W-based multilayer soft X-Ray Bragg optics

Synthesis and Characterization

Roman Medvedev

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LIST OF PUBLICATIONS

This thesis is based on the following publications:

- Chapter 2: R.V. Medvedev, K. V. Nikolaev, A. A. Zameshin, D. IJpes, I. A. Makhotkin, S. N. Yakunin, A. E. Yakshin, and F. Bijkerk. "Low-energy ion polishing of Si in W/Si soft X-ray multilayer structures" *Journal of Applied Physics* 126, no. 4: 045302 (2019)
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INTRODUCTION

Multilayer systems are widely used in various modern applications such as lithography, X-Ray microscopy, synchrotron-based research, space research, and X-Ray fluorescence analysis. They have been thoroughly studied and developed over the past 40 years, focusing on specific and stringent requirements for each application. Multilayer systems working in the extreme ultraviolet (EUV) range ($\lambda = 13.5$ nm) used in the photolithography industry [1–4] need to have a close to theoretical reflectance, combined with an almost infinite lifetime and a very good thermal stability. The same holds for multilayer mirrors for the so-called “water window” range ($\lambda = 2.4$ – 4.4 nm), used for X-Ray microscopy [5–9]. For multilayer structures used in monochromators the main requirements are a high spectral selectivity and a high reflectance. In addition they need to be thermally stable and to have a long lifetime. Same is required for multilayer structures designed for space applications such as astronomical X-Ray telescopes (NuSTAR, Hitomi, HEFT, Athena) working in the hard X-Ray range [10–15]. An extremely demanding application of a multilayer as monochromator is the use in X-Ray fluorescence (XRF) spectrometers. Because the emission lines of particularly low Z elements in the soft X-Ray range ($\lambda = 0.12$ nm– 5 nm), which is the range where multilayers are required as monochromators, differ only marginally in wavelength, the multilayer mirrors are required to have an extremely high selectivity in order to uniquely detect these elements. Selectivity requires a very narrow bandwidth of the reflection peak. This can be achieved by decreasing the period value of the multilayer mirror, in combination with a design to use it at a larger grazing angle to obey the Bragg’s condition, thus enabling the use of a larger number of periods which results in narrower reflectance peak, analogous to what is expressed in the Bragg formula for crystals. Furthermore, the thickness ratio of the layers within one period needs to be optimized. Apart from selectivity, to perform a fast, high-quality XRF analysis of the elements, high reflectance is needed, enabling a better signal-to-noise ratio. However, most of the multilayer materials have a strong photon absorption in the intended energy range, which makes it challenging. Therefore, material selection is a very important criterion to achieve the maximum reflectivity. Furthermore, as the period decreases, the systems become more sensitive to imperfections at interfaces and full control of the multilayer deposition process is required. This thesis is devoted to multilayer systems with a period $d = 2.5$ nm working in the spectral range from the O $K\alpha$ to Al $K\alpha$ (525 eV – 1486 eV, or $\lambda = 2.4$ nm– 0.84 nm, respectively) and angles of incidence in the range from $\theta = 9.7^\circ$ to $\theta = 29^\circ$. Working on multilayers in this energy regime is challenging because of the high absorption of radiation and a dramatic effect of imperfections at the multilayer interfaces. One of the suitable systems to achieve high reflectivity and narrow bandwidth in theoretical calculations is the W/Si multilayer system. W/Si is a well-studied system, but mostly for larger energies and period values [11, 13, 16–28]. According to computer modelling [29], for an ideal system (zero interfacial roughness) with a period $d = 2.5$ nm, a maximum reflectivity of 61% at $\lambda = 0.84$ nm and a grazing angle of incidence of 9.7° can be achieved for a tungsten layer thickness of only 0.5 nm (ratio of the W thickness to the period, or gamma value, is $\Gamma = 0.24$). In practice, the average interfacial roughness is in the range of 0.2 – 0.35 nm rms, according to previous research on similar systems [11, 13, 16, 30–33]. Therefore, the quality

of interfaces plays an especially important role in the synthesis of multilayer mirrors working in the soft X-Ray energy range. Since it is not possible to deposit an ideal multilayer system with zero roughness of the interfaces and no interactions between the materials deposited, a minimum roughness value of 0.2 nm should be taken into account when designing a multilayer system. The initially deposited multilayer mirror showed a reflectivity of 40% at $\lambda = 0.84$ nm and a grazing angle of incidence of 9.7° which is rather low compared to the theoretical value of 61% for an ideal multilayer system. The essential problem for short period multilayer systems is the incomplete understanding of roughness development and interfacial layer formation and the incapability of conventional methods such as atomic force microscopy (AFM) and transmission electron microscopy (TEM) to provide a precise analysis of roughness on the sub-nanometer scale. Previous studies have not yet provided full understanding of the formation of interfaces and a quantitative analysis of imperfections, know-how which is of crucial importance for further development of such systems. This thesis is primarily devoted to the analysis challenges for which a combination of cutting-edge methods is used, such as low energy ion scattering (LEIS), grazing-incidence small-angle X-Ray scattering (GISAXS), grazing incidence X-Ray reflectivity (GIXR) in combination with fluorescence X-Ray standing wave (XSW) analysis and X-Ray photoelectron spectroscopy (XPS) measurements. These methods allow a more precise qualitative and quantitative evaluation of interface formation and roughness characteristics on a sub-nanometer scale. All methods are described in detail in [Section 1.5](#).

1.1 Application: X-Ray fluorescence spectroscopy

X-Ray fluorescence spectroscopy (XRF) is a fast analytical method to determine the elemental and chemical composition of all kinds of materials (solid and liquid). XRF is a non-destructive method which does not require extensive sample preparation. The schematic principle of a wavelength-dispersive X-Ray fluorescence spectrometer (WDXRF) is shown in [Fig. 1.1](#). An X-Ray light source is used to excite fluorescence radiation from the sample which is then diffracted by the analyzing crystal (multilayer mirror, natural or synthetic crystal) to the detector with the use of primary and secondary collimators to limit unwanted radiation on the detector. The analyzing crystal is attached to a goniometer that rotates with an angle θ and a secondary collimator with a detector that rotate with the angle of 2θ in order to select the required photon energy for analysis. Most commonly an Ar flow counter is used as a detector for low energies, while for higher energies (>2 keV) a scintillation counter is used. The analyzing crystal can be a natural crystal such as, for example, LiF, Ge, KAP or RbAP used at glancing angles of incidence. This works very well for fluorescence radiation from high-Z elements, but the small lattice distance in natural crystals makes it impossible to measure the longer wavelength spectral lines emitted by low Z elements and limits the angular range. The use of multilayer mirrors, discussed in the following session, overcomes this limitation because the periodicity can be chosen. The main requirements for multilayer mirrors to be used as analyzing elements in XRF equipment are: a high reflectivity, uniformity (constant period value across the structure), a narrow bandwidth of the reflection

Figure 1.1: Schematic principle of WDXRF: a light source is used to excite fluorescence radiation from the sample which is spectrally resolved by an analyzing crystal and measured by the detector. Primary and secondary collimators are used for directionality. The spectral range is scanned by rotating the analyzing crystal with an angle θ and the secondary collimator and detector combination with an angle 2θ

peak, and a long lifetime.

1.2 Multilayer design

The principle of operation of crystal based monochromators is constructive interference from the crystal plains following Bragg's condition [34].

Periodic multilayer mirrors are designed as a stack of alternating thin layers with low and high refractive indices and a period d obeying Bragg's condition:

$$2d \sin \theta = n\lambda; \quad (1.1)$$

They can be considered as artificial crystals of which the periodicity can be chosen. For the design materials with high-Z (reflective layer) and low-Z (spacer layer) are chosen according to their optical constants (σ and β) for the working wavelength, or wavelength range, as is described elsewhere [35]. The X-Ray refractive indices are close to unity due to the weak interaction with matter at these wavelengths, thus, the refractive index is denoted as:

$$n = 1 - \sigma + i\beta; \quad (1.2)$$

The main criteria in choosing materials is to have high σ and low β values for the reflective layer, whereas both values have to be low for the spacer layers. Such a material combination provides a high optical contrast and thus a high reflectance due to the constructive interference from all interfaces. A second step in designing multilayer mirrors is to calculate the gamma value Γ (ratio of the metal layer to the period of the multilayer system) in order to optimize bandwidth and reflectivity at the required wavelength.

Figure 1.2: Schematic view of constructive interference from interfaces of a multilayer mirror

1.3 Multilayer synthesis

Magnetron sputtering [36] is a commonly used technique for multilayer deposition rather than techniques as electron beam evaporation [37], ion beam sputtering and others [38, 39], as it allows for a good control of the layer growth at room temperatures and a high stability of the process which is essential for the multilayer systems, especially with short periods. Various multilayer systems such as Mo/Si, W/B₄C, W/Si, La/B, Cr/Sc, etc. [40–48] with periods varying from 1 nm to 10 nm have been studied in order to improve the reflectivity at the required wavelengths, to study the formation of the interfaces and to investigate the thermal properties. However, most of the multilayer systems studied were designed for a wavelength much longer than 0.84 nm (mostly from “water window” to EUV range) where imperfections at interfaces in the sub-nanometer scale do not affect the reflectivity of the multilayer system as significantly as in short period systems.

1.4 Quality of interfaces

1.4.1 Interfacial roughness

The quality of the interfaces is determined by the interaction between surface atoms, ad-atoms and the substrate. For instance, upcoming particles arrive on the surface with a too high energy (up to 100eV in magnetron sputtering) and can cause ballistic intermixing, but when the energy of upcoming particles is not high enough for ad-atom mobility, it can result in the formation of clusters rather than a uniform distribution of atoms over the layer. In both cases, the roughness of the multilayer mirror will be increased which will result in a stronger scattering of the radiation and thus in a reduced specular reflectivity. For small periods, the effect of roughness at the interfaces on reflectivity is more pronounced. A slight change in roughness and roughness characteristics, such as lateral and vertical correlation length, and the Hurst parameter [31], can already result in a reduced reflectivity in the soft X-Ray range. A roughness value of approximately 0.3 nm was reported in many research studies on multilayer systems as W/Si, W/B₄C, and W/C [16, 30–33].

Figure 1.3: IMD simulations of W/Si reflectivity at 0.84 nm at 9.7° grazing incidence for an ideal system versus a W/Si multilayer system with a sigma value of 0.3 nm at both interfaces, included by using a Debye-Waller factor.

Fig. 1.3 shows a simulation, calculated with IMD [29] software, how a roughness of 0.3 nm on each interface of a W/Si multilayer affects the reflectivity of 0.84 nm radiation at 9.7° grazing incidence. A Debye-Waller factor was used to include the roughness values in the model. In terms of reflectance Debye-Waller factor can be presented as: $R = R_0 \times \exp(-(2\pi m\sigma/d)^2)$, with R_0 being the reflectance of an ideal structure with $\sigma = 0$ and m being a reflection order. Decreasing d -value makes the reflectance at some point being dominated by σ/d ratio [44]. Such interfacial roughness substantially reduces the reflectivity by around 18% in absolute value. WC/SiC studies for higher d -values ($d = 9 - 10$ nm) [11] reported a lower roughness of 0.19 nm while introducing C in the system. It allowed to deposit small d -spacing structures ($d = 1$ nm) with low surface roughness ($\sigma = 0.23$ nm). Therefore, it is very important to reduce the high spatial frequency roughness in order to obtain a high reflectivity for that specific wavelength.

1.4.2 Interdiffusion and compound formation

Other processes that can influence the reflectivity of multilayer systems are interdiffusion at the interfaces and chemical reactions between deposited materials. For example, many metals easily form silicide compounds in Si-based multilayers, or borides in B-based multilayers [49–54]. Usually, the compounds formed have a lower density than the metal layers which affects the optical contrast of the interface, and hence, reduces the reflectivity. Another effect is that the effective periodicity of the multilayer changes due to the interfacial layer. Typically, in multilayer systems with

Figure 1.4: IMD reflectivity simulations of ideal zero roughness W/Si and WSi₂/Si multilayers at 0.84 nm at 9.7° grazing incidence (Density of W $\rho = 19.3 \text{ g/cm}^3$ and WSi₂ $\rho = 9.3 \text{ g/cm}^3$)

larger periods only a part of a metal layer is consumed to form an interfacial layer. However, in the case of a 2.5 nm period the optimized W layers are thinner than 1 nm, thus one can assume the entire W layer to be transformed into a tungsten silicide compound. Fig. 1.4 shows an IMD simulation as an example of the effect of WSi₂ formation in an ideal W/Si multilayer. One can see that the reflectivity at $\lambda = 0.84 \text{ nm}$ reduces by almost the same amount of 18% absolute value as was found in simulations for the multilayer system with a roughness of 0.3 nm at both interfaces. As can be seen, both roughness and chemical interaction between materials lead to a significant loss in reflectivity. Therefore it is of high importance to control the interface growth and to keep the optical contrast high. For multilayer mirrors with a relatively large period ($d = 7 \text{ nm}$ and larger), one can prevent interlayer formation by using thermodynamically stable barrier layers consisting of alternative materials with a thickness of less than a nm. That can prevent the formation of the undesired compounds and can in some cases even enhance the optical contrast [55]. Another way to prevent compound formation is to passivate the layer before deposition of the next one in order to form a thin passivated layer which will serve as a barrier layer [45, 56–59]. Passivation of layers can be achieved in several ways: reactive sputtering in a reactive gas (i.e. O₂, N₂, etc.), sputtering from a compound target or by ion bombardment. In multilayer mirrors with a short period however, it is very challenging to do this, since the passivated layer thicknesses should only be a few tenth of a nm thick and any additional process involved enhances the risk to damage the structure and reduce its performance rather than improve it. In the case of passivation and using a barrier layer one should take into account the

formation enthalpy which can be used to assess the thermodynamic properties of the layer. Another factor which has to be taken into account is the surface energy of deposited atoms. When the surface energy of the substrate atoms (the underlying layer) is lower than the energy of the atoms of the film under growth, the interface width of the structure will be large and vice versa, when the surface energy of the substrate is higher the interface width of the structure will be small. Other processes, such as segregation, can occur during the growth when there is a large difference in surface energy between the film and substrate atoms which can affect the interface width [60]. Another effect that can reduce the multilayer performance is top surface oxidation when exposed to air, or even worse, radiation induced oxidation of the top layer. Both effects can be prevented by applying protective capping layers. Oxidation of surfaces was studied and shown elsewhere [50–52]. This work is focused on the analysis and development of W/Si and W/B multilayer systems designed to work in the soft X-Ray range of 0.84–2.4 nm. Engineering challenges included the synthesis of very thin, uniform metal layers in the range 0.3–0.7 nm with a subsequent treatment to obtain low roughness values. In order to minimize interface zones and to improve optical contrast, various approaches such as ion beam polishing, post-deposition ion beam passivation and applying an alternative spacer material were implemented. Analysis challenges included a combination of cutting-edge techniques to study qualitatively and quantitatively interface formation and its roughness characteristics.

1.5 Analysis techniques

Apart from the challenges in the synthesis of the multilayer mirrors listed above, there are many challenges in the analysis of such thin layers and the detection of slight changes at the interfaces which play a big role in the performance of the multilayer mirrors. Although some of the measurement techniques are sensitive to small imperfections at the interfaces, it is troublesome to unambiguously determine the nature of the imperfections. Therefore usually a combination of analysis methods is used. In this thesis we use the standard methods, added with two very sophisticated techniques: Low Energy Ion Scattering (LEIS) and analysis of the XRF signal generated by the X-Ray standing wave in the multilayer. As more instabilities in the deposition process occur with increasing number of periods, multilayers with a small number of periods ($N=50$) were deposited for analysis purposes to avoid distractions in the signal. Such multilayer systems were used in every chapter along with multilayer mirrors with a number of periods $N=200$ required for maximum reflectivity.

1.5.1 Grazing-incidence small-angle X-Ray scattering (GISAXS)

GISAXS is a roughness characterization technique based on diffuse X-Ray scattering measurements. Unlike AFM which allows a direct measurement of the top surface roughness only, GISAXS is sensitive to the statistical parameters of the structure which allows for a quantitative assessment of the internal structure. A

grazing incidence geometry is used in this method (the angle of incidence is in between the critical angle and the first Bragg angle) in order to achieve a high energy density. Correlated roughness leads to a coherent superposition of scattered X-Rays while scattering from uncorrelated roughness produces X-Rays with a random phase. In the case of periodic multilayers, coherent scattering results in an interference pattern on the detector – Bragg sheets. An ensemble of interface roughness characteristics such as the Hurst parameter and the lateral and vertical correlation length determines the shape of such Bragg sheets. A concise and straightforward way to estimate the statistical parameters of roughness was demonstrated in [31]. It is based on the analysis of the tails of the Bragg sheets: for longer lateral correlation lengths the tails of the Bragg sheets are narrower, therefore it is easier to resolve and analyze them. Multilayer mirrors with a short lateral correlation length require a higher brilliance source in order to resolve the tails, therefore GISAXS measurements were performed at a synchrotron at $\lambda = 0.1$ nm wavelength.

1.5.2 Low energy ion scattering (LEIS)

Low energy ion scattering (LEIS) was used to study W-on-Si and Si-on-W interfaces by the process described in detail in Chapter 3. In general LEIS allows to obtain information about the top surface layer: Low energy He ions scatter from the surface and their energy loss is a measure for the type of atoms they scatter from, thus enabling a very accurate determination of the top surface atomic composition. Some information about sub-surface material can also be obtained, albeit limited because of the high neutralization probability of incident ions. The analysis is described in detail in [61].

1.5.3 Grazing incidence X-Ray reflectivity + X-Ray standing wave (GIXR + XSW)

All multilayer systems were characterized by θ - 2θ grazing incidence X-Ray reflectivity (GIXR) measurements with Cu K α radiation with a wavelength $\lambda = 0.154$ nm, using a Malvern Panalytical Empyrean diffractometer. GIXR was used for calibration purposes of deposition rates of the materials and to determine the period of the multilayers. Very long GIXR measurements (small angular step size with a long data accumulation time per point) were used to obtain high resolution reflectivity data which was used to reconstruct the in depth material profiles by means of a free-model approach described in detail in Chapter 2. The X-Ray standing wave (XSW) technique was used in this work to obtain more accurate information about the atomic distribution in combination with GIXR measurements as described in detail in [62] and is discussed in Chapter 4. The XSW is formed in the film as a result of interference between the incident and reflected beams. The technique in XSW is based on the analysis of the yield of XRF radiation excited by the XSW in the film. When varying the angle of incidence of the X-Rays, the X-Ray fluorescence signal contains in depth information about the atomic profile inside the film while GIXR is sensitive to the average electron density of the film.

1.5.4 X-Ray photoelectron spectroscopy (XPS)

XPS analysis provides information about the atomic and chemical composition of the surface. This information is important for multilayer mirror synthesis as it allows for the detection of compounds formed at interfaces upon deposition as well as detection of contaminants in the structure. XPS is a non-destructive method which has a probing depth of about 5 nm which makes it possible to perform analysis of the chemical composition of the top 5 nm of the sample. It is possible to use XPS to investigate the composition of the entire multilayer stack by measuring a depth-profile of the sample. This is implemented by removing material by etching the surface in one spot with low energy (typically 0.25-0.5keV) Ar⁺ ions. However, due to the etching process, intermixing of layers takes place making it difficult to obtain information of the “as-deposited” status for structures with such thin layers. Information about chemical elements in the stack helps to see how interfaces are affected by, for example, passivation of a layer, the flux of ions (if applied) or a change in ad-atom energy. As an example, we performed such an analysis in [Chapter 4](#) where nitridation was applied to Si layers.

1.5.5 Diffuse X-Ray scattering

Diffuse X-Ray scattering (rocking curve) analysis was used as a fast qualitative assessment of the deposited multilayer systems. The measurements with the Malvern Panalytical Empyrean diffractometer using Cu-K α radiation are carried out by fixing the detector at the center of the Bragg reflection peak and rocking the sample in a wide angular range around the Bragg peak. It is common to measure diffuse scattering at high Bragg orders to obtain a more significant contribution from deeper interfaces rather than only from the top layers. In this work, diffuse scattering was measured around the 2nd Bragg peak.

1.5.6 Atomic force microscopy (AFM)

The roughness of the multilayer mirror top surface was measured by atomic force microscopy in order to verify the low roughness after applying surface treatment such as ion beam polishing or changing the spacer layer material. All AFM scans were performed using the tapping mode and a high-resolution tip. Typical roughness values measured are around 0.2 nm. However, in our case roughness values were about 0.14 nm which is in the resolution limit of the AFM. [63]

1.5.7 Soft X-Ray reflectivity

Reflectivity measurements at the wavelength and angle of incidence the multilayer is designed for (‘at wavelength’), are carried out to determine the performance of the multilayer, and can, in combination with GIXR measurements, also be used for the analysis of the multilayer stack. While hard X-Ray reflectivity is sensitive to parameters such as layer thickness, material density, and interfacial roughness, the “at wavelength” soft X-Ray result is more sensitive to the composition of the layers. Therefore, a combination of both hard and soft X-Ray reflectivity is used for a more precise analysis of multilayer systems. Soft X-Ray reflectivity at specific wavelengths

and grazing angles of incidence required for the application ($\lambda = 0.84$ nm, $\theta \approx 9.7^\circ$ and $\lambda = 2.4$ nm, $\theta \approx 29^\circ$) were measured by the Physikalisch-Technische Bundesanstalt (PTB) in Berlin-Adlershof, Germany, using radiation from the storage ring BESSY II.

1.6 Synthesis of multilayer mirrors

Synthesis of short period multilayer mirrors requires sub-nanometer precision and high stability of the deposition process in order to obtain periodic structures. Reproducibility of the thickness of the layers within an accuracy of ≈ 0.1 % is required because even a slight change in the period will affect properties of the system such as peak reflectance at a required wavelength and angular and spectral bandwidth. The sharpness of the interfaces is determined not only by chemical interaction between deposited materials but by the deposition process as well: atoms should have sufficient mobility upon arriving on the surface otherwise the growth will result in roughening of interfaces and will require additional smoothening of every layer, for instance by ion polishing. Thickness uniformity of the layers is an important requirement in many applications. If layers are not uniform it will affect the period values and, thus, the peak reflectance at the required wavelength locally. Thickness uniformity of the deposited layers is achieved by rotating the substrate holder during the deposition process and the use of an optimized speed profile when the sample moves in front of the particle source. In this thesis, depositions were carried out using a magnetron sputtering deposition set up operated at a vacuum base pressure of $1 \cdot 10^{-9}$ mbar. The vacuum conditions allowed to minimize contamination from residual gas molecules in the chamber. Mass spectrometry was used to monitor the mass-to-charge ratio of ionized particles, checking the level of contamination prior to the depositions [2, 57, 64]. The schematic configuration of the coater is provided in Chapter 2.

References

- [1] T. W. Barbee, S. Mrowka, and M. C. Hettrick, *Molybdenum-silicon multilayer mirrors for the extreme ultraviolet*, [Applied Optics](#) **24**, 883 (1985).
- [2] A. E. Yakshin, R. W. E. van de Kruijs, I. Nedelcu, E. Zoethout, E. Louis, F. Bijkerk, H. Enkisch, and S. Müllender, *Enhanced reflectance of interface engineered Mo/Si multilayers produced by thermal particle deposition*, [Emerging Lithographic Technologies XI](#) **6517**, 65170I (2007).
- [3] T. Feigl, S. Yulin, N. Benoit, and N. Kaiser, *EUV multilayer optics*, [Micro-electronic Engineering](#) **83**, 703 (2006).
- [4] E. Louis, A. E. Yakshin, T. Tsarfati, and F. Bijkerk, *Nanometer interface and materials control for multilayer EUV-optical applications*, [Progress in Surface Science](#) **86**, 255 (2011).
- [5] C. Burcklen, S. de Rossi, E. Meltchakov, D. Denetière, B. Capitanio, F. Polack, and F. Delmotte, *High-reflectance magnetron-sputtered scandium-based x-ray multilayer mirrors for the water window*, [Optics Letters](#) **42**, 1927 (2017).
- [6] S. S. Andreev, M. S. Bibishkin, N. I. Chkhalo, E. B. Klunokov, K. A. Prokhorov, N. N. Salashchenko, M. V. Zorina, F. Schafers, and L. A. Shmaenok, *Short-period multilayer X-ray mirrors*, [Journal of Synchrotron Radiation](#) **10**, 358 (2003).
- [7] G. A. Johansson, *Enhanced soft x-ray reflectivity of Cr/Sc multilayers by ion-assisted sputter deposition*, [Optical Engineering](#) **41**, 2903 (2002).
- [8] A. Nefedov and H. Zabel, *Sputtered V/Al₂O₃ multilayer X-ray mirrors for the water window*, Nuclear Instruments and Methods in Physics Research, Section A: Accelerators, Spectrometers, Detectors and Associated Equipment **468**, 345 (2001).
- [9] J. Birch, F. Eriksson, G. A. Johansson, and H. M. Hertz, *Recent advances in ion-assisted growth of Cr/Sc multilayer X-ray mirrors for the water window*, [Vacuum](#) **68**, 275 (2002).
- [10] K. Yamashita, K. Akiyama, K. Haga, H. Kunieda, G. S. Lodha, N. Nakajo, N. Nakamura, T. Okajima, K. Tamura, and Y. Tawara, *Fabrication and characterization of multilayer supermirrors for hard X-ray optics*, [Journal of Synchrotron Radiation](#) **5**, 711 (1998).
- [11] C. P. Jensen, K. K. Madsen, and F. E. Christensen, *Small D-spacing WC/SiC multilayers for future hard X-ray telescope designs*, [Experimental Astronomy](#) **20**, 93 (2005).
- [12] D. D. M. Ferreira, F. E. Christensen, A. C. Jakobsen, N. J. Westergaard, and B. Shortt, *ATHENA optimized coating design*, [Space Telescopes and Instrumentation 2012: Ultraviolet to Gamma Ray](#) **8443**, 84435L (2012).

- [13] P. H. Mao, F. A. Harrison, D. L. Windt, and F. E. Christensen, *Optimization of graded multilayer designs for astronomical x-ray telescopes*, [Applied Optics](#) **38**, 4766 (1999).
- [14] S. Svendsen, S. Massahi, D. Della Monica Ferreira, F. E. Christensen, A. Jafari, P. L. Henriksen, M. Collon, B. Landgraf, D. Girou, M. Krumrey, L. Cibik, A. Schubert, E. Handick, and B. Shortt, *Performance and time stability of Ir/SiC X-ray mirror coatings for ATHENA*, [Proceedings of SPIE 11119, Optics for EUV, X-Ray, and Gamma-Ray Astronomy IX 11119](#), 107 (2019).
- [15] K. Madsen, F. E. Christensen, B. W. Grefenstette, F. A. Harrison, A. Hornschemeier, H. Miyasaka, T. Okajima, S. M. Pike, T. T. Saha, W. W. Zhang, M. Pivovarov, J. Vogel, M.-A. Descalle, D. Broadway, D. Gurgew, D. Stern, D. Ferreira, and D. Windt, *Optical instrument design of the high-energy x-ray probe (HEX-P)*, [Space Telescopes and Instrumentation 2018: Ultraviolet to Gamma Ray 10699](#), 237 (2018).
- [16] C. Liu, R. Conley, A. T. Macrander, T. J. Graber, C. Morawe, C. Borel, and E. M. Dufresne, *Small-d-spacing WSi₂/Si narrow bandpass multilayers*, [X-Ray Sources and Optics 5537](#), 154 (2004).
- [17] F. Wang, B. Mu, H. Jin, X. Yang, and J. Zhu, *Effect of separating layer thickness on W/Si multilayer replication*, [Optics Express 19](#), 15929 (2011).
- [18] D. L. Windt, F. E. Christensen, W. W. Craig, C. Hailey, F. A. Harrison, M. Jimenez-Garate, R. Kalyanaraman, and P. H. Mao, *Growth, structure, and performance of depth-graded W/Si multilayers for hard x-ray optics*, [Journal of Applied Physics 88](#), 460 (2000).
- [19] K. V. Nikolaev, S. N. Yakunin, I. A. Makhotkin, J. de la Rie, R. V. Medvedev, A. V. Rogachev, I. N. Trunckin, A. L. Vasiliev, C. P. Hendrikx, M. Gateshki, R. W. E. van de Kruijs, F. Bijkerk, and IUCr, *Grazing-incidence small-angle X-ray scattering study of correlated lateral density fluctuations in W/Si multilayers*, [Acta Crystallographica Section A Foundations and Advances 75](#), 342 (2019).
- [20] S. K. Rai, A. Das, A. K. Srivastava, G. S. Lodha, and R. Dhawan, *Ion beam sputter deposited W/Si multilayers: Influence of re-sputtering on the interface structure and structure modification at ultra short periods*, [Applied Surface Science 257](#), 10704 (2011).
- [21] C. Eberl, T. Liese, F. Schlenkrich, F. Döring, H. Hofsäuss, and H. U. Krebs, *Enhanced resputtering and asymmetric interface mixing in W/Si multilayers*, [Applied Physics A: Materials Science and Processing 111](#), 431 (2013).
- [22] B. A. Vidal and J. C. Marfaing, *X-ray reflectivity and transmission electron microscopy studies on thin and ultrathin W/C and W/Si multilayers structures*, [Journal of Applied Physics 65](#), 3453 (1989).

- [23] Y. Y. Platonov, D. Broadway, B. DeGroot, P. Mao, F. Harrison, G. Gutman, and J. Rodriguez, *X-ray reflectivity and mechanical stress in W/Si multilayers deposited on thin substrates of glass, epoxy-replicated aluminum foil, and Si wafer*, *Grazing Incidence and Multilayer X-Ray Optical Systems*, 27-29 July 1997 **3113**, 469 (1997).
- [24] M. J. Kessels, J. Verhoeven, A. E. Yakshin, F. D. Tichelaar, and F. Bijkerk, *Ion beam induced intermixing of interface structures in W/Si multilayers*, *Nuclear Instruments and Methods in Physics Research, Section B: Beam Interactions with Materials and Atoms* **222**, 484 (2004).
- [25] D. Bhattacharyya, A. K. Poswal, G. K. Dey, and N. C. Das, *Investigation of Mo/Si and W/Si interfaces by phase modulated spectroscopic ellipsometry and cross-sectional transmission electron microscopy*, *Vacuum* **76**, 31 (2004).
- [26] C. K. Kim, Y. S. Park, S. J. Han, J. yool Chae, and B. K. Na, *Study and characterization of W/Si and W/B₄C multilayer for applications in hard X-rays mirror*, *Korean Journal of Chemical Engineering* **32**, 2124 (2015).
- [27] T. Salditt, D. Lott, T. Metzger, J. Peisl, and G. Vignaud, *Interfacial roughness and related growth mechanisms in sputtered W/Si multilayers*, *Physical Review B - Condensed Matter and Materials Physics* **54**, 5860 (1996).
- [28] Y. P. Wang, H. Zhou, L. Zhou, R. L. Headrick, A. T. MacRander, and A. S. Özcan, *Interface roughness evolution in sputtered W Si₂ Si multilayers*, *Journal of Applied Physics* **101** (2007), 10.1063/1.2422713.
- [29] D. L. Windt, *IMD—Software for modeling the optical properties of multilayer films*, *Computers in Physics* (1998), 10.1063/1.168689, arXiv:hec.3108 [10.1002] .
- [30] B. K. Gan, B. A. Latella, and R. W. Cheary, *Fabrication and characterisation of ultra-thin tungsten-carbon (W/C) and platinum-carbon (Pt/C) multilayers for X-ray mirrors*, *Applied Surface Science* **239**, 237 (2005).
- [31] P. Siffalovic, E. Majkova, L. Chitu, M. Jergel, S. Luby, J. Keckes, G. Maier, A. Timmann, S. V. Roth, T. Tsuru, T. Harada, M. Yamamoto, and U. Heinzmann, *Characterization of Mo/Si soft X-ray multilayer mirrors by grazing-incidence small-angle X-ray scattering*, *Vacuum* **84**, 19 (2009).
- [32] I. A. Kopylets, V. V. Kondratenko, E. N. Zubarev, and D. V. Roshchupkin, *Formation of short-period multilayer W/B₄C compositions*, *Technical Physics* **57**, 1709 (2012).
- [33] P. N. Rao, S. K. Rai, M. Nayak, and G. S. Lodha, *Stability and normal incidence reflectivity of W/B₄C multilayer mirror near the boron K absorption edge*, *Applied Optics* **52**, 6126 (2013).
- [34] C. G. Pope, *X-ray diffraction and the bragg equation*, *Journal of Chemical Education* **74**, 129 (1997).

- [35] M. Yamamoto, J. Cao, and T. Namioka, *Optical Criterion Of The Selection Of Material Pairs For High-Reflectance Soft X-Ray Multilayers*, *X-Ray Instrumentation in Medicine and Biology, Plasma Physics, Astrophysics, and Synchrotron Radiation* **1140**, 448 (1989).
- [36] Barbee Jr., Troy W., *Multilayers for x-ray optics*, *Optical Engineering* **25**, 898 (1986).
- [37] E. Spiller, A. Segmüller, J. Rife, and R. P. Haelbich, *Controlled fabrication of multilayer soft-x-ray mirrors*, *Applied Physics Letters* **37**, 1048 (1980).
- [38] M. P. Bruijn, J. Verhoeven, E. Puik, and M. J. van der Wiel, *Multilayer X-Ray Mirrors; The State Of The Art. X-Ray Multilayers in Diffractometers, Monochromators, and Spectrometers* **0984**, 54 (1988).
- [39] E. Spiller, S. L. Baker, P. B. Mirkarimi, V. Sperry, E. M. Gullikson, and D. G. Stearns, *High-performance Mo-Si multilayer coatings for extreme-ultraviolet lithography by ion-beam deposition*, *Applied optics* **42**, 4049 (2003).
- [40] Z. Jiang, X. Jiang, W. Liu, and Z. Wu, *Thermal stability of multilayer films Pt/Si, W/Si, Mo/Si, and W/C*, *Journal of Applied Physics* **65**, 196 (1989).
- [41] E. Louis, A. E. Yakshin, E. Zoethout, R. W. E. van de Kruijs, I. Nedelcu, S. A. van der Westen, T. Tsarfati, F. Bijkerk, H. Enkisch, S. Müllender, B. Wolschrijn, and B. Mertens, *Enhanced performance of EUV multilayer coatings*, *Proceedings of SPIE* **5900**, 590002 (2005).
- [42] S. Braun, P. Gawlitza, M. Menzel, A. Leson, M. Mertin, and F. Schäfers, *Reflectance and resolution of multilayer monochromators for photon energies from 400 - 6000 eV*, *AIP Conference Proceedings* **879**, 493 (2007).
- [43] D. E. Savage, J. Kleiner, N. Schimke, Y. H. Phang, T. Jankowski, J. Jacobs, R. Kariotis, and M. G. Lagally, *Determination of roughness correlations in multilayer films for x-ray mirrors*, *Journal of Applied Physics* **69**, 1411 (1991).
- [44] F. Schäfers, *Multilayers for the EUV/soft X-ray range*, *Physica B: Condensed Matter* **283**, 119 (2000).
- [45] T. Tsarfati, R. W. van de Kruijs, E. Zoethout, E. Louis, and F. Bijkerk, *Reflective multilayer optics for 6.7 nm wavelength radiation sources and next generation lithography*, *Thin Solid Films* **518**, 1365 (2009).
- [46] D. S. Kuznetsov, A. E. Yakshin, J. M. Sturm, R. W. E. van de Kruijs, E. Louis, and F. Bijkerk, *High-reflectance La/B-based multilayer mirror for 6nm wavelength*, *Optics Letters* **40**, 3778 (2015).
- [47] N. I. Chkhalo, S. Künstner, V. N. Polkovnikov, N. N. Salashchenko, F. Schäfers, and S. D. Starikov, *High performance La/B₄C multilayer mirrors with barrier layers for the next generation lithography*, *Applied Physics Letters* **102**, 4 (2013).

- [48] S. Fischer, A. Guggenmos, B. Nickel, E. M. Gullikson, M. Hofstetter, U. Kleineberg, A. Wochnik, R. Rauhut, S. Radünz, S. Venkatesan, and C. Scheu, *Ion polished Cr/Sc attosecond multilayer mirrors for high water window reflectivity*, *Optics Express* **22**, 26526 (2014).
- [49] R. Pretorius, *Phase sequence of silicide formation at metal-silicon interfaces*, *Vacuum* **41**, 1038 (1990).
- [50] M. Morita, T. Ohmi, E. Hasegawa, M. Kawakami, and M. Ohwada, *Growth of native oxide on a silicon surface*, *Journal of Applied Physics* **68**, 1272 (1990).
- [51] J. Iijima, J. W. Lim, S. H. Hong, S. Suzuki, K. Mimura, and M. Isshiki, *Native oxidation of ultra high purity Cu bulk and thin films*, *Applied Surface Science* **253**, 2825 (2006).
- [52] S. Suzuki, K. Yanagihara, and K. Hirokawa, *XPS study of oxides formed on the surface of high-purity iron exposed to air*, *Surface and Interface Analysis* **30**, 372 (2000).
- [53] S. V. Plyushcheva, G. M. Mikhailov, L. G. Shabel'nikov, and S. Y. Shapoval, *Tungsten thin-film deposition on a silicon wafer: The formation of silicides at W-Si interface*, *Inorganic Materials* **45**, 140 (2009).
- [54] I. A. Makhotkin, E. Zoethout, R. van de Kruijs, S. N. Yakunin, E. Louis, A. M. Yakunin, V. Banine, S. Müllender, and F. Bijkerk, *Short period La/B and LaN/B multilayer mirrors for ~ 68 nm wavelength*, *Optics Express* **21**, 29894 (2013).
- [55] S. S. Andreev, M. M. Barysheva, N. I. Chkhalo, S. A. Gusev, A. E. Pestov, V. N. Polkovnikov, D. N. Rogachev, N. N. Salashchenko, Y. A. Vainer, and S. Y. Zuev, *Multilayer X-ray mirrors based on La/B₄C and La/B₉C*, *Technical Physics* **55**, 1168 (2010).
- [56] I. A. Makhotkin, R. W. E. van de Kruijs, E. Zoethout, E. Louis, and F. Bijkerk, *Optimization of LaN/B multilayer mirrors for 6.x nm wavelength*, *Advances in X-Ray/EUV Optics and Components VIII* **8848**, 884800 (2013).
- [57] D. S. Kuznetsov, A. E. Yakshin, J. M. Sturm, R. W. Van De Kruijs, and F. Bijkerk, *Structure of high-reflectance La/B-based multilayer mirrors with partial la nitridation*, *AIP Advances* **6** (2016), 10.1063/1.4968175.
- [58] T. Tsarfati, E. Zoethout, E. Louis, R. van de Kruijs, A. Yakshin, S. Müllender, and F. Bijkerk, *Improved contrast and reflectivity of multilayer reflective optics for wavelengths beyond the extreme UV*, *Alternative Lithographic Technologies* **7271**, 72713V (2009).
- [59] T. Tsarfati, R. W. Van De Kruijs, E. Zoethout, E. Louis, and F. Bijkerk, *Nitridation and contrast of B₄C/La interfaces and X-ray multilayer optics*, *Thin Solid Films* **518**, 7249 (2010).

- [60] A. Chandrasekaran, R. W. E. V. D. Kruijs, J. M. Sturm, A. A. Zameshin, and F. Bijkerk, *Nanoscale Transition Metal Thin Films : Growth Characteristics and Scaling Law for Interlayer Formation*, *Applied materials & interfaces* (2019), [10.1021/acsami.9b14414](https://doi.org/10.1021/acsami.9b14414).
- [61] A. Zameshin, *Probing atomic scale interface processes using X-rays and ions (doctoral dissertation)*, *Ph.D. thesis* (2018).
- [62] A. Gerlach and F. Schreiber, *The X-Ray Standing Wave Technique*, *Handbook of Spectroscopy: Second, Enlarged Edition 4-4*, 1507 (2014).
- [63] L. C. Xu and C. A. Siedlecki, *Atomic force microscopy*, *Comprehensive Biomaterials* **3**, 23 (2011).
- [64] T. Tsarfati, *Surface and interface dynamics in multilayered systems*, *Ph.D. thesis* (2009).

2

LOW-ENERGY ION POLISHING OF SI IN W/SI SOFT X-RAY MULTILAYER STRUCTURES

The effect of ion polishing in sputter deposited W/Si multilayer mirrors with a d-spacing of 2.5 nm was studied. 0.1 to 0.5 nm of Si were etched with 100 eV Ar⁺ ions. This process resulted in a pronounced reduction in diffused scattering, measured at wavelengths about 0.1 nm. However, CuK α X-Ray specular reflectivity and AFM showed only a marginal reduction of the roughness amplitude in the systems. Furthermore, the soft X-Ray reflectivity at 0.84 and 2.4 nm did not show any changes after the ion polishing as compared to the non-polished structures. GIXR analysis revealed that there was no pure W present in the deposited multilayers, with WSi₂ being formed instead. As a result, it was concluded that the initial roughness in W/Si multilayers grown by magnetron sputtering is not the major factor in the reflectivity deviation from the calculated value for an ideal system. Nevertheless, the GISAXS analysis revealed that ion polishing reduces the vertical propagation of roughness from layer to layer by a factor of two, as well as favorably affecting the lateral correlation length and Hurst parameter. These improvements explain the reduction of diffused X-Ray scattering at 0.1 nm by more than an order of magnitude, which is relevant for applications like high resolution XRD analysis.

2.1 Introduction

Multilayers with nanoscale thick layers are used in a large variety of applications, for the reason that they can be tuned to a specific wavelength and working angle required for a particular task. One of the applications is X-Ray fluorescence spectroscopy, where multilayers serve as analyzing crystals to resolve fluorescence emission lines from the investigated material. In this work such analyzers are considered to resolve spectral lines from O $K\alpha$ to Al $K\alpha$ (525 eV – 1486 eV) in order to produce a qualitative analysis of materials in this range. This corresponds to the range of wavelengths 0.84 to 2.4 nm. The focus in this work is on W/Si multilayers prepared by magnetron sputtering, which have high reflectivity at these wavelengths. Multilayers are designed following Bragg's law in order to reflect the incident radiation by constructive interference. Therefore, to reflect at 0.84 nm and 2.4 nm wavelengths at specific angles of relevance for the application (9.7 and 29.5 degrees grazing incidence, correspondingly), a period of the multilayer of 2.5 nm is required. Apart from the optical indices of materials used, the reflectivity is determined by the quality of the interfaces between the layers. The shorter the period, the more sensitive the reflectivity is to imperfections at the interfaces. Interdiffusion and interfacial roughness are two limiting factors to achieve the maximum reflectivity. For instance, Liu et al. studied interface formations in W/Si and WSi_2 /Si multilayers where they showed that interdiffusion between W and Si in W/Si multilayers leads to a formation of less sharper interfaces than in WSi_2 /Si multilayers [1, 2]. One of the advantages of magnetron sputtering is that it can inherently produce low interfacial roughness. However, even a relatively low roughness might affect reflectivity of short period multilayers. Moreover, intermixing of the elements can contribute to an additional interfacial roughness formation, which will further reduce reflectivity. Therefore, even the multilayers produced by magnetron sputtering might need an additional roughness control. Ion beam polishing was reported to be an effective tool to reduce interfacial roughness in multilayers and single surfaces [3–13]. Soyama et al. [3] reported about a strong reduction of interfacial roughness from 0.7 nm to 0.35 nm in Ni/Ti multilayers deposited by ion beam sputtering with a period $d = 12$ nm after applying an ion beam polishing of 100 eV after deposition on either a Ni or Ti layer. Another successful experience of ion polishing was demonstrated by Puik et al. [4] for W/C and Ni/C short period $d = 7.4$ nm multilayers. Metal layers of W and Ni were deposited by e-beam evaporation and etched afterwards using Ar^+ ions at 200–300 eV energies. Etching a thickness of 2.8 nm of metal layers resulted in a significant gain in reflectivity detected by an in-situ soft X-Ray monitoring system. Spiller [6] obtained an increase in reflectivity from 8% to 16% at $\lambda = 4.8$ nm by using ion beam polishing in Rh-C, and around the same gain from 9% to 20% at $\lambda = 4.78$ nm in ReWCo-C multilayer mirrors deposited by electron beam evaporation for normal incidence X-Ray telescopes. Ar^+ ions with energies of 300 eV and 500 eV were used to polish Rh-C with $d = 6.17$ nm and ReWCo-C with $d = 3.64$ nm multilayers, respectively.

Ion beam polishing was reported to be an effective tool to reduce interfacial roughness in Mo/Si multilayers with a period $d = 7$ nm [4–6]. In these works, about 4 nm thick Si was exposed to Kr^+ ions with energies in the range of 100–

2000 eV to achieve smoothening of interfaces. The etched thicknesses of Si were in the range from 0.12 to 0.75 nm. It was found that low energies in the range of 100-150 eV are more favorable for reducing interfacial roughness. W/Si multilayers with a period of 4.1 nm were studied by Kessels et al. [8] who applied Kr⁺ ions on W and WRe layers with a thicknesses of 1.7 nm. The energy of 100 eV was found to be optimal to reduce interfacial roughness and increase the reflectivity of carbon-K radiation from 43% to 65% for 10-period stacks. Applying higher energies led to intermixing of layers and an increase of interfacial roughness, hence a reduced reflectivity for all multilayers.

Thus, ion polishing was shown to be a useful tool to increase reflectivity by reducing roughness at the interfaces for multilayers having a relatively long period. The main goal of this work was to investigate the possibility of increasing the reflectivity of multilayers having a much shorter periodicity. We investigated the effect of ion polishing of Si in W/Si multilayer mirrors with a period of 2.5 nm, deposited by magnetron sputtering.

2.2 Experiment

2.2.1 Multilayer deposition

All multilayers were deposited on super-polished silicon wafers 25 mm × 25 mm (RMS roughness $\approx$ 0.14 nm) using DC magnetron sputtering system with a base pressure of $1 \cdot 10^{-9}$ mbar. Ar⁺ gas was used as a working gas at the pressure of about $1 \cdot 10^{-4}$ mbar. The multilayers consisted of 200 periods with the period thickness $d = 2.5$ nm and Gamma values varying from 0.06 to 0.24. Every Si layer was polished with an ion source after its deposition, with the etched thickness being 0.1 to 0.5 nm. The ion source was mounted such that the ions arrive at normal incidence with respect to the substrate surface. The energy of ions was chosen to be 100 eV in order to keep the penetration of ions into the layer as low as possible to avoid intermixing with the underlying layer, but at the same time practical to avoid an extended polishing process. The etching rate was calibrated by depositing stacks varying the amount of etched Si. These stacks were measured with Cu K α ($\lambda = 0.154$ nm) reflectometry to determine the resulting periods and subsequently determine the etching rate. To avoid oxidation of the surface after exposure to the air, every multilayer was finished with a Si layer with the same thickness as in rest of the structure. Depositions were performed at the power of 30 W for W and 260 W for Si. Such a low power for W was chosen to minimize the deposition rate of W in order to have a better thickness control over thin W layers. The uniformity was achieved by spinning the holder with substrates at 90 rpm during the deposition process (see Fig. 2.1 for configuration of the deposition setup).

2.2.2 Multilayer characterization

The multilayers were characterized by $\theta - 2\theta$ grazing incidence reflectivity measurement at Cu K α wavelength ($\lambda = 0.154$ nm) using a Malvern Panalytical Empyrean diffractometer to determine the period. A hybrid monochromator consisting of a combination of an X-Ray mirror and a two-crystal Ge (220) two-bounce monochro-

Figure 2.1: Configuration of the deposition setup. The spinning substrate moves forward sequentially over the W and Si magnetrons, and further over the ion source for Si polishing step. The translational movement rate is fixed for each station and is adjusted individually to control the deposited or etched thickness. All the stations are mounted such that the deposited particles (atoms and ions) arrive at normal incidence with respect to the substrate surface.

mator was used.

For a fast qualitative assessment of multilayers X-Ray diffused scattering rocking curves were measured with a conventional X-Ray tube at the wavelength of 0.154 nm, with the procedure of the measurement being described elsewhere [14]. The rocking curves were taken at the second Bragg peak. For quantitative analysis of X-Ray diffused scattering GISAXS measurements were implemented. These measurements were carried out at the bending magnet beamline Langmuir of the synchrotron radiation source Siberia-2 at the Kurchatov Institute [15]. Monochromatization at the beamline was arranged by a thermally stabilized two bounce Si monochromator with (111) reflection. Higher harmonics of the monochromatized beam were suppressed with quartz and tungsten X-Ray mirrors. The synchrotron beam was collimated with three sets of slits. The resulting beam size was $50 \times 200 \mu\text{m}^2$, with the corresponding average direct beam intensity being approximately $2 \cdot 10^7$ cps (counts per second). The vertical beam divergence was 4 arcsec and the horizontal divergence was 20 arcsec. The diffuse scattering intensity was measured with a Pilatus 100k 2D detector. Measurement settings for both samples (sample with and without ion treatment) were identical. The measurements were taken at the wavelength $\lambda = 0.1$ nm in three exposures of 15 min each, in order to avoid detector saturation. The angle of incidence was set to $\theta_0 = 0.3^\circ$, in between the total external reflection and the first Bragg peak. The incident synchrotron beam intensity was monitored with an ionization chamber FMB Oxford IC plus 50.

To measure the top surface roughness of the samples, a Bruker Dimension EdgeTM Atomic Force Microscope (AFM) was used. A high resolution tip Hi'Res-C14/Cr-Au by MikroMasch was used (radius of the tip was ≈ 1 nm).

Soft X-Ray reflectivity at specific wavelengths and grazing angles of incidence required for the application (0.84 nm, $\theta \approx 9.7^\circ$ and 2.4 nm, $\theta \approx 28.7^\circ$) were measured at the storage ring BESSY II at Physikalisch-Technische Bundesanstalt (PTB) in Berlin-Adlershof, Germany. Since the reflectivity was measured at grazing incidence angle, a 0.5 mm exit slit on the monochromator was used in order to reduce the size of the beam footprint on a sample.

2.3 Results

2.3.1 Diffuse scattering

To determine the impact of ion polishing on roughness for the deposited structures, X-Ray diffuse scattering at Cu $K\alpha$ wavelength ($\lambda = 0.154$ nm) was measured by mean of the rocking curve scan. This measurement is done by fixing the detector at the center of the Bragg reflection and rocking the sample in a wide angular range. A perfect structure will produce a very sharp peak in the specular direction only, while a structure with diffused scattering will show wide wings around it. The rocking curve measurement from multilayer structures are described in more detail elsewhere [14]. It is common to measure diffuse scattering at higher orders to observe a wider range of angles, however, due to the low intensity of the high order Bragg peaks, all scans in this work were performed at the second Bragg peak of 3.2° ($2\theta = 6.4^\circ$). Fig. 2.2 shows the rocking curve scans for the multilayers deposited with and without ion polishing. The peaks at 3.2° correspond to the

Figure 2.2: Rocking curve scans for W/Si ($d = 2.5$ nm, $N = 100$, $\Gamma = 0.125$) multilayers deposited with and without ion polishing. For the polished multilayers the amount of etched Si is 0.1, 0.3, and 0.5 nm. The curves were normalized at the maximum intensity of the Bragg peak for comparison.

specular reflectivity at the second Bragg order, with the diffused scattering being on the left and right sides of the specular peak.

As seen a substantial decrease in diffuse scattering is observed as the amount of etched Si during the ion-polishing process increases. This implies that the interfacial roughness was affected significantly by the polishing process [10–12]. The integral diffuse scattering does not differ significantly between the samples with 0.3 nm and 0.5 nm of Si etched that indicates that the effect of ion polishing reaches saturation at 0.3 nm. For this reason we proceeded with a 0.3 nm ion polishing for further analysis.

2.3.2 Grazing incidence X-Ray reflectivity

In Fig. 2.3 GIXR at CuK α wavelength $\lambda = 0.154$ nm of the initial (unpolished) and 0.3 nm polished multilayers are shown. The main difference between the two multilayers is that the high-order peaks are more pronounced in the multilayers after polishing, which usually indicates a reduced roughness, which is in line with the diffused scattering measurement shown in the section above that suggests reduced roughness.

Figure 2.3: Cu K α GIXR reflectivity of unpolished and polished W/Si multilayers with 0.3 nm Si etched. The enhanced reflectance at high orders indicates an improvement in the structures with ion polishing.

2.3.3 Soft X-Ray reflectivity

Simulations in IMD [16] show that the optimum gamma value $\Gamma = d_W/[d_W + d_{Si}]$ for the maximum reflectivity of W/Si multilayers at 0.84 nm wavelength and the angle of incidence $\theta \approx 9.7^\circ$ is $\Gamma = 0.23$. For an ideal multilayer (no interfacial roughness)

Figure 2.4: (a) Peak reflectivity as a function of gamma for the unpolished and polished W/Si multilayers with 0.3 nm etched Si ($d = 2.5$ nm $N = 200$), measured at 0.84 nm and at the angle of incidence 9.7° ; (b) Reflectivity as a function of wavelength measured at 9.7° angle of incidence compared to an ideal multilayer (no interfacial roughness) simulated in IMD.

the maximum reflectivity is 60%. It was reported that W and Si tend to form a silicide $WxSix$ in W/Si multilayer structures, which means that certain changes in the period and thus in gamma values occur during deposition, depending on the amount of deposited materials [7, 13]. Therefore, in order to find the optimum gamma value resulting in the maximum reflectivity in our experiments, a series of multilayers in the range of gamma from 0.06 to 0.24 was deposited for every set of multilayers with polished and unpolished Si layers. Fig. 2.4 shows the reflectivity for these structures at 0.84 nm and at the angle of incidence $\theta \approx 9.7^\circ$. As seen in Fig. 2.4(a) the optimum gamma value obtained was $\Gamma = 0.12$, which is about a factor of two smaller than in our IMD calculations. Furthermore, the obtained maximum reflectivity did not differ for both types of structures.

The multilayers were also measured at 2.4 nm and showed the same dependency of reflectivity on gamma value. The same maximum reflectivity of 9.5% was obtained at 2.4 nm for the unpolished and polished structures at a gamma value of 0.12. This way both soft X-Ray measurements showed that the applied ion polishing did not result in any improvements in reflectivity. Spiller et al. [17] reported that implantation of Ar^+ species in Si layers could reduce reflectivity in their work. Similarly, the presence of Ar^+ could counterbalance possible reflectivity gain in our polished multilayers. However, XPS analysis did not reveal the presence of Ar^+ in our samples.

Further analysis was needed to understand the differences in the results obtained at 0.154 nm, 0.84 nm and at 2.4 nm. For that the studied structures were measured with AFM and GISAXS, which allowed us to extract parameters of roughness quantitatively.

Figure 2.5: AFM data of unpolished (left side) and 0.3 nm polished (right side) surfaces.

2.3.4 Atomic force microscopy

In Fig. 2.5 a comparison of AFM measurements is shown for the unpolished and polished structures with 0.3 nm etched Si. Both surfaces were measured several times at different spots for better statistics. The rms roughness value for the unpolished sample was $r_q = 0.134$ nm with a standard deviation of 0.01 nm. The rms roughness value for the polished sample was $r_q = 0.116$ nm with a standard deviation of 0.008 nm. This way the AFM measurements confirmed some reduction in roughness of the polished structures, although the difference in the surface roughness was found to be only about 0.02 nm.

2.3.5 Grazing incidence small-angle X-Ray scattering

AFM allows for direct measurements of the roughness of the outermost surface of the structure. However, the surface is oxidized after exposure to the atmosphere; consequently, the morphology of its roughness is different from that of the inner interfaces. Therefore, imperfections of the multilayer cannot be characterized in full by the sole use of AFM. For the characterization of the interface roughness, grazing incidence small-angle X-Ray scattering (GISAXS) has been employed.

The GISAXS method is based on the measurement of the diffuse scattering of the incident radiation. The GISAXS measurements for not polished (a) and polished (b) W/Si multilayers are shown in Fig. 2.6 at a logarithmic scale. In Fig. 2.6, one can note distinct features: sets of maxima which are commonly referred to as Bragg sheets in the literature [18]. The nature of the Bragg sheets is attributed to the scattering on the correlated roughness [19]. This scattering produces coherent superposition of the scattered radiation which subsequently diffracts on the multilayer structure, resulting in the Bragg sheets. In the opposite case of the not correlated roughness, radiation scatters with a random phase. No diffraction from the multilayer structure appears in the scattered radiation in that case. The shape of the Bragg sheets is dependent on the statistical parameters of the interface roughness, as opposed to AFM which allows for direct roughness measurements but only for the outermost surface of the structure.

The interface roughness in multilayers can be represented as a self-affine surface [20]. Within that approach the interface roughness morphology is defined with the following parameters: ξ_v – vertical correlation length, ξ_l – lateral correlation length

Figure 2.6: GISAXS maps measured for (a) sample prepared without ion polishing and (b) sample prepared with ion polishing. Measurement parameters $\lambda = 0.1$ nm, angle of incidence $\theta_0 = 0.3^\circ$; Exit angle range $\theta_f \in [0.61^\circ; 5.18^\circ]$, Azimuthal angle range $\phi \in [-1.28^\circ; 1.28^\circ]$

and Hurst parameter H . The lateral correlation length is the averaged characteristic size of the interface roughness in lateral direction. The vertical correlation is the effective depth within which the shape of roughness is maintained from interface to interface. The Hurst parameter defines jaggedness of the interface. Limiting cases: $H \rightarrow 1$ corresponds to a smooth roughness profile, while $H \rightarrow 0$ corresponds to a jagged roughness profile [21]. Concise explanation of the physical meaning of these parameters is given in [22]. Qualitatively, decrease of lateral correlation leads to a broadening of the Bragg sheet in q_x direction [21]. Similarly, increase of the vertical correlation leads to the broadening in q_z direction. It is apparent in Fig. 2.6 that the polished sample has a bigger lateral correlation length than the not polished one because of its narrower Bragg sheets. We estimated statistical parameters of the interface roughness using an approach, similar to what was used in [18]. The vertical correlation length was estimated using the equation: $\xi_v = 2\pi/\sigma_{q_z}$, where σ_{q_z} is a full width half maximum (FWHM) parameter [18]. The FWHMs were analyzed by fitting line extractions of the second Bragg peak along q_z axis taken in $q_x = 0$, see Fig. 2.7 (a) and (b). The second Bragg peak was chosen due to the low penetration depth of X-Rays at the first Bragg peak. These line extractions were fitted using pseudo Voigt profile, which is conventionally used in spectroscopy and diffraction data analysis [23]. Thus, the FWHMs of the second Bragg peak were estimated [23].

The parameters of Hurst and lateral correlation length were estimated by fitting line extractions of the second Bragg sheet taken along the q_x axis (see Figs. 2.7(c) and 2.7(d)). These line extractions were fitted with the use of a K-correlation

Figure 2.7: Line extractions calculated from Fig. 2.6: (a) and (b) are the line extractions for the second Bragg peak along the q_z axis taken at $q_x = 0$ nm⁻¹ for the unpolished and polished multilayer, respectively (red curve is a measurement, blue curve is a fitting including error bars) (c) and (d) are the line extractions for the second Bragg peak along the q_x axis for the unpolished (taken at $q_z = 4.9$ nm⁻¹) and polished multilayer (taken at $q_z = 4.7$ nm⁻¹), respectively (red curve is a measurement, blue curve is a fitting including error bars)

model. [24] There, the correlation function is given by

$$C(r) = \frac{\sigma^2 H}{2^{H-1} \Gamma(H+1)} \gamma^H K_H(\gamma); \quad (2.1)$$

where $\gamma = r\sqrt{2H}/\xi_l$, Γ is the gamma function, K_H is the modified Bessel function of H-th order of the second kind, and σ is the roughness rms amplitude. We approximated a corresponding power spectral density function as

$$P(q_{\parallel}) \propto \int_0^{\infty} r J_0(q_{\parallel} r) \exp(C(r) - 1) dr; \quad (2.2)$$

where J_0 is the 0-th order Bessel function of the first kind. Finally, we assumed that the scattering cross section in the region of line extraction along the q_x axis in the second Bragg peak is proportional to the PSD function $\sigma/d\Omega = I_0 P(q_{\parallel})$. This assumption imposes a restriction on the estimation of the absolute value of the roughness amplitude σ . Indeed, for the sufficiently small argument of exponent in Eq. 2.2, the diffuse scattering intensity is linearly scaled with the value of σ^2 (due to the Taylor expansion of exponent). Thereby, in this model, the intensity of

the incident beam I_0 is strongly correlated with σ . However, due to the normalization on the incident beam intensity, we can cross-compare roughness amplitudes of the measured samples. We estimate $\sigma_1 = 0.28$ nm (without ion polishing) and $\sigma_2 = 0.21$ nm (with ion polishing). These are effective parameters of roughness amplitude, nevertheless, we can conclude that the parameter of roughness changed insignificantly due to the polishing procedure. The results of the fit are presented in Table 2.1.

Table 2.1: Result of the line extractions fit.

	Not polished	Polished
ξ_v , nm	92.9 ± 0.9	36.5 ± 2
ξ_l , nm	10 ± 1	25 ± 2
H	0.54 ± 0.01	0.76 ± 0.04
σ , nm	0.28	0.21

Intensities of the diffuse scattering on the sample prepared with ion assistance were lower; therefore, uncertainties of the parameters for this sample are higher. Finally, it should be noticed that in Fig. 2.6(b) an enhancement of the scattering outside the Bragg sheets can be seen. This effect is more apparent in Fig. 2.8.

Figure 2.8: Line extractions in between Bragg sheets along the q_x direction averaged in between Bragg sheets in the range between $q_z = 3.4$ nm $^{-1}$ and $q_z = 3.7$ nm $^{-1}$.

In Fig. 2.8 line extractions along q_x directions averaged in between Bragg sheets in the range between $q_z = 3.4$ nm $^{-1}$ and $q_z = 3.7$ nm $^{-1}$ for both polished and not polished samples are shown. Line extraction for polished samples have maxima at $q_x \approx \pm 0.5$ nm. The peaks at $q_x \approx \pm 0.5$ nm correspond to the distribution of density fluctuations with the mean neighbors distance of about 10 nm. In our recent work [25] we showed that this scattering is associated with slight density fluctuations of Si in W/Si multilayers where the Si layers were polished with Ar $^{+}$ ions. Line extraction for the not polished sample in Fig. 2.8 have no visible peaks

outside the center $q_x = 0$, which indicates the absence of the density fluctuations in this sample. Note that similar density fluctuations were also observed inside the Ge layer in Fe/Ge multilayers and were attributed to the trapping of Ar⁺ inside the Ge layer [26]. Both observations indicate that Ar⁺ ion treatment may stimulate the formation of density fluctuations inside the Si layers that can be studied further in more details.

2.3.6 Free-form analysis of GIXR

Figure 2.9: Free-form approach fit of the GIXR curves for W/Si unpolished (a) and W/Si 0.3 nm polished (b) multilayers. Calculated curves are shown in solid blue lines, experimental curves in red points; Note that absorption is modulated the same way as refraction, which is not shown here; (c) The δ -profiles obtained with the free-form approach for W/Si unpolished (red line) and W/Si 0.3 nm polished (blue line) multilayers. Two consecutive periodic parts are shown; δ -values for bulk W and WSi_2 are shown by dashed lines.

To obtain additional information about the multilayer structure from GIXR curves presented in Fig. 2.3, we performed a model-independent (free-form) reconstruction of the structural profile, using the approach described in [27]. Compared

to conventional methods of fitting of XRR data, it allows for more freedom in modeling an interface profile, which is crucial for very thin multilayer structures where an interface profile width is comparable to the period thickness.

For treatment of GIXR curves from Fig. 2.3, the periodic part of the multilayer was divided into 13 sublayers, with the top layer being treated separately. The reconstruction started from a steplike profile and finished in about 200 steps with the results shown in Fig. 2.9. As can be seen from Fig. 2.9(a), the fit quality is good, with all the Bragg peaks and the shape of the XRR curve in between being properly described. The results of reconstruction are shown as delta-profiles where $\delta = 1 - \text{Re}(n)$, n is an optical constant [27].

As seen, the shape of the interface profiles between W and Si layers is almost identical in both samples. However, the width of the interface profile for the polished sample is slightly smaller. This can be attributed to somewhat lower roughness in the polished sample. It is important to note that this reconstruction also allows us to conclude that Ar⁺ ion bombardment of thin Si layers at 100 eV energy did not result in the ion penetration through the Si layer. Clearly, no ballistic intermixing takes place with the underlying W layer as a result of the applied ion beam polishing.

An interesting observation can be made about the composition of the W layers. The delta value for pure W based on the tabulated values [28] is $4.6 \cdot 10^{-5}$. However, the delta value of the highest density material in the stack was found to be about $2.4 \cdot 10^{-5}$, which corresponds to a W fraction of only 44%. It means that there is no pure W material within the multilayers.

The obtained delta value is close to the value of WSi₂, which is a consequence of the interaction between W and Si resulting in the formation of silicide as it was described by [7] and [13].

2.3.7 IMD model simulation

The model-independent approach resulted in a smooth delta profile that effectively describes the interface profile but does not allow to discriminate between the contribution of roughness and intermixing individually. Nevertheless, the carried out reconstruction could now be used as an input for some further estimations. Based on the reconstructed density profile, a two-layer model WSi₂/Si ($d = 2.5$ nm, $N = 200$, and $\Gamma = 0.33$) was used to fit our reflectivity data at 0.154 and 0.84 nm with IMD to estimate the roughness values before and after applied polishing. A σ parameter of the Debye–Waller factor was used to take into account the roughness values at interfaces [29]. The obtained results Fig. 2.10 are in a good agreement with experimental data: fittings at 0.154 nm look relatively good and reflectivity at 0.84 nm match the experimental reflectivity of 40%. Changes of the interface widths from $\sigma_{\text{WSi}_2/\text{Si}} = 0.23$ nm and $\sigma_{\text{Si}/\text{WSi}_2} = 0.2$ nm to $\sigma_{\text{WSi}_2/\text{Si}} = 0.22$ nm and $\sigma_{\text{Si}/\text{WSi}_2} = 0.18$ nm explain the high-order changes at 0.154 nm without affecting reflectivity in the soft X-Ray range.

Figure 2.10: The measured and fitted reflectivity of unpolished (a) and polished (b) W/Si multilayers at 0.154 nm (left) and 0.84 nm (right). WSi_2/Si model was used for the fit. The parameters were: ($d = 2.5$ nm, $N = 200$, and $\Gamma = 0.33$). The roughness values (Debye–Waller factor): $\sigma_{\text{WSi}_2/\text{Si}} = 0.23$ nm and $\sigma_{\text{Si}/\text{WSi}_2} = 0.2$ nm for the unpolished structures, and $\sigma_{\text{WSi}_2/\text{Si}} = 0.22$ nm and $\sigma_{\text{Si}/\text{WSi}_2} = 0.18$ nm for the polished structures. The dip in reflectivity below $\theta = 1^\circ$ is caused by oxidation of the surface. Surface oxidation only affect reflectivity between the Bragg peaks and does not affect reflectivity from the periodical part of the multilayer.

2.4 Discussion

We observed a substantial reduction in diffused scatter in the 0.154 nm X-Ray rocking curve measurements of the multilayers when polishing the Si layers. From that it could be expected that the roughness of the multilayers was reduced essentially as a result of the polishing process. The specular reflectivity from these multilayers was qualitatively in agreement with the diffuse scatter measurement results. However, the reflectance of these multilayers at soft X-Rays of 0.84 nm and 2.4 nm did not show any improvements. The highest reflectivity achieved was 40% and 9.5%, respectively, regardless of whether the multilayers received Si ion treatment or not, with the calculated maximum reflectivity for ideal structures to be 60% and 20.5%, correspondingly. Further AFM measurements of the multilayer surfaces suggested only a marginal smoothening effect for the polished structures of about 0.02 nm.

It is necessary to explain why so insignificant changes in roughness resulted in such a substantial reduction in 0.154 nm diffuse scattering. Subsequent GISAXS measurements allowed us to estimate parameters of roughness quantitatively. The lateral correlation length increased from 10 nm to 25 nm and the Hurst parameter

increased from 0.54 to 0.76 as a result of Si layer polishing. The effective parameters for roughness amplitude were estimated to be: $\sigma_1 = 0.28$ nm (without ion polishing) and $\sigma_2 = 0.21$ nm (with ion polishing). This indicates some smoothening effect, although these changes are indeed insignificant. More importantly, it was found that polishing also resulted in a substantial reduction in the vertical correlation length from 92.9 nm to 36.5 nm. This reduction means that the constrictive interference of diffused scattering from interfaces was significantly reduced. According to our simulations in IMD with the data obtained from GISAXS, the changes in the roughness parameters could explain the strong reduction in the diffused scattering observed in the 0.154 nm X-Ray rocking curve measurements. Consequently, we conclude that the amplitude of the initial roughness in W/Si multilayers grown by magnetron sputtering is not sufficiently high to be further reduced by applied ion polishing. Furthermore, this roughness did not seem to be the major factor resulting in a reflectivity loss in the deposited multilayers. Trying to identify this factor, a model-independent X-Ray analysis was applied to the measured GIXR curves from the unpolished and polished multilayers. The reconstructed refractive index profiles suggested that the W layers in the deposited multilayers do not reach bulk density. In fact, effectively only the presence of 44% of bulk W density could explain the observed refractive index of the reflective layer. If we presume that the reduced density is due to a formation of a compound between W and Si, notably the formation of WSi_2 could explain the observed effect. With this input we modelled the 0.154 nm and 0.84 nm reflectivity curves shown in Fig. 2.10(a) and Fig. 2.10(b) with a structure where W layers were replaced with WSi_2 : WSi_2 /Si. To account for the interface width or roughness between the layers Debye–Waller factors were introduced at every interface. Fitting with such a model resulted in the interface widths $\sigma_{\text{WSi}_2/\text{Si}} = 0.23$ nm and $\sigma_{\text{Si}/\text{WSi}_2} = 0.2$ nm for the structures before polishing. They changed to $\sigma_{\text{WSi}_2/\text{Si}} = 0.22$ nm and $\sigma_{\text{Si}/\text{WSi}_2} = 0.18$ nm after polishing. The difference in roughness before and after polishing is in a good agreement with the AFM measurements from the surfaces of the multilayers and estimations made by GISAXS.

As a result, we conclude that the initial roughness in W/Si multilayers grown by magnetron sputtering is not the major factor in the reflectivity deviation from an ideal system. Therefore, ion polishing cannot improve the reflectivity significantly. For a further improvement of reflectivity, the interaction between W and Si should be the key consideration. Nevertheless, if diffused scattering is an important mirror property, Si ion polishing can reduce the fraction of scattered radiation by more than an order of magnitude.

2.5 Conclusions

Previously, ion polishing was shown to be a useful tool to increase reflectivity by reducing roughness at the interfaces for multilayer soft X-Ray reflectors with period thicknesses above 3.5 nm. The main goal of this work was to investigate a possibility to reduce roughness and thus increase the reflectivity of shorter, 2.5 nm period, W/Si multilayers. The multilayers were deposited by magnetron sputtering and were polished with 100 eV Ar^+ ions for every Si layer directly after its deposition,

with the amount of etched Si being varied from 0.1 to 0.5 nm.

The procedure resulted in a pronounced reduction in diffused scattering measured with rocking scans at 0.154 nm and with GISAXS at 0.1 nm. Analysis of GISAXS revealed a strong reduction of the vertical interfacial roughness correlation length from 93 nm to 37 nm. Additionally, the lateral correlation length and the Hurst parameter were improved. The lateral correlation length increased from 10 nm to 25 nm and the Hurst parameter increased from 0.54 to 0.76. The effective parameters of the roughness amplitude reduced from 0.28 to 0.21 nm. AFM measurements showed only a marginal reduction in the surface roughness of about 0.02 nm for the polished multilayers.

Soft X-Ray reflectivity at 0.84 and 2.4 nm did not show any changes after ion polishing. A maximum reflectivity of 40% at 0.84 nm (AOI=9.7° grazing incidence) and 9.5% at 2.4 nm (AOI=29.5° grazing incidence) was achieved.

Free-form analysis of 0.154 nm GIXR measurements revealed there is no pure W present in the deposited multilayers. The obtained delta value of the optical index of the highest density material in the stack corresponded to a WSi₂ compound. Based on this, a two-layer model of WSi₂/Si ($d = 2.5$ nm, $N = 200$, and $\Gamma = 0.33$) was used in IMD to successfully fit both our reflectivity data at 0.154 and 0.84 nm. The small change in roughness amplitude of 0.015 nm could explain high-order changes for the X-Ray reflectivity at 0.154 nm while not affecting the reflectivity at 0.84 and 2.4 nm.

The initial goal of this work was to increase the reflectivity of W/Si multilayers deposited by magnetron sputtering applying ion beam polishing. However, 100 eV Ar⁺ ion polishing of Si in W/Si multilayers did not result in a significant reduction of the interfacial roughness due to the already small roughness present in the initial (unpolished) structures. However, roughness characteristics like the vertical and lateral correlation lengths and the Hurst parameter were significantly improved, which resulted in a reduction of diffused scattering by more than an order of magnitude at 0.1 – 0.15 nm. Such a strong reduction of diffuse scattering is very beneficial, for example, for applications of a multilayer mirror as a collimator or focusing element, e.g. for high resolution X-Ray diffraction analysis.

References

- [1] C. Liu, R. Conley, A. T. Macrander, T. J. Graber, C. Morawe, C. Borel, and E. M. Dufresne, *Small-d-spacing WSi₂/Si narrow bandpass multilayers*, in *X-Ray Sources and Optics*, Vol. 5537, International Society for Optics and Photonics (SPIE, 2004) pp. 154 – 160.
- [2] C. Liu, R. Conley, A. T. Macrander, J. Maser, H. C. Kang, M. A. Zurbuchen, and G. B. Stephenson, *Depth-graded multilayers for application in transmission geometry as linear zone plates*, *Journal of Applied Physics* **98**, 113519 (2005).
- [3] K. Soyama, W. Ishiyama, and K. Murakami, *Enhancement of reflectivity of multilayer neutron mirrors by ion polishing: optimization of the ion beam parameters*, *Journal of Physics and Chemistry of Solids* **60**, 1587 (1999).
- [4] E. J. Puik, M. J. van der Wiel, H. Zeijlemaker, and J. Verhoeven, *Ion bombardment of thin layers: The effect on the interface roughness and its X-ray reflectivity (invited)*, *Review of Scientific Instruments* **63**, 1415 (1992).
- [5] N. I. Chkhalo, S. A. Churin, A. E. Pestov, N. Salashchenko, Y. A. Vainer, and M. V. Zorina, *Roughness measurement and ion-beam polishing of super-smooth optical surfaces of fused quartz and optical ceramics*, *Opt. Express* **22**, 20094 (2014).
- [6] E. A. Spiller, *Enhancement of the reflectivity of multilayer x-ray mirrors by ion polishing*, *Optical Engineering* **29**, 609 (1990).
- [7] E. Louis, H.-J. Voorma, N. Koster, F. Bijkerk, Y. Platonov, S. Zuev, and S.S., *Multilayer coated reflective optics for extreme uv lithography*, *Microelectronic Engineering* **27**, 235 (1995).
- [8] M. Kessels, J. Verhoeven, F. Tichelaar, and F. Bijkerk, *Ion-induced interface layer formation in w/si and wre/si multilayers*, *Surface Science* **582**, 227 (2005).
- [9] E. Louis, A. Yakshin, T. Tsarfati, and F. Bijkerk, *Nanometer interface and materials control for multilayer euv-optical applications*, *Progress in Surface Science* **86**, 255 (2011).
- [10] A. Guggenmos, S. Radünz, R. Rauhut, M. Hofstetter, S. Venkatesan, A. Wochnik, E. M. Gullikson, S. Fischer, B. Nickel, C. Scheu, and U. Kleineberg, *Ion polished Cr/Sc attosecond multilayer mirrors for high water window reflectivity*, *Opt. Express* **22**, 26526 (2014).
- [11] M. M. Barysheva, Y. A. Vainer, B. A. Gribkov, M. V. Zorina, A. E. Pestov, N. N. Salashchenko, R. A. Khramkov, and N. I. Chkhalo, *The evolution of roughness of supersmooth surfaces by ion-beam etching*, *Bulletin of the Russian Academy of Sciences: Physics* **76**, 163 (2012).

- [12] W. Liao, Y. Dai, X. Xie, and L. Zhou, *Morphology evolution of fused silica surface during ion beam figuring of high-slope optical components*, *Appl. Opt.* **52**, 3719 (2013).
- [13] N. Chkhalo, M. Mikhailenko, A. Mil'kov, A. Pestov, V. Polkovnikov, N. Salashchenko, I. Strulya, M. Zorina, and S. Zuev, *Effect of ion beam etching on the surface roughness of bare and silicon covered beryllium films*, *Surface and Coatings Technology* **311**, 351 (2017).
- [14] D. E. Savage, J. Kleiner, N. Schimke, Y. Phang, T. Jankowski, J. Jacobs, R. Kariotis, and M. G. Lagally, *Determination of roughness correlations in multilayer films for X-ray mirrors*, *Journal of Applied Physics* **69**, 1411 (1991).
- [15] V. Korchuganov, A. Belkov, Y. Fomin, E. Kaportsev, G. Kovachev, M. Kovalchuk, Y. Krylov, K. Kuznetsov, V. Kvardakov, V. Leonov, *et al.*, *The development of synchrotron radiation source of NRC "Kurchatov Institute"*, (Russian Particle Accelerator Conference (RuPAC), 2012) pp. 24–28.
- [16] D. L. Windt, *IMD—Software for modeling the optical properties of multilayer films*, *Computers in Physics* (1998), 10.1063/1.168689, arXiv:hec.3108 [10.1002] .
- [17] E. Spiller, S. L. Baker, P. B. Mirkarimi, V. Sperry, E. M. Gullikson, and D. G. Stearns, *High-performance mo-si multilayer coatings for extreme-ultraviolet lithography by ion-beam deposition*, *Appl. Opt.* **42**, 4049 (2003).
- [18] P. Siffalovic, E. Majkova, L. Chitu, M. Jergel, S. Luby, J. Keckes, G. Maier, A. Timmann, S. Roth, T. Tsuru, *et al.*, *Characterization of Mo/Si soft X-ray multilayer mirrors by grazing-incidence small-angle X-ray scattering*, *Vacuum* **84**, 19 (2009).
- [19] V. Kaganer, S. Stepanov, and R. Köhler, *Effect of roughness correlations in multilayers on Bragg peaks in X-ray diffuse scattering*, *Physica B: Condensed Matter* **221**, 34 (1996).
- [20] D. G. Stearns, *Stochastic model for thin film growth and erosion*, *Applied Physics Letters* **62**, 1745 (1993).
- [21] M. Pelliccione and T.-M. Lu, *Evolution of thin film morphology*, Vol. 108 (Springer New York, 2008).
- [22] A. P. Payne and B. M. Clemens, *Influence of roughness distributions and correlations on X-ray diffraction from superlattices*, *Phys. Rev. B* **47**, 2289 (1993).
- [23] F. Sánchez-Bajo and F. L. Cumbreira, *The use of the pseudo-voigt function in the variance method of x-ray line-broadening analysis*, *Journal of Applied Crystallography* **30**, 427 (1997).
- [24] P. Siffalovic, M. Jergel, and E. Majkova, *GISAXS-probe of buried interfaces in multilayered thin films*, *X-ray Scattering* (2011).

- [25] K. V. Nikolaev, S. N. Yakunin, I. A. Makhotkin, J. d. I. Rie, R. V. Medvedev, A. V. Rogachev, I. N. Trunckin, A. L. Vasiliev, C. P. Hendrikx, M. Gateshki, R. W. E. v. d. Kruijs, and F. Bijkerk, *Grazing-incidence small-angle X-ray scattering study of correlated lateral density fluctuations in W/Si multilayers*, *Acta Crystallographica Section A* **75**, 342 (2019).
- [26] R. Maruyama, D. Yamazaki, K. Akutsu, T. Hanashima, N. Miyata, H. Aoki, M. Takeda, and K. Soyama, *Development of high-polarization Fe/Ge neutron polarizing supermirror: Possibility of fine-tuning of scattering length density in ion beam sputtering*, *Nuclear Instruments and Methods in Physics Research Section A: Accelerators, Spectrometers, Detectors and Associated Equipment* **888**, 70 (2018).
- [27] A. Zameshin, I. A. Makhotkin, S. N. Yakunin, R. W. E. van de Kruijs, A. E. Yakshin, and F. Bijkerk, *Reconstruction of interfaces of periodic multilayers from X-ray reflectivity using a free-form approach*, *Journal of Applied Crystallography* **49**, 1300 (2016).
- [28] E. Gullikson, *CXRO-Database*, (2015).
- [29] F. Schäfers, *Multilayers for the EUV/soft X-ray range*, *Physica B: Condensed Matter* **283**, 119 (2000).

3

INTERFACE FORMATION IN W/SI MULTILAYERS STUDIED BY LOW ENERGY ION SCATTERING

We studied the formation of interfaces in W/Si multilayer structures deposited by magnetron sputtering. In vacuo Low Energy Ion Scattering Spectroscopy was used to determine the materials growth profile with a close to atomic resolution. For that purpose, bi-layer structures, W-on-Si and Si-on-W were grown, with Si being deposited using Ar as the sputter gas and W being deposited in either Ar or Kr. The measurements revealed strongly asymmetric interfaces, with W-on-Si being significantly broader than Si-on-W. However, no difference was found in the W-on-Si interface width depending on the sputter gas, Ar or Kr, used for W deposition, suggesting that it is not a ballistic effect of the backscattered gas ions that is responsible for the wider W-on-Si interface. However, strong surface segregation of Si atoms upon the deposition of W in Kr on Si was observed. Mechanisms responsible for the observed effects are discussed.

3.1 Introduction

Multilayer structures are used in various applications due to their ability to be synthesized for a specifically required wavelength. One of the applications is to use multilayers as analyzing crystals in X-Ray fluorescence spectrometers for qualitative and quantitative elemental analysis of different materials. In this work, such multilayers are designed to resolve spectral lines from O $K\alpha$ to Al $K\alpha$ (525 eV – 1486 eV), which corresponds to the range of wavelengths between 0.84 nm to 2.4 nm. W/Si multilayers are investigated in this work due to their high reflectivity in this wavelength range. Reflectivity is a very important characteristic of the multilayer in spectroscopy as it allows for a fast and high sensitivity analysis. Multilayers are designed following Bragg's law in order to reflect the incident radiation by constructive interference. Therefore, to reflect at wavelengths in the range from 0.84 nm to 2.4 nm at specific angles of relevance for the application, a periodicity of the multilayer of 2.5 nm is required. Apart from the optical indices of the materials used, the reflectivity is determined by the quality of the interfaces between the layers. The shorter the period, the more sensitive the reflectivity is to imperfections at the interfaces. Previous studies on W/Si multilayers were devoted to analysis of the growth and evaluation of interfacial roughness at different deposition conditions which was considered to be one of the main obstacles to achieving high reflectivity at required wavelengths [1–10]. However, in our previous research [11] we found that interfacial roughness in W/Si multilayers deposited by magnetron sputtering was not the main factor limiting the reflectance for the range of wavelengths of interest in this work (0.84 to 2.4 nm). Instead, an interaction between W and Si appeared to be the dominant factor. In other studies, W/Si was claimed to be chemically unstable, and WSi_2 was used instead to avoid unfavorable chemical reactions [7, 12].

However, none of the previous studies provided a detailed investigation of the W-Si interface formation. Therefore, in this paper, we focused on a study of interface formation between W and Si at the initial stage of interface formation. For that, in vacuo Low Energy Ion Scattering (LEIS) was used. Due to a high neutralization rate of scattered low energy ions, LEIS has a high sensitivity for the outermost surface layer [13], and at the same time can provide information about the in-depth distribution of a given element. Combined with a magnetron sputtering deposition setup, it allowed us to perform in vacuo quantification of the surface composition for incremental thicknesses of the growing top layer. As such, a so-called layer growth profile could be composed with a close to atomic thickness resolution.

3.2 Experiment

3.2.1 Deposition and in vacuo LEIS

The samples to study interfaces were fabricated in a home-made UHV magnetron sputtering chamber with a base pressure of $2 \cdot 10^{-10}$ mbar. Bi-layer structures, W/Si and Si/W, were fabricated, with the top layer being deposited incrementally in thicknesses followed by LEIS analysis described below. A separate sample was fabricated for each thickness of the top layer to avoid an accumulation of contam-

ination. DC magnetron sputtering was used. Super-polished silicon wafers $25\text{ mm} \times 25\text{ mm}$ (AFM RMS roughness of about 0.14 nm) were used as substrates. The thicknesses of the deposited thin films were controlled by quartz crystal microbalances (QCM). QCM readings were calibrated in advance, using a set of thin films whose thicknesses were obtained by $\text{CuK}\alpha$ Grazing Incidence X-Ray Reflectometry. Thus, the thicknesses of the thin films presented in this paper are referred to as as-deposited thicknesses. These are not the actual thickness of the formed films because they will change due to an interaction between the deposited materials at interfaces.

The deposition chamber was connected with a UHV transfer system to the LEIS chamber, which allowed for in vacuo characterization of the surface composition of samples [14]. It took about 10 minutes to transfer a sample and start its measurement. The LEIS setup was a Qtac100 instrument by ION-TOF, with a base pressure of $1 \cdot 10^{-10}$ mbar, equipped with a double toroidal electrostatic analyzer and an electron impact ion source, with the ion incidence angle being normal to the surface of a sample and a scattering angle being of 145° . 3 keV He^+ primary ions were used to obtain LEIS spectra. A separate ion gun with 0.5 keV Ar^+ ions at an angle of incidence of 59° was used for ion sputtering.

The LEIS spectra feature binary collision peaks for each element heavier than the projectile ion. The information depth of these peaks is almost exclusively limited to the top surface layer, due to the very high neutralization probability of incident ions. Projectiles scattered from subsurface layers interact with the target material much longer than those scattered from the surface layer, therefore the majority of them become completely neutralized. Since only ions are detected in LEIS, the contribution of the subsurface collisions to the LEIS surface peak is negligible [13, 15–17]. Projectiles scattered from the deeper layers can still be detected if reionized upon exiting the sample surface, however, they lose additional energy in inelastic interaction with the electron clouds of the target atoms. Therefore they do not contribute to the main surface peak, forming instead a so-called tail at lower energies, separated from the main peak in both energy and intensity. The in-depth distribution of the tail-producing material is one of the main contributing factors to the shape of this tail, which allows for static depth profiling with LEIS measurements [18, 19].

3.2.2 Multilayer deposition

Full-stack W/Si multilayers were deposited on super-polished silicon wafers $25\text{ mm} \times 25\text{ mm}$ (AFM RMS roughness of about 0.14 nm) using a DC magnetron sputtering system with a base pressure of $1 \cdot 10^{-9}$ mbar. Ar and Kr were used as working gases at a pressure of about $1 \cdot 10^{-4}$ mbar. Ar gas was used to sputter Si, whereas tungsten was deposited by using either Ar or Kr. To distinguish between W films deposited in Ar or Kr we denote $\text{W}(\text{Ar})$ and $\text{W}(\text{Kr})$ films. Depositions were performed at the power of 85 W (330 V) for W and 205 W for Si for Ar gas. The power was reduced down to 35 W (350 V) for W in case of Kr gas, due to a higher sputter yield compared to Ar. Thicknesses of the deposited films were controlled by time following calibration procedures that involved measuring periods

of deposited calibration multilayers by CuK α Grazing Incidence X-Ray Reflectometry. Multilayers consisted of 200 periods with a period of $d=2.5$ nm and gamma values ($\Gamma=d_W/(d_W+d_{Si})$), where d_W and d_{Si} are layer thicknesses of W and Si correspondingly) varying from 0.06 to 0.36. To avoid uncontrolled oxidation of the surface after exposure to the air, every multilayer was finished with a Si layer with the same thickness as in the rest of the structure.

3.2.3 Multilayer characterization

Soft X-Ray reflectivity at a wavelength of 0.84 nm and grazing angle of incidence of about 9.7° was measured at the storage ring BESSY II at Physikalisch-Technische Bundesanstalt (PTB) in Berlin-Adlershof, Germany.

3.3 Results

3.3.1 LEIS study of W/Si in Ar

To study the intermixing between W and Si layers during the growth, we performed in-vacuo LEIS measurements of W-Si binary layer systems with an incremental thickness of the top layer. W/Si multilayers, optimized with respect to the reflectivity at a wavelength of 0.84 nm, have a period of 2.5 nm and gamma of 0.12 [11]. Taking into account the compaction of the period due to W-Si interaction, the as-deposited thicknesses of W and Si are 0.32 nm and 2.58 nm, respectively. As found in [11] this allows for a formation of pure Si layers, but not pure W layers, with the latter being closer in their composition to a tungsten silicide. This knowledge was used to select representative thicknesses of the layers for this research. As such to study W(Ar)-on-Si interface, W thin films with incremental thicknesses were deposited in Ar on a 10 nm amorphous Si substrate layer deposited on a Si wafer Fig. 3.1 (a). However, for a representative study of the Si-on-W(Ar) interface, the W layer should have been much thinner. So a thin layer system of 0.3 nm W(Ar) on 10 nm Si was used as a substrate for the following incremental deposition of Si Fig. 3.1 (b).

Raw LEIS spectra of W(Ar)-on-Si and Si-on-W(Ar) are shown in Fig. 3.2. LEIS surface peaks of W and Si are present, as well as some contamination of O and F. At the lower energy side of W and Si peaks a wide background (so-called LEIS tail, or depth signal) is also present, due to a contribution from reionized He projectiles that scattered from the sub-surface layers and lost additional energy proportionally to the travel length. In Fig. 3.2 (a), surface peaks and depth signal of W are visibly separated as a “peak” and monotonously decaying “tail.” In the case of W covered by Si in Fig. 3.2 (b), the depth signal of W also takes a shape of a “peak” due to a very thin W layer. It can be distinguished from the surface peak by its position.

We analyzed the surface peaks in the spectra by fitting Gaussian peaks with a fixed position, width, and isotope distribution to each of the elements. These values were fixed to that of corresponding reference samples. To enable quantification of the surface composition, we calculated the surface coverage of W and Si by dividing the LEIS surface peak intensity of each element by its intensity in a reference sample [13]. For the reference samples of Si and W we took 10 nm Si and 2.5 nm W on

Figure 3.1: Schematic representation of the sequence of layers deposited for LEIS measurements, given with the values of as-deposited thicknesses of these layers. Note that in the case of (b) no pure W film is formed in reality.

Si wafers, produced and transferred in exactly same manner as the samples in the actual series. This way we obtained 15200 and 3200 counts/nC as reference LEIS signals for W and Si, correspondingly. The surface coverages, determined in this manner, are presented in Fig. 3.3 (solid lines) as functions of as-deposited thicknesses of the top layer for both W(Ar)-on-Si and Si-on-W(Ar) interfaces. The general behavior of the surface coverage changes in Fig. 3.3 (solid lines) follows the expectations: the amount of substrate material decreases, the amount of growing material increases. The formation of W(Ar)-on-Si interface starts from the pure Si surface, and it takes 1.7 nm of W(Ar) to close Si completely, which we define as a point when the Si surface coverage reaches the detection limit. The formation of Si-on-W(Ar) interface, on the other hand, does not start from a pure W surface, because only 0.3 nm of W was deposited, and as seen from Fig. 3.3 (b) (solid lines), W appears to cover only a very small portion of the surface (13%). W surface coverage reaches the detection limit after about 0.3 nm of Si is deposited on top, which is much faster than for the reverse interface. The deposition of 0.3 nm layers takes less than 5 seconds, which limits the control over the desired material thickness, therefore smaller thicknesses of the Si layer were not attempted.

It must be noted that the sum of the surface coverages of the W and Si is larger than 1 for the intermediate surface compositions in Fig. 3.3 (solid lines). This is an indication that the rule of mixtures does not apply to this situation [13, 19], which may be caused by compaction due to the formation of tungsten silicides [20]. This effect limits the accuracy of the obtained profiles, however, it does not affect the main observations in Fig. 3.3 (solid lines).

As it is known from earlier work [19], the observed evolution of the surface composition can be affected by two processes: intermixing of the involved elements and additional surface segregation of the underlying element. Between W and Si, Si has significantly lower surface free energy [21], therefore if surface segregation is present, it is expected to be the surface segregation of Si on W. Since the surface segregation is purely a surface phenomenon, it should in principle be possible to reduce the surface enrichment by a limited sputtering of the surface layer. Therefore, a low-dose sputtering with 0.5 keV Ar⁺ ions of $3 \cdot 10^{-14}$ ions/cm² fluence was additionally applied to each surface to check for a potential presence of the surface segregation of Si on W. The surface coverages of the etched surfaces are added in

Figure 3.2: (a) LEIS spectra of thin films of W(Ar) with incremental thicknesses grown on 10 nm Si layer. (b) LEIS spectra of thin films of Si with incremental thicknesses grown on 0.3 nm W(Ar) layer on 10 nm Si

Fig. 3.3 as dashed lines. The results do not show any indication of segregation of Si, but instead can be described by intermixing effects and removal of contamination, as will be discussed below. It should be noted that the reference LEIS signals of W and Si chosen for quantification of the untreated surface do not apply to the

Figure 3.3: (a) The surface coverages of W and Si as a function of the as-deposited W thickness for W(Ar) on 10 nm Si. The surface coverages are shown for the untreated as-deposited surfaces after a 10-minute transfer, as well as for the surfaces etched with a $3 \cdot 10^{-14}$ ions/ cm^2 fluence of 0.5keV Ar $^+$ (b) The surface coverages of W and Si as a function of as-deposited Si thickness for Si on 0.3 nm W(Ar), as well as for the surfaces etched with a $3 \cdot 10^{-14}$ ions/ cm^2 fluence of 0.5keV Ar $^+$

ion etched surfaces, due to differences in surface purity, density, and roughness. We, therefore, use the measurements from the ion etched surfaces for qualitative

purposes only.

For the Si-on-W(Ar) interface Fig. 3.3 (b) each of the attempted thicknesses was small enough to allow for sputter-induced intermixing. For each point, it should increase the surface coverage of the substrate material and reduce the surface coverage of the top film material. For the starting point, where W is the top film material, intermixing should lead to an increase of the Si signal and a decrease of the W signal. For other points, where a certain amount of Si is deposited on top, intermixing should lead to an increase of the W signal and decrease of the Si signal. However, as can be seen in Fig. 3.3 (b), the data does not exactly follow this expectation – the Si signal after etching is increasing instead of decreasing. We attribute this discrepancy to the removal of surface contamination occurring during the sample transfer, which increases the signal. Therefore the behavior of the growth profiles in Fig. 3.3 (a) is explained by a combination of two effects: sputter-induced intermixing and surface contamination removal.

For the W(Ar)-on-Si interface Fig. 3.3 (a) three thickness ranges can be isolated. For W thicknesses below one nanometer, the etching step results in a slight decrease of the W signal and a slight increase of the Si signal, which can once again be attributed to sputter-induced intermixing. For the higher W thicknesses etching strongly increases the W signal and slightly increases the Si signal (below W thickness of 1.5 nm) or does not change the Si signal within error margins (above W thickness of 1.5 nm). The signal increase can be explained by the removal of surface contamination. The Si signal is not affected to the same extent as the W signal probably because of the lesser affinity of Si to the contaminants compared to W. Note that the increase of intensity of peaks of O and F with W increase in W thickness and intensity would also be consistent with the stronger affinity of contaminants to W.

3.3.2 Alternative sputter gas

In the previous section, we observed the formation of strongly asymmetric interfaces in the W-Si system deposited by magnetron sputtering. A possible reason for the asymmetry of interfaces in the magnetron sputtering can be the presence of high energy backscattered neutrals (reflected and neutralized ions) from the target. This effect will depend on the mass of the target: the higher the mass, the more ions, and neutrals of a gas species will recoil from the target [22]. The gas species are also of importance. Using heavier gas species results in a smaller amount and energy of the backscattered ions and neutrals on the surface of the deposited material. Available literature demonstrates that among other parameters a choice of gas species in magnetron sputtering affects the growth of thin films and their morphology [23–26]. It also affects roughness and intermixing in multilayers [27–30], which should be especially important for short period multilayers investigated in this work. However, we are not aware of such studies on W/Si multilayers, which is why it was decided to carry out such comparison as a part of this work.

In order to select appropriate gas species for this experiment, we performed Transmission of Ions in Matter (TRIM) simulations [31] for the backscattering of the Ar, Kr, and Xe ions from a W target. We chose an incident ion energy of 350 eV

that corresponds to the discharge voltage of 350 V used for deposition of W in our experiments. The normal angle of incidence was used. Fig. 3.4 (a) shows the TRIM calculation of the number of backscattered ions depending on their energy. Fig. 3.4 (b) and (c) show the total number of particles and their energy depending on the gas species. The number and energy of the recoiled Ar particles are correspondingly about a factor of three and a factor of two higher than for Kr. Further, the number and energy of the recoiled Ar are about a factor of seven higher than for Xe.

Figure 3.4: TRIM calculations of backscattered ions for three gas species, Ar, Kr, and Xe, from a W target: a) the number of backscattered ions depending on their energy, b) the total number of particles derived from a) and c) the average energy of the backscattered particles for each gas species

The figure shows that Ar and Xe have the largest difference in the number and energy of the backscattered particles and would be the most favorable species for an experiment to check the influence of reflected particles on the formation of interfaces. However, one has also to take into account the process of inclusion of the working gas in the growing film inherent to magnetron sputtering [32, 33]. During the deposition process, inert gas ions get trapped in the growing films, which might influence the optical properties of the multilayers. It turns out that Xe has a very strong absorption at 0.84 nm compared to Ar and Kr, therefore, optically it would be disadvantageous to use it in this experiment. At the same time, a selection of Ar and Kr is still a suitable choice for our test as these gas species also show significant differences in the number and energy of the backscattered ions.

3.3.3 LEIS study of W/Si in Kr

To check the influence of the backscattered particles on the formation of interfaces, the same experiments that were already performed for W(Ar)-on-Si and Si-on-W(Ar) were now repeated for W(Kr)-on-Si and Si-on-W(Kr). The raw LEIS

spectra are shown in Fig. 3.5, and the changes of the surface coverage with the incremental thickness of the top layer are shown in Fig. 3.6, together with the surface coverages of the etched surfaces. For the Si-on-W interface, there is no significant difference between W(Ar) and W(Kr) (Fig. 3.3 (b) vs Fig. 3.6 (b)). In both cases, W disappears after being covered by about 0.3 nm Si. We cannot exclude possible differences for lower thicknesses of Si, but due to high deposition rates, thicknesses lower than 0.3 nm were not attempted. For the W-on-Si interface, some noticeable differences are present between Fig. 3.3 (a) and Fig. 3.6 (a), especially in the surface coverage of Si. To highlight the differences, we also compose Fig. 3.7 where the growth profiles for the untreated surfaces from Fig. 3.3 and Fig. 3.6 are overlaid.

Si becomes closed by W after being covered by about 2.5 nm of W on the W(Kr)-on-Si interface, while 1.7 nm was enough for W(Ar)-on-Si interface. To investigate the reason for such difference, we plot LEIS spectra of untreated surfaces of 2.5 nm W(Ar) and W(Kr) on Si in Fig. 3.8. There is no noticeable difference between the LEIS tails of W for these two samples, which suggests that the actual interface width is the same for W(Ar)-on-Si and W(Kr)-on-Si. The surface peak of W also has the same intensity. However, the surface peak of Si is absent in W(Ar)-on-Si but present in W(Kr)-on-Si. Note that there also differences in the presence of O and F peaks but this will be discussed later.

The LEIS spectra in Fig. 3.8 can be explained by both layered stacks having the same internal structure (leading to the same W tail), with the only difference being the surface composition. Such a situation can be explained by Si surface segregation during W(Kr) deposition. The surface segregation of Si on W(Kr) becomes evident from the changes in the surface coverage of Si after an etching step (Fig. 3.6 (a)). This is clearly observed for the points with higher W thicknesses where the Si surface is significantly covered with W. Indeed, the surface coverage of Si in W(Ar)-on-Si growth profile in that area does not decrease after the low dose ion etching (Fig. 3.3 (a)). However, for Si in a W(Kr)-on-Si growth profile, it reduces significantly. This indicates stronger sputtering of Si for the W(Kr)-on-Si system compared to W(Ar)-on-Si system. Since the elemental combination is the same for both systems, the stronger sputtering of Si can only be explained when assuming a surface enrichment of Si taking place during the W(Kr)-on-Si growth.

If our assumption about the same interface width for W(Ar)-on-Si and W(Kr)-on-Si is correct, and the observed extra Si on W(Kr) is purely a surface effect, it should be possible to remove this extra Si by etching and arrive at the same surface. However, even after the etching step, Si does not fully disappear from 2.5 nm W(Kr), as evident from Fig. 3.6 (a). The reason for this can be an insufficient ion fluence. Increasing the ion fluence to $4 \cdot 10^{-14}$ ions/cm² further reduces the amount of Si twofold (see a single point at 2.58 nm W in Fig. 3.6 (a)). However, the higher the fluence, the stronger the sputter-induced intermixing. Therefore it is not possible to fully remove a large amount of segregating Si without intermixing.

The last observation to be made from the comparison of LEIS spectra of W(Ar)-on-Si and W(Kr)-on-Si, is the behavior of surface peaks of O and F contaminants alongside the surface peak of Si. For the two surfaces with the same deposited amount of W in Fig. 3.8, 2.5 nm W(Kr)-on-Si contains a Si peak, but no O and F peaks, while a 2.5 nm W(Ar)-on-Si spectrum contains O and F peaks, but no Si

Figure 3.5: a) LEIS spectra of thin films of W(Kr) with incremental thicknesses grown on 10 nm Si layer. b) LEIS spectra of thin films of Si with incremental thicknesses grown on 0.3 nm W(Kr) layer on 10 nm Si

peak. If we assume that there is only a limited number of active surface sites on W (e.g. vacancies), there should be a competition between Si surface segregation and O and F contamination. Since the surface contamination takes place only after deposition, for W(Kr) the active surface sites could already be occupied by the

Figure 3.6: a) The surface coverages of W and Si as a function of as-deposited W thickness for W(Kr) on 10 nm Si. The surface coverages are shown for the untreated as-deposited surfaces after 10-minute transfer, as well as for the surfaces etched with $3 \cdot 10^{-14}$ ions/cm² fluence of 0.5keV Ar⁺. The surface coverage of Si for the final point is also shown after an extra etching step of $4 \cdot 10^{-14}$ ions/cm². b) The surface coverages of W and Si as a function of Si as-deposited thickness for Si on 0.3 nm W(Kr).

segregated Si, reducing the contamination.

Figure 3.7: Comparison of growth profiles for W-on-Si interface, with W grown in Ar or Kr as a working gas.

Figure 3.8: Comparison of LEIS spectra for two samples of 2.5 nm W grown on 10 nm Si, with Ar or Kr as a working gas.

3.3.4 Reflectivity of full-stack multilayers

To determine the influence of the deposition of W in Ar or Kr on the reflectivity at-wavelength, we deposited a series of full-stack multilayers. As known from our

previous studies [11], due to an interaction between W and Si the optimum gamma value resulting in a maximum reflectivity will shift with respect to the theoretical value obtained by calculation with IMD software [34]. Therefore, multilayers with several gamma values from 0.06 to 0.36 were deposited. Fig. 3.9 shows the reflectivity of the deposited multilayers at 0.84 nm versus the gamma value in comparison to the theoretical dependence for an ideal multilayer (without intermixing or roughness).

Figure 3.9: Reflectance versus gamma ($\Gamma = d_W/[d_W + d_{Si}]$) at 0.84 nm for full-stack multilayers with W deposited in Ar and Kr and theoretical calculation in IMD for ideal multilayer (no interfacial roughness or intermixing)

As seen, both multilayers, with W deposited in Ar and Kr, have an optimum gamma value of about 0.15, while the calculated ideal multilayer has a value of about 0.25. This shift in gamma is associated with chemical interaction between W and Si and indicates that interaction processes are similar for both cases, of Ar and Kr. Furthermore, the highest reflectivity achieved for both types of structures is about 40 % at 0.84 nm, which means that using Kr did not result in a noticeable gain in reflectivity. The minor differences in reflectivity can be ascribed to a small difference in the periods of the deposited structures.

3.4 Discussion

LEIS measurements at different stages of the growth of W on Si and Si on W thin films revealed strongly asymmetric interfaces. The W layer grown on Si forms a

wide interface of about 1 nm. In contrast, Si on a thin non-pure W layer only forms an atomically thick layer resulting in a sharp transition. We should note that W-on-Si and Si-on-W interfaces were using different starting surface coverages to emulate the real multilayer, with the W layer being much thinner than the Si layer. Si signal drops by 50% after 0.85 nm of W deposition in W(Ar)-on-Si system and 1.25 nm in W(Kr)-on-Si system. W signal drops by 50% after less than 0.3 nm of Si deposition in Si-on-0.3 nm W. Therefore, the difference in structures alone cannot be the reason for the strong asymmetry, assuming a stochastic growth process. A very sharp transition at Si-on-W interface should be unresolvable by cross-section TEM, taking into account that all involved films are amorphous. Therefore, an in vacuo measurement that uses a surface-sensitive technique was essential to resolve the formed interfaces. The formation of a thick W-on-Si interface could be attributed to a ballistic effect of the backscattered ions from W due to its high mass compared to Si. In this case, changing the working gas species from Ar to Kr for W deposition would have a positive effect. However, our experiment showed a similar interface compared to the structure deposited in Ar. This suggests that it is not a ballistic effect of the backscattered gas ions that is responsible for the wide W-on-Si interface, but rather an atomic interaction between W and Si, which was already shown for metal-on-metal growth [35]. The interface formation can then be mainly driven by the reduction in the free energy of the system. The element with a lower surface free energy would tend to move to the surface of the element with a higher surface free energy upon deposition. This process can result in a significantly intermixed interface between the elements. The surface free energies for Si and W are 1.107 Jm^{-2} and 3.468 Jm^{-2} , respectively [21]. Additionally, the process of the wider W-on-Si interface formation could be explained by the large cohesive energy of W (8.9 eV/atom) [36]. Some energy is required to initiate a chemical reaction between W and Si. This energy should be higher than the energy barrier for the silicide formation reaction. Si cohesive energy of only 4.6 eV/atom [36] may not be sufficient for that.

Figure 3.10: Schematic representation of surface segregation and segregation removal during deposition of W in either Ar or Kr.

The next point to be discussed is the surface segregation effect found by the LEIS measurements. Although interface widths of W(Ar)-on-Si and W(Kr)-on-Si

appear to be the same from direct comparison of LEIS tails, there is a strong surface segregation of Si atoms upon W(Kr) deposition on Si. This observation may look counter-intuitive at first sight. Indeed, as TRIM calculations suggest, the number and energy of backscattered ions would be higher for the case of Ar. So it could be expected that due to a stronger ballistic effect for the Ar case, Si atoms would move more readily to the surface of the growing W layer above. However as we discussed this mechanism should also have led to a noticeably stronger intermixing at the interface, which we did not observe for Ar in comparison to Kr. In fact, the difference in Si segregation can essentially be explained (see Fig. 3.10) if we assume that the segregation of Si is independent of the gas species used for sputtering, i.e. the segregation of Si is equally present during deposition of W both in Ar and Kr. However, the segregated at the surface atoms can be preferentially removed from the surface by energetic particles arriving at the surface during a deposition. In the case of Ar, a larger number and higher energy neutrals are more efficient in sputtering the segregating Si atoms than in the case of Kr. This could explain why there is no Si segregation observed for the case of Ar. Note that we do not observe any effect of Si segregation on the W-on-Si interface width and, consequently, on the soft X-Ray reflectivity of multilayers. This can be explained by the fact that the segregated Si atoms become part of the deposited Si layer above and do not affect the formation of this interface. Still, this effect might be important in case of depositing e.g. a tri-layer structure, using a diffusion barrier, which would be one possible suggestion to improve the reflectivity of W/Si multilayers. As such, Si segregation might lead to unwanted compound formation and roughness buildup.

3.5 Conclusions

In vacuo LEIS was used to study the formation of interfaces in W/Si multilayer structures deposited by magnetron sputtering. Model layered structures, W-on-Si, and Si-on-W, were incrementally grown on Si substrates, with Si being deposited in Ar, and W being deposited in either Ar or Kr. The measurements revealed strongly asymmetric interfaces, with W-on-Si being significantly broader than Si-on-W. This seemed to be consistent with the initial notion that films would experience much more energetic bombardment during the deposition of W than during the deposition of Si. However, contrary to that no difference was found in the W-on-Si interface width for W deposited in Ar or Kr. This is in spite of the fact that according to TRIM calculations and available data in the literature, a heavier gas species should result in a significantly smaller energetic contribution and therefore less mixing effects at that interface. This suggests that it is not a ballistic effect of the backscattered gas ions that is responsible for the wide W-on-Si interface, but rather a direct atomic interaction between W and Si.

Furthermore, although the deposition of W in Kr did not result in noticeable changes in the W-on-Si interface width as compared to the deposition in Ar, it did result in strong surface segregation of Si atoms upon W deposition on Si. This can be explained if we assume that the segregation of Si is actually present for any gas species used, but the higher impact neutrals in the case of Ar can be more efficient in removing the segregating Si atoms than in the case of Kr. Surface segregation

of Si during growth did not have any effect on the reflectivity of the fabricated full-stack W/Si multilayers. A reflectivity of 40% was obtained at a wavelength of 0.84 nm for all investigated multilayers.

Finally, the obtained data about the studied interfaces suggests that further research should be focused on the improvement of the W-on-Si interface in the first place. An attempt should be done to reduce the direct interaction between W and Si, rather than trying to reduce the impact of the reflected neutrals from the W target. At the same time, the effect of Si segregation should be taken into account in case of an attempt to design structures with diffusion barriers between W and Si.

References

- [1] Z. Jiang, X. Jiang, W. Liu, and Z. Wu, *Thermal stability of multilayer films Pt/Si, W/Si, Mo/Si, and W/C*, [Journal of Applied Physics](#) **65**, 196 (1989).
- [2] T. Salditt, D. Lott, T. Metzger, J. Peisl, and G. Vignaud, *Interfacial roughness and related growth mechanisms in sputtered W/Si multilayers*, [Physical Review B - Condensed Matter and Materials Physics](#) **54**, 5860 (1996).
- [3] M. J. Kessels, J. Verhoeven, A. E. Yakshin, F. D. Tichelaar, and F. Bijkerk, *Ion beam induced intermixing of interface structures in W/Si multilayers*, [Nuclear Instruments and Methods in Physics Research, Section B: Beam Interactions with Materials and Atoms](#) **222**, 484 (2004).
- [4] M. J. Kessels, J. Verhoeven, F. D. Tichelaar, and F. Bijkerk, *Ion-induced interface layer formation in W/Si and WRe/Si multilayers*, [Surface Science](#) **582**, 227 (2005).
- [5] B. A. Vidal and J. C. Marfaing, *X-ray reflectivity and transmission electron microscopy studies on thin and ultrathin W/C and W/Si multilayers structures*, [Journal of Applied Physics](#) **65**, 3453 (1989).
- [6] A. Paul, T. Damm, D. E. Bürgler, D. Rafaja, and D. Simek, *Interface study of W-Si / Si and obliquely deposited W / Si multilayers by grazing-incidence high-resolution x-ray diffraction*, .
- [7] Y. P. Wang, H. Zhou, L. Zhou, R. L. Headrick, A. T. MacRander, and A. S. Özcan, *Interface roughness evolution in sputtered W Si₂ Si multilayers*, [Journal of Applied Physics](#) **101** (2007), 10.1063/1.2422713.
- [8] M. Jergel, V. Holý, E. Majkivá, Š. Luby, and R. Senderák, *Interface Evolution in a W/Si Multilayer after Rapid Thermal Annealing Studied by X-ray Reflectivity and Diffuse Scattering*, [J. Appl. Cryst.](#) **30**, 642 (1997).
- [9] P. Høghøi, J. Peisl, D. Lott, T. Metzger, G. Grübel, J. Legrand, O. Schärpf, G. Vignaud, and T. Salditt, *Characterization of interface roughness in W/Si multilayers by high resolution diffuse X-ray scattering*, [Physica B: Condensed Matter](#) **221**, 13 (2002).
- [10] B. Vidal, J. Marfaing, and P. Dhez, *Magnetron Sputtering Deposition Of Ultrathin W-Si Multilayers For X Rays Optics*, , 148 (1989).
- [11] R. V. Medvedev, K. V. Nikolaev, A. A. Zameshin, D. Ijpes, I. A. Makhotkin, S. N. Yakunin, A. E. Yakshin, and F. Bijkerk, *Ion polishing of Si in W / Si soft X-ray multilayer structures*, [Journal of Applied Physics](#) **045302**, 1 (2019).
- [12] C. Liu, R. Conley, A. T. Macrander, T. J. Graber, C. Morawe, C. Borel, and E. M. Dufresne, *Small-d-spacing WSi₂ /Si narrow bandpass multilayers*, [X-Ray Sources and Optics](#) **5537**, 154 (2004).

- [13] H. Brongersma, M. Draxler, M. de Ridder, and P. Bauer, *Surface composition analysis by low-energy ion scattering*, *Surface Science Reports* **62**, 63 (2007).
- [14] R. Coloma Ribera, R. W. E. van de Kruijs, J. M. Sturm, A. E. Yakshin, and F. Bijkerk, *In vacuo growth studies of Ru thin films on Si, SiN, and SiO₂ by high-sensitivity low energy ion scattering*, *Journal of Applied Physics* **120**, 065303 (2016).
- [15] D. Primetzhofer, M. Spitz, E. Taglauer, and P. Bauer, *Resonant charge transfer in low-energy ion scattering: Information depth in the reionization regime*, *Surface Science* **605**, 1913 (2011).
- [16] R. Cortenraad, A. W. Denier van der Gon, H. H. Brongersma, S. N. Ermolov, and V. G. Glebovsky, *Quantification of the surface composition of low-work function surfaces using low-energy ion scattering*, *Surface and Interface Analysis* **31**, 200 (2001).
- [17] D. Goebel, B. Bruckner, D. Roth, C. Ahamer, and P. Bauer, *Low-energy ion scattering: A quantitative method?* *Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms* **354**, 3 (2015).
- [18] V. I. T. A. de Rooij-Lohmann, A. E. Yakshin, R. W. E. van de Kruijs, E. Zoethout, A. W. Kley, E. G. Keim, M. Gorgoi, F. Schafers, H. H. Brongersma, and F. Bijkerk, *Enhanced diffusion upon amorphous-to-nanocrystalline phase transition in Mo/B₄C/Si layered systems*, *Journal of Applied Physics* **108**, 014314 (2010).
- [19] A. Zameshin, *Probing atomic scale interface processes using X-rays and ions (doctoral dissertation)*, *Ph.D. thesis*, University of Twente (2018).
- [20] W. M. Haynes, *CRC Handbook of Chemistry and Physics, 96th Edition* (CRC Press, 2015).
- [21] L. Z. Mezey and J. Gibber, *The surface free energies of solid chemical elements calculation from internal free enthalpies of atomization*, *Japanese Journal of Applied Physics* **21** (1982).
- [22] W. Eckstein and J. P. Biersack, *Reflection of heavy ions*, *Zeitschrift für Physik B Condensed Matter* **63**, 471 (1986).
- [23] I. Petrov, I. Ivanov, V. Orlinov, and J. Sundgren, *Comparison of magnetron sputter deposition conditions in neon, argon, krypton, and xenon discharges*, *Journal of Vacuum Science & Technology A: Vacuum, Surfaces, and Films* **11**, 2733 (1993).
- [24] Y. Takagi, Y. Sakashita, H. Toyoda, and H. Sugai, *Generation processes of super-high-energy atoms and ions in magnetron sputtering plasma*, *Vacuum* **80**, 581 (2006).

- [25] G. T. West and P. J. Kelly, *Influence of inert gas species on the growth of silver and molybdenum films via a magnetron discharge*, *Surface and Coatings Technology* **206**, 1648 (2011).
- [26] M. Novotný, J. Bulíř, P. Pokorný, J. Lančok, L. Fekete, J. Musil, and M. Čekada, *RF magnetron sputtering of silver thin film in Ne, Ar and Kr discharges-plasma characterisation and surface morphology*, *Surface and Coatings Technology* **228**, 466 (2013).
- [27] Y. Maeda, Y. Suzuki, Y. Sakashita, S. Iwata, T. Kato, S. Tsunashima, H. Toyoda, and H. Sugai, *Effect of sputtering deposition process on magnetic properties of magnetic multilayers*, *Japanese Journal of Applied Physics* **47**, 7879 (2008).
- [28] M. Shiraishi, N. Kandaka, and K. Murakami, *Mo/Si multilayers deposited by low-pressure rotary magnet cathode sputtering for extreme-ultraviolet lithography*, *Proceedings of SPIE Vol. 5037* **5037**, 249 (2003).
- [29] P. Sandström, E. B. Svedberg, M. P. Johansson, J. Birch, and J. E. Sundgren, *Structure evolution in Ag/Ni multilayers grown by ultra high vacuum DC magnetron sputtering*, *Thin Solid Films* **353**, 166 (1999).
- [30] E. B. Svedberg, J. Birch, I. Ivanov, E. P. Münger, and J.-E. Sundgren, *Asymmetric interface broadening in epitaxial Mo/W (001) superlattices grown by magnetron sputtering*, *Journal of Vacuum Science & Technology A: Vacuum, Surfaces, and Films* **16**, 633 (1998).
- [31] J. Biersack and L. Haggmark, *A Monte Carlo computer program for the transport of energetic ions in amorphous targets*, *Nuclear Instruments and Methods* **174**, 257 (1980).
- [32] J. A. Thornton and D. W. Hoffman, *The influence of discharge current on the intrinsic stress in Mo films deposited using cylindrical and planar magnetron sputtering sources*, *Journal of Vacuum Science & Technology A: Vacuum, Surfaces, and Films* **3**, 576 (2002).
- [33] D. M. Mattox, *Particle bombardment effects on thin-film deposition: A review*, *Journal of Vacuum Science & Technology A: Vacuum, Surfaces, and Films* **7**, 1105 (2002).
- [34] D. L. Windt, *IMD - Software for modeling the optical properties of multilayer films*, *Computers in Physics* **12**, 360 (1998).
- [35] A. Chandrasekaran, R. W. Van De Kruijs, J. M. Sturm, A. A. Zameshin, and F. Bijkerk, *Nanoscale Transition Metal Thin Films: Growth Characteristics and Scaling Law for Interlayer Formation*, *ACS Applied Materials and Interfaces* **11**, 46311 (2019).
- [36] C. Kittel, *John Wiley & Sons, Inc*, Vol. 8 (2005) p. 43.

4

POST DEPOSITION NITRIDATION OF SI IN W/SI SOFT X-RAY MULTILAYER SYSTEMS

Partial nitridation of W/Si multilayer systems with a 2.5 nm period was investigated in an attempt to reduce optically unfavorable tungsten silicide formation in the systems. Nitridation was applied directly after the deposition of every Si layer by exposing the Si surfaces to reactive nitrogen species from an ion source. As a result the formation of substantially sharper interfaces and a reduction in the silicide formation were observed in the systems. However, the passivation treatment caused a pronounced reduction in the X-Ray reflectivity at 0.84 nm wavelength because of deep nitrogen penetration in the Si layers. This reduced the optical contrast between the reflector and spacer layer, which compensated the effect of the improved interface profile.

4.1 Introduction

W/Si short-period multilayer systems (of about 2.5 nm) are widely used in X-Ray fluorescence (XRF) applications to achieve a high reflectivity in the wavelength range 0.84 nm–2.4 nm, which corresponds to spectral lines of O $K\alpha$ to Al $K\alpha$. The advantage of using multilayer mirrors is the ability to tune them to a specific wavelength required for a specific task. The shorter periods allow for a larger angular distance between the spectral peaks, which is beneficial for the analysis in XRF applications as it prevents overlapping of the peaks of interest. However, the short-period W/Si multilayer systems have limited reflectivity, which limits the sensitivity of XRF analysis. Currently the highest achieved reflectivity at 0.84 nm for W/Si is 40%, while the theoretical reflectivity is 60% for an ideal system that presumes no interfacial roughness or interdiffusion [1]. Roughness has significant effect on the optical contrast and therefore the reflectivity of these short-period multilayers. However, recent attempts to reduce it to below the currently achieved level of about 0.3 nm was not successful [1]. Interdiffusion is another factor that significantly reduces the reflectivity in short-period multilayers. It was found that a tungsten silicide compound is formed in W/Si multilayers that reduces the optical contrast considerably [1, 2]. The W-on-Si interface was proven to be significantly broader than the Si-on-W interface [3]. Therefore, research is needed on the improvement of the W-on-Si interface in the first place. In this work we used passivation of the Si layer surface with nitrogen as one of the possible solutions to prevent chemical interaction between the two materials. Passivation is used in many applications to prevent unwanted compound formations. In microelectronics passivation is used to improve lifetime and quality of elements, while in thin-film transistors it is used to create barrier layers preventing chemical interactions [4–6]. In X-Ray optics, the definition of the layer materials was efficiently improved, for example, by nitridation of every La layer, as in La/B multilayers [7–9]. Other examples of a successful nitridation was shown for Ru/B₄C, Pd/B₄C and Co/C multilayer systems [10–14]. A Si₃N₄ compound could be used to prevent W-Si interaction, while nitridation of Si was reported before in [15–17]. The nitridation was implemented by reactive sputtering of Si or Si₃N₄ in N₂ or applying ion assisted deposition using an ion source supplied with N₂. These studies were devoted to the passivation of the entire Si layer to obtain silicon nitride. However, for our application of W/Si at 0.84–2.4 nm, passivation of the entire Si layer is optically unfavorable. To avoid reflectivity loss in our case the thickness of Si₃N₄ at the W-on-Si interface should not exceed 0.3 nm. For this reason, in this work an attempt was made to nitrate only the surface of the Si layers by post deposition low energy ion treatment and to avoid full nitridation of the Si layers.

4.2 Experimental

4.2.1 Multilayer deposition

The multilayer mirrors were deposited on super-polished silicon wafers of 25 mm × 25 mm (RMS roughness of about 0.14 nm) using DC magnetron sputtering in a

system with a base pressure of $1 \cdot 10^{-7}$ Pa. Ar gas was used as a working gas at a pressure of about $1 \cdot 10^{-1}$ Pa (Ar flow of 26 sccm). Depositions were performed at a power of 84W for W and 213W for Si. Tungsten was deposited with a low power in order to have a better control on thickness. Deposition rates were 0.075 nm/s and 0.02 nm/s for Si and W, respectively. An ion source was used for passivation of the Si layers. The ion source was fed with Ar (flow of 14 sccm) and N₂ (flow of 7 sccm). The ion source was mounted at 60 degrees to the substrate at a distance of 70 cm. The following parameters were used: ion beam voltage of 60 eV, and ion current of 120 mA. The multilayer mirrors had a period of 2.5 nm and a gamma value ($\Gamma = d_W/[d_W + d_{Si}]$) $\Gamma = 0.12$. The thickness of the Si capping layer was the same as in the entire multilayer stack $d_{Si} = 2.2$ nm. The main set of the experimental multilayers consisted of 50 periods as it allowed for analysis that is more accurate. A selected number of multilayers consisted of 200 periods in order to achieve the maximum reflectivity. To avoid oxidation of the surfaces after exposure to the air, every mirror was finished with a Si layer with the same thickness as inside the stack. Uniformity of the deposition and ion treatment was achieved by rotating the holder with substrates at 60rpm during the entire deposition process. Configuration of the set-up is described elsewhere [18] .

4.2.2 Multilayer characterization

Soft X-Ray reflectivity at the specific wavelength and grazing angle of incidence required for the application (0.84 nm, $\theta \approx 9.7^\circ$ with respect to the surface) were measured at the storage ring BESSY II at the Physikalisch-Technische Bundesanstalt (PTB) in Berlin, Germany. For a qualitative assessment of the roughness of the multilayer systems, X-Ray diffused scattering rocking curves were measured with a conventional X-Ray tube at the wavelength of 0.154 nm. The rocking curves were taken at the second Bragg peak. The procedure of the measurement is described elsewhere [19]. The subsurface composition of the samples was determined by non-destructive X-ray Photoelectron Spectroscopy (XPS). A Thermo Scientific Theta Probe Instrument was used employing monochromatic Al-K α radiation, providing a typical full-width half maximum of the Ag 3d5/2 peak equal to 0.75 eV, as indication for the obtained energy resolution. The probing depth of the non-destructive measurement is about 6 nm. The photoelectron signal is integrated over the entire acceptance angle of the analyzer, corresponding to $\pm 30^\circ$ around an average take-off angle of 53° with respect to the surface normal. Spectra were evaluated with Thermo Advantage software, applying quantification based on analyzer transmission, Scofield sensitivity factors and inelastic electron mean free path values calculated according to the method of Cumpson and Seah [20]. The non-destructive measurement of subsurface composition was done after exposure of the samples to the air. In-depth distribution of the elements was assessed by XPS sputter depth-profiling with 0.25 keV Ar⁺ ions. Grazing incidence X-Ray reflectivity (GIXR) and X-Ray fluorescence from W modulated by an X-Ray standing wave (F-XSW) in the multilayer were measured using an in-house Malvern Panalytical Empyrean X-Ray diffractometer using a Cu-K α source (0.154 nm) [21]. A $4 \times$ Ge 220 monochromator was used between the source and the sample. The measurements were performed in two

steps. First, the X-Ray reflectivity curves were measured up to 8 degrees incidence. These measurements were performed in continuous scanning mode using various steps sizes and accumulation times in order to compromise between good measurement statistics for higher order Bragg peaks and reasonable total measurement time (Table 4.1). At the second step X-Ray fluorescence was measured as a function of the X-Ray angle of incidence on the sample. To capture these signals, we have equipped the diffractometer with an Amptek energy dispersive XR-100SDD Silicon Drift Detector. Only the angular range corresponding to the first Bragg peak was scanned since for larger angles fluorescence modulation could not be detected in the used measurement setup. The measurements were performed with an angular step of 0.0025 degree around the Bragg peak and 0.005 degrees outside the Bragg peak. To accumulate a sufficient number of fluorescent photons, the accumulation time was 5 minutes per angular step.

Table 4.1: XRR measurement configuration

Range (deg)	Step size (deg)	Accumulation time per point (s)
0.1 – 1.32	0.004	3.5
1.32 – 2.8	0.005	4.4
2.8 – 8	0.008	8.8

The data analysis was performed using a free-form approach similar to the one discussed in [22]. Within this approach the periodically repeated W-Si bi-layers were divided into a set of 0.3 nm thick sublayers [21]. While the thickness of the sublayers is fixed, the optical constant of each individual sublayer is varied during the fitting of GIXRR data. A minimizing procedure for cumulative mismatch between the measured and simulated data was applied for both GIXR and F-XSW simultaneously.

4.3 Results

4.3.1 Passivation of Si

In our previous studies [3] the W-on-Si interface was found to be significantly broader than Si-on-W interface in 2.5 nm W/Si multilayers. This was due to a W silicide formation during W deposition on Si. To minimize the interaction at the W-on-Si interface, the top part of every Si layer was passivated with nitrogen. Ideally, a silicon nitride layer with a thickness of about 0.3 nm on top of the Si layer was to be formed, as illustrated in Fig. 4.1.

According to simulations a layer of 0.3 nm of Si_3N_4 would only slightly reduce reflectivity ($R=58.8\%$) compared to the ideal bi-layer W/Si system ($R=60\%$). A thicker layer of silicon nitride would already affect the reflectivity too strongly due a reduced optical contrast at 0.84 nm. Note that a W silicide layer formed in W/Si multilayers reduces reflectivity by about 10 abs.%. To implement nitridation, the surface of every Si layer (after its deposition) was exposed to reactive nitrogen

Figure 4.1: Schematic representation of one period of the multilayer with a partially N-passivated Si layer.

species from the ion source. The growth mechanism of Si_3N_4 was not known for such thin layers and the treatment conditions used. Therefore, four multilayers with different passivation times (1 min, 2.5 min, 4 min, and 8 min) were synthesized (Table 4.2). All other parameters were fixed, with the N_2 flow being 7 sccm, the beam voltage 60 eV, and ion current density 0.68 mA/cm^2 (total ion current of 120 mA).

Table 4.2: Structure IDs with the corresponding passivation times

Structure ID	Passivation time	Number of periods	Period d-value
T_0	0 min (Reference)	50/200	2.52 nm
T_1	1 min	50	2.54 nm
T_2	2.5 min	50	2.63 nm
T_3	4 min	50/200	2.5 nm
T_4	8 min	50	2.5 nm

4.3.2 Soft X-Ray reflectivity at 0.84 nm

Fig. 4.2 shows the reflectivity in the first Bragg peak at 0.84 nm of the multilayer systems with 50 periods versus different passivation times. The maximum reflectivity is observed for the reference multilayer (structure T_0) and the multilayer with one minute of passivation (structure T_1). They both have about the same reflectivity (of about 18%) suggesting that no significant structural changes were present for 1-minute of passivation (structure T_1). This observation is supported by the reflectivity measurements at 0.154 nm that did not show any differences in the reflectivity curves either. However, for 2.5-minute passivation time (structure T_2), a significant reduction in reflectivity at 0.84 nm was observed. The reflectivity remained the same for the longer passivation times of 4 and 8 minutes (structures T_3 and T_4). Note that this abrupt reduction in the reflectivity at 0.84 nm was accompanied by significant changes in the reflectivity at 0.154 nm as well, which will be discussed in section Section 4.3.5.

A multilayer system with 4-minute passivation treatment and 200 periods was also fabricated. It had a reflectivity of about 29% at 0.84 nm, which is 11% absolute value lower than the reflectivity of our W/Si reference multilayer system with 200

Figure 4.2: Reflectivity of the passivated multilayer systems with various passivation times and the reference multilayer (time=0) at 0.84 nm and an angle of incidence $\theta \approx 9.7^\circ$. The period $d=2.5$ nm, the number of periods $N=50$ for all the multilayers.

periods.

In the following sections, we investigate possible reasons for the reduction of the reflectivity at 0.84 nm in systems with passivated Si.

4.3.3 Diffuse scattering

To determine the influence of passivation on roughness of the passivated multilayer systems, diffuse scattering at $\text{CuK}\alpha$ radiation ($\lambda=0.154$ nm) was measured. For that, we did rocking curve scans by fixing the detector at the center of a Bragg peak and rocking the sample in a wide angular range. A perfect structure will produce a very sharp peak in the specular direction only, while a structure with diffused scattering will show wide ‘wings’ around it. Rocking curve measurements from multilayer structures are described in more detail elsewhere [23]. It is common to measure diffuse scattering at higher Bragg orders to observe a wider range of angles. However, due to low intensity of the higher order peaks, all scans in this work were performed at a second Bragg peak at 3.2° ($2\theta = 6.4^\circ$). The observed diffused scattering was similar for all the multilayers. For example, Fig. 4.3 shows a comparison of the T1 and T3 multilayer with the reference T0 multilayer.

The observed differences are not significant and indicate negligible differences in roughness of the measured samples. The passivation of Si did not affect the roughness to a sufficient extent to explain the drop in reflectivity at 0.84 nm for the passivated samples.

Figure 4.3: Rocking curve scans for W/Si ($d=2.5$ nm, $N=50$) multilayers deposited with and without passivation of the Si layers. Passivation times were 1 and 4 min. The curves were normalized at the maximum intensity of the Bragg peak, for comparison.

4.3.4 X-Ray photoelectron spectroscopy (XPS)

In order to investigate an effect of the ion treatment on the composition and chemical state of the elements in the structures, the multilayers were analyzed by XPS. Fig. 4.4 shows an example of a sputter depth profile for the T3 structure (4 min of Si passivation). Since the probing depth of XPS is larger than the multilayer period, the sputter profile only shows a very weak modulation in the concentrations of W, Si and N. We used these profiles to determine an average concentration of N in every structure, which is plotted in Fig. 4.5. The concentration of N increases with the passivation time and reaches a saturation for 4- and 8-min passivation. This implies that the passivation procedure was effective in nitridation the structure.

To determine the chemical state of the elements, the W4f and Si_{2p} peaks were analyzed. In order to avoid intermixing induced formation of compounds by sputter depth profiling [24], the W4f and Si_{2p} peaks were measured on the deposited samples without applying ion etching. Fig. 4.6 and Fig. 4.8 illustrate the measured W4f and Si_{2p} spectra of the samples with selected passivation times compared to the reference sample without passivation. For the W4f peak, also a reference spectrum of a thick tungsten film is included, which was sputter cleaned by Ar ion-etching directly before the measurement.

In our previous work we showed that tungsten silicide formation results in a shift of the W4f peak to a lower binding energy by about 0.2 eV [18], compared to the reference position for bulk W. Since such small shifts are close to the resolution that can be obtained with laboratory XPS systems, we only provide a qualitative evaluation and do not attempt to deconvolute the W4f peak into different components. Fig. 4.7 shows that longer passivation leads to a higher fitted binding energy of

Figure 4.4: XPS depth profiles of multilayer systems with 4 min of nitridation of Si layers.

Figure 4.5: Average concentration of nitrogen (N1S peak) in the samples with different time of passivation determined from the XPS depth profiles after a 1000s etch time at 0.25 keV.

the W4f_{7/2} peak, approaching the W reference binding energy. This implies some reduction of the tungsten silicide formation. However, since the shifts are close to the resolution of the laboratory XPS equipment, it is not possible to determine how strong the effect of silicide suppression is. Lastly, the sample deposited with 4-min passivation shows some additional XPS intensity for the W4f_{7/2} peak around 32 eV, and for the W4f_{5/2} peak around 34 eV. The intensity around these binding energies

Figure 4.6: The measured XPS W4f doublet for a multilayer with 2.5-min (red line) and 4-min (green line) passivation compared to a multilayer without passivation (blue) and a W reference (dashed line). The signals are normalized to the W4f7/2 peak.

Figure 4.7: The fitted peak position of the XPS W4f7/2 peak as function of passivation time.

is in line with WN_x formation [25], which indicates that W may react with N. This intensity strongly increases with the passivation time. This indicates that WN_x is probably not a result of W reaction with N from the underlying SiN_x layer. Instead nitrogen may penetrate through Si into the underlying W layer during passivation.

Fig. 4.8 illustrates Si_{2p} spectral lines measured for selected samples. The W/Si

reference mirror showed a slightly different background intensity due to differences in secondary electrons. Therefore, a Shirley background [26] was subtracted to facilitate comparison.

Figure 4.8: Si 2p peaks for the multilayer structure with 2.5-min passivation (red), 4-min passivation (green), and a reference structure without passivation (blue). A Shirley background was subtracted from all spectra. No normalization of intensities was applied.

The peak around 99.5 eV is assigned to elemental Si and Si in WSi_x compounds. The peak around 103.5 eV is due to native SiO_2 formed because of the oxidation of the top surface after exposure to air. Due to the larger probing depth than the period of the multilayer system, it was possible to detect the formation of SiN_x species, which contribute to the signal between 101.5 and 102 eV. However, it should be noted that substoichiometric SiO_x , present at the interface between SiO_2 and Si, may also result in intensity in the same binding energy range. It can be seen that, as the passivation time increases, the intensity in the 101.5 to 102 eV binding energy range increases, confirming that SiN_x is formed by the passivation treatment. A decrease of the Si peak around 99.5 eV can be explained by the process of conversion of Si to SiN_x .

Note that possible Ar^+ implantation in Si layers during passivation treatment could also affect the reflectivity of the multilayer system [27]. However, XPS analysis did not reveal any presence of Ar^+ in our samples.

4.3.5 Grazing incidence X-Ray reflectivity and X-Ray fluorescence analysis

Although XPS analysis gave information about the presence of nitrogen and chemical interactions taking place in the systems upon the passivation treatment, the limited depth resolution of XPS analysis did not give accurate information about

the in-depth distribution of the materials.

Figure 4.9: Measured (dots) and simulated X-Ray reflectivity data based on best-fit solutions (lines) for the T2 (2.5-min passivation) multilayer.

Figure 4.10: Measured (dots) and simulated (lines) angular dependent X-Ray fluorescence yields around the first Bragg peak ($\theta = 1.71^\circ$) for W for the T2 (2.5-min passivation) multilayer sample

To analyze this, we used X-Ray reflectivity measurements (GIXR) in combination with X-Ray fluorescence modulated by the X-Ray standing wave analysis (F-XSW). This combination allowed us to reduce the cross-correlations between the model parameters during the analysis of X-Ray reflectivity by adding the X-Ray fluorescence dataset that is sensitive to the phase of the reflected waves. This approach partially solves [28] the well-known phase problem of X-Ray reflectivity

[29, 30].

We could not measure the fluorescence signal from N in our laboratory equipment. The fluorescence signal from Si from the multilayer would be mixed with the signal from the Si substrate. So only the fluorescence signal from W was measured. To fit the data, a so called free-form analysis was used [22]. Unlike the conventional model-based fitting method, it allows for more freedom in modelling interface profiles, which is essential for short-period multilayers where interaction zones are substantial compared to the period of the structure. We analyzed the structures T0 (no passivation), T2 (2.5-min passivation), and T3 (4-min passivation). The data analysis was performed as discussed in [21] with implementation of free-form multilayer parametrization approach described in [31]. The period of the reference multilayer T0 was modeled as a set of sublayers where the concentration of the elements in the sublayers, and consequently the optical constants were allowed to vary between W and Si. To account for nitridation for structures T2 (2.5-min passivation) and T3 (4-min passivation) the element concentration and layer density was allowed to vary from W to SiN to pure Si. Examples of the achieved fits are shown in Fig. 4.9 (for GIXR) and Fig. 4.10 (for F-XSW). The fitting curves are in a good agreement with the measured data for all three multilayer systems.

Figure 4.11: The real part of the optical constant decrements obtained for 0.84 nm wavelength for the structures T0 (no passivation), T2 (2.5 min-passivation), and T3 (4-min passivation). Due to slight differences in the periods of the samples, the depth values were normalized to corresponding period values of each sample.

As a result of this analysis, we obtained a set of the concentrations of the elements, and densities per sub layer. These were used for the calculation of the optical constants at 0.84 nm wavelength as described in [32]. Fig. 4.11 shows the real part of the optical constant profiles obtained for T0, T2, and T3, as derived from the simultaneous fit described above. These profiles were used to calculate the

Figure 4.12: Measured and simulated reflectivity at 0.84 nm using the optical constant profiles shown in Fig. 4.11 for the T0, T2 and T3 multilayer systems.

at-wavelength reflectivity shown in Fig. 4.12. A good match between the measured and calculated reflectivity was obtained.

Note that a small change in the period of the structure T3 is observed. This may be ascribed to the fact that the 0.154 nm X-Ray reflectivity measurements were done about two years after the 0.84 nm wavelength X-Ray reflectivity measurements. We suggest that interdiffusion process that may continue in the multilayer after deposition could have been more significant in the T3 structure. This phenomenon calls for a separate research.

4.4 Discussion

The passivation treatment procedure of using reactive nitrogen clearly resulted in some reduction of the silicide formation, as proven by XPS. However, it did not cause a reflectivity improvement at 0.84 nm wavelength. It is remarkable that the 1-minute passivation did not result in any changes in reflectivity detectable by either 0.154 nm or 0.84 nm measurements. This is in spite of the fact that the XPS measurements did detect some amount of N present in the systems. It could be argued that this treatment did not produce a continuous passivated Si layer, with the chemical processes at the W-on-Si interface being not affected significantly. However, the 2.5-min passivation treatment did result in a pronounced reduction in the reflectivity at 0.84 nm. This is in spite of the fact that it leads to the formation of sharper interfaces, as seen in the reconstructed refractive index profile (Fig. 4.11). Still, this also showed a reduced contrast between the reflector and spacer layer

because of an elevated plateau formed in the refractive index observed in the spacer layer. The occurrence of this plateau can be ascribed to the formation of a nitrated Si layer (Si_xN_y). Evidently, the observed improvement in the interface profile is compensated by the reduced optical contrast due to the formation of a thick Si_xN_y layer, resulting in a reduction of the reflectivity at 0.84 nm. The longer passivation time (4-min) improves the interfaces further and defines the reflecting layer better. The latter is visible by a plateau formed in the reflecting layer. At the same time, the thickness of the formed SiN_x layer increases as well. Furthermore, the formation of WN_x species is observed by XPS for the 4-min passivation treatment. This could be the reason the optical density of the absorber does not increase in spite of the formation of sharper interfaces.

Summarizing, it can be concluded that passivation of Si by nitrogen can result in improvement of the interfaces in W/Si multilayers. However, a gentler passivation procedure could be explored to avoid excessive penetration of nitrogen in the Si-layer which may reduce the thickness of the Si_xN_y layer.

4.5 Conclusion

We explored partial nitridation of W/Si multilayer systems with a 2.5 nm layer periodicity. The purpose was to reduce the optically unfavorable tungsten silicide formation in W/Si systems leading to X-Ray reflectivity loss. The multilayers were deposited by magnetron sputtering, and nitridation was applied directly after the deposition of every Si layer by exposing the Si surfaces to reactive nitrogen species from a Kaufman ion source operated at 60V. The passivation was in the range of 1 to 8 minutes.

The passivation treatment of 1-min did not result in any changes in X-Ray reflectivity, as detectable at 0.154 or 0.84 nm wavelength. The treatment of 2.5-min and longer did result in a reduced tungsten silicide formation (observed by XPS) and improved sharpness of the interfaces (detected by 0.154 nm X-Ray reflectometry). However, this was accompanied by a pronounced reduction in the reflectivity at 0.84 nm. The refractive index profile, reconstructed from 0.154 nm X-Ray reflectivity, revealed the formation of an elevated plateau in the refractive index of the spacer layer. This was attributed to the formation of a thicker than 0.5 nm silicon nitride layer that reduced the optical contrast of the multilayer at 0.84 nm.

We conclude that passivation of Si using nitrogen can result in improvement of interfaces in W/Si multilayers. However, in the tested conditions, this improvement was counterbalanced by a reduced optical contrast due to a relatively thick silicon nitride layer. This suggests that gentler passivation procedures should be tried to reduce nitrogen penetration in Si.

References

- [1] R. V. Medvedev, K. V. Nikolaev, A. A. Zameshin, D. Ijpes, I. A. Makhotkin, S. N. Yakunin, A. E. Yakshin, and F. Bijkerk, *Ion polishing of Si in W / Si soft X-ray multilayer structures*, *Journal of Applied Physics* , 1 (2019).
- [2] C. Liu, R. Conley, A. T. Macrander, T. J. Graber, C. Morawe, C. Borel, and E. M. Dufresne, *Small-d-spacing WSi₂ /Si narrow bandpass multilayers*, *X-Ray Sources and Optics* **5537**, 154 (2004).
- [3] A. A. Zameshin, R. V. Medvedev, A. E. Yakshin, and F. Bijkerk, *Interface formation in W / Si multilayers*, to be published in *Thin Solid Films* (2021).
- [4] T. P. Ma, *Making silicon nitride film a viable gate dielectric*, *IEEE Transactions on Electron Devices* **45**, 680 (1998).
- [5] S. Guruvanket, J. Ghatak, P. V. Satyam, and G. M. Rao, *Characterization of bias magnetron-sputtered silicon nitride films*, *Thin Solid Films* **478**, 256 (2005).
- [6] B. C. Kim, H. Kang, C. Y. Kim, and J. W. Chung, *Ion beam nitridation of a Si(111) surface: effects of ion reactivity and thermal treatment*, *Surface Science* **301**, 295 (1994).
- [7] I. A. Makhotkin, R. W. E. van de Kruijs, E. Zoethout, E. Louis, and F. Bijkerk, *Optimization of LaN/B multilayer mirrors for 6.x nm wavelength*, *Advances in X-Ray/EUV Optics and Components VIII* **8848**, 88480O (2013).
- [8] D. S. Kuznetsov, A. E. Yakshin, J. M. Sturm, R. W. E. van de Kruijs, E. Louis, and F. Bijkerk, *High-reflectance La/B-based multilayer mirror for 6xnm wavelength*, *Optics Letters* **40**, 3778 (2015).
- [9] D. S. Kuznetsov, A. E. Yakshin, J. M. Sturm, R. W. Van De Kruijs, and F. Bijkerk, *Structure of high-reflectance La/B-based multilayer mirrors with partial la nitridation*, *AIP Advances* **6** (2016), 10.1063/1.4968175.
- [10] T. Tsarfati, R. W. Van De Kruijs, E. Zoethout, E. Louis, and F. Bijkerk, *Nitridation and contrast of B₄C/La interfaces and X-ray multilayer optics*, *Thin Solid Films* **518**, 7249 (2010).
- [11] T. Tsarfati, E. Zoethout, E. Louis, R. van de Kruijs, A. Yakshin, S. Müllender, and F. Bijkerk, *Improved contrast and reflectivity of multilayer reflective optics for wavelengths beyond the extreme UV*, *Alternative Lithographic Technologies* **7271**, 72713V (2009).
- [12] Q. Huang, Y. Liu, Y. Yang, R. Qi, Y. Feng, I. V. Kozhevnikov, W. Li, Z. Zhang, H. Jiang, L. Zhang, A. Li, J. Wang, and Z. Wang, *Nitridated Ru/B₄C multilayer mirrors with improved interface structure, zero stress, and enhanced hard X-ray reflectance*, *Optics Express* **26**, 21803 (2018).

- [13] Y. Wang, Q. Huang, Q. Yi, I. V. Kozhevnikov, R. Qi, M. Wen, P. Jonnard, J. Zhang, A. Giglia, Z. Zhang, and Z. Wang, *Nitridated Pd/B₄C multilayer mirrors for soft X-ray region: internal structure and aging effects*, *Optics Express* **25**, 7749 (2017).
- [14] M. Wen, Q. Huang, S. Ma, W. Li, R. She, J. Peng, A. Giglia, I. V. Kozhevnikov, H. Feng, Z. Zhang, and Z. Wang, *Improvement of interface structure and polarization performance of Co/C multilayers by incorporation of nitrogen*, *Optics Express* **24**, 27166 (2016).
- [15] K. H. Park, B. C. Kim, and H. Kang, *Silicon nitride formation by low energy N⁺ and H₂⁺ ion beams*, *The Journal of Chemical Physics* **97**, 2742 (1992).
- [16] I. Kusunoki, T. Takaoka, Y. Igari, and K. Ohtsuka, *Nitridation of a Si(100) surface by 100-1000 eV N⁺ ion beams*, *The Journal of Chemical Physics* **8238**, 101 (1994).
- [17] O. C. Hellman, N. Herbots, and O. Vancauwenberghe, *Kinetics of ion beam nitridation (IBN) of Si and of MBE-grown Ge and Si_xGe_{1-x} alloys: The role of ion energy, ion dose and substrate temperature*, *Nuclear Inst. and Methods in Physics Research, B* **67**, 301 (1992).
- [18] R. V. Medvedev, A. A. Zameshin, J. M. Sturm, A. E. Yakshin, and F. Bijkerk, *W/B short period multilayer structures for soft x-rays*, *AIP Advances* **10** (2020), 10.1063/1.5143397.
- [19] D. E. Savage, Y. H. Phang, J. J. Rownd, J. F. MacKay, and M. G. Lagally, *Determination of interfacial roughness correlation in W/C multilayer films: Comparison using soft and hard x-ray diffraction*, *Journal of Applied Physics* **74**, 6158 (1993).
- [20] P. J. Cumpson and M. P. Seah, *Elastic scattering corrections in AES and XPS. II. Estimating attenuation lengths and conditions required for their valid use in overlayer/substrate experiments*, *Surface and Interface Analysis* **25**, 430 (1997).
- [21] S. N. Yakunin, I. A. Makhotkin, R. W. Van De Kruijs, M. A. Chuev, E. M. Pashaev, E. Zoethout, E. Louis, S. Y. Seregin, I. A. Subbotin, D. V. Novikov, F. Bijkerk, and M. V. Kovalchuk, *Model independent x-ray standing wave analysis of periodic multilayer structures*, *Journal of Applied Physics* **115** (2014), 10.1063/1.4869540.
- [22] A. Zameshin, I. A. Makhotkin, S. N. Yakunin, R. W. Van De Kruijs, A. E. Yakshin, and F. Bijkerk, *Reconstruction of interfaces of periodic multilayers from X-ray reflectivity using a free-form approach*, *Journal of Applied Crystallography* **49**, 1300 (2016).
- [23] D. E. Savage, J. Kleiner, N. Schimke, Y. H. Phang, T. Jankowski, J. Jacobs, R. Kariotis, and M. G. Lagally, *Determination of roughness correlations in multilayer films for x-ray mirrors*, *Journal of Applied Physics* **69**, 1411 (1991).

- [24] B. Chakraborty and S. Hofmann, *Ion bombardment induced silicide formation during sputter depth profiling of Ta/Si multilayer thin film structure as studied by x-ray photoelectron spectroscopy and auger electron spectroscopy*, *Thin Solid Films* **204**, 163 (1991).
- [25] R. J. Colton and J. W. Rabalais, *Electronic Structure to Tungsten and Some of its Borides, Carbides, Nitrides, and Oxides by X-ray Electron Spectroscopy*, *Inorganic Chemistry* **15**, 236 (1976).
- [26] D. A. Shirley, *High-resolution x-ray photoemission spectrum of the valence bands of gold*, *Physical Review B* **5**, 4709 (1972).
- [27] E. Spiller, S. L. Baker, P. B. Mirkarimi, V. Sperry, E. M. Gullikson, and D. G. Stearns, *High-performance Mo-Si multilayer coatings for extreme-ultraviolet lithography by ion-beam deposition*, *Applied Optics* **42**, 4049 (2003).
- [28] M. J. Bedzyk, G. M. Bommarito, and J. S. Schildkraut, *X-ray standing waves at a reflecting mirror surface*, *Physical Review Letters* **62**, 1376 (1989).
- [29] K. M. Zimmermann, M. Tolan, R. Weber, J. Stettner, A. K. Doerr, and W. Press, *Phase determination of x-ray reflection coefficients*, *Physical Review B - Condensed Matter and Materials Physics* **62**, 10377 (2000).
- [30] J. Ehlers, K. Hepp, R. Beig, W. Domcke, U. Frisch, W. Hillebrandt, and R. L. Jaffe, *X-ray and Neutron Reflectivity. Principles and Applications* (Springer, 2009) p. 360.
- [31] S. I.A. Makhotkin, *Model independent grazing incidence X-ray reflectivity*, US Patent US10416101B2 **2** (2016).
- [32] S. N. Yakunin, I. A. Makhotkin, K. V. Nikolaev, R. W. E. van de Kruijs, M. A. Chuev, and F. Bijkerk, *Combined EUV reflectance and X-ray reflectivity data analysis of periodic multilayer structures*, *Optics Express* **22**, 20076 (2014).

5

W/B SHORT PERIOD MULTILAYER STRUCTURES FOR SOFT X-RAYS

X-Ray W/B multilayer mirrors with a period of 2.5 nm were deposited by dc magnetron sputtering and studied in a comparison with W/Si multilayer systems of the same period. TEM, GIXR, and XPS analysis revealed that the layer quality and interfaces of the W/B multilayers are not better than the W/Si multilayers. Strong intermixing between W and B is present, which leads to compound formation with little or no pure W left after the interaction: an optically unfavorable boride formation and an increased roughness result in a reduced reflectivity. The deposited W/B multilayer mirrors showed a reflectivity of 34.5% at 0.84 nm and angle of incidence 9.7° compared to 40% obtained for W/Si multilayers. Ion polishing applied on the boron layers did not result in improvements of the reflectivity.

5.1 Introduction

Multilayer X-Ray mirrors working in the range Al $K\alpha$ to O $K\alpha$ (0.84 - 2.4 nm) are used in X-Ray fluorescent spectroscopy (XRF) as analyzing monochromators at the grazing angles of incidence in the range from 9.7° to 29° . An advantage of using multilayer systems is the possibility to tune their period for a specific wavelength. High reflectivity is required as it allows for a higher sensitivity of XRF. Several multilayer systems, W/Si, W/B₄C, W/C, and W/B are promising systems as they have theoretically high optical contrasts, hence high reflectivity in the range 0.84 - 2.4 nm. Shorter period multilayers would allow achieving higher resolution in XRF applications because they would allow obtaining a larger angular distance between the measured peaks corresponding to different elements. However, for the shorter periods, lower reflectivity is achieved in practice. As such, the period range 2 to 3 nm can be considered to be optimal to achieve acceptable resolution and reflectivity. However, limited literature is available on these multilayer systems for the discussed wavelength range. Most of these multilayer mirrors were studied thoroughly for other applications [1–10]. Gan et al. [1] studied W/C in the period range 1.5 to 4 nm. According to that, good quality periodic systems could be obtained when the W layers were thicker than 0.75 nm. Thinner W layers were found to show island-like growth, worsening the quality of the interfaces. In comparison, studies on W/B₄C showed a better periodicity and higher reflectivity than W/C [6, 8, 10, 11].

However, it was reported that W-B₄C interaction leads to a W_xC_y compound formation and an increase of thickness errors which negatively affected the reflectivity and quality of the multilayer mirrors. All systems, W/C, W/B₄C, and W/Si were found to have a decreased density of the reflector layers as a result of a chemical interaction between the spacer and the metal layer, for thicknesses of the W layer less than 0.75 nm. As such, the optical contrast of the multilayer mirrors was lower than theoretically expected, limiting the reflectivity. However, no measurements of the reflectivity in the soft X-Ray range were done for those multilayer systems, except for W/Si. Therefore, we took the W/Si system from our previous research, as a reference for our studies [3]. So far the highest reported reflectivity (40 %) was achieved for W/Si at 0.84 nm which is 20 abs. % lower than the theoretical value for a W/Si multilayer mirror without any interfacial roughness ($\sigma = 0$). The main reason for the reduced reflectivity was an interaction between W and Si which led to a tungsten silicide formation and an interfacial roughness which could not be reduced further.

In this work, we synthesized and analyzed short-period W/B multilayer systems that to our knowledge have not been experimentally studied before. Theoretically, i.e. when taking again $\sigma = 0$, W/B shows the highest reflectivity, 62.6 % at 0.84 nm, compared to about 60 % for W/Si, W/B₄C, and W/C systems. The purpose was to study the interaction between the layers in the system and determine if a higher optical contrast between the layers could be obtained in comparison to a reference W/Si multilayer.

Figure 5.1: Configuration of the deposition setup. The spinning substrate is fixed in the middle of the deposition chamber 30 cm above the magnetrons. The magnetrons move to the center of the chamber before the deposition of the layer and back once the deposition of the layer is finished. An ion source is mounted at 60 degrees with respect to the substrate.

5.2 Experiment

5.2.1 Multilayer deposition

All multilayer mirrors were deposited on super-polished silicon wafers 25 mm x 25 mm (RMS roughness ≈ 0.14 nm) using DC magnetron sputtering system with a base pressure of $1 \cdot 10^{-9}$ mbar. Ar was used as a working gas at the pressure of about $1 \cdot 10^{-4}$ mbar. Depositions were performed at the power of 84 W for W and 575 W for B, with the areas of the targets being 78.5 cm^2 . W was deposited with lower power in order to have better control of thickness. The deposition rates were 0.05 nm/s and 0.031 nm/s for B and W, respectively. A 15 cm DC Kaufman-type ion source (Veeco Instruments) with a molybdenum three-grid lensing system was used for the experiments. The ion source was operated at Ar flow of 5 sccm, with the energy of extracted ions being 100 eV, and the current density of the ions on the substrate being $566 \mu\text{A/cm}^2$. The ion gun was mounted at 60 degrees grazing to the substrate at a distance of 70 cm. The multilayer mirrors consisted of 200 periods with a period of 2.5 nm and gamma values ($\Gamma = d_W / (d_W + d_B)$) varying from 0.08 to 0.36. To avoid uncontrolled oxidation of the surfaces after exposure to the air, every mirror was finished with a B layer of the same thickness as in the stack. The substrate holder was rotating at 60rpm during the deposition process. The schematic configuration of the chamber is illustrated in the Fig. 5.1

5.2.2 Multilayer characterization

The multilayer mirrors were characterized by θ - 2θ grazing incidence reflectivity measurement at CuK α wavelength ($\lambda = 0.154 \text{ nm}$) using a Malvern Panalytical

Empyrean diffractometer. Fast measurements for period thickness determination were performed with a hybrid monochromator consisting of a combination of an X-Ray mirror and a 2-crystal Ge(220) 2-bounce monochromator. Longer measurements for structural reconstruction were performed with a 4-bounce Ge(220) monochromator to achieve the highest angular resolution. For the reconstruction we used a model-independent approach described in [12], where the multilayer period is segmented into multiple sublayers that can be adjusted semi-independently. This allows for a more versatile representation of structural profiles in comparison to rigid models, i.e. without sub-layer division, which is important for working with strongly intermixed films.

To measure the top surface roughness of the samples, a Bruker Dimension EdgeTM Atomic Force Microscope (AFM) was used. A high-resolution tip Hi'Res-C14/Cr-Au by MikroMasch was used (radius of the tip was ≈ 1 nm).

For a qualitative assessment of interfacial roughness in the multilayer systems X-Ray diffused scattering rocking curves were measured with a conventional X-Ray tube at the wavelength of 0.154 nm, with the procedure of the measurement being described elsewhere [13]. It is common to measure diffuse scattering at higher orders to observe a wider range of angles. However, due to the low intensity of the high order Bragg peaks, the scans in this work were performed at the second Bragg peaks. The surface composition of the samples was determined by non-destructive X-Ray Photoelectron Spectroscopy (XPS), using a Thermo Scientific Theta Probe Instrument employing monochromatic Al-K α radiation. Base pressure in the XPS chamber was $5 \cdot 10^{-10}$ mbar.

Cross-sectional transmission electron microscope images of the multilayers were obtained with Philips CM30T instrument used in a bright field mode at 300kV with a point resolution of 0.2 nm and line resolution of 0.14 nm. All samples were prepared by mechanical polishing (Dimple Grinding/Polishing) followed by argon ion thinning at 600 eV. The minimal thickness of the samples was 250 nm.

Soft X-Ray reflectivity at 0.84 nm and grazing angle of incidence of $\theta_0 = 9.7^\circ$ was measured at the storage ring BESSY II at Physikalisch-Technische Bundesanstalt (PTB) in Berlin-Adlershof, Germany [14]. Since the reflectivity was measured at a grazing incidence angle, a 0.5 mm exit slit on the monochromator was used in order to reduce the size of the beam footprint on a sample.

5.3 Results and discussions

5.3.1 Soft X-Ray reflectivity

Previously, it was reported that in W/Si, W/B₄C and W/C multilayer systems compound formation takes place, which has a significant influence on the formed thicknesses of the layers and thus the gamma values ($\Gamma = d_{\text{metal}}/(d_{\text{metal}} + d_{\text{spacer}})$) of the formed stacks [3, 4, 10, 13, 15]. Therefore, in order to find the optimum gamma value resulting in the maximum reflectivity at 0.84 nm, a series of multilayer mirrors in a range of gamma values from 0.06 to 0.36 was deposited. According to IMD simulations [16] the optimum Γ for an ideal W/B multilayer system is 0.23 at which the maximum reflectivity of 62.6% at $\lambda = 0.84$ nm and the angle of incidence 9.7°

Figure 5.2: The measured and calculated reflectivity versus wavelength for the deposited W/B multilayer (blue line) and an ideal multilayer (no interfacial roughness, dashed line), correspondingly. The angle of incidence is 9.7° .

is achieved. Fig. 5.2 shows the highest measured reflectivity of the deposited W/B ($\Gamma=0.12$) together with the simulation of an ideal multilayer system (interfacial roughness $\sigma=0$) at 9.7° .

Note that the highest measured reflectivity was obtained for $\Gamma=0.12$, rather than $\Gamma=0.23$ expected based on the calculations. This strong difference can be explained by the interactions taking place between layers that have a significant influence on the formed thicknesses of the layers. This effect was previously observed for W/Si systems as well [3]. As it can be seen from Fig. 5.2 the maximum reflectivity at 0.84 nm is $R=34.5\%$ which is 28 % (absolute value) lower than the theoretical value for an ideal multilayer system, and 5.5 % (absolute value) lower than the reflectivity of W/Si reported previously [3]. The reflectivity data at 0.84 nm and angle of incidence 9.7° for all the deposited W/B multilayer systems is provided in the Table 5.1.

Table 5.1: Reflectivity data at 0.84 nm and AOI= 9.7° for gamma values in the range from 0.06 to 0.18

Gamma value	Reflectivity at 0.84 nm
0.06	22.21%
0.08	29.54%
0.12	34.5%
0.18	32.66%

Spiller et al [17] reported that implantation of Ar species in the Si layers could

reduce reflectivity. The presence of Ar in the B layers could affect the reflectivity too. However, XPS analysis did not reveal the presence of Ar or any other contaminant in our samples. So the relatively low reflectivity of the W/B multilayers could not be explained by contamination. Other possible reasons could be roughness and/or interaction between the layers, which is addressed in the following sections.

5.3.2 Atomic force microscopy measurements

In order to verify the role of layer roughness, we did AFM measurements. The measurements were done both for W/B ($\Gamma=0.12$, $N=200$) and W/Si ($\Gamma=0.12$, $N=200$) multilayer systems to also be able to make a comparison between them. The measured absolute rms values for W/B and W/Si were 0.143 and 0.134 nm, respectively, which is at the limit of the AFM sensitivity. The probed area for both samples was $1 \times 1 \mu\text{m}$. So no differences in roughness were determined within the resolution of AFM. Note that surface roughness can in some cases be affected by oxidation of the surface. Keeping in mind that the B and Si oxides may reconstruct or smoothen the surface, other methods of analysis to study the layer roughness were required.

5.3.3 Transmission electron microscopy

The interfaces were additionally analyzed by means of TEM. Fig. 5.3 shows TEM images of W/B (left) and W/Si (right) multilayer structures with the following characteristics: $d=2.5$ nm, $N=200$, and $\Gamma=0.12$. Both multilayer systems seem to have relatively sharp interfaces. Another point evident from the TEM pictures, is that the as-deposited gamma value is significantly higher than the nominal gamma $\Gamma=0.12$ in both systems. This substantial difference cannot be explained by errors in the calibration of thicknesses in the deposition process but should be associated with interactions between the layers.

These interactions can considerably modify thicknesses of the deposited reflector and spacer layers e.g. via an intermixing process or compound formation. As a result, the optical index profile can substantially deviate from the intended profile, which will affect the X-Ray reflectivity of the structures. TEM did not reveal significant differences in the density profiles of the W/B and W/B multilayers as judged by the intensity modulation (Fig. 5.3). However it is not possible to extract quantitative information from such measurements due to a difficulty to have a proper reference intensity level in TEM. To look into this further, this point has been addressed by GIXR described in the following section.

5.3.4 Model-independent analysis of GIXR

To obtain quantitative data on the interface and layer profiles for the investigated systems, GIXR analysis was applied. We used a model-independent method of structural reconstruction, described in detail elsewhere [12]. Our method assumes an ideal periodicity, which puts requirements on the period-to-period reproducibility of the multilayer samples. Thickness errors lead to the broadening of the Bragg peaks and/or splitting of them, which cannot be simulated in our layer reconstruction method. Accumulation of small instabilities in the deposition process [18]

Figure 5.3: (a) TEM cross-sectional pictures of W/B ($\Gamma=0.12$, $N=200$) (left) and W/Si ($\Gamma=0.12$, $N=200$) (right) multilayers. (b) Intensity profiles of the TEM images

leads to a stronger peak broadening in the structures with larger number of periods. Furthermore, the larger the total thickness of the multilayer film, the larger the curvature of the sample due to the internal stress in the film. A strongly curved sample does not allow for accurate measurement of the total external reflection and can modify the critical angle. Note, that the W/B systems were found to have about a factor of four higher sample curvature than W/Si as checked by white light interferometry. For both of these reasons, the multilayer structures with 200 periods could not be used for GIXR analysis.

We, therefore, deposited an additional multilayer structure W/B, with $d=2.5$ nm, $\Gamma=0.12$, and the number of periods $N=50$, and measured GIXR data. The reference multilayer system, W/Si with $d=2.5$ nm, $\Gamma=0.12$ and $N=50$, was deposited and analyzed in our previous research [3]. Fig. 5.4 (a) and (b) (red points) show the corresponding reflectivity curves of these systems. The model-independent approach was used to reconstruct the multilayer structure from these measurements. For fitting the GIXR curves from Fig. 5.4 (a) and (b), the periodic part of the

multilayer mirrors was divided in 13 sublayers. The reconstruction started from a step-like profile and finished in about 200 iterations with the profiles shown in Fig. 5.4 (c). As can be seen from Fig. 5.4 (a) and (b), the calculated GIXR curves fit well the experimental ones, with all the Bragg peaks fully described and the shape of the XRR curve in between the Bragg peaks mostly matching. The results of the reconstruction are shown as delta-profiles in Fig. 5.4 (c) where $\sigma = 1 - \text{Real}(n)$, n - optical constant [12].

Figure 5.4: (a) CuK GIXR measured reflectivity (red dots) and fitting curve (blue line) for W/Si multilayer. (b) CuK GIXR measured reflectivity (red dots) and fitting curve (blue line) for W/B multilayer; (c) Reconstructed delta profile of W/Si (red line) and W/B (blue line) multilayers. Note that the analysis of the W/Si multilayer shown here is taken from our earlier research [3].

As seen, the shape of the reconstructed interface profiles in W/B and W/Si is almost identical, which is qualitatively in agreement with the TEM data. The only noticeable difference is the highest delta values. The tabulated delta value for pure W is $4.6 \cdot 10^{-5}$ [19], whereas the highest delta values from the reconstructed profiles are only $2.7 \cdot 10^{-5}$ and $2.8 \cdot 10^{-5}$ for W/B and W/Si systems, respectively. This means that there is no pure W present in any of the multilayer systems, with the difference in the highest delta values for the two systems being rather small.

The maximum delta value for W/B corresponds to the tabulated value of W_2B_5 of $2.75 \cdot 10^{-5}$. The maximum delta value for W/Si comes close to the tabulated value of WSi_2 of $2.5 \cdot 10^{-5}$, although it does not match it exactly. This can be explained by a formation of a mixture of several compounds, e.g. two neighboring silicides found in the W-Si phase diagram, WSi_2 , and W_5Si_3 .

Thus, based on TEM and GIXR analysis, the W/B system did not prove to be structurally better than W/Si multilayer. This explains its relatively low reflectivity at 0.84 nm. In both systems, compounds are suggested to be formed due to strong intermixing. To check the formation of these compounds and the fact that no pure W is present in the multilayers we performed XPS measurement, which is described in the following section.

5.3.5 X-Ray photoelectron spectroscopy measurements

GIXR analysis of W/B and W/Si multilayers ($d = 2.5$ nm, $\Gamma = 0.12$) suggested there is no pure W present and indicated the formation of certain compounds in the structures. To check that, non-destructive XPS measurements were done on the surface of these multilayers. Taking into account 5-7 nm depth of information for XPS, the signal was obtained from about two top periods of the stacks. Fig. 5.5 shows the signal from W4f peaks, obtained for the multilayers and a reference W film that was sputter cleaned directly before the measurements. In order to facilitate comparison of the peaks, the intensity scale is normalized to the W4f7/2 peak.

Figure 5.5: W4f XPS measurements for W/Si ($\Gamma = 0.12$) and W/B ($\Gamma = 0.12$) compared to a reference measurement for pure W metal. All spectra are normalized on the W4f7/2 peak. A shift of the W peak indicates the consumption of W in the multilayers to form WB_x and WSi_x compounds. A shift towards lower binding energies indicates a silicide formation; a shift towards higher binding energies indicates a boride formation

To our knowledge, there are no studies in literature that unambiguously relate

the binding energy of the W4f peak to WB_x composition. However, most literature results on tungsten-boron and tungsten-boron-carbon compounds indicate a positive change in binding energy between 0.3 and 0.8 for WB_x compounds, relative to W metal [20–22]. This is consistent with a peak position of the W4f7/2 peak at 31.5 eV binding energy observed here for W/B multilayers, compared to 31.1 eV for a W metal reference. Similarly, a shift of the W4f peak to lower binding energy (30.9 eV) upon silicide formation is in line with reported XPS studies on metal silicide formation for W/Si systems [23, 24]. These differences in binding energy are small compared to the typical resolution achievable with laboratory XPS systems, which complicates the use of peak fitting to separate the formed WB_x and WSi_x compounds from a possible fraction of unreacted W metal. When the W4f spectral region of the W/B multilayer from Fig. 5.5 is fitted with a W4f doublet corresponding to WB_x and a W4f doublet of W metal, with the fixed peak position, width and shape according to a fit of a clean W reference sample, the fit indicates that around 6% of the W4f signal may be attributed to unreacted W metal. Similarly, a fit of the W4f spectrum from W/Si with doublets corresponding to WSi_x and W metal indicates a potential contribution of unreacted W metal of 7%, compared to the total W signal. However, a virtually equally good fit is obtained without adding a peak component of W metal. Due to the low intensity of the signal from boron and a broadness of its peak it was not possible to detect small shifts in its binding energy. Analysis of oxygen spectral line was not performed due to the fact that only the top surface oxidizes and there is no diffusion of oxygen in the layers beneath.

The XPS results are thus in line with a negligibly small fraction of unreacted W metal, as concluded from GIXR data in both W/B and W/Si multilayer structures. The high density layers formed during the deposition are made of certain W compounds. However according to the reconstructed delta profiles from GIXR, the difference in the highest delta values at 0.154 nm for the two systems was rather small, and this did not explain why the reflectivity of the W/B multilayer was significantly (by 5.5 abs.%) lower than that of W/Si at 0.84 nm. To further look into that, we did model simulations at 0.84 nm wavelength which are described in the following section.

5.3.6 Model simulations at 0.84 nm wavelength

The delta profiles (shown in Fig. 5.4 (c)) obtained from GIXR, indicated the formation of W_2B_5 instead of a pure W layer, suggesting the formation of W_2B_5/B instead of a W/B multilayer. Similarly, WSi_x/Si was formed instead of a W/Si multilayer. We used this data to asses if such compositions of the multilayers could explain the experimental reflectivity obtained at 0.84 nm, by IMD model simulations.

We started our simulations with the WSi_x/Si system. A two-layer model WSi_x/Si with $d=2.5$ nm, $\Gamma=0.315$, and $N=200$ was used to fit the reflectivity. The $\Gamma=0.315$ was chosen based on the reconstructed delta profiles in Fig. 5.4 (c). The obtained maximum delta value for W/Si in Fig. 5.4 (c) did not match the tabulated delta values of any of the pure silicides but was found in between the values of WSi_2 and W_5Si_3 . So we used a mixture of these two silicides to match the obtained

maximum delta value. As such an effective stoichiometry of $x=1.28$ and a density of $\rho = 10.68$ was calculated and used for the reflectivity simulations. The roughness of the interfaces was taken into account by applying a Debye-Waller factor at each of the interfaces. The calculations showed that the 40% reflectivity (measured on the experimental multilayer) can be obtained for the modeled system with the Debye-Waller factor being $\sigma = 0.25$ nm. We used this as a reference for further calculations.

At the next step, we replaced WSi_x with W_2B_5 in our simulations. A two-layer model $\text{W}_2\text{B}_5/\text{B}$ was used, with $d=2.5$ nm, $\Gamma=0.315$, $N=200$, and Debye-Waller factor $\sigma=0.25$ nm. The tabulated density $\rho(\text{W}_2\text{B}_5)=11$ g/cm³ was used. This calculation resulted in the reflectivity of 37.5%. So the W_2B_5 compound reduced reflectivity by 2.5 abs.% compared to the WSi_x silicide used in the simulations above. The remaining 3 abs.% of 5.5 abs.% could be explained if we would increase the Debye-Waller factor from $\sigma=0.25$ to $\sigma=0.31$ nm. XPS depth-profile measurements revealed presence of oxygen in the top B layer, which is a result of the surface oxidation after the exposure of the structure to air. Oxygen was not found in the deeper layers. Therefore, we added a layer of boron oxide (B_2O_3) in our model with a thickness of 2 nm. The layer of B_2O_3 did not cause reduction in reflectivity by more than 0.5% at wavelength, therefore, we could conclude that oxidation of the top surface was not the reason for the strongly reduced reflectivity.

Figure 5.6: The simulated reflectivity of W/B multilayers at an angle of incidence of 9.7° , compared to the highest measured reflectivity of a W/B multilayer ($N=200$, $d=2.5$ nm, $\Gamma=0.12$). Parameters used for the simulation: two layer $\text{W}_2\text{B}_5/\text{B}$ model, $N=200$, $d=2.5$ nm, $\Gamma=0.315$, $\sigma=0.312$ nm.

Fig. 5.6 shows the simulated and measured reflectivity for the W/B multilayer. As it can be seen the width of the simulated reflectivity peak is narrower than the one measured at 0.84 nm. It could be explained by an accumulated effect of the thickness errors occurring during the deposition of the 200-period stack. Although

such a peak cannot be uniquely fit, our simulations showed that such broadening can be caused by RMS random thickness error of the layers in the range 0.04 - 0.05 nm. However, our data obtained on the multilayers with a smaller number of periods do not support such a large thickness error. Based on GIXR we estimate the actual random thickness errors to be about a factor of three smaller. Alternatively, systematic period shift could explain the observed data. Unfortunately, there cannot be a unique solution found for the systematic period shift. However, we could estimate that in the worst case such period shift could result in about 3 abs.% reflectivity loss.

Thus, the model simulations showed that the reduced reflection of W/B with respect to W/Si at 0.84 nm can be explained by a combination of several factors: formation of a compound unfavorable for 0.84 nm wavelength, higher interfacial roughness, and somewhat larger layer thickness errors. But TEM and AFM did not reveal any differences in the roughness of the two systems. To verify this further, we performed diffuse scatter measurements that have a very high sensitivity to roughness in multilayers.

5

5.3.7 Diffuse scatter measurements and ion polishing

To compare interfacial roughness in the W/B and W/Si multilayers, X-Ray diffuse scattering at $\text{CuK}\alpha$ wavelength ($\lambda = 0.154 \text{ nm}$) was measured by mean of the rocking curve scan. The measurement was done by rocking the sample around a second Bragg position $\theta = 3.48^\circ$ in a wide angular range, with the detector being fixing at $2\theta = 6.96^\circ$ (Fig. 5.7).

Figure 5.7: Rocking curve scans for W/B ($d=2.5 \text{ nm}$, $N=200$, $\Gamma=0.12$) and W/Si ($d=2.5 \text{ nm}$, $N=200$, $\Gamma=0.12$) around the position of the second Bragg peak $\theta = 3.48^\circ$ and detector a $2\theta = 6.96^\circ$.

Although we were not able to extract quantitative data from these measure-

ments, the higher diffuse scattering from W/B in the entire angular range is qualitatively in agreement with the model simulation (section 3.6) that suggested a higher interfacial roughness in W/B compared to W/Si.

Figure 5.8: Rocking curve scans for the W/B ($d=2.5$ nm, $N=200$, $\Gamma=0.12$) multilayers with (blue line) and W/B ($d=2.5$ nm, $N=200$, $\Gamma=0.12$) without (red line) ion polishing of B layers. The polishing was done with 100 eV Ar⁺ ions, with the etched thickness of 0.3 nm.

As it was reported [15, 25–27], ion polishing is an effective tool to reduce interfacial roughness in some of the multilayer systems and hence improve reflectivity. To test this possibility for W/B multilayers, we performed an experiment where every B layer was polished with 100 eV Ar⁺ ions, with an etched thickness of 0.3 nm. The energy of 100 eV was selected as it is high enough to initiate mobility of the surface atoms but not too high to cause ballistic intermixing with the underlying layer. To compare interfacial roughness in the polished and unpolished structures, X-Ray diffuse scattering at CuK α wavelength ($\lambda=0.154$ nm) was measured by mean of the rocking curve scan, shown in Fig. 5.8.

A substantial reduction in diffuse scattering is observed after applying the ion-polishing, which usually implies a reduction of roughness. However, the measured reflectivity of the ion-polished multilayer did not result in any reflectivity changes at 0.84 nm wavelength – both unpolished and polished multilayer systems showed reflectivity of about 34.5% at 0.84 nm. A similar effect was observed in our previous work on the W/Si systems where a substantial decrease of diffuse scattering was caused by a strong reduction in the vertical correlation length of roughness, but insignificant changes in the amplitude of roughness [3]. We presume that the same effect is also observed in the ion-polished W/B multilayers. Nevertheless, it cannot be excluded that other parameters can be found, including the ion species, ion energy, and the amount of etched material, which will still allow further reduction of roughness in W/B multilayers.

5.4 Conclusions

We have synthesized and analyzed 2.5 nm period W/B multilayer X-Ray mirrors and compared these with more established 2.5 nm period W/Si mirrors. The main goal was to study the interaction between the layers in the system and determine if a higher optical contrast between the layers could be obtained in comparison to reference W/Si multilayers. However, the deposited W/B multilayers mirrors showed a reduced reflectivity of 34.5% at 0.84 nm compared to 40% obtained for W/Si multilayers.

Based on TEM, GIXR, and XPS analysis, the W/B multilayers did not prove to be structurally better than W/Si multilayers. We have identified strong intermixing between W and B leading to a compound formation, with little or no pure W left after the interaction. A similar process occurs in W/Si multilayers, although the reflectivity of W/B multilayers is lower than that of W/Si multilayers by about 5.5 abs.%. This is mainly because of optically unfavorable boride formation and a slightly increased roughness. Ion polishing of boron layers resulted in a significant reduction in the diffuse scattering of the W/B multilayer at 0.154 nm wavelength, but did not improve its reflectivity at 0.84 nm.

References

- [1] B. K. Gan, B. A. Latella, and R. W. Cheary, *Fabrication and characterisation of ultra-thin tungsten-carbon (W/C) and platinum-carbon (Pt/C) multilayers for X-ray mirrors*, *Applied Surface Science* **239**, 237 (2005).
- [2] J. F. MacKay, D. W. Pearson, B. E. Nelms, P. M. DeLuca, M. N. Gould, and M. G. Lagally, *A double mirror W/C multilayer monochromator for radiation biology applications*, *Medical Physics* **25**, 773 (1998).
- [3] R. V. Medvedev, K. V. Nikolaev, A. A. Zameshin, D. Ijpes, I. A. Makhotkin, S. N. Yakunin, A. E. Yakshin, and F. Bijkerk, *Low-energy ion polishing of Si in W/Si soft X-ray multilayer structures*, *Journal of Applied Physics* **045302**, 1 (2019).
- [4] C. Liu, R. Conley, A. T. Macrander, T. J. Graber, C. Morawe, C. Borel, and E. M. Dufresne, *Small-d-spacing WSi₂/Si narrow bandpass multilayers*, *X-Ray Sources and Optics* **5537**, 154 (2004).
- [5] B. Vidal, J. Marfaing, and P. Dhez, *Magnetron Sputtering Deposition Of Ultrathin W-Si Multilayers For X Rays Optics*, , 148 (1989).
- [6] A. F. Jankowski, L. R. Schrawyer, and M. A. Wall, *Structural stability of heat-treated W/C and W/B₄C multilayers*, *Journal of Applied Physics* **68**, 5162 (1990).
- [7] A. F. Jankowski, L. R. Schrawyer, M. A. Wall, W. W. Craig, R. I. Morales, and D. M. Makowiecki, *Interfacial bonding in W/C and W/B₄C multilayers*, *Journal of Vacuum Science & Technology A: Vacuum, Surfaces, and Films* **7**, 2914 (2002).
- [8] I. A. Kopylets, V. V. Kondratenko, E. N. Zubarev, and D. V. Roshchupkin, *Formation of short-period multilayer W/B₄C compositions*, *Technical Physics* **57**, 1709 (2012).
- [9] A. Jankowski and D. Makowiecki, *W/B₄C multilayer x-ray mirrors*, *Optical Engineering* **30(12)** (1991).
- [10] P. C. Pradhan, D. Gangir, A. Majhi, M. Nayak, A. Biswas, D. Bhattacharyya, and G. S. Lodha, *Fabrication and performance of a high resolution ultra-short period W/B₄C multilayer structure*, *Journal of Physics D: Applied Physics* **49** (2016), 10.1088/0022-3727/49/13/135305.
- [11] P. N. Rao, S. K. Rai, M. Nayak, and G. S. Lodha, *Stability and normal incidence reflectivity of W/B₄C multilayer mirror near the boron K absorption edge*, *Applied Optics* **52**, 6126 (2013).
- [12] A. Zameshin, I. A. Makhotkin, S. N. Yakunin, R. W. Van De Kruijs, A. E. Yakshin, and F. Bijkerk, *Reconstruction of interfaces of periodic multilayers from X-ray reflectivity using a free-form approach*, *Journal of Applied Crystallography* **49**, 1300 (2016).

- [13] D. E. Savage, J. Kleiner, N. Schimke, Y. H. Phang, T. Jankowski, J. Jacobs, R. Kariotis, and M. G. Lagally, *Determination of roughness correlations in multilayer films for x-ray mirrors*, [Journal of Applied Physics](#) **69**, 1411 (1991).
- [14] G. Ulm, B. Beckhoff, R. Klein, M. K. Krumrey, H. Rabus, and R. Thornagel, *PTB radiometry laboratory at the BESSY II electron storage ring*, [X-Ray Optics, Instruments, and Missions](#) **3444**, 610 (1998).
- [15] N. S. E.Louis, H.-J.Voorma, N.B. Koster, F. Bijkerk, Yu.Ya.Platonov, S.Yu.Zuev, S.S.Andreev, E.A. Shamov, *Multilayer coated reflective optics for Extreme UV lithography*, [Microelectronic Engineering](#) **27**, 235 (1995).
- [16] D. L. Windt, *IMD—Software for modeling the optical properties of multilayer films*, [Computers in Physics](#) (1998), 10.1063/1.168689, [arXiv:hec.3108 \[10.1002\]](#) .
- [17] E. Spiller, S. L. Baker, P. B. Mirkarimi, V. Sperry, E. M. Gullikson, and D. G. Stearns, *High-performance Mo-Si multilayer coatings for extreme-ultraviolet lithography by ion-beam deposition*, [Applied Optics](#) **42**, 4049 (2003).
- [18] E. Spiller, D. Stearns, and M. Krumrey, *Multilayer x-ray mirrors: Interfacial roughness, scattering, and image quality*, [Journal of Applied Physics](#) **74**, 107 (1993).
- [19] E. Gullikson, [CXRO-Database](#), (2015).
- [20] D. Radev, I. Avramova, D. Kovacheva, D. Gautam, and I. Radev, *Synthesis of Boron Carbide by Reactive-Pulsed Electric Current Sintering in the Presence of Tungsten Boride*, [International Journal of Applied Ceramic Technology](#) **13**, 997 (2016).
- [21] T. Dash and B. B. Nayak, *Preparation of multi-phase composite of tungsten carbide, tungsten boride and carbon by arc plasma melting: characterization of melt-cast product*, [Ceramics International](#) **42**, 445 (2016).
- [22] J. Chrzanowska-Giżyńska, P. Denis, S. Woźniacka, and Ł. Kurpaska, *Mechanical properties and thermal stability of tungsten boride films deposited by radio frequency magnetron sputtering*, [Ceramics International](#) **44**, 19603 (2018).
- [23] E. Zoethout, E. Louis, and F. Bijkerk, *In depth study of molybdenum silicon compound formation at buried interfaces*, [Journal of Applied Physics](#) **120** (2016), 10.1063/1.4962541.
- [24] D. R. Wheeler and W. A. Brainard, *Composition of rf-sputtered refractory compounds determined by x-ray photoelectron spectroscopy*, [J Vac Sci Technol](#) **15**, 24 (1978).
- [25] K. Soyama, W. Ishiyama, and K. Murakami, *Enhancement of reflectivity of multilayer neutron mirrors by ion polishing: optimization of the ion beam parameters*, [Journal of Physics and Chemistry of Solids](#) **60**, 1587 (1999).

- [26] E. J. Puik, M. J. Van Der Wiel, H. Zeijlemaker, and J. Verhoeven, *Ion bombardment of thin layers: The effect on the interface roughness and its x-ray reflectivity*, *Review of Scientific Instruments* **63**, 1415 (1992).
- [27] E.Spiller, *Enhancement of the reflectivity of multilayer x-ray mirrors by ion polishing*, *Optical Engineering* (1990).

VALORIZATION AND OUTLOOK

Development of new X-ray optics requires solving complex layer deposition issues which become more challenging the shorter the multilayer periodicity is. To solve these issues it is necessary to understand what happens at the interfaces during and after deposition of the layers. In this work, we demonstrate that the analysis of thin multilayer structures is not possible using a single conventional method due to limitations in resolution. A combination of many analytical methods is required. The main motivation for this work is to investigate how to use state-of-the-art analysis techniques, such as grazing incidence X-ray reflectivity (GIXR) in combination with X-ray standing wave (XSW) generated X-ray fluorescence (XRF), grazing-incidence small-angle X-ray scattering (GISAXS) and low-energy ion scattering (LEIS) in combination with X-ray photoelectron spectroscopy (XPS), and combine them to construct a reliable picture of the multilayer stack and its interfaces.

In this thesis we demonstrate the value of combining the techniques in the process of developing W/Si and W/B multilayers: Reconstruction of profiles using a free-model approach fitting of GIXR data allowed us to compare interfaces of two different structures and to discover the lack of bulk tungsten in the systems, which reveals the problem of reduced optical contrast. Such a method is very useful for straightforward comparison of different multilayer systems in terms of changes at interfaces and of optical contrast.

LEIS studies revealed the asymmetric formation of interfaces which led us to focus on the treatment of the Si layers. For instance, the type of surface nitridation applied, has a significant effect on the sharpness of the interfaces in the multilayers. The GISAXS method enabled us to investigate ensembles of correlated nanostructures in multilayer systems. It is sensitive to the distribution of shapes of the nano-particles, their location, and orientation. We showed that GISAXS is a very useful tool that provides data about interfacial roughness characteristics such as vertical and lateral correlation lengths and jaggedness of roughness resulting in a quantitative analysis of all three parameters and effective parameters of the roughness amplitude which was later confirmed by a model-independent simulation. We show that a combination of various nano-metrology methods enables a qualitative and quantitative analysis of the internal structure of W/Si and W/B multilayer mirrors. This makes it possible to develop a new dedicated analyzer for industrial application of X-ray spectroscopy.

In this work we investigated the limits in reflectance of the bi-layer system W/Si and its alternative W/B. There is room for improvement which will lead to a higher at-wavelength reflectance. The next step to reach higher reflectance should be to use barrier layers in order to prevent strong WSix formation and to form an optically

favorable compound. Possible candidates for barrier layers are C, B, B₄C and post deposition nitridation with a more gentle energy than was used in this research. In the case of increased roughness at the interfaces, the deposition process can be combined with ion polishing and the use of alternative working gases.

The research described in this thesis may serve as a roadmap for engineers and researchers who are tasked to design and make such X-ray optics. One of examples is X-Ray optics for astronomy. Despite the focus on much higher energies, the technology for production, modelling and characterization has large overlap with this field. Key of this work is that most of the methods besides GISAXS can be applied on in-house lab-scale equipment as we used in this work. Only the GISAXS measurements, requiring higher intensity, have to be carried out at a synchrotron facility.

SUMMARY

This work is dedicated to thin film reflective multilayer optics working in the range between the O $K\alpha$ and the Al $K\alpha$ absorption edges (525 eV-1486 eV) to be used in spectroscopic applications. The main requirements for multilayer optics in spectroscopy are a high peak reflectance and a narrow bandwidth. The periodicity of the multilayer system designed for such an energy range is only 2.5 nm with individual layers being thinner than 1 nm. This makes the performance of such systems extremely sensitive to any imperfection at the interfaces. Analysis of such short period structures is very challenging due to the limitations of conventional methods that are commonly used for multilayer systems with larger periodicities. Therefore, this research faced two main challenges: engineering and analysis. In the engineering part, to improve the optical contrast and the quality of the interfaces various techniques such as ion beam polishing of layers, alternative working gas, and the use of alternative material combinations were applied. The analysis part required a combination of several state-of-the-art analytical methods in order to obtain reliable information about interfaces and film growth. Roughness at interfaces is one of the main factors that lead to reduced reflectivity. Ion beam polishing was applied to the W/Si multilayer system in order to reduce interfacial roughness. Treatment of every Si layer with 100 eV Ar⁺ ions led to a strong reduction of the vertical interfacial roughness correlation length as well as favourable changes in the lateral correlation length as well as jaggedness of roughness. However, despite strong changes of more than an order of magnitude in the diffuse scattering of hard X-rays, ion polishing did not result in a significant reduction of the amplitude of the interfacial roughness, mainly because the initial roughness was already at the atomic scale level, which is difficult to reduce further. Furthermore, analysis of the GIXR data revealed a lack of bulk W in the W/Si system, indicating the formation of a WSi_x compound, which reduced the overall optical contrast. Therefore, improvement of the optical contrast by preventing this strong compound formation became the next goal. In order to study interface formation in W/Si multilayer systems an in vacuo low-energy ion scattering (LEIS) set-up, connected to a magnetron deposition system, was used. Two working gases, Ar⁺ and Kr⁺, were used for W deposition. The measurements revealed strongly asymmetric interfaces, with W-on-Si being significantly broader than Si-on-W. Changing to a heavier gas (Kr) for W deposition was considered as a method to improve the W-on-Si interface because of the lower energetic contribution of backscattered neutralized Kr⁺ ions, resulting in a weaker intermixing at the interface. However, no difference was found between interfaces deposited in different gases. Therefore, it was concluded that the asymmetry was caused by direct atomic interaction between W and Si rather than by a ballistic effect. The results obtained suggested focusing further research on the improvement of the W-on-Si interface in the first place, trying to reduce direct W-Si interaction.

Post deposition nitridation of Si by means of implantation of 60eV N⁺ ions from a Kaufman ion source was applied on every Si layer in order to form a thin Si₃N₄ layer which could reduce the strong W-Si interaction. A gradual increase of the passivation time while keeping the rest of the parameters fixed, showed an improvement of the interfaces. However, the effect of the improved sharpness of the interfaces was counterbalanced by the formation of a relatively thick Si₃N₄ layer which reduced the overall optical contrast. This result suggested using lower ion energies in order to reduce the nitrogen penetration depth in the Si layers.

High optical contrast can be achieved by using different material combinations that have a less pronounced interaction compared to tungsten and silicon. Among several materials, boron was chosen as an alternative to silicon. In contrast with other suitable materials, this combination had not been studied before, thus, the main goal was to investigate the W-B interaction and the possibility of using W/B as an alternative to W/Si systems. W/B multilayers were synthesized successfully, however, GIXR analysis revealed the substantial formation of tungsten boride due to W-B chemical interaction. Furthermore, an increased interfacial roughness was observed. Ion polishing of the boron layers resulted in a significant reduction of the diffuse scattering of hard X-rays but did not improve the reflectivity for soft X-rays. These results indicate that B is not a favourable material to substitute Si in the investigated multilayer systems.

A comprehensive analysis of the short-period W/Si and W/B multilayer systems was carried out in this work. A combination of various state-of-the-art analysis techniques was used to obtain reliable information about the internal structure of the multilayers. Understanding the physics of thin-film growth at the atomic scale helped to define the next steps in improving the performance of such systems as discussed in the *"valorization and outlook"* section. This thesis is a basis for further studies on this type of multilayer mirrors.

SAMENVATTING

Dit proefschrift is geheel gewijd aan reflecterende multilaagoptieken voor spectroscopische toepassingen in het energiegebied tussen de O K en de Al K absorptiekanten (525 eV-1486 eV). De belangrijkste criteria waar de multilagen dan aan moeten voldoen zijn een hoge reflectie en een smalle bandbreedte. De periodiciteit van het multilaagsysteem dat in dit proefschrift wordt beschreven en dat is ontworpen voor het bovengenoemde energiegebied is slechts 2.5 nm, waarbij de afzonderlijke lagen dunner kunnen zijn dan 1 nm. Dit maakt dergelijke systemen uiterst gevoelig voor eventuele onvolkomenheden van de grensvlakken tussen de materialen. De analyse van dergelijke systemen met zeer dunne lagen is bovendien niet eenvoudig omdat conventionele methodes, die vaak worden gebruikt voor multilagen met een grotere periodiciteit, onvoldoende resolutie hebben. Dit proefschrift beschrijft het onderzoek aan twee belangrijke aspecten: het maken en de analyse van multilaagsystemen met een periodiciteit van 2.5 nm. Het engineering gedeelte betreft het verbeteren van het optische contrast en de kwaliteit van de grenslagen. Hiertoe hebben we andere sputtergassen en alternatieve materiaalcombinaties toegepast en hebben we de lagen met een bundel ionen behandeld. Voor de analyse hebben we een combinatie van verscheidene conventionele en nieuwe analytische state-of-the-art methodes gebruikt om betrouwbare informatie te verkrijgen over de grensvlakken en de samenstelling van de gevormde lagen. Een van de belangrijkste factoren die leiden tot een verminderde reflectie is ruwheid van de grensvlakken. Om deze ruwheid te verminderen hebben we de silicium lagen in het W/Si multilaagsysteem met ionen behandeld. Het etsen van elke Si laag met een bundel van 100 eV Ar⁺ ionen leidde tot een sterke reductie van de verticale correlatielengte van de ruwheid van het grensvlak en bovendien tot een verbetering van de laterale correlatielengte en van de karakteristieke vorm, of “hoekigheid”, van de ruwheid. De ionenbehandeling leidde weliswaar tot een sterke afname van de diffuse verstrooiing van harde röntgenstraling met meer dan een orde van grootte, maar het resulteerde niet in een significante vermindering van de amplitude van de ruwheid van de grensvlakken. Dit komt waarschijnlijk omdat de initiële ruwheid wanneer er geen ionen worden gebruikt al op atomaire schaal is en dus moeilijk te verbeteren. Analyse van de GIXR-data (scherende inval röntgen-data) laat echter zien dat er geen puur W meer in het systeem aanwezig is, wat duidt op de vorming van een WSix-verbinding die het optische contrast vermindert. Daarom hebben we ons vervolgens gericht op het zoveel mogelijk voorkomen van WSix-vorming om zo het optisch contrast tussen de lagen te verhogen. Om het ontstaan van de grenslagen tussen de beide materialen in W/Si multilaagsystemen te onderzoeken hebben we gebruik gemaakt van een opstelling die verstrooiing van lage energie edelgasionen (LEIS) gebruikt om informatie te verkrijgen over de bovenste monolaag van een preparaat. Dit LEIS systeem is in vacuo gekoppeld aan een magnetron sputter systeem waarin we W hebben gedeponereerd met twee verschillende sputtergassen, Ar⁺ en Kr⁺. De metin-

gen laten sterk asymmetrische grenslagen zien, waarbij de grenslaag van W-op-Si significant dikker is dan die van Si-on-W. De verwachting was dat gebruik van een zwaarder gas, Kr, de grenslaag bij W-op-Si zou verbeteren vanwege de lagere energetische bijdrage van de verstrooide geneutraliseerde Kr^+ ionen, hetgeen in minder vermenging op het grensvlak zou moeten resulteren. Er werd echter geen verschil gevonden tussen de W-op-Si grenslagen bij gebruik van de verschillende gassen. Daarom kunnen we concluderen dat de asymmetrie vooral wordt veroorzaakt door atomaire interactie tussen W en Si en in veel mindere mate door een ballistisch effect van verstrooide geneutraliseerde ionen. De resultaten leidden tot de conclusie is dat verder onderzoek naar W/Si systemen in de eerste plaats gericht moest zijn op het verbeteren van het W-op-Si grensvlak door de directe interactie tussen W en Si te verminderen. De sterke interactie tussen W en Si zou kunnen worden verminderd door het aanbrengen van een dunne Si_3N_4 -laag voordat er W gedeponereerd wordt. Hiertoe hebben elke Si-laag direct na de depositie behandeld met 60 eV N^+ -ionen uit een Kaufman-ionenbron. De ionendosis hebben we geleidelijk verhoogd door de behandel tijd op te laten lopen en daarbij alle andere parameters constant te houden. Hiermee verbeterden we de grensvlakken, maar het effect hiervan werd teniet gedaan omdat er een relatief dikke Si_3N_4 -laag werd gevormd die het totale optische contract verminderde. Dit pleitte voor toepassing van een lagere ionenenergie en dus een geringere indringdiepte van de N^+ -ionen in het Si. Een verbetering van het optische contrast kan ook worden bereikt door andere materiaalcombinaties die minder mengen dan wolfram en silicium te gebruiken. Uit verscheidene materialen werd borium gekozen als alternatief voor silicium. Deze combinatie was, in tegenstelling tot andere geschikte materialen, nog niet eerder bestudeerd, zodat ons eerste doel was de interactie tussen W en B te onderzoeken om W/B te kunnen gebruiken als alternatief voor W/Si. We slaagden erin de W/B multilagen te deponeren, maar helaas bleek uit de GIXR analyse dat er een aanzienlijke mate van wolfram-boridevorming optreedt ten gevolge van de chemische interactie tussen W en B. Bovendien vonden we dat de ruwheid van de grensvlakken toenam. Ionen polijsten van de boorlagen resulteerde in een significante vermindering van de diffuse verstrooiing van harde röntgenstraling, maar verbeterde niet het reflectievermogen voor zachte röntgenstralen. Uit deze resultaten kunnen we dus concluderen dat B niet het beste alternatief is voor Si in de in dit proefschrift beschreven multilagen. Dit proefschrift beschrijft een uitgebreide analyse van W/Si en W/B multilaagsystemen met een kleine periodiciteit. Een combinatie van verscheidene state-of-the-art analysetechnieken werd gebruikt voor het verkrijgen van betrouwbare informatie over de interne structuur van de multilagen. Inzicht in de fysica van de aangroei van dunne lagen op atomaire schaal hielp bij het bepalen van de volgende stappen om de prestaties van dergelijke systemen te verbeteren, zoals besproken wordt in de paragraaf "*Valorization and Outlook*". Dit proefschrift vormt een basis voor verdere studie naar dit type multilaag optieken.

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CURRICULUM VITAE

Roman Viktorovich Medvedev was born on 4th August 1990 in Petrozavodsk, Republic of Karelia, USSR. He studied at the highschool 42 with emphasis on mathematics and english language. In 2008 he started his education at St.Petersburg National Research University of Information Technologies, Mechanics and Optics (ITMO) in the faculty of Optoelectronics where he obtained a bachelor's degree. Later in 2013, he was enrolled to a Master's program in Photonics at Aalen University of Applied Science in Aalen, Germany. The Master's thesis project was carried out at Fraunhofer institute for Physical Measurement Techniques (IPM) in Freiburg im Breisgau, Germany. The topic of the project was "Development and characterisation of a system for two-photon absorption by IR-excitation and subsequent measurement of luminescence lifetime of rare earth oxide pigments by lifetime imaging analysis". From 2016 until 2020 he worked as a PhD student at Industrial Focus XUV Optics Group at University of Twente, Enschede, The Netherlands.