

High reflectance La/B based multilayer mirrors for 6.x nm wavelength*

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For future photolithography processes, the wavelength of 6 nm may offer improved imaging specs. The perspective of this technology however, will depend critically on the performance of multilayer reflective mirrors, which are likely to be based on La/B. One of the issues is formation of La_xB_y compounds at the interfaces, which decreases the optical contrast and reduce the reflectivity. To prevent such chemical interaction, passivation of La by nitrogen has been investigated. We successfully synthesized LaN layers that resulted in a new world record reflectivity of 64% at 6.6 nm at near normal incidence. This reduces the gap to the target of 70%, desired for a next generation lithography.

**D.S. Kuznetsov et al., Optics Letters, Vol. 40, No. 16 (2015)*

High-reflectance La/B based mirror for 6.x nm wavelength

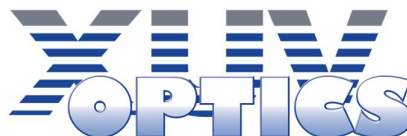
(details: D.S. Kuznetsov et al., Optics Letters, Vol. 40, No. 16 (2015))

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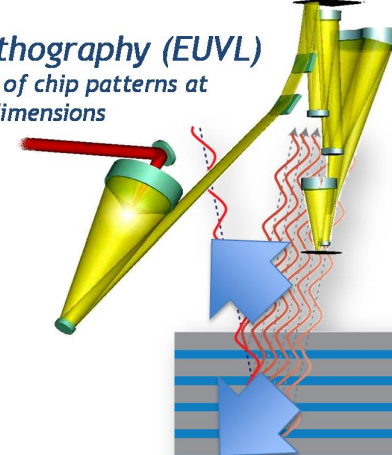
SPIE Advances in X-ray/EUV optics and components
11/12-08-2015



In this presentation we briefly describe our recent research results on the 6.x nm (beyond-EUV) La/B-based multilayers that shows a new reflectivity record for this wavelength. This material was published in *D.S. Kuznetsov et al., Optics Letters, Vol. 40, No. 16 (2015)*

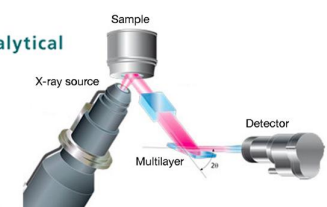
Motivation: many applications

EUV Photolithography (EUVL)
Fabrication of chip patterns at nanoscale dimensions




ZEISS
ASML

XRF Material analysis
Ultrasensitive detection using X-ray Fluorescence

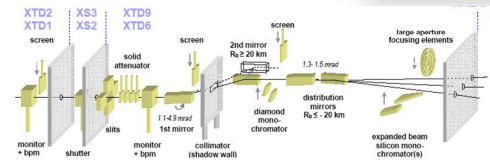











PANalytical

Space research
XUV telescopes



Optics for high intensity light sources
X-ray Free Electron lasers

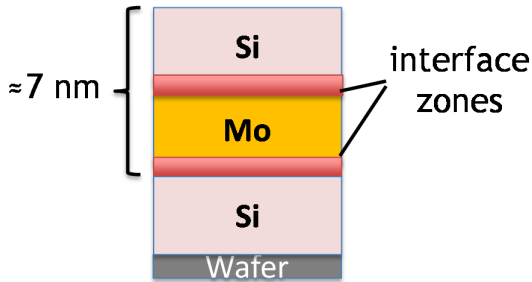


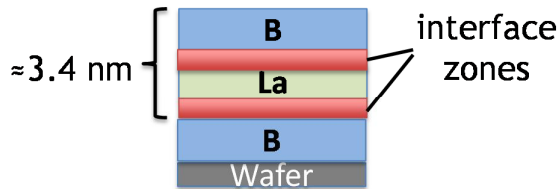
X-ray multilayer mirrors are employed for X-ray fluorescence material analysis, as optics in space research, for high-intensity free-electron lasers (FEL), and for extreme ultraviolet photolithography (EUVL). Those applications determine the main motivation for the research on x-ray multilayers.

Challenges on the atomic scale

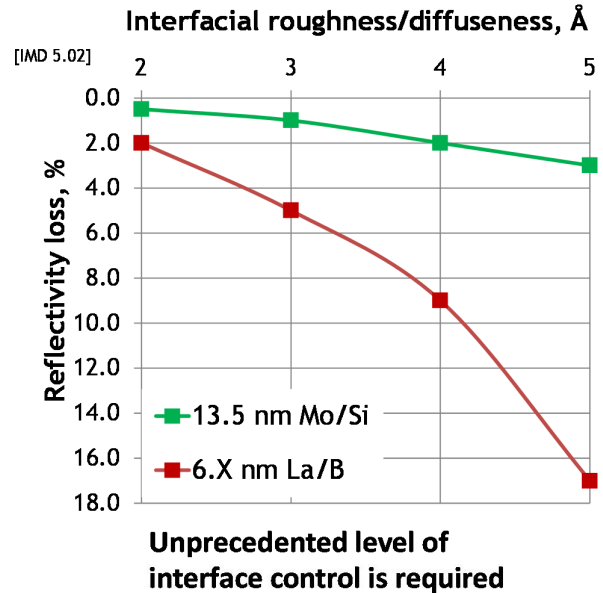
13.5 nm XUV multilayers



6.X nm XUV multilayers



Each layer ~ (5-10) atomic layers!



(details: D.S. Kuznetsov et al., *Optics Letters*, Vol. 40, No. 16 (2015))

XUV

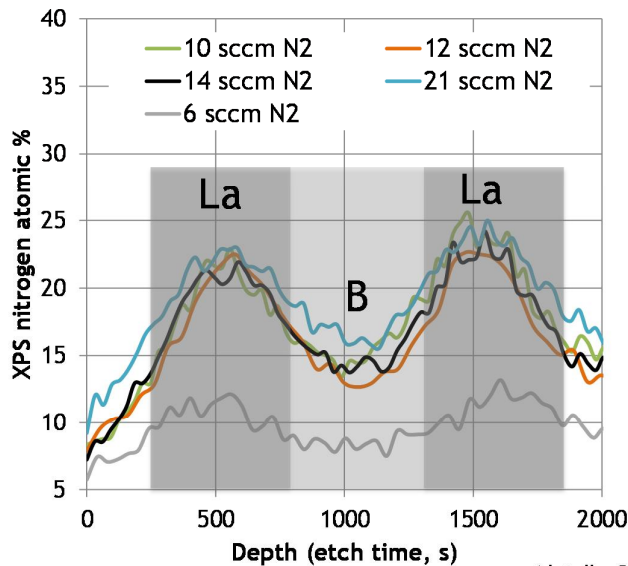
The previously developed Mo/Si multilayers for the wavelength around 13.5 nm had the bilayer thickness about 7 nm. Between two different deposited materials interfaces are formed (intermixing, interdiffusion, roughness-morphology,..), that significantly reduces the optical contrast and the reflectance of the multilayer. The newly developed La/B-based multilayers for the wavelength around 6.7 nm (called “6.x nm”) have the bilayer thickness about 3.4 nm which is about two times thinner than for Mo/Si multilayers. Therefore the naturally formed interface of the same width should logically result in the significantly larger reflectivity loss. This is supported by the presented calculations shown at the graph. So, to obtain significant reflectance the new 6.x nm generation of multilayers requires unprecedented level of the interface control.

Saturation of La with nitrogen

Issue: LaB_6 (LaB_x) compound formation
[S.L.Nyabero, 2014, thesis]

Solution: La passivation with N

[Igor A. Makhotkin et al., Optics Express, Vol. 21, No. 24 (2013)]



Idea: all possible La atoms' bonds occupied with N.

→ **LaN can not take more N than needed to form stoichiometric LaN.**

→ **High N₂ pressure -> longer exposure to N through non-closed/thin La(N) layer.**

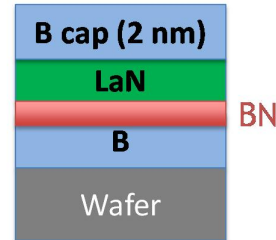
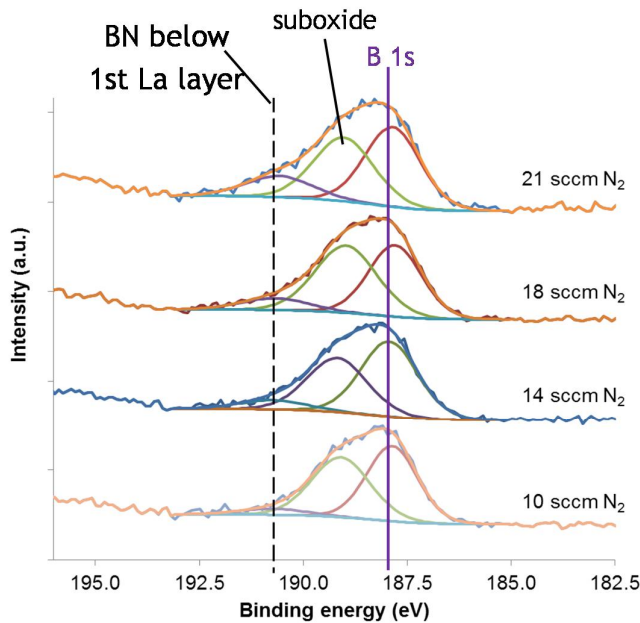
(details: D.S. Kuznetsov et al., Optics Letters, Vol. 40, No. 16 (2015))



It is known that interdiffusion between La and B that causes LaB_6 compound formation reduces the optical contrast in La/B multilayers. One of the solutions successfully implemented by Igor A. Makhotkin et al. [*Optics Express, Vol. 21, No. 24 (2013)*] was the reactive magnetron sputtering of La in nitrogen environment. But to obtain the most chemically inert lanthanum-nitride, La should be passivated with N to the maximum extent. Here the XPS depth-profiles are presented of the nitrogen profile for different flow of N₂ gas during the deposition. After La is saturated with N, it does not take more N.

BN formation: angular-resolved XPS

BN formation: during deposition or sputter-induced by depth-profile?



→ **BN is mostly present in deeper layers** (from AR-XPS)

→ **More BN is formed for deposition at higher N₂ partial pressure**

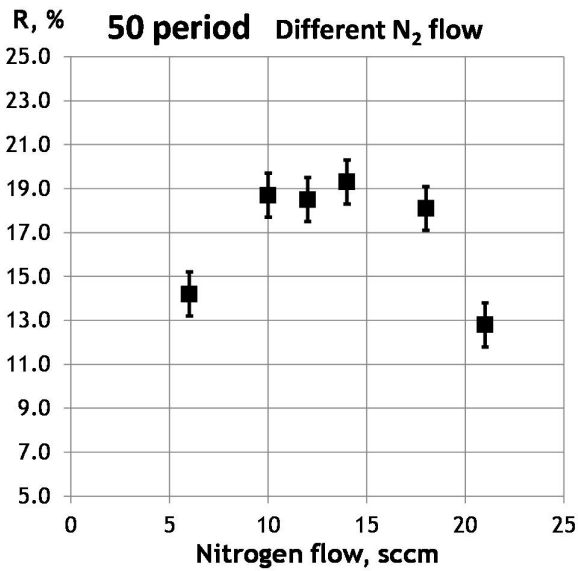
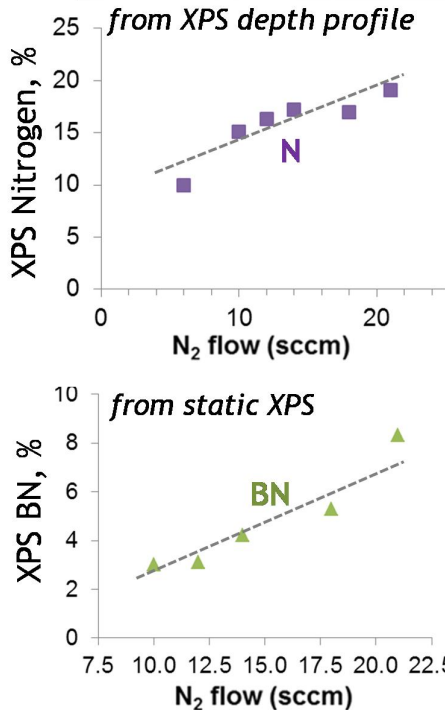
XUV

(details: D.S. Kuznetsov et al., Optics Letters, Vol. 40, No. 16 (2015))

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During the depth-profiling of the samples where LaN was deposited at different N₂ flows, boron-nitride (BN) signal was discovered inside the samples. But this compound could be formed due to sputter-induced effects during the depth-profiling. For this reasons non-destructive angular-resolved XPS (AR-XPS) was performed and confirm that this compound did already form on LaN-on-B interface during the deposition. Its amount increases with N₂ flows used during LaN deposition.

La passivation vs. BN formation



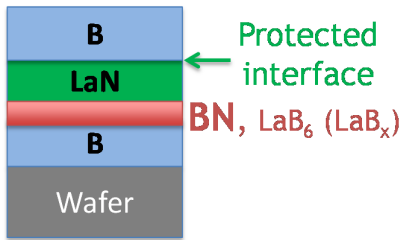
→ Trade-off between La passivation and BN formation



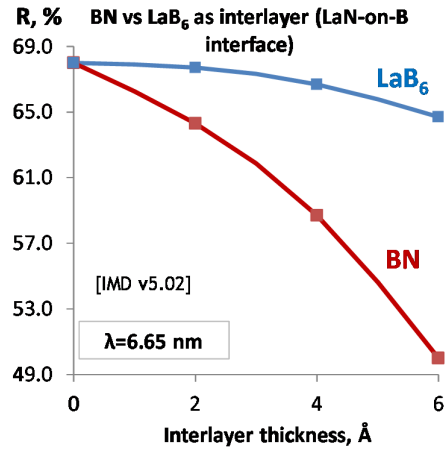
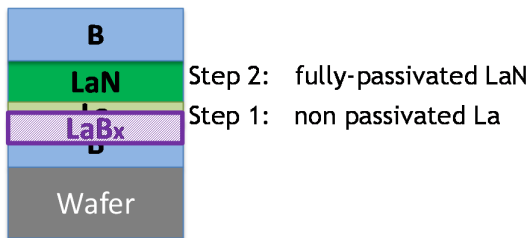
As shown at the left bottom slide the boron nitride on LaN-on-B interface increases with N₂ flow. Reflectivity of the multilayer, however, first increases, then decreases, showing a clearly pronounced maximum. This is explained by two counteracting processes. First, the reflectivity increases with the N₂ flow as the extent of LaN layer passivation increases. This improves protection of the B-on-LaN interface from the natural interlayer formation. As the N₂ flow increases further, the reflectivity starts to decrease due to the significant amount of BN formation at the LaN-on-B interface. 50-periods multilayers were used in this experiment.

LaN/B and delayed nitridation

Initial system: LaN/B



New system: LaN/La/B



Formation of LaB_6 (LaB_x) very favorable ($\Delta H(\text{LaB}_6) \approx -130 \text{ kJ/mol}^*$), proven** for La/B
 *[A. I. Efimov Handbook, Khimiya, Leningrad, 1983]
 **[I. A. Makhotkin et al., Optics Express 20(11), 11778 (2012)]
 **[T. Tsarjati et al., Thin Solid Films 518(5), 1365 (2009)]

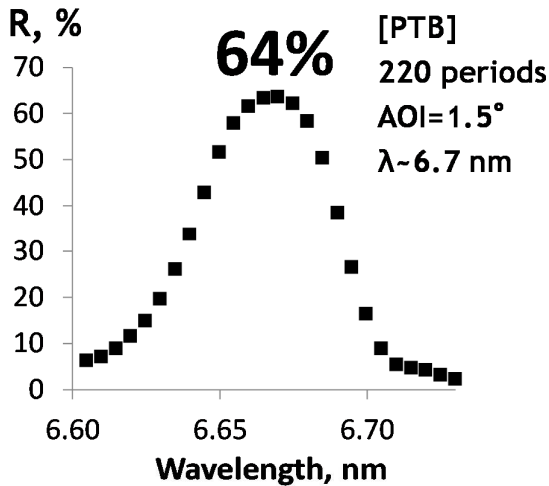
=>Delayed nitridation should improve reflectance.

(details: D.S. Kuznetsov et al., Optics Letters, Vol. 40, No. 16 (2015))



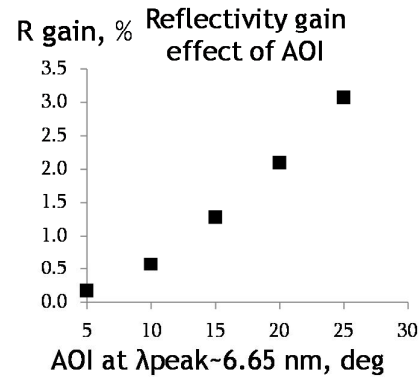
The calculations presented on the graph show a detrimental effect of BN formation on LaN-on-B interface. Based on these findings, we synthesized a structure that excludes direct contact of nitrogen species with the underlying B layer at the LaN-on-B interface. The simplest way to realize that was to initially delay lanthanum nitridation. This effectively introduced a lanthanum interlayer at the LaN-on-B interface. It is known that in this case, chemical interaction of lanthanum with the underlying boron layer will result in the formation of a LaB_x interlayer. However the calculation presented at the graph show that the reflectivity loss due to the LaB_6 formation at that interface is significantly smaller. (for further details see D.S. Kuznetsov et al., Optics Letters, Vol. 40, No. 16 (2015))

6.x nm reflectivity world record



Previous records
 R=58.6%, AOI*=20.9°
 (~56.5% at AOI*=1.5°)
 [N. I. Chkalo et al., *Applied Physics Letters* 102, 011602 (2013)]

R=58.1%, AOI*=10°
 (~57.5% at AOI*=1.5°)
 [P. Naujok et al., *Proc. SPIE*, Vol. 9422, 94221K (2015)]



(details: D.S. Kuznetsov et al., *Optics Letters*, Vol. 40, No. 16 (2015))



The soft x-ray reflectivity of the fabricated multilayer was measured at the radiometry laboratory of the Physikalisch Technische Bundesanstalt (PTB) using synchrotron radiation of the BESSY storage ring in Berlin, Germany. It showed that the used approach yielded 64.1% at 1.5° off normal AOI. The previously reported highest values are presented on this slide, and these values were measured at higher off-normal angles-of incidence (AOI). For proper comparison the gain in reflectivity due to the higher off-normal angle measurements is presented on the right bottom graph (calculations, IMD 5.02 software).

Summary

Passivation of La with nitrogen investigated (LaN saturation vs. BN formation);

Adverse effect of BN compound formation minimized by “delayed” nitridation;

6.x nm reflectivity world record achieved:
64.1%, AOI=1.5° off-normal, λ -6.7 nm [PTB];

Achieved record reduces the gap to application-desired performance.



(details: D.S. Kuznetsov et al., *Optics Letters*, Vol. 40, No. 16 (2015))



To summarize, nitridation of the lanthanum layer in La/B multilayers is shown to protect the B-on-La interface from the formation of optically unfavorable LaB_x compounds at that interface. However, XPS measurements showed that the nitridation process results in the formation of an unfavorable BN compound at the opposite LaN-on-B interface. To prevent interaction of nitrogen species with boron atoms of the underneath layer, a short delay in the nitridation was used at the initial stage of the La layer passivation. The thus synthesized B\La\LaN multilayer mirrors showed a reflectivity of 64.1% at 6.65 nm measured at 1.5 degrees off-normal incidence. The gain in reflectance is explained by formation of a more-optically favorable lanthanum boride compound instead of BN at LaNon-B interface. The gain in reflectance shown and the analysis of the obtained structures are expected to lead to further gains in reflectance, a process similar to Mo/Si-based multilayers at 13.5 nm used in extreme ultraviolet lithography.

The presented results are published in *D.S. Kuznetsov et al., Optics Letters, Vol. 40, No. 16 (2015)*

References

The presentation is based on *D.S. Kuznetsov et al., Optics Letters, Vol. 40, No. 16 (2015)*

1. S.L.Nyabero, 2014, thesis
2. Igor A. Makhotkin et al., *Optics Express*, Vol. 21, No. 24 (2013)
3. David L. Windt, *Comput. Phys*, 12, 360 (1998)
4. N. I. Chkalo et al., *Applied Physics Letters* 102, 011602 (2013)
5. P. Naujok et al., *Proc. SPIE*, Vol. 9422, 94221K (2015)