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Growth and optical performance of short-period W/Al and polished W/Si/Al/Si multilayers

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ABSTRACT
Short-period multilayer mirrors are used in wavelength-dispersive x-ray fluorescence to reflect and disperse elements in the O-Kα–Al-Kα range. In this work, we investigated sputter-deposited 2.5 nm W/Al with 20 periods. Our results show that W/Al is a poor reflector due to a combination of high interfacial roughness and strong W–Al intermixing. To address this, we introduced 0.5 nm Si seed layers at the W-on-Al and Al-on-W interfaces each consecutive period, while reducing the Al thickness from ∼2.0 to ∼1.0 nm. The Si seed layers significantly reduced interfacial roughness and W–Al intermixing, which led to an increase in the reflectance of the first Bragg peak at λ = 0.154 nm. To further reduce interfacial roughness, ion beam polishing of the top Si layer was applied at each period. The resulting structure of W/Si/Al/Si with ion beam polishing showed that the reflection coefficient of the first Bragg peak at λ = 0.154 nm was comparable to that of standard W/Si. These findings demonstrate the effectiveness of seed layers combined with polishing techniques in synthesizing smooth, high-reflectance multilayers containing two materials that are otherwise challenging to synthesize.

I. INTRODUCTION
Short-period multilayer (ML) mirrors are artificial structures containing repeating layers of low and high refractive indices that reflect photons in a Bragg mirror geometry. They are widely used in applications such as space astronomy, x-ray microscopy, synchrotron research, and wavelength-dispersive x-ray fluorescence (WD-XRF). In WD-XRF, a short-period ML is used as an analyzing crystal to resolve emission lines of light elements. This then allows elemental quantification in samples used in, for example, biology and soil research. In this work, MLs designed for reflection and dispersion of the O-Kα–Al-Kα (2.36–0.834 nm) emission lines are investigated. An essential requirement is that the ML needs high reflectance over the entire angular range, but also provides enough angular dispersion in order to separate specific emission lines. High reflectance is achieved in practice by increasing the ML period, but angular dispersion will decrease as a result. A period of 2.5 nm is considered a best-compromise between sufficient reflectance and angular dispersion for the chosen wavelength range.

Material combinations such as W/Si, W/B₄C, and W/B provide high theoretical reflectance in the entire emission range and are well studied at the short-period scale. The theoretical reflectance at λ = 0.834 nm for these material combinations is 60%–62% using an ideal two-layer IMD model, assuming bulk layer densities and step-like interfaces, with 200 bi-layers. In reality, however, the measured reflectivity is far from theoretical due to nanoscale intermixing and/or rough growth of the sub-nm thin layers. Research on 2.5 nm W/Si showed that the W layer completely reacts with Si to form optically unfavorable WSiₓ, limiting reflectance to 40% at λ = 0.834 nm. Similarly, in 2.5 nm, W/B strong intermixing between W and B caused formation of optically unfavorable WBₓ, resulting in a reflectance of only 35%. In 2.5 nm W/B₄C, the interaction is lower than for W/Si, but an increase in interfacial roughness limits reflectance to 39%. In all these cases, a moderate to strong interaction between W and the spacer, a promising strategy is to choose a spacer material that exhibits lower affinity toward W. In this regard, W/Al offers great potential as a highly reflective ML. This is primarily based on the assumption that the interaction between W and Al is comparatively weaker than that between W and other materials such as Si, C, or B. In addition, tungsten aluminides are difficult to prepare using...
common processes and at low temperatures\textsuperscript{11}. Therefore, formation of optically unfavorable W\textsubscript{x}Al\textsubscript{y} in the W absorber during sputtering is expected to be low. Moreover, the theoretical reflectivity of W/Al in the O-K\textsubscript{α}-Al-K\textsubscript{α} emission range exceeds that of W/Si by \( \sim 1.5\% \) absolute. Only a few publications report synthesizing sputter-deposited W/Al MLs, showing thicker periods ranging from 50 nm\textsuperscript{12} down to 4.5 nm\textsuperscript{13}. The purpose of this work is to synthesize and study sputter-deposited 2.5 nm W/Al, with the goal of obtaining soft x-ray reflectance that exceeds that of the current record values at 2.5 nm\textsuperscript{10}.

The layers are deposited by DC magnetron sputtering and characterized using grazing-incidence x-ray reflectivity (GI-XRR), x-ray diffuse scattering, atomic force microscopy (AFM), x-ray photoelectron spectroscopy (XPS), and transmission electron microscopy (TEM). In Sec. III A, we present the growth, analysis, and reflectance performance of 2.5 nm W/Al MLs. In Sec. III B, we present an improvement in the growth and optical performance of W/Al by introducing a third material,\textsuperscript{14,15} in our case silicon,\textsuperscript{16,17} which is deposited at W-on-Al and Al-on-W interfaces. The Si layer on the top of the W-on-Al interface is polished by an ion treatment\textsuperscript{8,18} to remove any roughness accumulation from the Al layer. The resulting structure is compared to W/Al and W/Si reference MLs.

II. EXPERIMENT

A. Deposition

The MLs were deposited onto single-side polished 25 \( \times \) 25 mm\textsuperscript{2} Si(100) wafers with a native oxide thickness of approximately 1.5 nm. The surface roughness was measured using AFM at 0.13 \( \pm \) 0.05 nm rms. For deposition of MLs, a DC magnetron sputtering system (MS1600 designed by Roth & Rau) was used with a base pressure of \( \sim 1 \times 10^{-8} \) mbar. The sputter deposition process uses krypton gas at a working pressure of 1.5 \( \times \) 10\textsuperscript{-3} mbar. The deposition targets, measuring 381 \( \times \) 89 mm\textsuperscript{2}, were positioned in front of the substrate holder at a target–substrate distance of 8 cm such that the particles arrive at normal incidence with respect to the sample surface, as described in Ref. 8. For deposition of the W/Si/Al/Si structure, two Si targets were used; one was positioned before and one was positioned after the Al target. The Si substrates were mounted on a 35 cm diameter circular substrate holder at a radius of 7.5 cm. During the deposition process, the substrate holder was rotated at 1.5 revolutions per second, while moving over each target by a substrate arm. The deposited film thicknesses were determined by the inverse of the velocity of the substrate arm. The magnetrons were power regulated to maintain a stable deposition flux, with sputter powers of 30, 80, and 130 W used for W, Al, and Si, respectively, and corresponding voltages of 326, 397, and 496 V. The power levels were selected such that the required minimum thickness could be achieved without exceeding the maximum speed of the substrate arm.

MLs with 20 periods were deposited with a period of 2.5 nm. The structures, illustrated in Fig. 1, contain W/Al, W/Si, W/Si/Al/Si, and W/Si/Al/Si with ion polishing. The deposited thickness of the spacer layer was chosen at \( \sim 2 \) nm, and the deposited thickness of W was 0.5 nm for all structures. In the case of compaction as a result of interaction between W and the spacer, Si (in the case of W/Si) and Al (in the case of W/Al and W/Si/Al/Si) are added such that the period remains 2.5 nm. Before each deposition, a 3 nm amorphous Si layer was deposited on the Si(100) substrate in order to promote smoother growth of the initial Al layer, which was found to grow rough when deposited directly on the Si substrate\textsuperscript{19,20}. To prevent further roughness accumulation in the ML as a result of inhomogeneous crystallization of Al\textsuperscript{21} we used an \( \sim 1\% \) Si-doped Al target. In the W/Si/Al/Si structure, the thickness of Al was reduced from \( \sim 2 \) to \( \sim 1 \) nm, and the thickness of the Si layers was fixed at 0.5 nm. The Si layers act as a...
seeding layer to promote smooth, layer-by-layer growth of W and Al as well as act as a protective barrier against W-Al intermixing.

To reduce roughness accumulation from the sandwiched Al layer, ion beam polishing (IBP) was applied on the top Si layer of each period with 80 eV Kr⁺ ions. The ion current during polishing was 141 mA, with an ion flux of approximately 2.45 × 10¹⁷ ions/(m²·s). 0.3 nm of extra Si was added before each polishing step and then removed such that the resulting top Si thickness remained 0.5 nm (Fig. 1, right). For polishing, a microwave Kaufman-type ion source (ECR ion beam source Tamiris 400-f) with a carbon three-grid lensing system was used. The ion source was operated using the same gas (krypton) and at the same working pressure (1.5 × 10⁻³ mbar) as magnetrons. The source, with grids measuring 360 × 100 mm², was oriented such that the ions arrive at normal incidence with respect to the substrate surface (also see Ref. 8) at a source–substrate distance of 8 cm. The substrate holder moves over the ion source while spinning with 1.5 revolutions per second. The deposition rate of each material was calibrated using ex situ GI-XRR on W/Si and W/Al stacks containing three different thicknesses of the to-be-calibrated material. The Si etch rate was calibrated on a W/Si stack with three different Si etch thicknesses (0.5, 0.6, and 0.9 nm each).

B. Characterization

An in-lab Malvern Panalytical Empyrean diffractometer with Cu-Kα radiation (λ = 0.154 nm) is used for x-ray diffuse scattering and GI-XRR measurements. A hybrid monochromator consisting of a parallel beam x-ray mirror and a 2-bounce Ge(220) monochromator was used at the source side. To qualitatively assess the interfacial roughness, x-ray diffuse scattering rocking curves were measured around the first Bragg peak, corresponding to θ ≈ 1.8° grazing angle of incidence (AoI). An in-depth explanation of ML rocking curves is presented in Ref. 22. GI-XRR was measured in θ – 2θ geometry from θ = 0°–8° grazing AoI.

To obtain additional information about the ML structure, a model-independent (free-form) optical constant reconstruction of the measured GI-XRR curves is performed, as described in more detail in Ref. 23. Free-form fitting of GI-XRR data allows freedom in the modeling of the interface, without a priori knowledge of the sample structure. This is especially beneficial in modeling short-period MLs, where the width of the interfaces can be comparable to the thickness of the layer. The model-independent approach was done by dividing the periodic part of the ML into 15 sublayers, with the top layer being treated separately to account for surface oxidation. The optical constant nᵢ of each sublayer is varied during the GI-XRR fitting. The optimization algorithm finds the final optical constant profile that satisfies the δ₂ minimum, which is represented by a sum of squares of residuals of the measured and simulated GI-XRR curves, as described in Refs. 23 and 24. The reconstructed profile is represented as a delta profile, where

\[ \delta = 1 - \text{Real}(n). \]

To analyze the chemical bonding of elements, non-destructive x-ray photoelectron spectroscopy (XPS) was used. A Thermo Scientific Theta Probe instrument with monochromatic Al-Kα radiation (1486.7 eV) was used with a base pressure of 5 × 10⁻¹⁰ mbar. The energy resolution was better than 0.8 eV, with an average probing depth of 6 nm. All ML samples were measured after exposure to air, without surface treatment. A thick W metal film was cleaned by 1 keV Ar ion bombardment until the oxygen content dropped below one atomic percent (1 at. %) to serve as a reference sample for the binding energy (BE) of clean W. The photoelectron signal was evaluated at a takeoff angle of 34.25° with respect to the surface normal. Peak fitting of the measured W 4f spectra was performed using Thermo Avantage software by fitting Gaussian-Lorentzian peaks, with asymmetric parameters based on the fit of the sputter-cleaned W reference sample.

A Bruker Dimension Edge atomic force microscope was used with a high-resolution tip (Mikro-Mash HiRes-C15/Cr-Au) to characterize the surface roughness. The radius of the tip was ~1 nm. The samples were measured after deposition and in ambient conditions. For measurement of the surface roughness, the tapping mode was used. The samples were measured with a scan area of 1 × 1 μm.

High-resolution TEM was used to study the structure and interfaces of the deposited MLs. The scanning TEM analysis was performed with a Thermo Scientific probe corrected Spectra 300, equipped with a Super-X EDS detection system. All measurements were done at an acceleration voltage of 300 kV, with the primary electron beam aligned along the Si[110] zone axis of the silicon substrate of the lamella. TEM bright-field imaging was carried out at sub-Angstrom resolution. Cross-sectional lamellae were extracted from the multilayer sample using a Helios 5 dual beam focused ion beam (Thermo Scientific). The lamellae were cut at 30 kV, followed by thinning of back and front sides at 5, 2, and 1 kV.

III. RESULTS

A. W/Al

1. GI-XRR and free-form analysis

The GI-XRR, measured from θ = 0° to 8° grazing AoI, of W/Al and W/Si is shown in the blue dots in Figs. 1(a) and 1(b), respectively. As shown in the figure, the Cu-Kα reflectivity of W/Al is substantially lower compared to the W/Si reference. The first Bragg peak reflectance of W/Al is only 2.8%, while the first Bragg peak reflectance of W/Si is 13%. To note, the theoretical reflectance at Cu-Kα of an ideal, W/Al ML with 20 bi-layers is 30%. Additionally, in W/Al, there is no presence of Bragg peaks beyond the second order. This implies that interfacial intermixing/roughness is high within the structure.

To obtain additional structural information from the GI-XRR, a model independent reconstruction of the optical constant profile is performed. As can be seen in Figs. 1(a) and 1(b), a good fit is obtained between the simulation (red curve) and measurement (blue dots), with the critical angle, Bragg peaks, and modulation in reflectance of the Kessig fringes properly fitted. In Fig. 1(c), the delta profile of the periodic part of the ML of W/Si and W/Al is shown. W/Al shows very low modulation of the delta profile. The peak delta of the absorber layer is only ~46% of pure W, while delta of the spacer has increased relative to pure Al. This means no pure Al or W is present in the ML, and there is strong W–Al intermixing. In W/Si, the modulation of the delta profile is much higher, with a spacer delta close to pure Si and an absorber delta that is ~65% of pure W.
2. X-ray diffuse scattering

To compare the interfacial roughness in W/Al relative to W/Si, x-ray diffuse scattering was measured by performing a Cu-Kα rocking scan. Due to insufficient higher Bragg peak orders in W/Al, the rocking scan was measured around the first Bragg peak. The rocking scan was measured by fixing the detector at the first Bragg peak (θ = ~1.8° grazing AoI) and rocking the sample around ω from 0° to 3.7° grazing AoI. The resulting rocking curves are shown in Fig. 2.

The appearance of broad wings around the Bragg peak in diffuse scattering scans is indicative of interface roughness. By comparing the diffuse scattering intensity, a qualitative comparison of the interfacial roughness can be made between W/Al and W/Si. The rocking curves reveal that the interfacial roughness in W/Al is higher compared to W/Si. This means that W–Al interfaces are likely rougher than W–Si interfaces. However, it has to be noted that with this technique, we cannot obtain a reliable value of the interfacial roughness amplitude.

3. Atomic force microscopy

In order to quantitatively determine roughness, the surface of each ML was measured with AFM. The samples were measured in air after deposition. Figure 3 shows the obtained topography and calculated surface roughness σ_{rms} for W/Al and W/Si. W/Al has a...
**4. Transmission electron microscopy**

To study the layer and interface morphology of MLs, bright-field TEM images were taken. Figure 4 shows the TEM image of W/Al (Fig. 4, left) and W/Si (Fig. 4, right). The dark regions correspond to W, while the bright regions correspond to Al (Fig. 4, left) and Si (Fig. 4, right). The TEM image of W/Al shows some dramatic features. First, the layered structure contains a long-range waviness, which seems to increase as the number of layers increases. In comparison, the TEM image of W/Si shows very flat layers, without any visible long-range waviness. Second, the layered structure of W/Al contains regions that appear to show strong intermixing of W with Al. Some parts of the W layer look almost completely intermixed with Al, while other parts of the W layer show clear separation of W and Al. The Al layer also shows some regions where W has intermixed. This is in qualitative agreement with the delta profile of W/Al [Fig. 5(c)], which showed a spacer delta that was higher than pure Al. The presence of strong W–Al and Al–W intermixed regions causes a severe reduction in optical contrast [Fig. 5(c)], resulting in a loss of ML reflectance [Fig. 5(a)].

The local regions of strong W–Al intermixing from the TEM image might indicate that there is island formation or discontinuous layer growth. The increase in roughness measured with AFM, coupled with the increase in spacer delta from the delta profile in Fig. 5(c) would suggest a contribution of island formation and/or discontinuous layer growth. However, the possible presence of such features, specifically island formation, cannot be directly imaged in our case. The thickness of a single TEM lamella is about 100 nm, meaning that the cross-sectional image of the sample is strongly averaged over this length. Similarly, the delta profile of W/Al [Fig. 5(c)] arises from GI-XRR data, which is averaged both laterally and in-depth. Finally, with AFM, we cannot always observe...
the islands directly if they have coalesced into a closed—but rough—layer. Since W/Al has both high interfacial roughness and intermixing, there is a strong indication that one or both of these mechanisms are at play.

A final observation is that some parts of the W and Al layer in W/Al seem to form a polycrystalline structure. For W, this is unexpected, since the nominally deposited thickness of W is only 0.5 nm. This is well below the typical crystallization threshold of ∼2–3 nm for a metal layer. The Al layer also appears to show some crystallinity, which means that ∼1% Si dopant did not fully prevent Al from crystallizing. However, the presence of Al and W crystallites in W/Al is not expected to be a large contributor to the lower reflectance presented in Fig. 5 for W/Al. Instead, the lower reflectance of W/Al is explained by a combination of high interfacial roughness—backed by diffuse scattering and AFM measurements—as well as strong W–Al intermixing—evidenced by GI-XRR delta profile and TEM.

B. W/Si/Al/Si

In Sec. III A, we found that a 2.5 nm W/Al ML is a poor reflector due to a combination of high interfacial roughness and strong W–Al intermixing, which we hypothesized to be caused by island formation and/or discontinuous layer growth. The possible presence of discontinuous layer growth and/or island growth indicates that there is weaker atomic interaction between Al and W relative to the interaction between Al–Al and W–W. A solution to the weak interaction between W and Al is to use a third material that acts as a seeding or wetting layer. Si is a well-studied material and is known to form a smooth interface with W. For this reason, we chose to use Si as a seeding layer in W/Al—with the idea to promote smooth growth of both W and Al.

The thickness of the Si seed layers is chosen at 0.5 nm because of the short period. Since it is unclear whether the island growth/discontinuous layer growth is caused by the W or the Al layer, a Si seed layer is deposited at both W-on-Al and Al-on-W interfaces (Fig. 1, W/Si/Al/Si). The thickness of Al is reduced to ∼1 nm to maintain the 2.5 nm period. In order to reduce the roughness of W/Si/Al/Si further, another structure of W/Si/Al/Si is deposited where 0.3 nm of the top Si layer is etched by IBP with 80 eV Kr+ ions (Fig. 1, W/Si/Al/Si IBP) and compared to W/Si/Al/Si without Si etching.

1. GI-XRR and free-form analysis

Figures 6(a) and 6(b) show the GI-XRR of W/Si/Al/Si and W/Si/Al/Si with IBP, respectively. A substantial increase in reflectance is found in both structures, relative to W/Al. The first Bragg peak reflectance of unpolished W/Si/Al/Si is 9.2%, while the first Bragg reflectance of W/Si/Al/Si with IBP is 13%. The first Bragg peak reflectance of W/Si/Al/Si with IBP is comparable to that of W/Al. However, the higher-order Bragg peaks in W/Si/Al/Si with IBP are more pronounced than W/Al as a result of polishing.

To obtain additional structural information from W/Si/Al/Si and W/Si/Al/Si with IBP, a model independent reconstruction of the optical constant profile is performed. The fitted curves of
W/Si/Al/Si, as shown in Fig. 6(a), and of W/Si/Al/Si with IBP, as shown in Fig. 6(b), show a decent fit with the measurement (dots). In Fig. 6(c), the delta profile of the periodic part of the ML of W/Si/Al/Si and W/Si/Al/Si with IBP is shown. The delta profiles of W/Al and W/Si are added for comparison. The figure shows that the modulation of the profile is much higher for both structures compared to W/Al. Applying two Si seed layers reduces the spacer delta to that of pure Si/pure Al. Moreover, delta of the absorber has increased from ~46% to ~56% of pure W. This indicates that the Si seed layers partially inhibit W–Al intermixing. The significant improvement in optical contrast resulting from the use of Si seed layers strongly supports our initial hypothesis that the formation of islands and/or discontinuous layer growth in W/Al contributes significantly to the loss in reflectance. Polishing the top Si in W/Si/Al/Si [Fig. 6(b)] increases delta of the absorber further to ~69% of pure W—increasing it above the W delta of W/Si. Such a substantial gain in W delta after polishing implies that interfacial roughness is still high in W/Si/Al/Si and will be discussed in later paragraphs.

In both delta profiles, a moderate interface asymmetry is present. In W/Si/Al/Si, the Si-on-W interface is sharper, while the W-on-Si interface is broader. This can be explained by interfacial roughness in case the roughness builds on the Al-on-Si interface in the Si/Al/Si sandwich, although a firm conclusion cannot be made.
here. In contrast, W/Si/Al/Si with IBP has a broader Si-on-W interface, while the W-on-Si interface is sharper. A sharper W-on-Si interface is explained by a reduction in interfacial roughness if we assume that this interface is smoothened as a result of polishing. The broader Si-on-W interface, however, is somewhat unexpected. It is not unreasonable, however, to assume that ballistic intermixing could take place with the underlying W layer as a result penetrating Kr\(^+\) ions, leading to a more intermixed interface.\(^{28,29}\) It is important to keep in mind that due to the lack of phase information from x-ray reflectometry,\(^{30,31}\) the reconstruction of GI-XRR may result in another solution where the interfaces of the delta profile are inverted. Nevertheless, a clear increase in absorber delta and a decrease in spacer delta relative to W/Al for both W/Si/Al/Si and W/Si/Al/Si with IBP are present, leading to an increased reflectance.

2. X-ray diffuse scattering

The Cu-K\(_{\alpha}\) rocking scans of W/Si/Al/Si, W/Si/Al/Si with IBP, W/Al, and W/Si are shown in Fig. 7. The rocking curves show that in both W/Si/Al/Si and W/Si/Al/Si with IBP the diffuse scattering intensity reduced relative to W/Al. The diffuse scattering intensity of unpolished W/Si/Al/Si is close to that of W/Si. In W/Si/Al/Si with IBP, the diffuse scattering intensity is by far the lowest, which seems to imply that interfacial roughness is lowest in this ML. However, a reduction in diffuse scattering as a result of polishing can also be caused by a reduction in vertical interfacial roughness correlation length, rather than interfacial roughness amplitude, as was shown in Ref. 8. For this reason, additional AFM measurements are done to characterize the roughness amplitude of the surface.

3. Atomic force microscopy

To check whether the roughness amplitude of the surface is reduced as a result of Si seed layers and polishing, AFM was measured on the samples. Figure 8 shows the obtained topography and calculated surface roughness \(\sigma_{\text{rms}}\) for unpolished W/Si/Al/Si and W/Si/Al/Si with IBP. W/Si/Al/Si has a roughness of \(\sigma_{\text{rms}} = 0.21\) nm with a standard deviation of 0.02 nm, while W/Si/Al/Si with IBP has a roughness of \(\sigma_{\text{rms}} = 0.13\) nm with a standard deviation of 0.01 nm. The AFM measurements show...
that the surface roughness of W/Si/Al/Si reduced significantly relative to W/Al ($\sigma_{\text{rms}} = 0.35 \text{ nm}$). However, the surface roughness of W/Si/Al/Si is higher than standard W/Si ($\sigma_{\text{rms}} = 0.16 \text{ nm}$). This means that the Al layer is likely still causing some roughness development in the stack. Applying IBP in W/Si/Al/Si reduces the surface roughness to below that of the W/Si reference.

4. Transmission electron microscopy

The bright-field TEM image of the W/Al ML (Fig. 4, left) revealed a wavy structure as well as regions within the W layer that are strongly intermixed with Al. To find out whether the internal structure was modified by the polished Si seed layers, a cross-sectional TEM image was obtained for W/Si/Al/Si with IBP (Fig. 9, right) and compared to the W/Al reference (Fig. 9, left).

The TEM image of W/Si/Al/Si with IBP shows a dramatic change in the layered structure compared to W/Al. The layers are relatively flat and without presence of long-range waviness observed in W/Al. This is also corroborated by diffuse scattering and AFM data, which pointed to a reduction in the interface roughness. Additionally, the W layer is more uniform compared to W/Al and does not contain local regions of high Al intermixing with W. The spacer layer (Si/Al/Si) is also more uniform and does not show regions of high W intermixing. This result is in line with the delta profile from Fig. 6(c), which shows greatly increased optical contrast as well as pure Al/pure Si in the spacer.

5. X-ray photoelectron spectroscopy

To measure the chemical environment of W, the XPS analysis has been performed on W/Al, W/Si/Al/Si IBP, and W/Si. The signal was collected from the top 2–3 periods, and the intensity was normalized to the W 4f/2 peak. Samples were measured within the same measurement run to ensure shifts in BE between samples could not be attributed to a temporal drift in the BE scale of the instrument. The W 4f/2 peaks of W/Al, W/Si/Al/Si IBP, and W/Si are shown in Fig. 10, along with a pure, sputter-cleaned W film.

The XPS spectra of all samples show shifts in the W 4f/2 BE relative to pure W. Previous research from our group$^{10}$ compared the W 4f/2 BE of 2.5 nm W/Si with a pure W layer reference (31.5 eV) and found a negative shift of 0.2 eV, which was associated to the formation of W silicide. In this work, a similar shift of 0.2 eV is found for W/Si (31.3 eV). The W 4f/2 BE of W/Si/Al/Si with IBP (31.3 eV) is overlapping with the W 4f/2 BE of W/Si. This means that the W inside the ML is bonded to Si rather than to Al and forming WSi$_x$. The W–Si bonds present in W/Si/Al/Si with IBP correlates with a reduction in the interface roughness as well as a reduction in W–Al intermixing.

Interestingly, the W 4f/2 BE of W/Al (31.2 eV) relative to pure W is a negative shift of 0.3 eV, which is larger than W/Si. The relatively large W 4f/2 shift in W/Al may look surprising, since our initial hypothesis suggested a weaker atomic interaction between Al and W relative to the interaction between Al–Al and W–W, leading to the growth of W or Al islands and/or discontinuous layer.
growth. Instead, a significant portion of W appears to form bonds with Al, resulting in a shift in the W4f7/2 BE. There are several explanations for this effect. The first is that even in an ideal, non-mixed system, there will be chemical interaction between the adatoms of the growing film and the substrate, i.e., at the W–Al interfaces. Since the W layer in our structures is only 0.5 nm thick, a significant portion of W atoms is situated at the W–Al interface.

The second is that the shift in W4f7/2 BE may be caused by a metastable W–Al mixture in the ML, which is not stable as the bulk phase. During sputter deposition at room temperature, energetic particles are deposited as the film grows, facilitating the formation of such metastable mixtures.

The three-dimensional island growth mode that we hypothesize to be present in W/Al would also suggest the presence of W–W and Al–Al bonds in addition to W–Al bonds. Therefore, the W4f7/2 XPS signal (Fig. 10, blue line) likely contains a superposition of signals from W–Al and W–W bonds. Since it is unclear what kind of W–Al bonds are present, i.e., from the W–Al mixture or from the W–Al interface, it is difficult to estimate the shift in W4f7/2 BE and, consequently, the proportion of W–W and W–Al bonds.

IV. CONCLUSIONS

We have synthesized 2.5 nm W/Al MLs with 20 periods using magnetron sputtering. Our results show that, in spite of expectations, W/Al is a poor reflector due to a combination of high interfacial roughness and strong W–Al intermixing, with no pure Al or pure W present within the structure. As a result, the first Bragg peak reflectance is limited to 2.8% at λ = 0.154 nm. To address this issue, we have applied two 0.5 nm Si seed layers at the W-on-Al and Al-on-W interfaces, while the thickness of Al was reduced from ~2 to ~1 nm. The Si seed layers cause a significant reduction in interfacial roughness and W–Al intermixing, increasing the first Bragg peak reflectance to 9.2%. In order to reduce interfacial roughness of the structure further, the top Si layer was polished using 80 eV krypton ions. The resulting ML structure of W/Si/Al/Si with IBP showed a first Bragg peak reflectance of 13% at λ = 0.154 nm—comparable to the reflectance of standard W/Si. The increase in first Bragg peak reflectance is explained by a reduction in interfacial roughness as a result of polishing.

The results of this study serve as a use case for the implementation of seed layers with polishing techniques, aimed at achieving smooth, high-reflectance MLs containing two materials that are otherwise challenging to synthesize. Examples of such ML systems are W/Be, Ni/Ti, and Al/X (X = transition metal), where a high degree of roughness/intermixing is expected. Using the right selection of seed layer and polishing conditions, a significant increase in optical performance can be achieved in such ML systems.

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AUTHOR DECLARATIONS

Conflict of Interest

The authors have no conflicts to disclose.

Author Contributions

D. IJpes: Conceptualization (lead); Data curation (lead); Formal analysis (lead); Investigation (lead); Methodology (lead); Writing – original draft (lead); Writing – review & editing (lead).

A. E. Yakshin: Conceptualization (supporting); Supervision (lead); Writing – review & editing (equal).

J. M. Sturm: Investigation (supporting); Writing – review & editing (supporting).

M. Ackermann: Project administration (lead); Supervision (supporting); Writing – review & editing (supporting).

DATA AVAILABILITY

The data that support the findings of this study are available from the corresponding author upon reasonable request.
REFERENCES


