Angle resolved x-ray photoelectron spectroscopy has been employed to determine non-destructively the in-depth interface formation during thin film growth. Buried interfaces underneath nanometer thick layers are probed by identifying the chemical shift of compound materials in photoelectron spectroscopy and using the angular response to quantify compound amounts from the measured intensities. The thin interfaces in molybdenum-silicon multilayers grown at ambient temperature are investigated. This system is an example of an almost perfect 1D-system where the interface region is only a small part of the individual layer thicknesses of 3 to 5 nanometer. Despite the low growth temperature, both interfaces of this multilayer show layer thickness dependent interface formation. Where the silicon-on-molybdenum interface shows a limited interface thickness of 0.4 nm of Mo$_5$Si$_3$, the molybdenum-on-silicon interface shows a more complex evolution. For this interface the composition of the first 2.0 nm of deposited layer thickness is best described as a molybdenum-silicon compound layer with a molybdenum rich top and a Mo$_5$Si$_3$ bottom layer. After 2.5 nm of deposited layer thickness the molybdenum rich compound at the top has transformed into polycrystalline molybdenum on top of 1.8 nm Mo$_5$Si$_3$ at the interface. The formation of the 1.8 nm Mo$_5$Si$_3$ precedes the formation of polycrystalline molybdenum on top. Angle resolved x-ray photoelectron spectroscopy (ARXPS) is shown to be a good tool to study interface phenomena beneath nanometer thick top layers. In the case of Mo/Si multilayer mirrors this ARXPS study shows that the compound formation at the interface accounts for the majority of the extreme ultraviolet reflectance loss.

I. Introduction

The study of the composition of an interface during formation below a top layer that is only a few nanometers thick, is inherently difficult because it is often outside the range of surface sensitive techniques (scanning tunneling microscopy, atomic force microscopy, low energy ion scattering, auger electron spectroscopy, low energy electron microscopy) and a marginal fraction of more bulk like techniques (Rutherford backscattering, energy dispersive x-ray spectroscopy, x-ray diffraction). In order to investigate these interfaces in systems where the only inhomogeneity in composition is in-depth, angle resolved x-ray photoemission spectroscopy can be a powerful tool. The probing depth of this technique is determined by the attenuation length of the escaping electrons used for spectroscopy and for the used monochromatic Al-K$_\alpha$ radiation is of the order of 1.5-3 nm, depending on the composition of the system under investigation. This medium surface sensitivity enables to detect both top and substrate layer over a range of top layer thickness of several times the attenuation length. The possibility to identify chemical states and quantify the amounts of top layer material makes x-ray photoemission spectroscopy the suited tool to study buried interfaces below a few nanometer thin layers.

A good example of such a 1D-system of thin layers is a molybdenum-silicon multilayer. Mo/Si multilayers are the enabling elements of the optical systems applied in extreme ultraviolet photolithography (EUVL), employing radiation with a wavelength of 13.5 nm. In order to achieve a high reflectance, positive interference of the reflections from all interfaces is required (thus reflecting a specific wavelength), alternating layers of molybdenum and silicon are used with individual layer thicknesses of 3 to 5 nm. Although a reflection of 75% is theoretically possible in this artificial Bragg reflector, imperfect interfaces
between the two materials are mainly responsible for a limited practical reflectivity. Layer growth at room temperature has been shown to achieve optimal performance for Mo/Si multilayers. A procedure of periodic noble gas ion treatment of the silicon layers after deposition has resulted in a reflectivity of 69%. In-situ x-ray reflectometry, used to monitor layer deposition, has enabled an impression of the interface roughness development during the build-up of multilayer systems. Interlayer and crystallite formation in molybdenum silicon multilayers have been studied ex-situ extensively using grazing-incidence X-ray reflectivity (XRR), X-ray diffraction (XRD) and transmission electron microscopy (TEM). From these studies it has been concluded that the polycrystalline nature of the molybdenum layers is the main cause of interlayer roughness. Furthermore these studies conclude that the interface region between the molybdenum and silicon layers of this room temperature grown multilayer occupies a volume up to 20% of the multilayer period. Recently we reported on a study of direct measurement of the surface morphology during the deposition process. We have shown that the periodic ion treatment of the silicon layers in the multilayer production procedure is capable of reducing growth induced height differences down to the morphology of the first ion treated silicon layer, reducing the need of interface study of this multilayer to the interface study of bi-layers. Furthermore, for the growth of molybdenum-on-silicon, the height differences evolving with increasing amounts is lacking behind compared to expected values for polycrystalline growth. This most likely is due to compound formation at the interfaces. The interfaces have been investigated on crystalline substrates extensively with the help of dedicated surface science equipment. Near ambient temperature an approximately 0.5 nm thick MoSi interface layer is formed. Only after a deposited amount of 2 nm layer closure is suspected. At growth temperatures between 400-700°C and sub-monolayer amounts of molybdenum deposit, MoSi island growth has been reported on crystalline silicon substrates with islands elevating 1.2 nm above the surface. Both are exemplary for the complexities that can arise during interface formation in molybdenum silicon systems.

In this work we investigate the deposition of both multilayer components in vacuo with angle resolved x-ray photoelectron spectroscopy (ARXPS) to provide insight in the nanometer scale processes of the buried interface below the nanometers thick layers. By quantifying both the layer morphology and composition at different stages of the deposition process for dimensions down to the nanometer scale, the “intermixed” zone between two materials can be estimated. All deposited layers are prepared under relevant conditions by using a deposition set-up that is also used for the development of multilayer films for EUV optics. The in vacuo approach prevents exposure to atmosphere which usually modifies the top layer to a significant part of the XPS probing depth, both in composition as well as in morphology. The chemical shift in XPS data for molybdenum silicon systems will be explored by investigating room temperature grown mixed-molybdenum-silicon (Mo_xSi) films with x in the range of 0.1 to 4. The resulting identification of molybdenum-silicon compound formation will be used in the discussion on the silicon-on-molybdenum and molybdenum-on-silicon interface formation. Investigation of the top morphology and modelling of the ARXPS data of bi-layer systems will show that even at growth temperatures as low as room temperature, compound formation between molybdenum and silicon is a dynamic process determined by the deposited amount.

II. Experimental details

Throughout the paper molybdenum and silicon bi-layers as well as mixed-molybdenum-silicon films are deposited at room temperature onto the native oxide of super-polished silicon substrates in an ultra-high vacuum (UHV) environment better than 10^-8 mbar. Silicon and molybdenum were deposited by electron beam evaporation. A Kaufman type hot cathode ion source, providing 100 eV krypton ions, was used to modify the surface of freshly deposited silicon layers when silicon was used as substrate layer. A fluence of 1.5 x 10^16 ions/cm² under 45° angle of incidence was used, resulting in removal of 0.5 nm of silicon. Quartz crystal oscillator microbalances were used to control the amount of deposited material with an accuracy better than 1% of the reported value. Amounts (and rates) are reported as layer thickness assuming bulk
density. Constant deposition rates are employed for both materials during bi-layer formation at a rate of 0.025 nm/s. Samples were transported from the coating facility via a vacuum transfer system, base pressure 1x10^{-9} mbar, to be analyzed with the aid of either an scanning tunneling microscope (STM, Leiden Probe Microscopy) or x-ray photoelectron spectroscopy (XPS, Thermo Fisher Scientific Theta Probe). The composition of the top surface was studied in a vacuum environment of 1x10^{-9} mbar. Monochromatic Al-Kα radiation has been used to investigate the surface. For quantification XPS sensitivity factors from the Scofield library are used together with attenuation lengths that are determined using bulk densities. Finally, machine specific calibration factors are applied (e.g. analyzer transmission function, source-detector geometry). The Theta Probe XPS used in this study employs an angle resolved lens, enabling measurement from different analyzer angles simultaneously from the same footprint. This lens type is routinely used to analyze smooth thin film in for example high-k/semiconductor interfaces. It enables relative fast measurement from a wide angular range. Photoelectrons measured by more grazing angles originate from a more shallow depth, making them more surface sensitive compared to more normal angles. Comparing top layer/substrate layer intensity ratios at different angles allows in-depth concentration modelling of the different components. This only hold true for flat films. The sensitivity of the angular response to morphology is determined by the angular binning of the detector. Throughout this paper the 60 degrees acceptance angle of the analyzer is divided into 8 sub-regions. In this paper the same division of analyzer angles is used as reported previously on influence of surface morphology on ARXPS measurements of nanometer thin overlayers. The most grazing angle regions (all angles above 60°) are discarded because of the potentially large contribution of elastic scattering or the lack of intensity of one of the components. ARXPS data was analyzed with the Avantage software (Thermo Fisher Scientific), but the three-layer-model or box-model used in this paper is described in the supplementary material. The best model fit to the data always matches the measured data within the statistical noise of the measurement. The supplementary material also describes the relation to the reported error bars in more detail. For this paper the acquisition time was chosen such that statistical noise allowed a relative intensity errors to be in the range of 1% to 10%. The STM chamber was operated at a base pressure of 1x10^{-9} mbar as well. The STM imaging was performed with mechanically cut Pt/Ir tips, using a sample bias of 2 V and a current of 0.2 nA as typical tunnel parameters. STM performance was verified on Highly Ordered Pyrolytic Graphic (HOPG), where the observed atomic spacing was used for lateral calibration and on polycrystalline gold where the step heights on the grains were used to calibrate heights. In order to prevent possible influences on the film growth by previously deposited layers and/or prolonged exposure to residual gas during transport and analysis, a fresh silicon wafer was used for every bi-layer or mixed-film experiment.

III. Results

A. Co-deposition of molybdenum and silicon

Two electron beam evaporator sources have been operated simultaneously to co-deposit silicon and molybdenum at different ratio’s at ambient growth temperature. Approximately 10 nm thick films with different molybdenum content (Mo_{x}Si_{1-x}) have been produced. With growth near room temperature, the silicide formed is assumed to be governed by the arriving species and less by bulk diffusion events. Only limited atomic mobility at the surface needs to be assumed for the arriving species to form the energetically most favored compound. Three stable Mo_{x}Si compounds can be found in literature: MoSi_{2} (x=0.5), Mo_{x}Si_{3} (x=1.67) and Mo_{x}Si (x=3). With growth temperature low compared to the melting temperatures of molybdenum (10%) and silicon (18%) and assuming the thermodynamically most favored compound to be formed from the arriving atom flux, three regions can be distinguished. For x smaller than 1 the MoSi_{2} compound is favored. For x between 1 and 2.7 the Mo_{x}Si_{3} compound is favored. Finally for x larger than 2.7 the Mo_{x}Si compound is the favored compound to be formed. This will require some atomic surface mobility, which will be present at room temperature. The small leftovers are assumed to remain in their elemental state.
Figure 1(a) shows the XPS data of the Mo3d peaks of a reference layer of 7 nm thick polycrystalline molybdenum and of three Mo\(_x\)Si films with different ratio’s. The molybdenum peak shifts towards lower binding energy for the films with lower metal content. Figure 1(b) depicts the Si2p peaks of a reference layer of 10 nm thick amorphous silicon and the Mo\(_x\)Si films corresponding to figure 1(a). There is no clear trend in silicon peak position with molybdenum content although small shifts are observed. In order to assess the binding energy more accurately, both the Mo3d and Si2p peaks are fitted with their respective spin-orbit states. Where for molybdenum the states are clearly separated, for silicon they are only visible in the asymmetric shape of the Si2p peak. In both cases textbook values for the positional difference and peak intensity ratios are used. Furthermore, the Mo3d\(_{5/2}\) peak shows an asymmetry typical for metal peaks under XPS observation. This asymmetry is located at binding energies higher than the elemental peak position and is taken into account by determining the asymmetry for the reference layer and compensating with the background level. This asymmetric shape is assumed to be present for all molybdenum peaks and only has a minor impact on the peak position or on peak area. The peak position associated with molybdenum in the elemental state (Mo3d\(_{5/2}\)) is 227.9 eV and that of silicon in the elemental state (Si2p\(_{3/2}\)) is 99.1 eV. Both are obtained from the reference layers.

In order to establish possible chemical shifts in the peak positions of silicon and molybdenum, the binding energy difference with respect to the elemental peak position is plotted in figure 2. On the horizontal axis the metal ratio is plotted based on XPS measurement. This ratio is consistent with the deposited amounts of molybdenum and silicon monitored during production of these mixed films. Furthermore, a 1 micrometer thick film of MoSi\(_2\) reference material has been characterized and is plotted in figure 2 as well (open symbol). The reference material has been exposed to atmosphere and consequently the MoSi\(_2\) compound peaks needed to be decomposed from their oxides, decreasing the accuracy of the peak position. This reaction with atmosphere is the main reason for conducting this study of compound formation underneath nanometer thin layers in vacuum. In figure 2 the Mo3d\(_{5/2}\) position shows the largest shift for the lowest metal concentration, -0.4eV, overlapping with the MoSi\(_2\) reference at x=0.5. This value is consistent with literature references on MoSi\(_2\). The Si2p\(_{3/2}\) position corresponding to the MoSi\(_2\) compound (around x=0.5) shows a chemical shift of +0.15 eV with respect to the elemental position. A small positive chemical shift can be found in literature as well.

In figure 2 the center region, corresponding to a Mo\(_5\)Si\(_3\) compound, shows a slightly different chemical shift. Here the Mo3d\(_{5/2}\) has shifted -0.25 eV and the Si2p\(_{3/2}\) shows a -0.15 eV shift. Even at an x value larger than 3, the region corresponding to Mo\(_3\)Si, the Mo3d\(_{5/2}\) position is shifted 0.13 eV towards lower binding energy. The silicon peak shift is shown here to be almost absent, but the low intensity makes an accurate estimate difficult.

These shifts are used in the rest of the paper to identify the presence of Mo\(_x\)Si at the interface of the bi-layer systems. Before this can be done, the peak shapes, most importantly the peak width, needs to be discussed. The width of an XPS peak is determined by many factors of which the used source and detector are the main ingredients. All reported data in this paper have been recorded with the same source and detector settings. Furthermore, peaks are broadened due to the amorphous nature of some materials compared to their crystalline state. In this work, the full-width-half-maximum (fwhm) of amorphous and crystalline silicon for the Si2p\(_{3/2}\) peak are 0.8eV and 0.6eV respectively, showing the latitude of structure on peak width. From the co-deposition results a similar broadening is observed for molybdenum when compared to the large grain (typical grain dimensions 10 nm) polycrystalline reference film. Where for the reference film the Mo3d\(_{5/2}\) shows a fwhm of 0.6eV, the co-deposited results show a width of 0.7-0.8eV. With the ambient growth temperature used here, it is very well possible that the evolving MoSi\(_x\) compound occupies a structure with grains small enough to be considered amorphous. In the next sections, the full width of a peak becomes important when small amounts of compound need to be identified together with their bulk species. The amount of a compound is identified by the chemical shift of the Mo3d\(_{5/2}\) peak only, because the molybdenum peak’s photo-ionization probability is an order of magnitude higher than for silicon. Furthermore the fwhm of a possible compound is assumed the same for all compounds and is fixed at a width of 0.7eV, which is the smallest value observed in the mixed films.
Bi-layer systems: Mo-on-Si

Amorphous silicon substrate layers are prepared in vacuum before covering it with different amounts of molybdenum. The deposited molybdenum thickness (t) is plotted in figure 3 together with the Mo3d\(_{5/2}\) chemical shift. In order to validate the reported +/- 0.05 eV accuracy of the chemical shift, the peak position of Si2p\(_{3/2}\) of the silicon substrate layer is used as a reference. The deposited amount is determined during preparation using a quartz micro mass balance at bulk density (10.2 g/cc for molybdenum). All molybdenum amounts below t= 2.5 nm exhibit a chemical shift, suggesting a compound state for all molybdenum. Starting at a shift of -0.4 eV for t=0.2 nm it decreases to a shift of -0.25 eV around t= 0.7 nm. Between t= 0.7 nm and t= 2 nm the shift remains constant around -0.25 eV. The chemical shifts presented in figure 3 are similar to results reported by Slaughter et al. 13 on crystalline silicon, suggesting that the amorphous nature of the silicon substrate layer used here is irrelevant for the range t=0-2 nm covered in both studies.

Before continuing with a more detailed in-depth modelling of the ARXPS results, the morphology of the films needs to be considered. Surface morphology can change the angular response significantly 20, 27-30, depending on both the lateral dimensions and on the magnitude of the height fluctuations. This study has been carried out on super-polished silicon wafers that are relatively flat. Nevertheless height fluctuations on the nanometer scale can be expected. The sensitivity of the angular response of XPS to morphology is determined by the angular binning of the detector. In this paper the same division of analyzer angles (7.5° bins of the 60° acceptance angle) is used as reported previously on angular photo-electron spectroscopy measurements of nanometer thin overlayers 20. In this case the surface morphology similar to that of the super-polished wafer is smooth enough to be modelled with a top layer without taking roughness into account. Figure 4 shows the morphologies of the silicon substrate layer and that of about 3 nm deposited molybdenum on top of this substrate layer. The in vacuum characterization ensures that the system under observation of the STM is the same as observed by ARXPS. The surface morphology of the substrate layer is quite similar to that of the bi-layer. In both cases height differences show an isotropic landscape with a root-mean-square of 0.20 nm for the silicon layer and 0.23 nm for the molybdenum layer. These values are similar to the reported value for the super-polished wafer 20 and can therefore be considered smooth enough for XPS modelling without roughness influencing the result. The evolution of the morphology of this system is described elsewhere 12 and is not discussed in this paper.

To identify the composition of the molybdenum-silicon compound, de-convoluting XPS peaks is required. For a reliable composition both peak position and peak width of a chemical state need to be known. This is especially true when the compound is a minority fraction of the total, as is depicted in figure 5 where the components of the Mo3d peak for the system Si/Mo(2nm) are displayed. Where the MoSi\(_2\) component has a fixed chemical shift of -0.4 eV and a fixed width of 0.7 eV, the peak for the Mo3d(top) is allowed optimum position to fit best. The resulting envelope is shown together with the measurement next to the components and shows a good fit. Also plotted is a small peak labelled Mo3d(O2) that occupies the position of the MoO\(_2\) compound. Where a small amount of metallic oxygen (in the O1s peak) is detected in the XPS measurements corresponding to roughly a monolayer coverage, the area of the Mo3d(O2) peak is twice the amount metallic oxygen would allow for a MoO\(_2\) compound. The Mo3d(O2) peak is therefore partly attributed to background signal. This peak is omitted from quantification since the compound of interest, MoSi, is identified at the lower binding energy positions where background signal is unambiguous. Furthermore, a monolayer of metallic oxide can be expected on a molybdenum layer with the used vacuum transport time (5 minutes) and base pressure (1x10\(^{-9}\)mbar).

The model used for quantifying the ARXPS results is a simple three layer model and described in detail in the supplementary material 22. From the vacuum interface downwards, the model consists of a top molybdenum layer, a MoSi\(_2\) interface layer and a silicon substrate layer. In order to assign a layer thickness to XPS data modelling, a material density needs to be assumed. For molybdenum and silicon bulk densities are applied and for the compound MoSi\(_2\) a density of 6.24 g/cm\(^3\) is used. Detector angles up to 60° are used for which the good fit quality of the used model to the measured angular response confirms the in-depth
order of the layers. Figure 6 shows the thickness results obtained from best fit of the box-model to the data with only the compound fraction of the deposited material as parameter (see supplementary material for details). The reported total thickness is the sum of the molybdenum top layer and the compound interface layer. The model total thickness is inherently consistent with the monitored amount of material during preparation and is presented to illustrate the timing of the top layer evolution. The evolution of the MoSi$_2$ interface thickness shows a more complex behavior. A MoSi$_2$ interface thickness of 0.25 nm evolves instantly when 0.1 nm molybdenum is deposited. This interface thickness remains intact up to about $t=1.0$ nm. This amount of interface has incorporated 1 monolayer (accuracy of +/-10%) of the substrate silicon, suggesting that mainly the former vacuum interface of the silicon substrate layer has reacted. In the range $t=1.0-2.0$ nm the MoSi$_2$ thickness is increased with respect to the initial amount to a 1.8 nm thick interface layer. This amount of interface now incorporates around 7 monolayers of substrate silicon, suggesting significant in-depth materials redistribution. In this range the MoSi$_2$ interface thickness accounts for most of the added film thickness. For amounts larger than $t=2.0$ nm the MoSi$_2$ interface thickness is no longer increasing (indicated by the blue solid line). Besides the thickness dependent behavior of the MoSi$_2$ at the interface, the chemical shift of the top molybdenum layer also holds information. For deposited amounts below 2.0 nm, the top layer is in a compound state as well. A shift of -0.20 eV suggests this top layer to be Mo$_5$Si$_3$, although a mixed Mo$_5$Si$_3$-Mo$_3$Si composition cannot be excluded. Only after $t=2.5$ nm the top molybdenum layer exhibits a peak signature of bulk poly-crystalline molybdenum. The combined results suggest a complex molybdenum silicide to exist below $t=2.5$ nm.

According to in-depth analysis of ARXPS data the evolution of this molybdenum compound layer is a stepwise process. The first sub-monolayer amount of molybdenum reacts with the former vacuum interface of the silicon substrate layer to form a MoSi$_2$ compound. This amount remains constant up until 1.0 nm deposited molybdenum (4 monolayers). After the initial 0.25 nm thick MoSi$_2$ compound formation, the arriving molybdenum contributes to the formation of a (most likely) Mo$_5$Si$_3$ top layer. Between 1.0 nm up to 2.0 nm deposited molybdenum, the arriving molybdenum contributes mainly to an increase of the MoSi$_2$ compound at the silicon substrate layer’s interface, keeping the amount of Mo$_5$Si$_3$ compound in this range almost constant. Only at larger amounts of 2.5 to 3 nm deposited, a more straightforward model of bulk molybdenum on top of a 1.8 nm thick MoSi$_2$ interface layer emerges. The results show that the interface between molybdenum and silicon evolves underneath the top layer at growth temperatures as low as room temperature. To confirm that the interface formation is mainly deposited amount dependent and not time dependent, a bi-layer at $t=2.5$ nm has been produced with a factor 10 slower deposition rate of the molybdenum. The MoSi$_2$ interface thickness of this slower bi-layer matches within the 10% accuracy typical for these measurements. The exact pathways through which the compounds are formed are beyond the scope of this paper, but first results on the atomic details of this system have already been provided by Fokkema.

In his thesis on STM study of molybdenum on crystalline silicon it is clearly shown that initial molybdenum deposition modifies the underlying silicon surface and opens up the silicon facets, providing new pathways for materials diffusion.

### Bi-layer systems: Si-on-Mo

In order to investigate the reverse interface, molybdenum substrate layers are prepared in vacuum before covering it with different amounts of silicon. In order to avoid signal intensities of the supporting silicon wafer, 7 nm thick (poly-)crystalline layers are used as substrate layer. To validate the reported +/- 0.05eV accuracy of the chemical shift, the peak position of Mo3d of the molybdenum substrate layer is used as a reference. The Si2p$_{3/2}$ chemical shift for different silicon top layers up to 6 nm thickness is not showing any significant shift with respect to a silicon reference film. Only for the smallest deposited amount of 0.15 nm the chemical shift in the silicon peak is significantly different from reference amorphous silicon. The shift of -0.26eV would suggest a Mo$_5$Si$_3$ compound based on the compound identification proposed in section “co-deposition”. In order to have a closer look at compound formation in the system silicon on molybdenum, the same approach as the previous section is deployed.
Before using ARXPS modelling, the surface morphologies of these bi-layers are probed. Figure 7 shows the results of the molybdenum substrate layer and 6 nm deposited silicon on top of this substrate. The surface morphology of the substrate layer is similar to that of the bi-layer. In both cases height differences show an isotropic landscape with a root-mean-square of 0.44 nm for the molybdenum layer and 0.51 nm for the silicon layer. These values are larger than the reported value for the super-polished wafer and can therefore no longer be considered flat for XPS modelling. The picture also shows that lateral correlation lengths (from height-difference correlation) are slightly different with 2.3 nm and 3.5 nm for the molybdenum and silicon layer respectively. These are of the same order of magnitude as the attenuation lengths of XPS. Consequently modelling ARXPS data will be influenced similar for both morphologies. The extent of height differences in these systems prevent the unique identification of the in-depth layer position from ARXPS data for this bi-layer, but a simple three layer model can still be used. Provided the assumed in-depth layer order is right and omitting the most grazing detector angles, in this case all angles above 45°, a compound interface amount can be estimated when the compound can be identified via a chemical shift. In the system silicon-on-molybdenum, the Mo3d peak is again used to identify possible compound formation. With the peak shape (mainly position and fwhm) of the substrate layer known, peak broadening of the envelope can be assigned to compound formation. The molybdenum peak composition is assumed to consist of three components, a bulk molybdenum component with bulk peak constrains, a MoSi2 component with chemical shift of -0.4eV and fwhm of 0.7eV and a Mo5Si3 components with chemical shift of -0.25eV and fwhm of 0.7eV. For all deposited silicon amounts, best fit of the molybdenum peak show the MoSi2 component to be only a marginal fraction (smaller than 0.1 nm). Therefore, this component is omitted in the quantification. From the vacuum interface down, the model consists of a top silicon layer, a Mo5Si3 interface layer and a molybdenum substrate layer. To assign a layer thickness to the Mo5Si3 compound, a density of 8.24 g/cm3 is assumed. The resulting layer thicknesses are plotted in figure 8. The amount of interface layer thickness is significantly smaller for this bi-layer compared to the previous section. Below t= 0.8 nm, the Mo5Si3 interface is only 0.25 nm thick. For deposited amounts above t= 1.3 nm the interface layer thickness saturates at 0.4 nm. This is roughly a quarter of the thickness of the molybdenum-on-silicon of the previous section. The initial Mo5Si3 interface thickness of 0.25 nm has consumed only 0.7 monolayers of the molybdenum substrate. Consequently the final interface layer thickness consumes 1.0 monolayers worth of substrate atoms. Although on a smaller scale, also this buried interface shows evolution underneath nanometer thick layers.

IV. Summary and discussion

All facets of angle resolved x-ray photoelectron spectroscopy (ARXPS) have been employed to determine non-destructively the molybdenum-silicon compound formation at buried interfaces. Thin compound films are produced and analyzed in vacuo to identify the chemical shifts of the Mo3d and Si2p peaks. The MoSi2, Mo5Si3, and Mo3Si compounds can be distinguished from their elemental state by careful analysis of the molybdenum peak. Buried interface amounts are estimated by using chemical shift identification of the compounds and quantifying ARXPS results. Room temperature deposition of molybdenum and silicon bi-layers show an evolution of the interface depending on the deposited amount of top layer material. This indicates both the meta-stable state of the initially formed interface as well as the potential for (limited) in-depth materials transport across the interface.

The Mo-on-Si interface shows two distinct in-depth compositions, depending on the deposited amount. For Molybdenum layer thickness above 2.5 nm a (poly-)crystalline top layer exists on top of a 1.8 nm thick MoSi2 interface layer. For smaller amounts all molybdenum is in a compound state. This compound state consists of a 0.25 nm thick MoSi2 part at the interface with the silicon substrate layer and a molybdenum rich top layer. Around 2.0 nm deposited (8 monolayers) the molybdenum compound layer consists of about 1.8 nm MoSi2 and 1 nm Mo5Si3. With increasing molybdenum amounts the MoSi2 remains at 1.8 nm layer thickness, while the molybdenum rich top layer transforms to (poly-)crystalline molybdenum after 2.5 nm deposited (10 monolayers). The saturation of MoSi2 formation seems prerequisite before the top layer
can crystalize. This deposition amount dependent complex behavior of interface formation at room temperature requires significant interaction of the silicon substrate layer and the molybdenum top layer. This can be achieved by diffusion of atomic species across the interface together with morphology changes due to compound formation.

The Si-on-Mo interface shows a smaller amount of interface formation than the Mo-on-Si interface, but a deposited amount dependent evolution is observed nevertheless. An initial Mo$_5$Si$_3$ interface of 0.25 nm thickness is formed from the arriving silicon. This amount consumes about 0.7 monolayers of the molybdenum substrate layer. Only when the silicon deposition exceeds 1.0 nm the interface thickness increases to 0.4 nm. This interface thickness remains constant with increasing amount.

Comparing compound formation at both interfaces the Mo-on-Si interface has a larger impact on the substrate layer, consuming up to 7 monolayers worth of substrate material. This is significantly more than at the Si-on-Mo interface where 1.0 monolayer of substrate material is consumed. The relatively larger amount of substrate material transformed for the Mo-on-Si interface compared to the reverse interface can partly be explained by the amorphous nature of the silicon substrate layer. This allows easier binding sites for the arriving atoms due to more dangling bonds when compared to the (poly-)crystalline texture of the molybdenum substrate layer of the reverse interface. This argument is especially true for the first arriving atoms. The main promoter for Mo$_5$Si$_3$ compound formation on the Mo-on-Si interface is however found when deposition exceeds 1.0 nm. Where the reverse interface shows hardly any increase in compound amount over the initial amount, the Mo-on-Si interface continues its transformation towards more Mo$_5$Si$_3$ compound. This can only happen when (part of) the compound formation energy is used to free up fresh, unreacted substrate material. This could occur by, for example, creating small clusters of Mo$_5$Si$_3$ that partly cover the substrate layer. The saturation point would now indicate the stage where these clusters of Mo$_5$Si$_3$ cover the substrate layer sufficiently to block further materials transport for compound formation. This process is clearly absent on the reverse Si-on-Mo interface.

For EUV multilayers this mixed composition of the interface region will reduce its performance. The amount of molybdenum and silicon in the multilayers in every period is about 3 nm and 5 nm respectively. At these amounts the Mo-on-Si interface will consist out of 1.8 nm Mo$_5$Si$_3$ and the Si-on-Mo interface consists out of 0.4 nm Mo$_5$Si$_3$. This study in line with previously reported values for these multilayers. IMD reflectance simulations show that this amount of interface will reduce the maximum EUV reflectance of 75% with about 5%. The compound formation therefore accounts for the majority of the reflectance loss in the observed 69% surface morphology during the deposition process.

V. Conclusions

Where the presented results show the dynamic interface behavior at relatively low growth temperature (room temperature) in Mo/Si multilayer systems, this is but an example for the potential the employed technique harbors for characterizing buried interfaces underneath nanometer thick layers. Thanks to an in-depth probing volume that is sensitive to both the top as well as the substrate layer and the possibility to identify compound states via chemical shifts, angle resolved x-ray photoelectron spectroscopy (ARXPS) is a good tool to start the study of any interface problem at the nanometer scale.

VI. Supplementary material

The three-layer-model or box-model used in this paper to quantify the measured angle resolved photoelectron data is described in the supplementary material. The supplementary material also describes the relation to the reported error bars in more detail.
Part of this work was carried out in the framework of the STW program “Nano-engineering rules for X-ray and EUV optics: Atomic-scale controlled deposition”, which was carried out in cooperation with Leiden University. Furthermore this work was part of the FOM Industrial Partnership Programs I10 (‘XMO’) and I23 (‘CP3E’) which were carried out under contract with Carl Zeiss SMT GmbH, Oberkochen, ASML, Veldhoven, and the ‘Stichting voor Fundamenteel Onderzoek der Materie (FOM)’, the latter being financially supported by the ‘Nederlandse Organisatie voor Wetenschappelijk Onderzoek (NWO)’.
VIII. Figure captions

FIG. 1. Mo3d (a) and Si2p (b) peaks of co-deposited molybdenum silicide layers (Mo₅Si) and of reference layers of polycrystalline molybdenum and amorphous silicon.

FIG. 2. Chemical shift of silicon and molybdenum binding energy for different Mo/Si ratios in mixed layers.

FIG. 3. Chemical shift of molybdenum for different deposited thickness of molybdenum on a silicon substrate layer.

FIG. 4. 100 nm x 100 nm STM image of (a) initial silicon substrate layer surface (rms 0.20 nm) and (b) 3 nm molybdenum deposited on this initial silicon surface (rms 0.23 nm).

FIG. 5. Si/Mo(2nm) decomposition of Mo3d peak with in (a) the individual components and in (b) the match between the measured data points and the envelope of the fit.

FIG. 6. Thicknesses obtained from three layer modelling of the ARXPS data. The total thickness matches the total deposited amount whereas the evolution of the Mo₅Si₃ interface thickness between the molybdenum and silicon shows non-linear behavior: the initial 0.25 nm interface thickness evolves into 1.8 nm interface thickness. Solid blue line indicates the approximate deposited thickness where the Mo₅Si₃ interface formation saturates.

FIG. 7. 100 nm x 100 nm STM pictures of (a) molybdenum substrate layer (rms 0.44 nm) and (b) of 6 nm silicon deposited on the molybdenum substrate layer (rms 0.51 nm).

FIG. 8. Thicknesses obtained from three layer modelling of the ARXPS data. The silicon thickness matches the total deposited amount whereas the Mo₅Si₃ interface evolves underneath the silicon top layer. Solid blue line indicates the approximate deposited thickness where the Mo₅Si₃ interface formation saturates.
IX. References


