



Nitridation and contrast of B₄C/La interfaces and X-ray multilayer optics

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ABSTRACT

Chemical diffusion and interlayer formation in thin layers and at interfaces is of increasing influence in nanoscopic devices such as nano-electronics, magneto-optical storage and multilayer X-ray optics. We show that with the nitridation of reactive B₄C/La interfaces, both the chemical and optical contrast can be greatly enhanced. Although interaction and diffusion of N₂ from the substrate towards the adlayer does occur, this surfactant mediated growth contributes to chemical and optical interface properties that enable major reflectivity improvements of multilayer optics for 6.7 < λ < 7.0 nm.

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In recent years there have been numerous reports on multilayer optics for a variety of applications [1–3]. Chemical reactivity and differences in lattice parameters and surface free energy are of significant influence on the morphology and kinetics in layer-on-layer growth [4,5]. Interfaces in e.g. B₄C/La multilayer optics for B-K_α reflectivity (λ = 6.65 nm) [6–8] suffer from surface segregation and exothermic interlayer formation via 7La + 6B₄C → 4LaB₆ + 3LaC₂ [9]. Vapor or sputter deposition of B₄C occurs in separate B and C atoms [10,11], making the B₄C-on-La interface even more reactive. Chemically inactive, high contrast interfaces are however essential for the optics. For reflectivity at near-normal angle of incidence (AOI), La/B₄C multilayers considered as highly reflective coatings operating at λ = 6.65 nm typically require 200 periods of 2.0 nm thick B₄C and 1.6 nm thick La layers. Considering the formation enthalpy (ΔH^{for}), refractive index (n) and absorption constant (β) at λ = 6.65 nm for LaN, BN, LaB₆, LaC₂, B₄C, and La as shown in Table 1 [12–16], we observe that passivation of the B₄C/La interface is possible by nitridation, which would simultaneously improve the optical contrast, i.e. the reflectivity. Nitridation could also suppress roughening by grain formation [17,18] and diffusion at elevated temperatures.

The ΔH^{for} values imply that B₄C/LaN and BN/LaN interfaces are chemically inactive and do not suffer from LaB₆ and LaC₂ interlayer formation. Calculations [19] indicate that a relative increase of 20% in peak reflectivity and bandwidth can be achieved in comparison to a 200 period B₄C/La multilayers when 0.3 nm of both the top and bottom side of the La layer is replaced by LaN in a B₄C/LaN/La/LaN multilayer.

To verify the calculations on kinetic and optical properties, we investigated the nitridation and chemical reactivity in La and B₄C layers. These were grown by magnetron sputter deposition at a variable current between 1 and 2 A onto natively oxidized super polished Si (100) substrates in a Leybold Optics A1105 ultra high vacuum facility with a base pressure of 1 · 10⁻⁶ Pa [20]. A Kaufmann source was used for N₂⁺-treatment, with a N₂ working gas pressure of 1 · 10⁻³ Pa. To study the depth and diffusion range of the nitridation process, N₂⁺-treatment was applied either during deposition (NIBAD), or after deposition of individual layers. The nitridation of La and B₄C single-, bi- and multilayers is investigated using, angular resolved photoelectron spectroscopy (ARPES), cross-section transmission electron microscopy (CS-TEM) and selected area electron diffraction (SAED). For in-vacuo ARPES layer analysis and quantification [21–23], we assume the bulk densities of 6.73, 6.17, 2.25 and 2.37 g/cc for respectively LaN, La, BN and B₄C [24]. Optical analysis of seven multilayers with nitridation steps at various stages is done with grazing incidence X-ray reflectometry (GIXR) and at-wavelength reflectivity measurements.

For a post N-treatment of the B₄C layer, we observe that the BN overlayer thickness is linearly dependant on the N₂⁺ beam voltage (V_b) in the 15 V to 120 V range. Over this range, we form 0.45 to 2.7 nm thick BN overlayers of similar composition as the BN obtained by NIBAD. In the case of La, already for the lowest N₂⁺ beam voltage applied, two additional La4d doublets can be identified at ~2 eV higher and lower than the elemental electron binding energy. We identify three N1s peaks at 395.8, 396.9 and 398.5 eV. The spectral peaks hint at partial recombination to N₂ that forms dinitrogen complexes and intermediates such as La(N₂) [25,26]. Above a V_b of ~100 V, the doublet that represents elemental La decreases. The La3d doublet shows only a slight increase at the low binding energy side, similar as observed for La₂O₃. With ARPES, we model [27–29] that

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Table 1
The values of ΔH^{for} , n and β ($\lambda = 6.65$ nm) for LaN, BN, LaB₆, LaC₂, B₄C, and La.

Compound	LaN	BN	LaB ₆	LaC ₂	B ₄ C	La
ΔH^{for} (kJ/mol)	-303	-255	-130	-89	-71	0
n	0.981	0.995	0.992	0.986	0.999	0.984
β ($\times 10^3$)	1.420	0.894	0.853	0.996	0.528	1.075

post N-treatment with $V_b = 70$ V for 60 s. yields a 1.5 nm thick BN film on a B₄C substrate layer, and a ~ 1.3 nm thick LaN film on a La substrate layer, i.e. slightly thinner than the 2.0 nm thick B₄C and 1.6 nm thick La layers that are required for the multilayer.

The chemical interaction in B₄C/La interfaces is now investigated in three La-on-B₄C and three B₄C-on-La bilayers; either with post N-treatment or NIBAD of the substrate layer, or without N-treatment. For both post N-treatment and NIBAD, $V_b = 70$ V was used.

Fig. 1 shows the La3d_{5/2} and La4d XPS peaks for the three La-on-B₄C bilayers. It reveals that upon nitridation of the B₄C substrate layer on which the La layer is grown, the La3d_{5/2} peak at 835.8 eV decreases while peaks at 835.0 and ~ 838.8 eV emerge. The La4d_{5/2} peak at 102.8 eV also decreases while a second doublet emerges at ~ 2 eV higher binding energy. Since both N⁻ and N⁺ are highly reactive, this suggests that N₂ diffuses from the B₄C substrate layer, into the La layer to form a LaN or La(N₂) film that is approximately 0.3 nm thick. The observed nitridation of La is theoretically beneficial for the optical contrast, as earlier concluded from Table 1. The La-on-BN interface, with NIBAD of the B₄C substrate layer, is observed to suffer least from diffuseness and yields superior chemical contrast.

For the case when a B₄C layer is deposited onto a La layer, the highest contrast B₄C-on-La interface is obtained with NIBAD of the La substrate layer. Only in that case we observe a clear second La4d doublet at ~ 2 eV lower binding energy from LaN in addition to the elemental La4d doublet. There is no indication of La(N₂) presence, possibly due to surface free energy driven diffusion [30] of N₂ into the B₄C adlayer. By occupying the surface, the diffusing N₂ could improve the B₄C-on-LaN growth. With ARPES we observe that the N₂ diffusion results in a BN film with a thickness of 0.6 nm for post-La deposition N-treatment, and of ~ 0.9 nm for NIBAD of the La. Due to the diffusion, the substrate layer retains only a 0.4 nm thick LaN film. From the bilayer experiments, we conclude that nitridation can enhance layer-by-layer growth both via chemical passivation and surfactant-mediated growth [25] of diffusing N₂ that is loosely bonded in dinitrogen complexes.

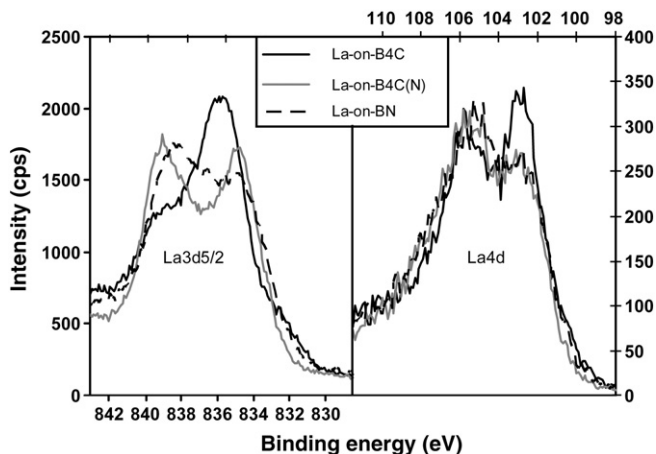


Fig. 1. The La3d_{5/2} and La4d peaks of the three discussed bilayers. For the La-on-B₄C(N) interface, the B₄C substrate layer was post N-treated, for the La-on-BN interface, it was grown by NIBAD.

For optical analysis of the interfaces, we have grown seven multilayers with 51 B₄C/La periods; without nitridation (ML1), with NIBAD of both B₄C and La (ML2), NIBAD of only the B₄C (ML3), NIBAD of only the La (ML4), post N-treatment of both B₄C and La (ML5), post N-treatment of only B₄C (ML6), and post N-treatment of only La (ML7). In all cases, the same magnetron deposition times were used in order to investigate the effect of the N-treatment on layer thickness. We used XPS depth profiling with 0.5 keV Ar⁺ to determine the in-depth material distribution and compound formation in these multilayers. Noting that the relocation range of the ions can occasionally exceed the calculated penetration depth, the low energy sputtering induces only moderate ion beam mixing compared to the XPS probing depth [31].

Fig. 2 shows the XPS depth profile of the reference non-nitridated B₄C/La multilayer (ML1) with a period of 3.540 nm thick and a La-ratio (r) of 0.52, as established with GIXR at $\lambda = 0.154$ nm. The approximate multilayer profile can be reconstructed with the mixing-roughness-information depth (MRI) model [32]. By using a calculated atomic mixing (g_w) of 2 nm and an information depth (g_λ) of 3 nm in linear approximation, we model a 0–100% interface gradient of 1 nm, leaving pure B₄C and La layers of ~ 0.6 and 0.8 nm thick respectively. These findings are supported by reflectometry, CS-TEM and XPS measurements and suggest that the interface gradient can partially be regarded as a LaB₆ and LaC₂ interlayer, which is thickest for the B₄C-on-La interface. For individual layer thicknesses of up to 5.0 nm, no crystallization is visible in XRD [9] and CS-TEM [33]. The reflectivity of 5.94% at $\lambda = 7.00$ nm, 1.5° AOI can be modeled [19] by 1.5 and 0.5 nm thick interlayers at the B₄C-on-La and La-on-B₄C interfaces respectively, with an interface diffuseness of 0.47 nm. The values are in good agreement with GIXR results of André et al. [8]. An extrapolated 37% reflectivity at $\lambda = 7.00$ nm for a 200 period multilayer would also be in accordance with results obtained by other growth methods [34].

To investigate the effect of N-treatment on the chemical reactivity and optical performance of a B₄C/La multilayer, NIBAD of B₄C and La is now applied (ML2). A N1s peak around 397.4 eV, a B1s peak at 190.0 eV, and two C1s peaks at 282.7 and 286.0 eV indicate that all B and 40% of the C is bonded to N, possibly in a BN:C complex [35]. Judging from the C content, chemical etching via formation of volatile CN and C₂N₂ is limited, while sputtering or lower sticking of BN yields a more than 50% lower B content in the multilayer upon NIBAD. Modeling of the two doublets with La4d_{5/2} at 102.2 and 104.5 eV suggests that the majority of the La is nitridated and possibly in equilibrium with a La(N₂) dinitrogen complex. GIXR confirms the very poor layer contrast, although a net period thickness increase to 4.460 nm can still be determined, attributable to significant layer

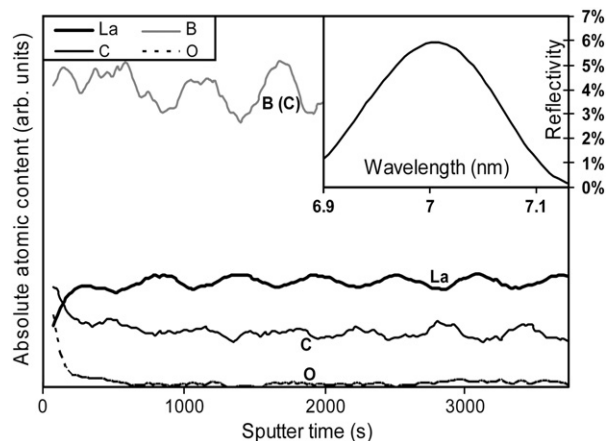


Fig. 2. XPS depth profile of a La/B₄C multilayer. The inset shows the reflectivity curve at 1.5° AOI.

swelling upon BN formation. The peak reflectance is only 0.04% at $\lambda = 8.80$ nm, 1.5° AOI.

With NIBAD of only the B_4C layer (ML3), the peak positions and the nitride quantity are similar to when NIBAD is used for B_4C and La (ML2). The nitridation of La is only marginally decreased, confirming the significant N_2 diffusion that we observed in the La-on-BN bilayer. The XPS depth profile, CS-TEM, GIXR, and the peak reflectivity of 0.09% at $\lambda = 10.88$ nm, 1.5° AOI all reveal severe interdiffusion of the layers. The period thickness of 5.302 nm compared to 3.540 nm (ML2) confirms that NIBAD of B_4C results in significant layer expansion.

NIBAD of only the La layers (ML4) yields a multilayer period of 3.388 nm thick and $\Gamma < 0.3$. We observe two La4d doublets with the La4d_{5/2} peak at 101.6 and 103.9 eV in a 2:3 ratio. The combined peak area suggests a 25% lower La content compared to the non-nitridated multilayer (ML1). The peaks for B1s at 188.0 eV, C1s at 282.7 eV and N1s at 397.4 eV indicate that no nitridation of B_4C occurs and that the N resides in the midst of the La layer. In Cr/Sc multilayers that were grown in a N_2 rich background vacuum, N was also observed to reside in the midst of the layers [36,37]. MRI reconstruction of the asymmetric multilayer depth profiles and GIXR modeling suggest that the 0–100% interface gradients are less than 0.2 and 0.6 nm thick for respectively the La-on- B_4C and the B_4C -on-La interface. CS-TEM and the 11.52% peak reflectivity at $\lambda = 6.74$ nm, 1.5° AOI confirm the lower diffusion and better layer localization than without nitridation (ML1), or with NIBAD of B_4C (ML2, ML3). We model a reflectivity of 43% at $\lambda = 6.72$ nm for a 200 period multilayer. Nitridation of La thus appears the key step to obtain a major increase in reflectivity.

We now address the effects of N-treatment after deposition of the La and B_4C layers. A 60 s N-treatment both after completion of B_4C and La (ML5) results in a period thickness increase to 4.34 nm and a decrease in Γ to 0.30, again attributed to layer expansion upon N-treatment of B_4C . The peak reflectance of 15.37% at 8.47 nm, 1.5° AOI suggests a high degree of periodicity and low interface diffuseness. The XPS depth profile of ML5 is shown in Fig. 3. Fig. 3 reveals a high degree of localization for the B_4C and BN, with possibly surfactant-mediated growth by N or N_2 . Based on MRI reconstruction and GIXR modeling, we estimate that the 0–100% interface gradients are less than 0.3 nm thick. The nitride content in the La layer shows a modest gradient from about 50% at the N-treated top to 60% at the bottom of the layer. This suggests that N_2^+ is implanted deeper into the La layer and that nitridation starts from there, similar as in Si [38]. A 200 period multilayer is modeled to yield 51% reflectivity at $\lambda = 6.72$ nm and 44% at $\lambda = 7.00$ nm.

With post N-treatment of only the B_4C layers (ML6), we observe a lower BN content at the La-on- B_4C than when also the La layer is post

N-treated (ML5). This confirms surfactant-mediated growth of B_4C -on-La(N) interfaces by N or N_2 and subsequent nitridation of B_4C . The prominent nitridation of the La implies a similar process at the other interface, with N_2 diffusion from the previously N-treated B_4C layer surface. The period is 4.190 nm thick, Γ is 0.44 and the peak reflectivity is 11.48% at $\lambda = 8.22$ nm. A 200 period multilayer is modeled to reflect 29% at $\lambda = 6.72$ nm and 23% at $\lambda = 7.00$ nm.

Finally, when only the La layers are post N-treated (ML7) we observe that about 60% of the La is nitridated, and in addition BN is observed at the La-on- B_4C interface. This suggests N implantation deep into the La layer and diffusion to the subsurface interface that possibly acts as precursor for nitridation [10,39]. Fig. 4 shows the CS-TEM and SAED image for this multilayer, revealing an amorphous structure and high layer contrast. The period is 4.000 nm thick and Γ is 0.46 for this multilayer. The increase in period thickness compared to 3.540 nm (ML1) appears solely attributable to the BN formation that was observed in the B_4C -on-La(N) bilayer and in Fig. 3. The peak reflectance is 15.53% at $\lambda = 7.85$ nm. A 200 period multilayer is modeled to yield 45% reflectivity at $\lambda = 6.72$ nm and 39% at $\lambda = 7.00$ nm. The dramatic reflectivity improvement that is obtained with post N-treatment of B_4C and/or La in comparison to NIBAD is partially explained by better localization of the nitrides at the interfaces. Especially BN has a higher optical absorption than B_4C (Table 1).

In conclusion, the investigations on B_4C and La layer nitridation by N_2^+ -treatment have shown that the B_4C /La interface gradient can be substantially decreased by nitridation of the interface. The best results are achieved when the La and B_4C , or only the La layers are post N-treated. From the experimental results, extrapolated IMD modeling suggests peak reflectivities of up to 51% at $\lambda = 6.72$ nm for a 200 period multilayer. Complete interdiffusion is observed upon NIBAD of B_4C . The N_2^+ -treatment of La appears to yield an equilibrium that involves dinitrogen complexes. The loosely bound N or N_2 in the B_4C or La substrate layers partially diffuses into the adlayer, resulting in surfactant mediated adlayer growth. Subsequent nitridation of the adlayer is observed, yielding nitridated interfaces that are chemically inactive to LaB_6 and LaC_2 interlayer formation. B_4C swells considerably upon nitridation, while the B content is significantly lower. Reflectometry and CS-TEM reveal that these processes occur without significantly affecting interface diffuseness in the case of post N_2^+ -treatment.

In effect, we substantially improved optical contrast, reflectivity maximum and bandwidth in La/ B_4C multilayers by applying N-treatment after individual layer growth. This makes application in reflective optics highly advantageous for e.g. free electron lasers such as FLASH, next generation photolithography, soft X-ray spectroscopy, fluorescence analysis and imaging.

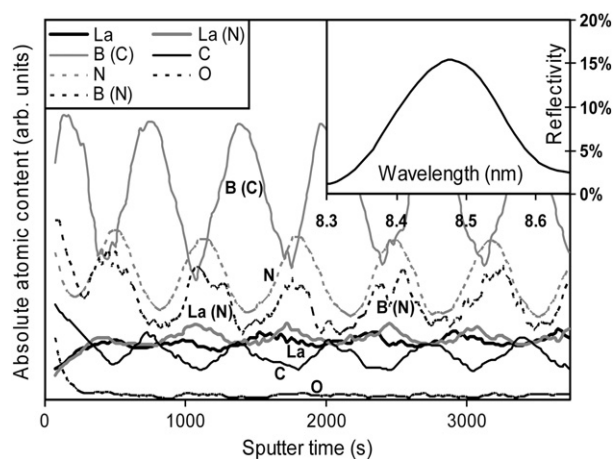


Fig. 3. XPS depth profile of a La/ B_4C multilayer with 60 s N-treatment after each layer. Brackets denote chemical bonds to other elements. The inset shows the reflectivity curve at 1.5° AOI.

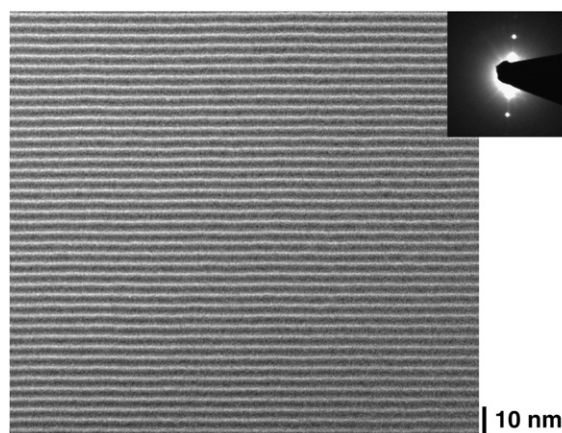


Fig. 4. CS-TEM image of a La/ B_4C multilayer with 60 s N-treatment after each La layer. The inset at the upper right shows the SAED image for this multilayer.

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