where thicker multilayers correspond to the smaller grazing angle (left side). It can be noticed that incorporating B₄C at either or both interfaces leads to higher reflectivity, namely, improves multilayer quality. In particular, it is better to incorporate B₄C at the Cr-on-Ti interfaces than at the Ti-on-Cr interfaces, and incorporating B₄C at both types of interfaces is the best of all. Thickness of 0.13 nm B₄C is chosen because the fitted roughness is lowest.

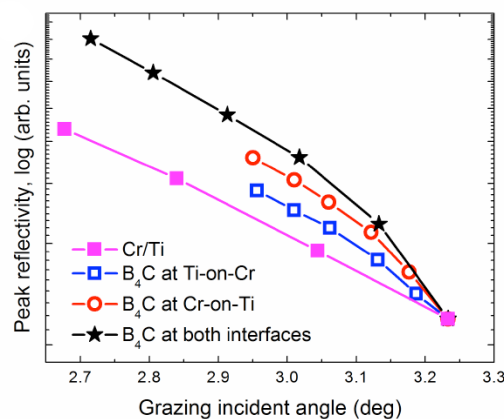


Figure 1 (color online) Peak reflectivity versus peak angle of the first order Bragg peaks in the XRR curves of the Cr/Ti multilayers. Symbols represent the data and solid lines are only guides for the eyes.

In order to study the interface stoichiometry, we performed x-ray photoelectron spectroscopy (XPS) on two samples. One had no B₄C incorporated and the other had 0.13 nm thick B₄C at both interfaces. The measurements were performed on a Thermo Scientific K-Alpha system with an Al K α source. The binding energy scale was calibrated from hydrocarbon contamination using the C 1s peak at 285.0 eV. A non-linear Shirley-type background was subtracted from the raw spectra. The peak positions and areas of core level peaks were optimized by a weighted least-squares fitting method using 70% Gaussian, 30% Lorentzian line shapes. Atomic concentrations were calculated on the basis of Scofield's relative sensitivity factors. To eliminate the contamination of the multilayer such as the oxidation at the surface, the XPS spectra were recorded after ~10 nm were removed at the surface by argon etching. Considering the ultra-short period and the estimated analysed depth it is safe to regard the recorded spectra as averaged over the whole multilayer period. It should be, for some material combinations, that the chemical interaction of materials in the multilayer may change after energetic Ar⁺ ion bombardment. However, in a previous research on XPS study of Pb/B₄C multilayer (Supruangnet *et al.*, 2016), C1s core level remained the same as pure carbon after Ar⁺ etching. B1s core level shifts only because of the change from boride phase to oxide compound. Pb 3d_{3/2} and Pb 3d_{5/2} core levels for pure plumbum remained the same while the only change occurs in the oxidation of Pb compound. It can be confirmed that Ar⁺ etching will not introduce extra chemical interaction in B₄C-based multilayers.

(new paragraph)The Cr 2p and Ti 2p spectra of the two multilayers show no difference in peak position, which is probably due to the small chemical shifts of possible compounds (<0.2eV for CrB₂ or TiB₂). (Wanger *et al.*, 1979) The B 1s and C 1s spectra of the multilayer with B₄C are shown in Figure 2 along with the spectra of a B₄C monolayer reference sample which was deposited and measured by the same method described above. The B 1s spectrum of the monolayer consists of two peaks at 188.4 eV, characteristic of B–B or B–C bond from B atoms in the B₁₂ icosahedra, and 190.6 eV, characteristic of B–C bond from B atoms in the C–B–C chain. The B 1s spectrum of the Cr/Ti multilayer is dominated by a peak at 187.4 eV which is attributed to TiB₂ (187.5 eV) (Mavel *et al.*, 1973) rather than CrB₂ (188.0 eV). (Mavel *et al.*, 1973) The C 1s spectrum of the monolayer consists of two peaks at 282.8 eV, characteristic of B–C bond in the icosahedra, and 284.1 eV, characteristic of B–C bond in the C–B–C chain. The C 1s spectra of the Cr/Ti multilayer is dominated by a peak at 281.9 eV which is attributed to TiC (281.7 eV) (Galuska *et al.*, 1988) rather than Cr₃C₂ (282.9 eV). (Goretzki *et al.*, 1989) For the pure Cr/Ti multilayer, the atomic concentrations of Cr, Ti, and O are 58.9%, 27.8%, and 13.4%, respectively. For the Cr/Ti multilayer with B₄C, the atomic concentrations of Cr, Ti, B, C, and O are 47.8%, 22.9%, 17.1%, 4.4% and 7.9%, respectively. There are two reasons why there is less oxygen in Cr/B₄C/Ti/B₄C multilayer: firstly, B₄C can hinder the diffusion of oxygen to inner layers; secondly, with the deposition of B₄C, imperfection of grain boundary

can be decreased and thus there occur less ways of oxygen diffusing into inner layers. According to the calculated results, different concentrations of oxygen will not influence the reflectivity.

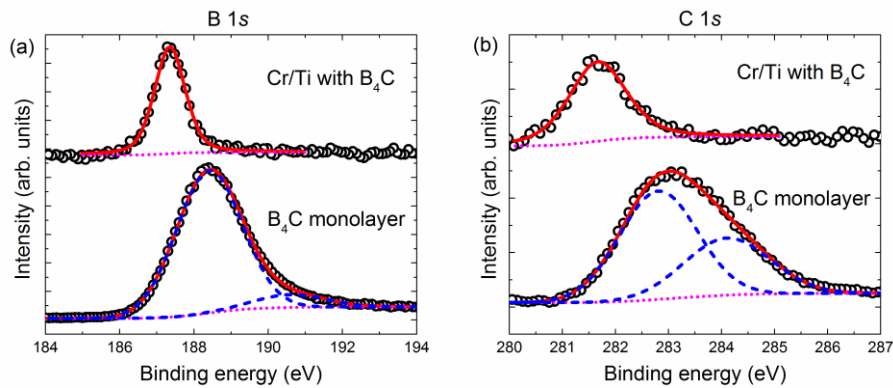


Figure 2 (color online) (a) B 1s and (b) C 1s XPS spectra of the B₄C monolayer and Cr/Ti multilayer with B₄C. Open symbols represent the measured data, solid lines the fitted spectra, short dashed lines the background, and long dashed lines the peaks used in the fitting if more than one peak is involved.

Encouraged by the preliminary results, we deposited two Cr/Ti multilayers, one without B₄C and the other with 0.13 nm thick B₄C at both interfaces, which can work as high reflection mirror for wavelength $\lambda=2.73$ nm (453.5 eV photon energy). The period number is $N=600$ and the designed period thickness is $\Lambda=1.38$ nm. Figure 3 shows the cross-section transmission electron microscopy (TEM) images of the two samples measured using an FEI microscope (Tecnai G2 F20). The multilayer with B₄C shows much better contrast between Cr layers and Ti layers although the flatness is similar. Figure 4 presents the selected area electron diffraction (SAED) results of Cr/Ti multilayers with and without B₄C. The diffraction ring and spots weakened after e^- -deposition of B₄C. The crystallization in Cr/Ti multilayer has been suppressed. These results ~~confirm~~ show that the TiB_xC_y formation prevents diffusion of Cr.

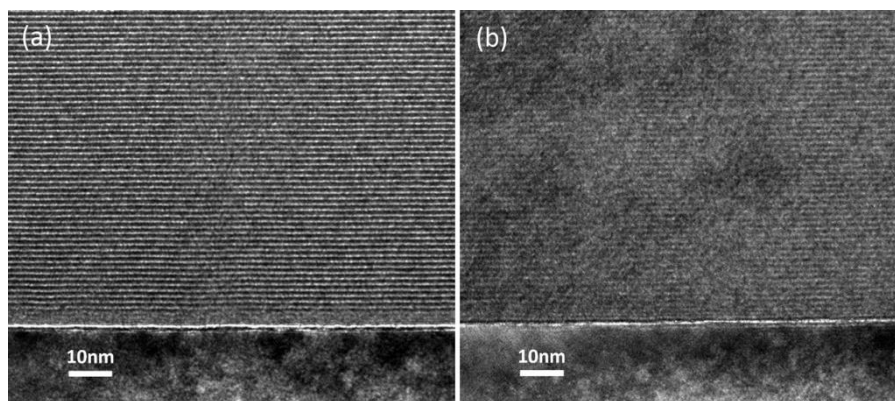


Figure 3 Cross-section TEM graphs of Cr/Ti multilayers (a) with and (b) without B₄C.

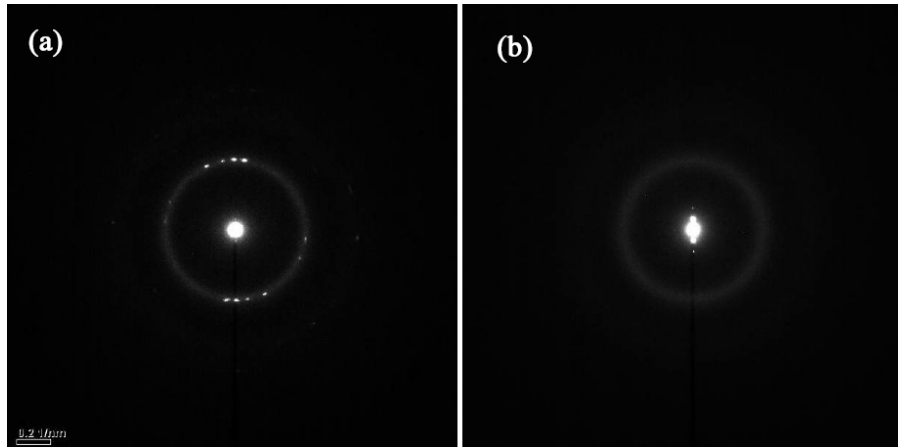


Figure 4 SAED (selected area electron diffraction) results of (a) Cr/Ti multilayer and (b) Cr/B₄C/Ti/B₄C multilayer.

4. Reflectivity measurements in water window range

The soft x-ray reflectivity measurements were performed by using a high precision polarimeter on Beamline I06 at the Diamond Light Source, United Kingdom. (Wang *et al.*, 2011) The Cr filter was selected to suppress the high harmonic contamination from the collimated plane grating monochromator. Linear horizontal polarization synchrotron radiation with energy of 453.5 eV was used in the measurements. The reflectivity curves are plotted in Figure 4 as a function of the glancing angle, close to the near-normal incidence. The reflectivity of the pure Cr/Ti multilayer is 4.48% (at 79.95°) and the interface width is determined to be 0.41 nm by simulation using the IMD code. (Windt, 1998) The reflectivity of the Cr/Ti multilayer with B₄C is 15.75% (at 82.75°) and the interface width is determined to be 0.30 nm. The required optical constants were generated following the method in the reference (*Berkeley center for x-ray optics*). The large improvement of the reflectivity, by a factor 3, is due to the reduced diffusion between Cr and Ti layer and the suppression of crystallization.

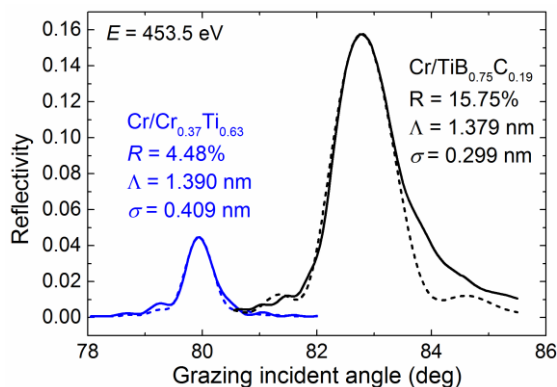


Figure 5 (color online) Soft x-ray reflectivity of the Cr/Ti multilayers with (black) and without (blue) B₄C. Solid lines represent the measured data and dashed lines show the calculated reflectivities.

5. Summary

In this paper, we have considered Cr/Ti multilayers with ultra-short period ($\Lambda \sim 1.4$ nm). We intentionally incorporated B and C into Cr/Ti multilayers by depositing ultra-thin B₄C at the interfaces. We found that incorporating 0.13 nm thick B₄C at both interfaces dramatically improves the structure and composition of the Cr/Ti multilayers. B and C incorporated during deposition is mainly bonded to Ti. The formation of non-stoichiometric Ti compound hinders the diffusion and improves the interface quality of the multilayer. The crystallization is also suppressed after introduction of B₄C. As a result, Cr/B₄C/Ti/B₄C multilayers (with period number N=600) exhibits a reflectivity 3.5 higher near-normal incidence soft x-ray reflectivity (15.75% absolute reflectivity) than pure Cr/Ti multilayers.

Acknowledgements The authors acknowledge Francesco Maccherozzi for the support during the reflectivity measurements, Kawal Sawhney for helpful discussion and Yuchun Tu for the experimental suggestions.

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