Specific aspects of roughness and interface diffusion in non-periodic Mo/Si multilayers

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ABSTRACT

Most of the currently used reflective coatings for EUV and X-ray mirrors are periodic nanometer multilayers. Depending on the number of periods and the absorption in the multilayer stack a certain band width of the incoming radiation can be reflected. In order to increase the integral reflectance or to accept larger ranges of incidence angles, non-periodic multilayers are needed. With the transition from periodic to non-periodic multilayers new challenges arise for the deposition process. Since the reflectance spectra are sensitive to every single layer thickness a precise coating control and an exact knowledge of the interface reactions are required. Furthermore substrate roughness influences the reflectance spectra. With an advanced coating process using additional ion bombardment during thin film growth the integrated reflectance of broadband mirrors can be conserved even for an initial substrate roughness of about 0.7 nm rms.

Keywords: Mo/Si multilayer, extreme ultraviolet (EUV), mirror, nanometer coating, broadband reflection

1. INTRODUCTION

Periodic multilayers are routinely used as reflection coatings for EUV and X-ray mirrors. Due to the application of Mo/Si multilayers in optical systems of EUV lithography tools huge research and development activities have been focused on this material combination. Currently, near normal incidence reflectances of about 70 % can be obtained for a photon wavelength of $\lambda = 13.5$ nm. Periodic multilayers are a proper choice for mirror coatings if at every mirror position one fixed wavelength λ at one fixed incidence angle α is given. In this case the maximum reflectance can be obtained by using thicknesses d_P that fulfill the Bragg condition $\lambda = 2\ d_P \cos(\alpha)$ for the first reflection order at every mirror position. However, the condition of monochromatic waves with fixed incidence angles is hardly fulfilled in optical systems. A spread of incidence angles and/or wavelengths like as shown in Figure 1 results in non-uniform reflectance values for the different angle/wavelength combinations.

In order to overcome these restrictions the bandwidth of the reflection peaks has to be increased by changing the multilayer design from a periodic to a non-periodic layer arrangement [1-3]. This approach is already often used for multilayer mirrors in the hard X-ray range [4,5] or for mirrors for attosecond spectroscopy [6,7]. Due to lower absorption in the hard X-ray range a high number of layers (up to 1000) can be used for the broadband multilayer design. In the case of EUV radiation the low penetration depth of the light restricts the number of useful layers to about 100. For the EUV range two different approaches have already been applied for broadband reflectors: piecewise periodical multilayers [8] and depth-graded multilayers fabricated with in-situ thickness control [9]. In this work EUV broadband multilayer mirrors have been investigated that were fabricated just by controlling the deposition time. Additionally the impact of surface roughness on the resulting reflectance spectra is emphasized.

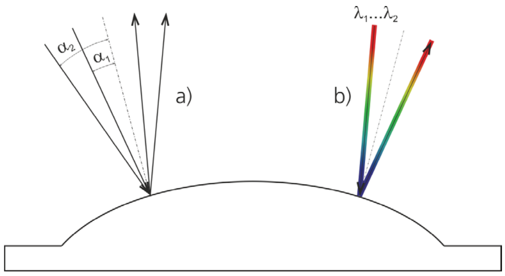

Figure 1: Scheme of multiangular (a) and polychromatic (b) reflection of radiation at mirrors.

2. MODEL CALCULATIONS

2.1 Roughness and interdiffusion in depth-graded Mo/Si multilayers for EUV broadband reflection

For the calculation of depth-graded thickness distributions in multilayers several algorithms have been developed [2,3,10]. Very recently Windt implemented the algorithm of Kozhevnikov in the IMD software for modeling the optical properties of multilayers [11,12]. Starting with a periodic multilayer and a target profile R(Θ) for $\Theta \in [\Theta_1,\Theta_2]$ or R(λ) for $\lambda \in [\lambda_1,\lambda_2]$ it is iteratively possible to calculate the layer thicknesses, that result in reflectance spectra that show the best fit to the target profile. In the case of the multilayers investigated in this work all the single layer thicknesses are unconditionally varied for optimization except the C and/or B_4C barrier layer thicknesses between the Mo and Si layers. The C and B_4C barrier layer thicknesses have been kept fixed at constant values. The initial calculations have been performed with ideal interfaces (no roughness σ_r and no diffusion σ_d) and with the optical parameters given in the Henke tables [13].

Real nanometer multilayers always have non-negligible deviations as compared to the ideal situation. One of the most important aspects are the interfaces: Roughness and interdiffusion always negatively affect the reflectance. For specular reflectance measurements both aspects cannot be separated. Therefore, the parameters σ_r and σ_d describing roughness and diffusion are combined to the so-called interface width σ with $\sigma^2 = \sigma_r^2 + \sigma_d^2$. For periodic multilayers increasing σ values result in reflectance damping according to the Debye-Waller factor. In case of broadband multilayers not only the reflectance for one combination of Θ and λ is important. In fact, the whole reflectance spectrum R(Θ) and/or R(λ) is decisive for the optical behavior of the mirrors. Therefore, model calculations have been performed in order to investigate the influence of the interface width to the reflectance spectra. The easiest case is that the interface width is constant for all interfaces. This assumption is roughly fulfilled if barrier layers are used and if the coating replicates the initial substrate roughness. As expected, the calculation for three different interface widths σ = 0, 0.3 nm and 0.5 nm shows decreasing reflected intensities (Figure 2, above). However, the normalized reflectance spectra show that the reduction cannot simply be described by a scaling factor. With increasing σ values the relative deviations of highest and lowest reflectance values become larger (Figure 2, below). In the wavelength/angle spectra the lower wavelengths/angles are relatively enhanced as compared to the higher ones.

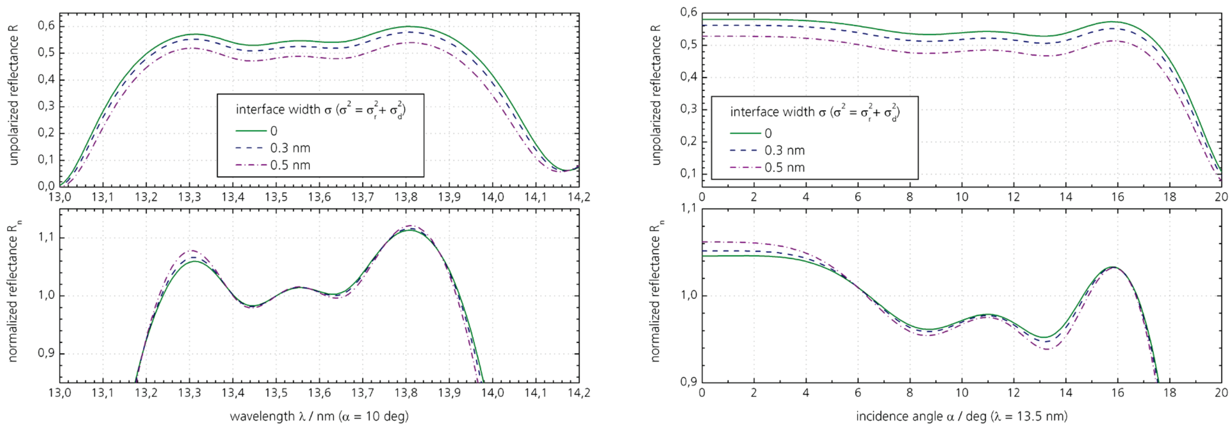

Figure 2: Calculated reflectance spectra R(λ) (left) and R(Θ) (right) for different interface widths σ: 0, 0.3 and 0.5 nm. The graphs above show the absolute reflectance, the graphs below the normalized spectra.

In most of the real cases the interface width is not constant throughout the whole multilayer. For strongly curved substrates it is often observed that surface regions tilted against the incoming particle flow show increasing film roughness with increasing thickness. The opposite case – smoothing of initially rough substrates by thin film coating – is also possible if process parameters are used that activate surface diffusion of the particles arriving at the surface. For the calculations we therefore assumed two cases: 1) linear increase of σ from 0.1 to 0.5 nm with growing film thickness and

2) linear decrease of σ from 0.5 to 0.1 nm. Of course, in both cases the reflectance is lower as for the ideal situation without roughness and interdiffusion, but the deviation from the ideal situation is significantly smaller in the case of self-smoothing films (Figure 3). Even with a substrate roughness of 0.5 nm rms only small reflectance losses and spectral changes are possible if coating processes are available that smooth the roughness down to about 0.1 nm rms.

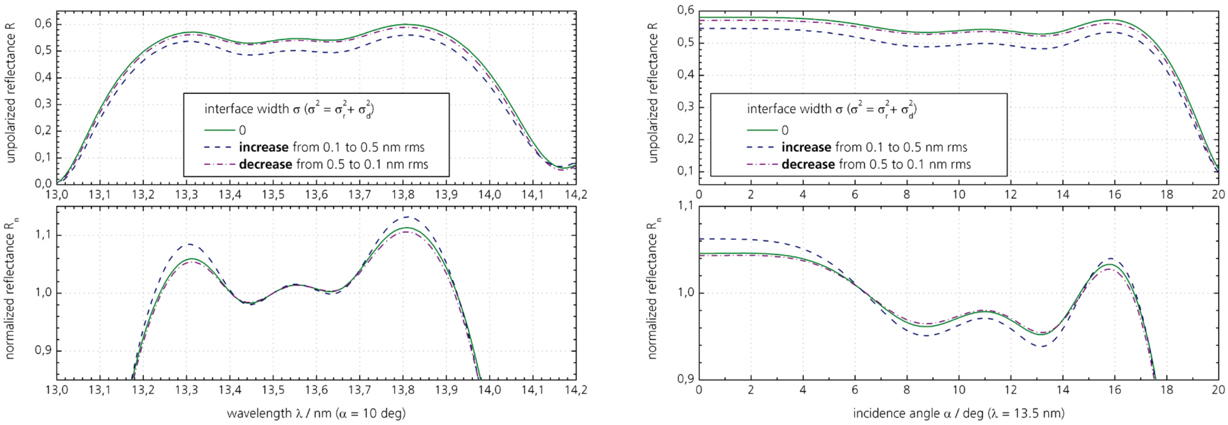

Figure 3: Calculated reflectance spectra R(λ) (left) and R(Θ) (right) for linear increasing and decreasing interface widths σ. The graphs above show the absolute reflectance, the graphs below the normalized spectra.

As a consequence of the model calculations the following statements can be made:

- Interface roughness and diffusion in depth-graded multilayers not only affect the overall reflectance of broadband mirrors but also the shape of the reflectance spectrum.
- Increasing roughness with growing film thickness on smooth substrates is much more critical than decreasing film roughness on rather rough substrates.
- Even higher substrate roughness values in the order of 0.3-0.5 nm rms can possibly be tolerated if self-smoothing coating processes are available.

3. EXPERIMENTAL

3.1 Multilayer coating

The fabrication of all coatings described in this work has been made by magnetron sputter deposition (MSD). We used two different deposition machines. The first one – MSD1 – is equipped with 4 linear sputter sources (target size: 304.8 mm x 88.9 mm) and can handle substrates with diameters of up to 150 mm. This machine has already been described elsewhere [14]. The second machine MSD2 is a commercially available machine and contains 6 linear sputter sources (target size: 400 mm x 88.9 mm) radially arranged in an octagonal vacuum chamber. The basic layout is shown in Figure 4.

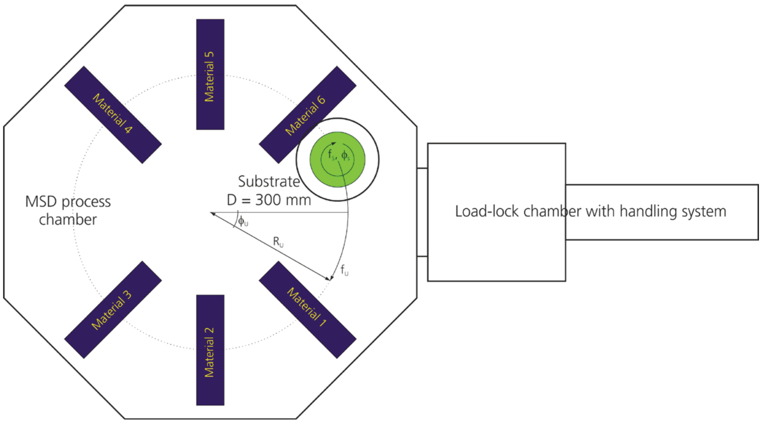

Figure 4: Schematic view of the arrangement of sputtering targets and substrate within the deposition machine with R_U = 625 mm, f_S = 1…3 Hz and f_U = 0.001…5 deg/s.

In order to have well-defined vacuum conditions the process chamber is equipped with two turbo pumps and one cryo pump. This results in a base pressure prior to the multilayer deposition in the range of $1…3 \cdot 10^{-8}$ mbar. During the coating process the sputtering sources are operated at constant power: P = 150…400 W, depending on the materials and their deposition rates. Accordingly, discharge current and voltage are variable and depend on the used sputter gas pressure which is typically within $0.9…1.1 \cdot 10^{-3}$ mbar. The distance between the surfaces of sputtering target and substrate is 70 mm. The thicknesses of the layers are controlled by the frequencies f_U that are used for the movement across the individual materials. Since everything in the machine is optimized for the highest possible stability and reproducibility no in-situ thickness monitoring is necessary.

For the determination of the deposition rates of the multilayer materials periodic multilayers have been fabricated. Using Cu-Kα reflectometry the period thicknesses can precisely be measured and the deposition rates can be calculated. However, the sum of the individual layer thicknesses calculated from the deposition rates is not exactly equal to the real period thickness measured by reflectometry. Due to atomic diffusion at the interfaces thickness contraction occurs. The quantification of the contraction has been calculated from the difference of the thickness sum calculated from the deposition rates and the real period thickness measured by reflectometry. For given design values of the layer thicknesses and with known deposition rates and thickness contraction all information is available that is needed to calculate the deposition time and the corresponding frequency f_U for a specific material.

Using standard process parameters of the machine, smooth Mo/Si multilayers can be fabricated on smooth substrates (R_q = 0.1…0.2 nm rms). The smoothest films have been obtained at the lowest possible sputter gas pressures of about $0.9 \cdot 10^{-3}$ mbar. In order to further improve the film growth a so-called advanced coating process has been developed. In this case an additional ion bombardment is introduced during deposition. This results in a transition from conformal film growth to activated film growth with surface diffusion of the particles arriving at the surface as illustrated in Figure 5.

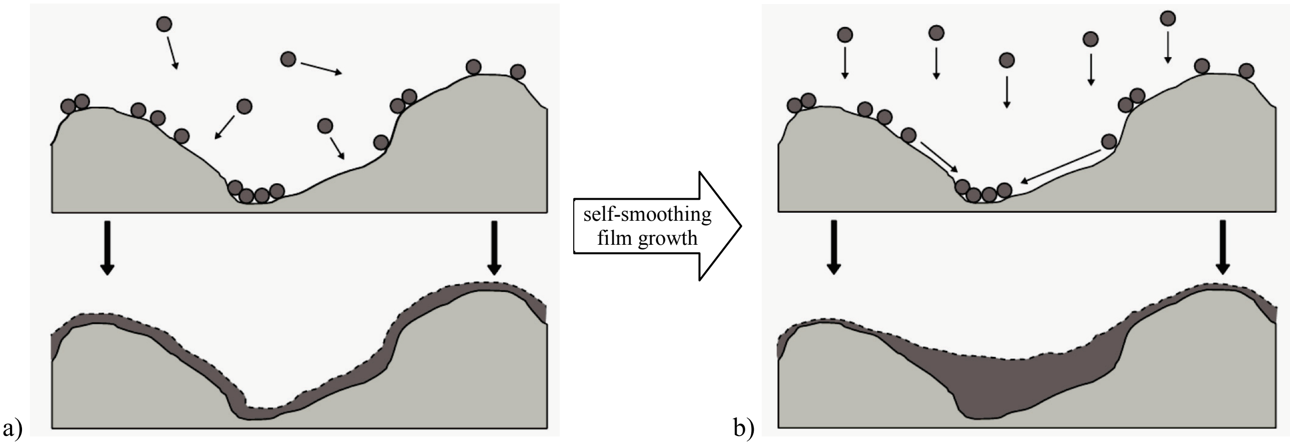

Figure 5: Transition from the standard process with conformal film growth for MSD at low sputter gas pressures (a) to advanced coating processes with additional ion bombardment and activated surface diffusion of the atoms resulting in self-smoothing of the thin films (b). (Pictures taken from Pellicione and Lu [15])

The experimental implementation can be made in different ways: 1) applying a BIAS voltage at the substrate surface connected with an acceleration of ions from the plasma to the film surface [16] or 2) using additional ion sources for the direct bombardment during or after the film growth [17,18]. In both cases the kinetic energies have to be tuned very carefully since any volume diffusion resulting in intermixing of the materials has to be avoided. For an optimum performance of Mo/Si multilayers rather low kinetic energies of the bombarding particles in the range of 50…100 eV have been used.

3.2 Reflectance measurements

The specular reflectance of the mirrors has been characterized by X-ray reflectometry under grazing incidence with Cu-Kα radiation (λ = 0.154 nm, Bruker D8) and at near-normal incidence with EUV radiation (λ = 12-15 nm, laboratory reflectometer based on a laser produced plasma source [19]).

3.3 Atomic force microscopy

The high-spatial frequency roughness (HSFR) has been characterized by atomic force microscopy (AFM) using the commercial tool Dimension 3100 from Veeco. All samples have been measured in non-contact mode (= tapping mode). Typical scan sizes are in the range between 1 µm x 1 µm and 10 µm x 10 µm.

4. RESULTS AND DISCUSSION

4.1 Broadband reflectance spectra of Mo/Si multilayers

Using the deposition rates and taking into account the interface contraction as described in section 3.1 non-periodic multilayers have been fabricated by time-controlled deposition. The first attempts have been made in a way that half of the contraction has been added to the thicknesses of molybdenum and silicon. However, the Cu-Kα reflectographs of these samples show a higher Γ value than expected ($\Gamma = d_{Mo}/d_P$ with d_{Mo} = thickness of the molybdenum layer and d_P = period thickness). This indicates that the layer thickness consumed for the formation of the interdiffusion zone is larger for silicon than for molybdenum. By varying the amount of added silicon and molybdenum layer thickness as compared to the design values Γ can be tuned. Finally it turned out that the best agreement with the model calculation can be obtained if the value of the multilayer contraction is completely added to the silicon layer thickness and if the molybdenum thickness of the design remains unchanged (Figure 6). As can be seen in the Cu-Kα reflectograph the agreement of the measured and calculated reflectance spectra is almost perfect for small grazing angles up to 2 degree.

For larger angles the differences become larger. Since the main features of the spectra can also be detected in the measurement it is concluded that the single layer thicknesses of the multilayer should be correct. The deviations between measurement and calculation are attributed to a non-perfect description of the interfaces in the model.

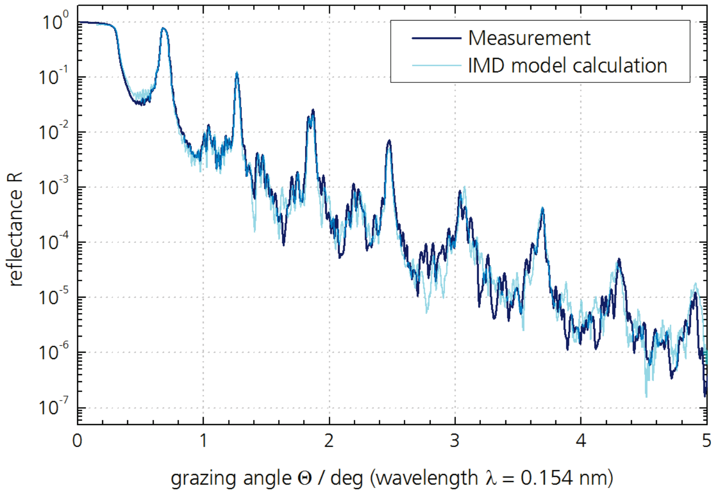

Figure 6: Comparison of a typical X-ray reflectograph taken with Cu-Kα radiation (λ = 0.154 nm) with the calculated spectrum of the depth-graded multilayer design.

After verifying the correct single layer thicknesses and the proper Γ value, EUV reflectance measurements have been performed. Initially, the reflectance spectra have not been perfectly uniform. Because of oxidation of the silicon layer on top of the multilayer stack a disagreement between measured and calculated spectra appeared. The measured reflectance spectra exhibited an almost linear gradient of the reflectance. Since oxidation cannot be avoided, the only chance to solve this problem is the tuning of the last silicon layer. With a reduction of the design value of the last-Si thickness of about 1 nm an acceptable agreement between design and measured EUV spectra has been obtained (Figure 7).

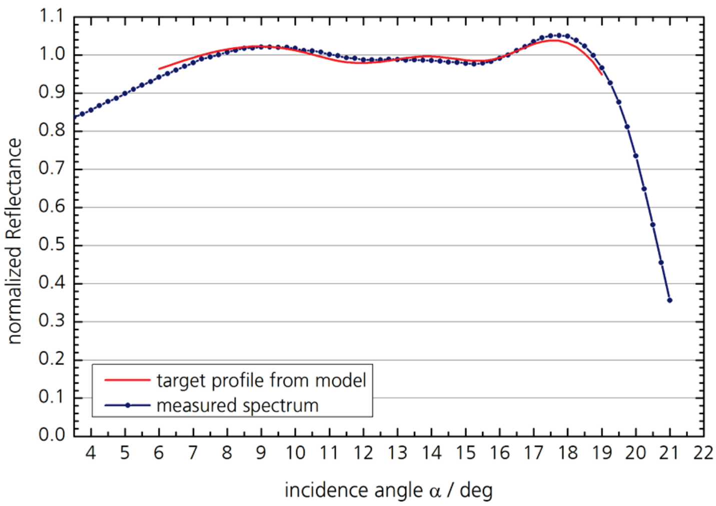

Figure 7: Normalized EUV reflectance spectrum and the corresponding spectrum from the theoretical model.

4.2 Reproducibility of broadband coatings

For the application of broadband reflection coatings in an industrial environment the reproducibility is tremendously important. Since already small deviations of only a few layer thicknesses can have significant impact on the reflectance spectra, the sensitivity to thickness errors is larger than for periodic multilayers. Nevertheless, the great advantage of high temporal stability of the MSD is also beneficial for broadband coatings. EUV reflectance measurements have shown, that three nominal identical coatings differ only by 5 pm for the central wavelength ctw50 (Figure 8).

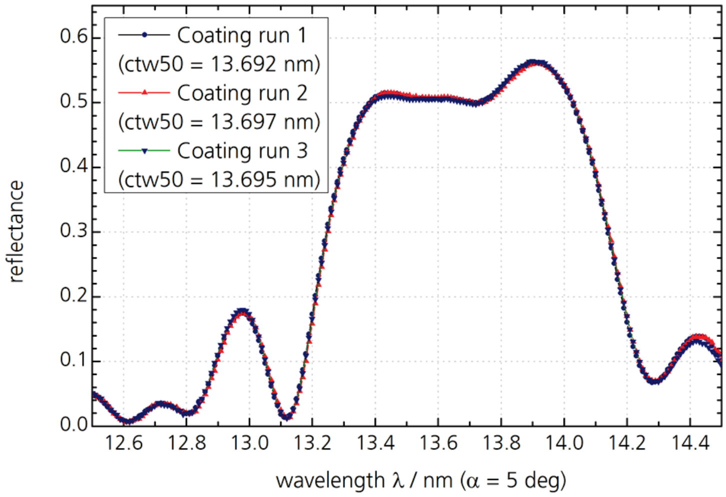

Figure 8: Run-to-run reproducibility of EUV broadband reflection coatings. The variation of the central wavelength ctw50 is only 5 pm for three nominal identical coatings.

4.3 Influence of substrate roughness to broadband reflectance spectra

<u>Fabrication of surfaces with defined and uniform roughness</u>

In order to investigate the influence of substrate roughness to the EUV broadband spectra, well-defined and uniform substrate roughness is needed. Since most of the substrate suppliers polish their substrates to a roughness below a certain specification it is hardly possible to buy substrates with other roughnesses. Additionally it has to be ensured that the roughness is uniform across the whole substrate surface. Otherwise AFM measurements are not meaningful since only small areas of 1 µm x 1 µm or 5 µm x 5 µm are measured that have to be representative for the whole surface.

Because of the difficulties to get substrates with defined and uniform roughness we decided to produce dedicated roughness “standards”. For this purpose silicon wafers have been coated with molybdenum single layers. Since the surface roughness of molybdenum layers increases with increasing thicknesses, the thickness can be used for controlling the surface roughness (Figure 9). By using these coatings perfectly uniform, well-defined and reproducible surface roughnesses are available. In order to prevent changes of the surface morphology the molybdenum layers were covered with an amorphous silicon layer with a thickness of ~ 5 nm. After contact to air a stable silicon oxide layer with a thickness of 2.5…3 nm is formed that finally results in a chemically saturated surface without altering the roughness.

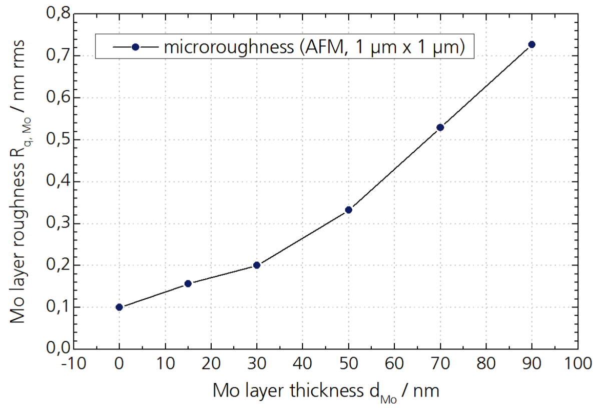

Figure 9: Roughness $R_{q,Mo}$ versus thickness d_{Mo} of molybdenum layers fabricated by MSD.

<u>Multilayers with and without smoothing properties</u>

In a first experiment samples with 6 different roughness values have been coated with a typical Mo/Si/C broadband design in one and the same deposition run using standard parameters. The EUV reflectance measurements show the expected results: With increasing substrate roughness the reflectance decreases (Figure 10, left hand side). Only up to a surface roughness of about 0.2 nm rms acceptable reflectance losses are observed. Using the same substrates and applying advanced process parameters, a significant improvement can be obtained. In this case the broadband reflectance spectra are almost independent from the substrate roughness (Figure 10, right hand side).

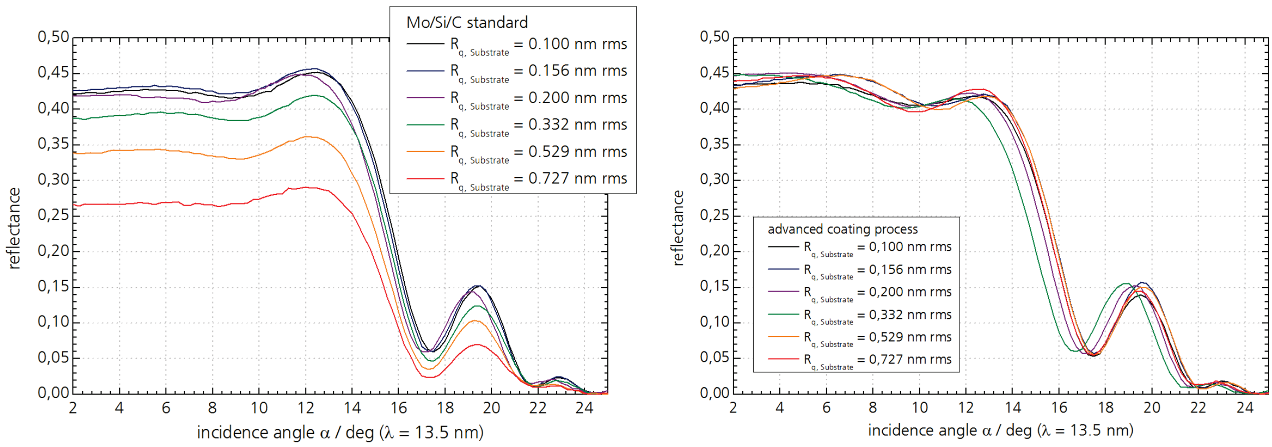

Figure 10: EUV reflectance measurements of broadband coatings on substrates with different roughness.
Left hand side: Results for the standard deposition process showing reflectance decrease with roughness.
Right hand side: Advanced deposition process with additional ion bombardment during film growth resulting in similar reflectance spectra only weakly dependent on the substrate roughness.

Using standard coating parameters the calculation of the integral reflectance from the spectra in Figure 10 shows a nearly linear reflectance decrease for roughness values > 0.15 nm rms. For $R_{q,substrate}$ = 0.3 nm rms a relative reflectance loss of about 10 % has to be taken into account (Figure 11, left hand side). With advanced coating parameters the impact of the substrate roughness can largely be reduced: Even for $R_{q,substrate}$ = 0.7 nm rms almost the same integral reflectance has been obtained as in the case of perfectly smooth wafer surfaces with $R_{q,substrate}$ = 0.1 nm rms (Figure 11, right hand side).

The corresponding AFM measurements on the mirror surfaces confirm the results of the reflectance measurements. In case of the standard coating process the substrate roughness is increased by 0.03 – 0.05 nm for initially smooth surfaces (0.1…0.2 nm rms) and replicated for larger substrate roughness (Figure 11, right hand side). Using the advanced coating parameters the initial substrate roughness can be significantly smoothed by the multilayer coating. Even for a substrate roughness of 0.7 nm rms the roughness of the coating is well below 0.2 nm rms (Figure 11, right hand side).

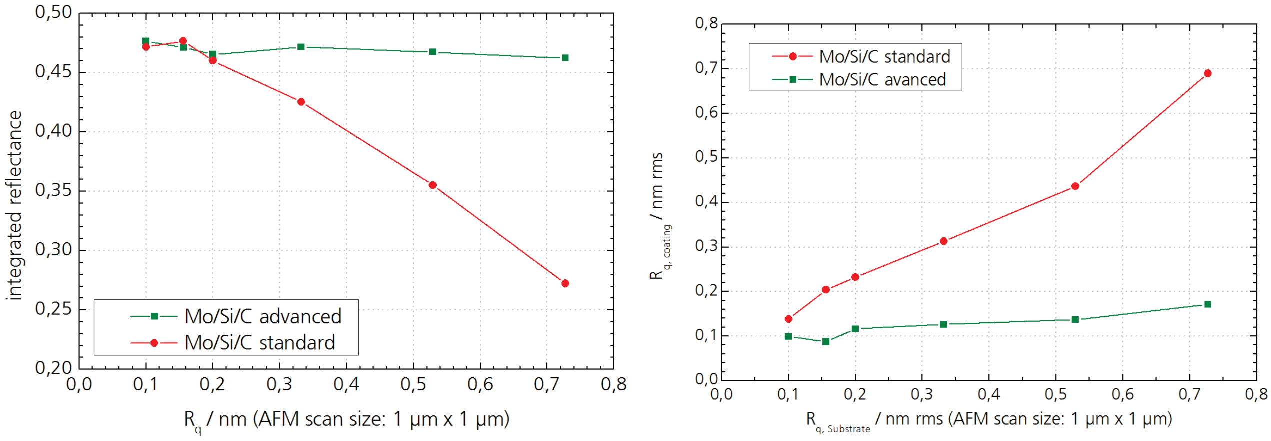

Figure 11: Left hand side: Integrated reflectance calculated from the spectra in Figure 10. Right hand side: AFM roughness of the Mo/Si/C multilayer coatings (standard and advanced process parameters) versus initial substrate roughness. Using the advanced coating parameters reflectance and mirror roughness is almost independent on the initial substrate roughness.

5. SUMMARY AND CONCLUSIONS

EUV broadband multilayer mirrors have been developed using magnetron sputter deposition. It has been shown that with a precise rate and contraction calibration non-periodic multilayers can be fabricated in a time-controlled regime which show good agreement with the calculated reflectance spectra. Additionally, it could be proven that such broadband coatings can be fabricated with a high reproducibility. The central wavelength of three nominal identical coatings differs only by 5 pm which corresponds to a reproducibility of > 99.95 %.

Another important result of the work is that high spatial frequency roughness of the substrate can be smoothed out by using advanced coating parameters with an additional ion bombardment during the multilayer fabrication process. Even with substrates showing initial roughness values of up to 0.7 nm rms the mirror roughness is < 0.2 nm rms. Correspondingly the reflectance of these broadband coatings remains high even for such high surface roughnesses.

ACKNOWLEDGEMENTS

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