Eindhoven University of Technology

MASTER

Thermal stabilization of Mo/Si multilayers

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Summary

Molybdenum-silicon (Mo/Si) multilayers, applied as optical elements for extreme ultraviolet (EUV) radiation, suffer from a decreasing reflectivity following exposure to elevated temperatures. To improve the thermal stability of Mo/Si multilayers, a novel method, based on the formation of carbides at the interfaces, has been developed. This is achieved by implantation of carbon ions of various energies. The multilayers were deposited by e-beam evaporation and the growth as well as the implantation procedure was monitored by in-situ x-ray reflectometry. For determination of the surface composition Auger electron spectroscopy (AES) was used. From AES it was observed that a silicon carbide was formed, with a strong correlation between the carbon content and the implantation energy. Independent of the carbon content (implantation energy), ex-situ x-ray reflectometry showed a thermal stability of both reflectivity and multilayer period up to 425 K. The untreated multilayers in comparison are unstable above 375 K. The application of a high implantation energy turned out to result in a reduction of the reflected intensity due to intermixing of the interface underneath.
2. Introduction.

2.1. General introduction

Molybdenum-silicon (Mo/Si) multilayers are currently the most promising reflective coatings for extreme-ultraviolet (EUV) lithography, a technology that is aimed to replace the current optical technologies used to print microelectronic circuits\(^1\) in the coming decade. Mo/Si multilayers mirrors will be used in a EUV lithography prototype system called the Alpha tool. This tool is designed to be capable of printing 70 nm dense features and to support the exposure of ten 300mm wafers per hour under ultra-high vacuum conditions.

The reflective coating of EUV lithography optics must have high reflectance, constant period (\(d\)) and low stress. The dependency of these properties on time, temperature and radiation must remain within very tight specifications (changes within 0.1\%). The reflectance \(R\) of the multilayer is very critical, because of the dependency of the throughput \(T\) of the optical system on the number of reflections the light experiences throughout the optical system\(^2\). For the past fifteen years the reflectance of Mo/Si multilayers has therefore been optimised throughout extensive studies of their structural dependency on the deposition conditions and post-deposition treatments. With Mo/Si multilayers mirrors comprising 51 layer pairs, near-normal incidence (NIR) values above 69\% are nowadays routinely achieved at wavelengths around 13.5 nm.

The preferred material choice for the fabrication of extreme-ultraviolet (EUV) multilayer mirrors for the 13-25 nm wavelength regions is molybdenum-silicon (Mo/Si). This material pair produces the most stable multilayer reflectivity and period known with relatively smooth interfaces, combined with the highest reflectance in the above-mentioned spectral region. A wide range of deposition techniques and conditions can be used to obtain multilayer structures of equivalent quality, and the materials do not present health hazards. Mo/Si was the first material pair to produce multilayer mirrors with sufficiently high reflectivity to be used in lithography tools.

2.2. Project definition: interface engineering

A well-known problem of Mo/Si multilayers is that characteristics like reflectivity and multilayer period deteriorate, when exposed to elevated temperatures and under high loads of photons and particles\(^3\)\(^4\). The mechanisms behind these changes are diverse, but the most prominent are compound formation at the interfaces between Mo and Si, intermixing of the two materials and compaction of the Si layer. These effects on the multilayers are already manifest for temperatures below 375 K that may occur during exposure to EUV and bake-out of the vacuum system.

This report presents a study of carbon barriers to stabilize the multilayer reflectivity and period. This is done through an introduction of thin carbon barrier layers (< 10\% of the total period with thickness of 6.9 nm) between the Mo and Si layers. To produce these thin layers carbon is not deposited but implanted via ion-bombardment of just deposited Mo or Si layers. To achieve this a mixture of methane and neon gas is fed to a Kaufman gun\(^5\). The motivation for using carbon is that its optical properties are very close to silicon so that it does not compromise the reflectivity and a carbide layer is expected to form a so-called diffusion barrier.

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5. H. Kaufman, "Broad-beam ion sources: present and future directions"
In this report, the reflectivity of the multilayers etched by the neon-methane mixture is compared to the reflectivity of two multilayers etched by the noble gases Kr and Ne. The reason is that a second effect of the use of the Kaufman gun is smoothening of deposited silicon layers resulting in an increase in multilayer reflectivity\(^6\). The Ne and Kr etched samples are therefore made to distinguish between the effects of carbon implantation from the smoothing effect on reflectivity. From the in-situ reflectivity signal, reflectivity data can be obtained as well as from the first Bragg peak observed in grazing incidence x-ray reflectometry using Cu-K radiation\(^7\).

The thermal stability of the carbon-implanted multilayers is investigated. For this purpose the initial reflectivity and period are measured using a Philips X’pert MRD system. Subsequently the multilayers are annealed for eight hours at 425 K under vacuum conditions (during annealing \(p<1\text{e}^{-7}\) mbar). After annealing the reflectivity and \(d\) spacing are again measured to check the thermal stability. It is concluded that an implanted multilayer is more stable, if the net change in \(d\) spacing (measured by a shift in the positions of the Bragg maxima) is less for the carbon treated multilayer in comparison to the untreated one.

\(^6\) H.-J. Voorma, E. Louis, N.B. Koster and F. Bijkerk, "Temperature induced diffusion in Mo/Si multilayer mirrors"  
3. Theory

3.1. Introduction

The key property of X-rays that prohibits the use of normal mirrors and lenses for reflection or focussing is their weak interaction with matter. The result is that it deeply penetrates any body that it encounters. In case of EUV mirrors and lenses, though this feature presents a problem. The weak interaction with matter can be described by stating that for X-rays the optical constant $n$ of all materials is very close to unity, $n = 1 - \delta$, the deviation $\delta$ being proportional to $\lambda^2$.

The Fresnel equations\(^8\) that will be described below dictate for $r$, at normal incidence:

$$r = \frac{(n_1 - n_2)}{(n_1 + n_2)} \approx \frac{(\delta_2 - \delta_1)}{2}.$$ 

Consequently the reflected amplitude $r$ of an X-ray beam on encountering a boundary between two materials with optical constants $n_1$ and $n_2$ is very small. Unless the grazing angle of incidence $\phi$ is below a so-called critical angle ($\phi_c$) the reflected intensity $|r|^2$ will be of the order of 1% or less.

To obtain high reflectivity, multilayer mirrors are designed. These multilayers are described extensively in literature\(^9\) and are based on constructive interference amplitude addition. For the mirror this is achieved via many reflecting boundaries that are spaced such, that the optical path length difference between reflected amplitudes from each of the consecutive boundaries equals one wavelength, resulting in a phase difference of $2\pi$. Therefore a large number of regularly spaced layers of alternating composition are deposited. The optical contrast between the two materials ascertains the multilayer reflection.

For a periodic multilayer a significant reflection will only occur for specific combinations of X-ray wavelength and angle of incidence, that is given by the Bragg equation

$$2d \sin(\phi) = \lambda,$$

with $d$ representing the multilayer period. This relation is deduced both via x-ray diffraction theory and classical optics. Numerous textbooks on x-ray optics give a detailed description of x-ray diffraction, for example the books by Compton and Allison\(^1\) and the review by Slater\(^1\).

3.2. Reflection from a single interface

The reflectivity of an X-ray multilayer mirror is determined by the optical contrast between its constituting materials. These two materials are usually referred to as absorber and spacer. In this section a formula is derived, describing this reflectivity. The complex refractive index $n'$ can be written as

$$n' = 1 - \delta + i\beta,$$

The values of $\delta$ and $\beta$ are directly proportional to the atomic density of the material

$$\delta = \rho_{at} r_e \lambda^2 f_1 / 2\pi, \quad \beta = \rho_{at} r_e \lambda^2 f_2 / 2\pi,$$

where $\rho_{at}$ is the atomic density, $r_e$ is the classical electron radius and $\lambda$ the wavelength of the radiation. The factors $f_1$ and $f_2$ are the real and imaginary parts of the atomic scattering factor.

\(^9\) F.L. Pedrotti en L.S. Pedrotti, "Introduction to Optics"
\(^1\) A.H. Compton and S. Allison, "X-rays in theory and experiment", van Nostrand, New York, 1935
\(^1\) J.C. Slater, "Interaction of waves in crystals", Review Modern Physics, 30, 1958
which represent coherent and incoherent scattering and absorption, respectively. The terms extinction coefficient or absorption coefficient are both used for $\beta$. It will be shown that the optical contrast is determined by the difference in optical constants $n'$ of the absorber and the spacer.

<table>
<thead>
<tr>
<th>Material</th>
<th>$1 - \delta$</th>
<th>$\beta$</th>
<th>$\delta$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon</td>
<td>0.9622</td>
<td>0.0067</td>
<td>0.0378</td>
</tr>
<tr>
<td>Silicon</td>
<td>0.9999</td>
<td>0.0018</td>
<td>0.0001</td>
</tr>
<tr>
<td>SiC</td>
<td>0.9831</td>
<td>0.0047</td>
<td>0.0169</td>
</tr>
<tr>
<td>Si3N4</td>
<td>0.9741</td>
<td>0.0092</td>
<td>0.0259</td>
</tr>
<tr>
<td>SiO2</td>
<td>0.9787</td>
<td>0.0106</td>
<td>0.0213</td>
</tr>
<tr>
<td>Mo</td>
<td>0.9227</td>
<td>0.0062</td>
<td>0.0773</td>
</tr>
</tbody>
</table>

Table 3-1. Optical constants for typical multilayer materials at $\lambda=13.6\text{nm}$. The meaning of the constants $\delta = (1-n)$ and $\beta$ (extinction or absorption coefficient) are described in the text.

The use of the complex refractive index is illustrated by the following example. An electromagnetic wave propagating in the z-direction through a homogeneous slab of material of thickness $z$ can be described by

$$E(z, t) = E_0 \exp\left(-\frac{2\pi\beta z}{\lambda}\right) \exp\left[\frac{2\pi i}{\lambda} (nz - ct)\right],$$

with $E$ representing the field amplitude at position $z$ and time $t$, $E_0$ is the field amplitude at $z=0$, $\lambda$ is the vacuum wavelength and $c$ is the speed of light. The extinction of the wave is described by the first exponential, the periodic behaviour by the second.

Upon specular reflection from a boundary, see Figure 3-1, the wave vector transfer is given by

$$q = \Delta k = (4\pi n_1/\lambda) \sin(\theta),$$

Figure 3-1. Reflection at the interface between two materials of indices $n_1$ and $n_2$.  

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13 Data taken from the Centre of X-ray Optics (CXRO), Berkeley Lab, http://www-cxro.lbl.gov/optical_constants/
with symbols defined in the above figure. The refraction and transmission coefficients for the amplitudes are given\textsuperscript{14, 15} by the Fresnel formulas (s-polarisation)

\textbf{Eq. 3-6} \quad r^2_{12} = \left[ n_1 \cos \phi_1 - n_2 \cos \phi_2 \right] / \left[ n_1 \cos \phi_1 + n_2 \cos \phi_2 \right],

\textbf{Eq. 3-7} \quad t^2_{12} = 2 \frac{n_1 \cos \phi_1}{n_1 \cos \phi_1 + n_2 \cos \phi_2},

From the momentum transfer vector (Eq. 3-5) and from (Eq. 3-6) a simple form of the Fresnel equation is obtained

\textbf{Eq. 3-8} \quad r^2_{12} = \frac{[q_1 - q_2]}{[q_1 + q_2]},

Total reflection will occur for small grazing angles below a critical angle \( \theta_{\text{crit}} \) for incidence from vacuum with \( n_0 = 1 \). This critical angle between vacuum \( (n_0 = 1) \) and a material with index \( n = 1 - \delta \) is defined by the requirement that \( \cos \phi_2 \) in Eq. 3-6 becomes zero, and in combination with Snell's law the following relation is obtained

\textbf{Eq. 3-9} \quad \sin \phi_{\text{crit}} = \cos \phi_{\text{crit}} = n'

Using this critical angle we can write the critical value of the momentum transfer

\textbf{Eq. 3-10} \quad q_{\text{cr}} = (4\pi n/\lambda) \sin(\theta_{\text{crit}}),

For angles much larger than the critical angles \( (q >> q_{\text{cr}}) \) we obtain for the reflected amplitude

\textbf{Eq. 3-11} \quad r_{12} = \frac{[q^2_{\text{cr1}} - q^2_{\text{cr2}}]}{4q^2},

and for the intensity

\textbf{Eq. 3-12} \quad R_{12} = \left| q^2_{\text{cr1}} - q^2_{\text{cr2}} \right|^2 / 16 q^4,

with the optical constants as variables, for the reflectivity is finally obtained using \( \delta, \beta << 1 \)

\textbf{Eq. 3-13} \quad R = \left[ (\delta_2 - \delta_1)^2 + (\beta_2 - \beta_1)^2 / 4 \sin^4 \theta_0,\right]

This is the formula describing the relation between the reflectivity and the optical contrast. From the definition of the refractive index (Eq. 3-2) we find that upon reducing the density of the spacer (Eq. 3-3), the contrast and the reflectivity for a fixed angle of incidence are enhanced.

\textsuperscript{14} L.G. Parratt, "Surface studies of solids by total reflection of X-rays," Phys. Rev. 95, pp.359-368, 1954

The gamma ratio for multilayers is defined as

\[ \Gamma = \frac{d_1}{d_1 + d_2}, \]

where \( d_1 \) and \( d_2 \) are the thickness of the absorber and spacer respectively. The influence of gamma is noticed e.g. on GIXR curves via a modulation of the Bragg intensities. This means that minima in the Bragg peaks appear when \( n \) is a multiple of \( 1/\Gamma \), where \( 1/\Gamma \) is an integer and \( n \) is the reflectivity order.

### 3.3. Full stack simulations

From the Fresnel formulas described in the previous section, the amplitude reflection coefficient for each boundary can be calculated. By adding several layers the reflectivity of a complete multilayer is obtained.

![Figure 3-2. A simulation of the grazing incidence x-ray reflectivity of a fifty bi-layer Mo/Si multilayer. The grazing incidence angle varies between 0 and 10 degrees. The multilayer period is 6.9 nm and the x-ray wavelength is 0.154 nm.](image)

In this section the results are shown for calculations using simulations\(^{16}\) of multilayers having fifty periods. The absorber (Mo) and the spacer (Si) each define two layers. Two additional layers have been simulated at the interfaces to account for the naturally formed silicide interlayers. This way each period comprises a four-layer structure. By repeating this structure fifty times the reflectivity of the entire stack is calculated. In advance of the discussion in the next section regarding the implantation of carbon interlayers, simulations have also been carried out using carbon interlayers at the positions of the original silicide layers.

\(^{16}\) IMD, version 4.1.1, august 2000, written by David L. Windt.
Figure 3-3. Representation of the repetitive part of the multilayer, $d=6.9 \text{ nm}$, used in the simulation of a 50 bi-layer Mo/Si multilayer. In the right graph amorphous carbon layers have replaced the Mo$_5$Si$_3$ interfaces.

Figure 3-4. Representation of the repetitive part of the multilayer, $d=6.9 \text{ nm}$, used in the simulation of a 50 bi-layer Mo/Si multilayer. In the left graph an amorphous carbon layer has replaced the Mo-on-Si interface. In the right one the amorphous carbon layer has replaced the Si-on-Mo interface.

The results of the different simulations are summarized in the table below.

<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Reflectivity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.2-left</td>
<td>Two Mo$_5$Si$_3$ interfaces</td>
<td>72.1</td>
</tr>
<tr>
<td>2.2-right</td>
<td>Two carbon interfaces</td>
<td>69.5</td>
</tr>
<tr>
<td>2.3-left</td>
<td>Carbon on Si interface</td>
<td>71.8</td>
</tr>
<tr>
<td>2.3-right</td>
<td>Carbon on Mo interface</td>
<td>70.2</td>
</tr>
</tbody>
</table>

Table 3-2. Multilayer reflectivity obtained from simulations of different interlayers.

Notice that replacing the silicide interlayer on the Mo-on-Si interface by a carbon interlayer does not compromise the reflectivity. The use of a carbon interlayer at the Si-on-Mo interface leads to a notable decrease in reflectivity. This decrease in reflected intensity is explained by the fact that at the molybdenum layer the standing wave x-ray field reaches a maximum. The result is a high absorption of the carbon layer that is situated on the molybdenum layer. At the silicon layer however an electric field interference minimum is situated, which results in a lower absorption of the carbon interlayer that is situated at this Si layer. It is therefore advantageous to study the thermal stability of a multilayer where only the silicon layer is implanted.
3.4. Definition of the Bragg relation with correction term

A simple model describing the multilayer structure consists of a succession of planes and each of these planes is described by the reflection coefficients and transmission coefficients of the field amplitude. These planes are the boundaries of the material in an optical coating. Between the boundaries the film materials are assumed to be homogeneous and are not producing any secondary scattered waves. The reflection and transmission coefficients are obtained from the Fresnel relations (Eq. 3-6). The phase shift \( \varphi \) produced by the propagation of the wave through one layer of the film is given by

\[
\varphi_n = (2\pi n' / \lambda) d_n \cos \varphi_n
\]

with \( d_n \) representing the thickness of the film layer \( n \).

For a multilayer film the reflectivity can be described\(^\text{17}\) by

\[
|r| = \sqrt{|1 + r_t r_b \exp(i\varphi)|}
\]

were \( r_t \) and \( r_b \) represent the Fresnel coefficients that represent the amplitudes of the multilayer structure, which can be considered as the top and bottom of a new structure.

If we consider a multilayer structure made of two film materials of complex index \( n_1 \) and \( n_2 \), thicknesses \( d_1 \) and \( d_2 \) and period \( d = d_1 + d_2 \). With \( n_0 = 1 \) and \( n' = 1 - 6 + i\delta \) and neglecting quadratic terms in \( \delta \) an \( \beta \) we obtain

\[
m \lambda = 2 d \sin(\theta_0) \sqrt{1 - 2 \delta / \sin^2(\theta_0)}
\]

where: \( m \) is the Bragg order.

The refractive index is the weighted index of the two materials in the coating

\[
\delta_{eff} = (d_1 \cdot \delta_1 + d_2 \cdot \delta_2) / d,
\]

Eq. 3-17 is called the Bragg equation in X-ray diffraction and appears often in the form without the square root (Eq. 3-1), which is an approximation for the case that \( \delta = \beta = 0 \). The influence of the optical constants on the position of the reflectivity curve can become substantial, especially for grazing angles. This change in the angle due to refraction has been used to determine the real part of the refractive index of multilayer coating materials\(^\text{18,19}\).

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\(^{17}\) O.S. Heavens, "Optical properties of thin solid films", Dover, New York, 1996


4. Experiments + results

4.1. Introduction

The optical properties of EUV multilayers depend substantially on the structure of the interfaces. Key characteristics in this context are roughness and degree of layer interdiffusion. The reflectivity is directly related to the structure of the interface\textsuperscript{20,21}. If the interface thickness is increased due to roughness and layer interdiffusion, the reflectivity is significantly reduced. Mo/Si multilayers show a finite solubility and forms alloys, therefore interdiffusion and compound formation at the interfaces is energetically favourable. Structural analysis has shown that even multilayers, which exhibit a high near-normal incidence (NIR), form amorphous interdiffusion zones. The thickness of these zones is expected to be 0.8±0.2 nm\textsuperscript{22}; a value determined from x-ray reflectivity data. Upon annealing of multilayers the interface thickness increases substantially, which is concluded from simulations. When the interface width is larger than ~10% of the period the reflectivity will decrease dramatically. At present this process of interlayer formation is considered as an intrinsic property of Mo/Si material and presents a fundamental barrier to achieving the maximum theoretical NIR\textsuperscript{23}.

4.2. Multilayer deposition

At FOM, two electron-beam deposition facilities are in use to produce Mo/Si multilayers. One is situated at FOM-rijnhuizen in Nieuwegein, near Utrecht and one at Amolf, in Amsterdam. The e-beam coating facility at Nieuwegein consists of two ultra-high vacuum chambers of which the lower chamber contains the multilayer materials and the e-beam evaporator. The upper chamber contains the sample holder, an in situ reflectometer and an ion gun. The ion gun is used to remove excess material. This process is known as etching. The base pressure in both chambers is better than 10\textsuperscript{-9} mbar. The coating facility is described in ref \textsuperscript{24}.

At Amolf the multilayer depositions were carried out in an ultrahigh vacuum (UHV) deposition chamber with an ultimate vacuum in the low 10\textsuperscript{-8} mbar range after baking. Two electron beam evaporation sources were used to deposit the materials. During evaporation the pressure did not exceed 10\textsuperscript{-7} mbar. A differentially pumped Kaufman ion source was used for carbon implantation and smoothing of the interfaces. During ion bombardment a vacuum of 10\textsuperscript{-5} mbar could be maintained. The angle of incidence of the ions was set to 45°. Ion currents densities of a few \mu A/cm\textsuperscript{2} were used. Commercially available Si(100) wavers were used for substrates. The film thickness during layer deposition as well as during etching was measured continuously by in-situ reflectometry using carbon-K radiation (\lambda = 4.47 nm). More information on the Amolf facility can be found in ref \textsuperscript{25}. In this study samples at Rijnhuizen were made without carbon implantation, whereas at Amolf samples were made having carbon interfaces.

\textsuperscript{20} "Thermally induced structural modifications of Mo/Si multilayers", D.G. Stearns, M.B. Stearns and Y. Cheng, J.H. Smith, N.M. Ceglio.
\textsuperscript{21} "Interfacial reactions of annealing molybdenum-silicon multilayers", K. Holloway, Khiem Ba Do and R. Sinclair.
\textsuperscript{22} "Determination of the layered structure in Mo/Si multilayers by grazing incidence X-ray reflectometry", A.E. Yakshin, E. Louis, P.C. Görts, E.L.G. Maas, F. Bijkerk.
\textsuperscript{23} "Magnetron sputtered EUV mirrors with high thermal stability", T. Feigl, S. Yulin, N. Kaiser, R. Thielsch.
4.3. Determination of multilayer period and reflectivity

Five samples have been examined, to find changes in reflectivity and period as a function of annealing temperatures. Since the optical properties of multilayers (like reflectivity) are strongly wavelength dependent, they are characterized at the wavelength at which they will be used in future lithography tools. This wavelength is 135 nm. For this purpose the multilayers are sent to a laboratory called "Physikalisch-Technische Bundesanstalt (PTB)". At the specified wavelength the multilayers are measured with an accuracy of less than 0.2%. The incidence wavelength is varied at fixed angle of incidence, 1.5 degrees of normal, and the reflectance is measured. From the wavelength with maximum reflectivity, called λ-max, a value for the period of the ML can be found from the Bragg equation. Note that the accuracy in the wavelength measurement is typically higher than that in the reflectivity, due to so-called beam instabilities and statistics. To check the uniformity of the coating, the reflectivity is measured at three points along a line through the centre, one in the hart and two 8 mm out of centre.

4.4. Annealing experiments

4.4.1. Temporal behaviour

The aim of this chapter is to indicate that small effects on reflectivity and multilayer period are already observed at annealing temperatures below 400 K. We will examine and quantify these changes for existing multilayers, having a period of 6.9 nm and having only naturally formed silicide interlayers at the Mo/Si interfaces. For temperatures below 375 K, the effects of annealing on both reflectivity and period become rather marginal, indicating that a safe temperature can be found below this value.

Annealing of five multilayers in the temperature range of 315 K to 375 K is done to survey the temperature behaviour. The annealing experiments are performed in a vacuum chamber. A residual gas analyser (RGA) is used to determine the rest gas composition in the chamber, a thermocouple to measure the sample temperature during annealing, a pressure gauge and a Peltier element for heating of the samples. This element is a high temperature resistant semiconductor device that can reach an annealing temperature of up to 475 K. The advantage of the Peltier element over an ohmic heater (NTC) is that the full range of 295 K to 475 K can be reached by one component. In addition, the Peltier element can also be used for active cooling purposes of the sample.

During annealing pressures are reached in the 10⁻⁶ mbar region. This way contamination of the top layer via contaminants in the gas (e.g. carbon) is avoided. The composition of the residual gas is analysed during annealing via the RGA analyser. After the annealing session, the mirrors are measured a second time at PTB. The post characterisation data are normalised to the pre characterisation data. Figure 4-1 and Figure 4-2 summarize the results for period and reflectivity.
Figure 4-1 Normalised reflectivity as a function of annealing temperature. Note that annealing times are indicated in the legend.

Figure 4-2 Normalised values of λ-max versus temperature.

The overall trend indicates a decreasing reflectivity at higher temperatures; the effect of the annealing on reflectivity is small (typically less than 0.2% which is in measurement uncertainties). The effect of annealing becomes substantial for temperatures above 375 K. Furthermore a decisive trend towards both lower reflectivity's and lower λ-max is noticed due to compaction of the silicon layers and silicide forming. In addition to the experimental data in the temperature range 295 K to 375 K that are presented here, previous studies have yielded temperature results in the range of 295 K to 475 K. Figure 4-3 and Figure 4-4 show the combined data sets. The general trend of a decrease in λ-max and reflectivity is continued in this set.

We conclude that a noticeable decrease of reflectivity and period occur starting at 375 K. From Figure 4-3 an interesting phenomenon can be noted. Although the annealing time may vary, there is no influence on the measured change in $\lambda$-max and reflectivity. All data points happen to follow the same trend. The line is very decisive. There is however one parameter that differs for all multilayers, but seems to be of no influence. This parameter is the annealing time. To investigate this phenomenon in more detail, three samples have been annealed at 375 K. The only difference is the annealing time. Using the Peltier element it is possible to achieve very short annealing trajectories of half an hour ramp-up and ramp-down. The result is shown in Figure 4-5.
Figure 4-5 Normalised wavelength as a function of annealing time. All three samples have been annealed at 375 K. The point at zero hours has been heated to 375 K.

Figure 4-6 Normalised reflectivity as a function versus annealing time. The data have been taken from the same samples as Figure 4-5.

As can be seen, the differences are very small. The normalised $\lambda$ shows a consequent trend down, the differences in reflectivity are too small to be substantial.
4.4.2. Repetitive annealing

A second topic that is addressed is whether the decrease of the reflectivity and multilayer period are stabilised after the first annealing session. If this question is answered affirmatively, the annealing procedure can be used to increase the thermal stability. In this case the deliberate annealing of a multilayer compromises the reflectivity, but a more stable multilayer is obtained afterwards.

In order to study the effects of repetitive annealing, three samples that were annealed previously, are annealed a second time. Two samples will be heated two times at 425 K, one sample during four hours and the other during 48 hours. The third one will be heated two times during 48 hours at 365 K. This way insight is gained in both repetitive and temporal effects.

![Figure 4-7 Normalised reflectivity for Mo/Si multilayers after two successive annealing sessions.](image1)

![Figure 4-8 Normalised λ-max for Mo/Si multilayers after two successive annealing sessions.](image2)
Figure 4-7 and Figure 4-8 show the effect of repetitive annealing on the reflectivity and period. In both cases the decrease is less than 0.5 percent, which is significant given the accuracy of the experiment. A stabilization of the negative effect of annealing on reflectivity and λ-max has been observed after the first annealing session. It is again observed that the annealing effect is independent of annealing time. The similarities between the two samples annealed at 425 K. occur notwithstanding the large difference in annealing time of 44 hours. The normalised decrease in both reflectivity and period is the same. We conclude that the annealing effect is largely independent of time.
5. Interface engineering.

5.1. Introduction.

In the previous chapter it has been shown that Mo/Si multilayers have insufficient thermal stability. The decrease in reflectivity is found to be more than 1.5% after annealing above 390 K. In the planned lithography tool a series of six multilayer mirrors, in addition to four multilayer masks are needed. The decrease in total throughput amounts to 16% (i.e. \((0.985)^{10}\)), which is intolerable. Annealing above 425 K results in a total loss much higher than 16%. It is known from literature that a SiC interface presents a chemically much more stable interface than a MoSi$_2$ interface. Additional calculations using the Miedema model\(^{27}\) based on reaction enthalpies support this idea. Therefore the formation of carbides at the interfaces is proposed to increase the thermal stability. In this section, experiments are presented, in which the multilayers are stabilized using carbon implantation of the Mo-on-Si and the Si-on-Mo interfaces using methane ions. At every etching step two effects are combined: smoothing of the interfaces and implantation of carbon. Single monolayers have been grown, to study the carbon implantation process at the interfaces in more detail.

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\(^{27}\) Boer, F.R. de, "Cohesion in metals: transition metal alloys"
5.2. Carbide implantation at the interfaces

In order to test the feasibility of carbon-implantation of deposited monolayers via the Kaufman source, at first single layers of Mo and Si have been investigated. The decision to produce a full-size stack multilayer is made, if the implantation of single layers turns out to be successful. The Mo and Si layers were deposited on Si(111) substrates. For the deposition we used two electron beam evaporators in a UHV system with a base pressure $p = 10^{-8}$ mbar and $p = 10^{-7}$ mbar during deposition. The Mo layers were deposited at a rate of 0.6 Å/s and at a substrate temperature around 300 K. For the Si layers the deposition rate was 0.3 Å/s, using the same substrate temperature.

For ion-implantation a gas mixture consisting of 50% methane / 50% neon was fed to the Kaufman gun. The motivation for a mixture is that the Ne component assures a stable discharge, whereas the carbon atoms are obtained from the methane component. The Kaufman gun offers the possibility to mix the positively charged ion beam with negatively charged electrons. This way a broad beam (3 cm) is obtained that has a neutral overall electric charge.

The characterization techniques that were used are in-situ Auger Electron Spectroscopy (AES) and in-situ soft X-ray reflectivity. The AES system makes use of a retarding field analyser that has an overall instrument energy resolution of 3%. For the in-situ reflection soft X-rays of $\lambda = 4.47$ nm (carbon-K line) from a carbon anode were used, incident at an angle $\theta = 23.5^\circ$ with the surface. The Bragg equation describes a periodic behaviour of the reflection signal that is measured during deposition or erosion of a layer with optical constant $n$, as a function of its thickness $d$. From the combination of angle and wavelength used, a period of 6.1 nm is calculated. The reflected X-rays were detected with a proportional counter, operated at 1450V containing a gas mixture of 90% Ar and 10% CO$_2$ ($p=1.05\times10^7$ mbar). An Ortec 550 electronic upper level filter is used to create a window to select the C-K line.

Layer thicknesses have also been determined using an in-situ crystal monitor. During the deposition process, material evaporated by the electron beam evaporator was simultaneously deposited on the crystal. By measuring a change in the crystal oscillation due to the deposited material, the deposited layer thickness is obtained.
During the first experiment several layers of molybdenum and silicon have been deposited. Because the deposition and ion sputtering rates are constant, the measured time scale can be converted into a thickness scale, see Figure 5-1:

![Graph showing in-situ signal](image)

**Figure 5-1 In-situ signal showing the first deposition run**

In the experiment layer thicknesses were determined using fractions of the period of the reflected x-ray signal. Therefore this nomenclature is kept for indicating layer thicknesses, instead of using nanometres. In Figure 5-1 the following deposition steps can be recognized:

First step: deposition via e-beam evaporation of four-and-a-quarter period (i.e. ~20 nm) of Si, followed by an in-situ Auger analysis of the fresh deposited surface.

Second step: simultaneous removing and implantation of carbon, a process that is commonly known as etching, of one-quarter period of the silicon layer, using the CH₄/Ne mixture. This step is directly followed by a second Auger analysis, to test if the carbon implantation has been successful. The results of the Auger analysis are shown in Figure 5-2, below. The analysis of the fresh deposited silicon layer is shown in the left graph, dashed line. The data of the silicon surface, after etching with the CH₄/Ne mixture is also shown (solid line). The left graph displays the low energy spectrum; the right one displays the high energies, between 230 and 300eV. It is concluded from the presence of the carbon KLL peak at 263 and 268eV that the implantation of the carbon has been successful. Notice also the shift of the Si LMM peak from 88 to 83eV. This shift is tentatively explained by SiC compound forming.
Figure 5-2. Auger plot of the clean (dashed) and carbon (solid line) etched silicon surface. The high-energy data on the clean silicon surface showed no additional AES peaks and has therefore been omitted.

After the analysis of the Si layer, the growth of molybdenum on the carbon etched silicon surface was investigated. The deposition of the molybdenum layer was controlled using the in-situ reflectivity signal. By depositing the layer from an interference minimum, due to interference of reflected x-rays from the stack and the top layer, to an interference maximum of the x-ray signal, a layer thickness of approximately 0.4 period, i.e. ~2.4 nm, is obtained. This method is called the ‘min/max method’.

It is clear from Figure 5-1, the deposition of half a period (from min to max) was successfully completed. The resulting Mo surface was again examined by Auger, followed by an etching step, where one quarter period of the molybdenum layer was eroded by the CH₄/Ne mix. A consecutive Auger measurement was performed to check the carbon presence of the surface.

Figure 5-3 (right) shows that the etching step with CH₄/Ne has resulted in the presence of carbon on the molybdenum surfaces (C KLL peak at 263 and 268eV). The intensity of the carbon peak is much lower on the Mo surface than on the Si surface. This is shown in more detail in Figure 5-4. It is difficult to make a quantitative analysis of the Auger data, but an indication is found of lower carbon content on the Mo surface than on the silicon surface.
Figure 5-3 AES plot of the clean molybdenum surface (dashed line) and after carbon implantation (solid line). At the top of the graph the energies expected from literature are indicated.

The final step in Figure 5-1 is the deposition of two-three-quarter period of silicon, followed by etching of one-quarter period of the silicon by the methane / neon mixture. The intention of this final step is to cap the multilayer with a carbon top layer. This capping layer can be used in future surface analysis experiments.

Figure 5-4. Comparison of the AES plots of both the Si (solid) and Mo (dashed) surface after etching.
Figure 5-1 shows that silicon has been grown twice. The first silicon layer, deposited between 0 and 625 seconds, is directly deposited on the substrate (SiO₂). The second layer, deposited between 1450 and 1750 seconds, is grown on the carbon treated molybdenum layer. The use of this layer is to study the growth of silicon on the carbon implanted molybdenum layer. The reflected intensity of the in-situ x-rays from the second silicon layer is much higher because of the higher optical contrast between molybdenum and silicon, in comparison to the contrast between the silicon layer and the silicon-oxide layer on top of the substrate. The reflectivity from the second silicon layer drops much faster, than that of the first silicon layer. This decrease cannot be explained by absorption alone. The much faster decrease of the reflectivity from the second silicon layer is explained by roughness. It indicates that the carbon implanted molybdenum layer underneath the second silicon layer is much rougher than the substrate layer.

Figure 5-5. Detail of Figure 5-1, showing the decrease of the reflected intensity that occurs during the deposition of the second silicon layer on the carbon treated molybdenum layer.

Figure 5-6 shows the in-situ signal of a second experiment that is carried out to study the etching process at a lower energy of 500eV. To obtain a more stable etching result the built-in neutralizer of the Kaufman gun is applied. Figure 5-6 shows the following steps.
First step: deposition of one-and-a-half period of molybdenum, followed by an etching step of half a period of the molybdenum layer with the CH₄ / Ne mixture. The etching-energy is set to 500eV.

![Graph showing deposition and etching processes]

**Figure 5-6.** In-situ signal from the second deposition run, deposition details are given in the text. The experiment is designed to investigate the carbon implantation at a lower etching energy.

The etching of the molybdenum is followed by the deposition of three periods of silicon. On this silicon layer again one layer of molybdenum was deposited. The thickness of this layer is controlled using the in-situ x-ray signal by depositing from an interference minimum to interference maximum. This method results in a molybdenum layer thickness of approximately 0.4 periods, i.e. ~2.4 nm. The molybdenum deposition was followed by an etching step with the CH₄ / Ne mixture. The etching-energy of this second step is set to 1000eV, to study differences in etching yield due to the different etching energies. An interesting phenomenon that is seen in Figure 5-6 is the increase in reflectivity after etching of the molybdenum. To see this more clearly the detail below (Figure 5-7) is available. The increase in reflected intensity is not seen in previous etching cycles that used the noble gas krypton²⁸. Thus Kr does not smooth the Mo interface.

Figure 5-7. Comparison of the etch process of molybdenum for 500eV and 1000eV ions.

The increase in reflected intensity after etching is the highest (~50%), after etching with energy of 1000eV. Etching of the molybdenum with an energy of 500eV results in an increased reflectivity of ~20%. The increase can be attributed to smoothening of the molybdenum layer. A second explanation based on calculations, is that the favourable optical contrast between the molybdenum and the carbon surface layer results in the increased reflectivity due to a higher carbon content after etching with 1000eV ions.

From Figure 5-6 a second effect at the etching step between 800 and 1500 seconds can be seen. The peak at 850 seconds relates to the molybdenum layer. The peak at 1050 seconds relates to the Si layer situated at 600 seconds that was situated under the molybdenum. An increase in reflected intensity of this peak relative to the peak at 600 seconds is observed. This increase could be explained via both smoothing of the silicon layer as well as to intermixing of the molybdenum and the silicon. This last effect results also in better optical properties resulting in a higher reflectivity. To decide which effect is prominent, a clean Si layer was deposited, followed by a second etching step with beam energy of 1000eV. Since on this last silicon layer no molybdenum top layer has been deposited, the intermixing effect of molybdenum and silicon is absent during the second experiment. Again an increase in reflectivity from the Si surface was observed. In this case the rise can no longer be attributed to intermixing. It is observed that etching of the Si with the mixture of CH₄/Ne results in an increase of reflectivity. So it must be concluded that smoothing is the cause of the increase in reflectivity. The etching is continued until the whole multilayer was removed, to test the stability of the etching procedure.
5.3. Reflectivity and period of the carbon implanted Mo/Si multilayers

In this section the results are presented of carbon injection on full stack multilayers. In the first experiment a multilayer has been deposited having twenty periods (Figure 5-8).

![Figure 5-8 In-situ reflectivity signal measured during the deposition of the full stack multilayer.](image)

It is investigated whether the carbon implantation procedure does not compromise the reflectivity of the Mo/Si multilayer in comparison to the non-injected one. For a EUV tool a multilayer is needed that combines a high thermal stability with a reflectivity comparable to the non-implanted multilayer. To quantify the as-deposited reflectivity of the carbon-injected multilayer, two independent methods are used. A first indication is obtained from the in-situ monitor signal. This signal measures the reflectivity for x-rays with a wavelength of $\lambda = 4.47$ nm.

A second result on the multilayer reflectivity is obtained from ex-situ GIXR, using Cu-Kα radiation with a wavelength of 0.154 nm. Since this short wavelength radiation penetrates much deeper into the structure, the deeper layers contribute relatively stronger to the reflectivity. From the in-situ signal information is obtained on the top-layer, whereas the ex-situ GIXR measurement averages over more layers and offers better statistics.

As a reference, two multilayers have been prepared without carbon interlayers. These samples are used to compare the reflectivity of the carbon-implanted samples with samples etched by neon and krypton. The Kr etched sample is fabricated because Kr is currently used in Nieuwegein.

5.3.1. In situ reflectivity results

To extract the reflectivity from the in-situ signal, a few problems have to be addressed. The yield of the x-ray source varies over a time period of weeks. Furthermore the yield will or can be manually adjusted. At the start of every deposition, a standard, one and a half period silicon layer is deposited. The in-situ signal is normalised to the reflection maximum of this first layer.
Figure 5-9 In-situ monitor signal of the deposited silicon and molybdenum layer.

The results of the in-situ reflectivity data of five multilayers are summarized in Table 5-1. All five samples are deposited via the so-called min/max method, which was described in section 4.2. Using this method the layer thickness is controlled using the in-situ x-ray monitor signal. The molybdenum layer is deposited from an interference minimum to interference maximum; the silicon layer fills the period from the maximum to the minimum.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Etch gas</th>
<th>Energy</th>
<th># Layers</th>
<th>Normalized in-situ R</th>
</tr>
</thead>
<tbody>
<tr>
<td>150502#1</td>
<td>Kr</td>
<td>300</td>
<td>38</td>
<td>10.0</td>
</tr>
<tr>
<td>190302#2</td>
<td>Ne+CH4</td>
<td>500</td>
<td>40</td>
<td>10.5</td>
</tr>
<tr>
<td>260202#2</td>
<td>Ne+CH4</td>
<td>1000</td>
<td>40</td>
<td>10.0</td>
</tr>
<tr>
<td>210302#1</td>
<td>Ne+CH4</td>
<td>1500</td>
<td>40</td>
<td>6.28</td>
</tr>
<tr>
<td>170402#4</td>
<td>Ne</td>
<td>500</td>
<td>50</td>
<td>7.55</td>
</tr>
</tbody>
</table>

Table 5-1 Measured in-situ x-ray reflectivity of the full stack multilayer. The in-situ reflectivity signal has been normalized to the reflectivity of the first Si layer.

From Table 5-1 it can be observed that the lowest etch energy of 500eV results in the highest final multilayer reflectivity. The lower reflectivity observed for samples etched with a higher energy of 1000eV and 1500eV is due to intermixing at the interfaces. The Ne etched sample seems to show a lower reflectivity at 500eV. The lower reflectivity of the Ne sample is due to layer errors, which were observed from the in-situ signal.

5.3.2. Copper-Kα reflectivity results

Table 5-2 shows all samples that have been deposited. The samples listed in Table 5-1 have been deposited using the min/max method. In addition to these min/max samples (entries 1, 4, 6, 8, 9), that were etched at an energy of 500, 1000 and 1500eV, additional samples have been made using the same etch energies, but with a variation of one parameter (Γ-ratio) of the multilayer (entries 2, 3, 5, 7). The in-situ reflectivity data of these samples cannot be used to quantify the reflectivity of the multilayer, because the reflectivity also depends on Γ. All samples
have been measured using GIXR. The data are summarized in Table 5-2. The normalised amplitude of the first Bragg peak is shown in the eighth column.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Sample ID</th>
<th>Etch gas</th>
<th>Energy</th>
<th># layers</th>
<th>period (Å)</th>
<th># Bragg peaks</th>
<th>amplitude</th>
<th>Method</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>190302#2</td>
<td>Ne+CH4</td>
<td>500</td>
<td>40</td>
<td>62.17</td>
<td>6</td>
<td>0.976</td>
<td>Min/max</td>
</tr>
<tr>
<td>2</td>
<td>270302#4</td>
<td>Ne+CH4</td>
<td>500</td>
<td>40</td>
<td>62.65</td>
<td>7</td>
<td>0.990</td>
<td>Crystal</td>
</tr>
<tr>
<td>3</td>
<td>270302#3</td>
<td>Ne+CH4</td>
<td>500</td>
<td>40</td>
<td>65.33</td>
<td>7</td>
<td>0.980</td>
<td>Crystal</td>
</tr>
<tr>
<td>4</td>
<td>260202#2</td>
<td>Ne+CH4</td>
<td>1000</td>
<td>40</td>
<td>61.37</td>
<td>7</td>
<td>0.913</td>
<td>Min/max</td>
</tr>
<tr>
<td>5</td>
<td>030402#4</td>
<td>Ne+CH4</td>
<td>1000</td>
<td>40</td>
<td>65.79</td>
<td>7</td>
<td>0.765</td>
<td>Crystal</td>
</tr>
<tr>
<td>6</td>
<td>210302#1</td>
<td>Ne+CH4</td>
<td>1500</td>
<td>40</td>
<td>60.29</td>
<td>7</td>
<td>0.661</td>
<td>Min/max</td>
</tr>
<tr>
<td>7</td>
<td>030402#3</td>
<td>Ne+CH4</td>
<td>1500</td>
<td>40</td>
<td>67.40</td>
<td>7</td>
<td>0.765</td>
<td>Crystal</td>
</tr>
<tr>
<td>8</td>
<td>170402#4</td>
<td>Ne+CH4</td>
<td>500</td>
<td>50</td>
<td>62.55</td>
<td>5</td>
<td>0.982</td>
<td>Min/max</td>
</tr>
<tr>
<td>9</td>
<td>150502#1</td>
<td>Kr</td>
<td>300</td>
<td>38</td>
<td>62.23</td>
<td>6</td>
<td>0.985</td>
<td>Min/max</td>
</tr>
</tbody>
</table>

Table 5-2. Characteristics of the carbon implanted samples. The decrease in period using higher etch energies is eminent. Also listed is the decrease in reflectivity at higher etching energy.

The samples from entries one, two and six will be used to compare the reflectivity from GIXR. When we want to create a different molybdenum fraction (i.e. $\Gamma$-ratio) in the multilayer period, than the one obtained using the min/max method, a different way to monitor the deposition process is needed. The varying gamma ratio is obtained by deposition of a different Mo thickness using the crystal monitor. The Si thickness is still controlled using the in-situ monitor signal, filling a complete period from max to min. This way a constant period is obtained.

Figure 5-10 presents a plot showing the reflectivity data for x-rays with a wavelength of 4.47 nm and 0.154 nm. Clearly visible is a noticeable drop in reflectivity for etching energies higher than 1keV.

![Figure 5-10](image)

Figure 5-10 The normalised reflectivity signal as a function of etching energy. Note that the measurements for the two different wavelengths are in good agreement.
The overall trend of a decreasing reflectivity is found for both wavelengths. The decrease in reflectivity from the top layer as a function of etching energy is the same at that from the full stack. It is concluded that the characteristics like roughness and gamma ratio of the top layer match the characteristics of the average of the complete stack. Table 5-2 shows the change in multilayer period for multilayers that have been etched using different energies. An indication of the nature of this shift is found by simulating the growth of multilayers with different spacer materials (see Table 5-3). The simulations have been done using the simulation program Multimul\textsuperscript{29}. This is a program that simulates the growth of a multilayer. The optical constants used in this program are obtained from ref [30]. The obtained periods have to be taken with considerable care though, since only two materials are taken into account and no interfaces are considered. In reality though two additional interfaces are formed.

From the calculations it is observed that the multilayer period is dependant on the composition of the spacer. The smallest period e.g. is observed with a simulation of pure carbon as the spacer material. The thickness of the period obtained with a Si spacer lies in-between. If we assume the whole spacer to be turned into SiC, then the highest thickness for the period is obtained. These values therefore provide insight in the composition of the spacer material.

<table>
<thead>
<tr>
<th>Material</th>
<th>Period (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mo/C</td>
<td>5.74</td>
</tr>
<tr>
<td>Mo/Si</td>
<td>6.20</td>
</tr>
<tr>
<td>Mo/SiC</td>
<td>6.29</td>
</tr>
<tr>
<td>Mo/MoSi2</td>
<td>7.24</td>
</tr>
</tbody>
</table>

Table 5-3 Results of simulations on the multilayer period obtained through deposition using the min/max method. This method is described in section 4.2.

As can be seen from Table 5-2, a higher etching energy results in a decrease in period. The decrease in period form a silicide interlayer to a carbide interlayer explains this decrease in period.

\textsuperscript{29} R. Schlatman, "Control of multilayer X-ray mirror properties", ISBN 90-9008724-9

5.4. Thermal stability of carbon injected multilayers

In this section one of the main issues of this survey is presented, i.e. whether the carbon-implanted multilayers are thermally more stable than the non-implanted ones. From the first part of the experiments it is found that changes in both reflectivity and period are observed after annealing of Mo/Si multilayers at temperatures above roughly 380 K. Therefore to investigate the thermal stability, the carbon treated samples are subjected to the following annealing procedure.

First the samples are characterized via GIXR. Then the samples are annealed during eight hours at 430 K in an UHV oven. From the evolution of the curves of a consecutive GIXR measurement the decrease in both reflectivity and multilayer period due to the annealing procedure is analysed. The period is obtained from the GIXR data using the Bragg equation, the reflectivity from the first order Bragg peak. For reference a multilayer sample has been made which has not been implanted by carbon. Instead it was etched using Ne.

Figure 5-10 shows the GIXR curve before and after annealing for a Mo/Si multilayer without carbon implanted at the interface. On annealing of this multilayers a shift of the Bragg curve is observed. From the data a contraction of the multilayer stack is concluded. The multilayer period has changed from 6.30 nm before annealing to 6.28 nm after annealing. Note that a contraction of the multilayer structure results in an expansion of the GIXR plot.

![Figure 5-11](image_url)

Figure 5-11 Two GIXR curves measured on a sample without carbon implantation. The dark curve was obtained before annealing and the light one after annealing. Note that the curves do not overlap precisely, changes have occurred both in height and position of the peaks.
Figure 5-12 Two GIXR curves of the carbon implanted sample measured before (dark) and after annealing (light). Note that in this case the position of the curves overlap. Changes occur however in height of the separate peaks (see text).

In general the decrease in multilayer period can be attributed to contraction of separate layers. The phenomenon of contraction is extensively described in literature\(^{31,32}\) and it is commonly conceived as due to both contraction of the silicon layer due to the extinction of voids and forming of large silicide interlayers. Because of the higher density of a silicide layer, in contrast to non-compound Mo and Si, a compaction of the multilayer structure is observed. Figure 5-12 shows that the carbon-implanted multilayer was more stable than the non-implanted multilayer. No changes in multilayer period on annealing were found for all carbon-implanted multilayers.

Figure 5-12 shows another interesting phenomenon. The position of the separate maxima remains at a fixed angle. Looking carefully though differences are observed in the height of the Bragg peaks of the GIXR curves made before and after annealing. It is noted that the height of the light peaks are not consequently lower (or higher) than those of the dark peaks. A redistribution of the peaks is observed instead. The GIXR curves can be calculated using the


optical thin film theory\textsuperscript{33}. For ideal multilayers with sharp interfaces only two layers are present per period. The composition is described by a factor $\gamma$

\textbf{Eq. 3-14} \quad $\Gamma = d_1 / (d_1 + d_2)$,

where $d_1$ and $d_2$ are the thickness of the absorber and spacer respectively. For deposited multilayers the reflectivity will be lower than the theoretical maximum, due to imperfections of the interfaces like roughness and intermixed zones or interlayers. To describe these non-ideal multilayers currently two models are used. The first method uses a two-layer model, using a so-called Névaut-Croce factor\textsuperscript{34} that multiplies the Fresnel reflectance coefficients of the interfaces with a statistical coefficient. This factor depends on the wavelength and the width ($\sigma$) of the density profile at the interlayer. For the composition gradient an error function is used.

The second method uses a four-layer model that takes into account the presence of real interlayers at the reflecting interfaces. In case of the carbon injected multilayer sample, see Figure 5-12, a carbide formation is assumed at the molybdenum on silicon interface. At the silicon on molybdenum interface silicide formation is assumed. The first method shows a uniform modulation of all the Bragg peaks as a function of the Bragg order in a GIXR curve, while the second method accounts for a redistribution of the height of individual Bragg peaks that is also observed in Figure 5-12.

An analysis of the effect of a change in $\Gamma$ on the GIXR plot of a multilayer explains how a redistribution of the peak heights can be present, while the positions of the maxima remain fixed. It is important to note that the modulation of the reflectivity is described by an envelope\textsuperscript{35} which is described by

\textbf{Eq. 5-1.} \quad $R_i = R_0 \sin^2 (m \pi \Gamma)$,

$R_i$ denoting the reflectivity of a single film at the reflectivity maximum, $R_0$ the reflectivity calculated from the Fresnel coefficients and $m$ the peak order.

\textbf{Eq. 5-1} shows that the reflectivity of a multilayer is modulated if we consider $\Gamma$ as a continuously varying variable. With $\Gamma=0.5$ it is found that $R_i = 0$ for all even orders. At the zeros of $R_i$ the reflected amplitudes of each film add up to zero and the reflectivity of the multilayer remains low, even for the case that the amplitudes from all periods add in phase.

\textsuperscript{34} for a complete description see e.g. http://www.kri.physik.uni-muenchen.de/crystal/teaching/content.html
From Eq. 5-1, the redistribution of Bragg peak heights can be explained. Statistical representations of the interlayers cause a reduction of the Bragg peaks. The reduction will simply be higher for higher order Bragg peaks. It will not cause a redistribution of the height of different Bragg orders.

![Graph of Reflected intensity vs Angle of incidence]

**Figure 5-13** Expansion of the GIXR curve due to contraction of the multilayer period. Note the difference with Figure 5-14.

![Graph of Reflected intensity vs Angle of incidence]

**Figure 5-14.** Modulation of the reflectivity. The dashed line indicates the modulation envelope. The multilayer period remains fixed, since the Bragg peaks are only redistributed within the modulation envelope.

Changes in the $\Gamma$-ratio will cause a shift in the modulation envelope and therefore a redistribution of the Bragg peaks. From experiments it is shown that a redistribution of peak heights occurs on annealing. Therefore it is concluded that small changes occur in $\Gamma$ during annealing. The mechanism behind this changing $\Gamma$ is a varying optical index of the interlayers. From the observations it is concluded that the period of the carbon-injected multilayers is stable. The small changes in the GIXR curve can be explained by a change in $\Gamma$, resulting in a shift of the modulation envelope.
5.5. Determination of the refractive index of the multilayer

It is found from simulations\textsuperscript{36} that a carbon interlayer thickness of one or two monolayers yields the highest reflectivity. The composition and thickness of this thin interlayer are very hard to determine. The refractive index of a multilayer\textsuperscript{37} can be found from the Bragg equation with correction term (Eq. 3-17). From a measured GIXR curve, the positions of the Bragg peaks of various orders are obtained. Eq. 3-17 can be rewritten as

\begin{equation}
[m \lambda / 2 d \sin (\theta)]^2 = [1 - 2 \delta_{\text{eff}} / \sin^2 (\theta_b)],
\end{equation}

The refractive index $\delta_{\text{eff}}$ in this formula is the weighted average index of the four materials in the coating

\begin{equation}
d \delta_{\text{eff}} = d_1 \delta_1 + d_{12} \delta_{12} + d_2 \delta_2 + d_{21} \delta_{21},
\end{equation}

The variables are described in Figure 5-15.

<table>
<thead>
<tr>
<th>Spacer</th>
<th>$d_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Interlayer</td>
<td>$d_{12}$</td>
</tr>
<tr>
<td>Absorber</td>
<td>$d_1$</td>
</tr>
<tr>
<td>Interlayer</td>
<td>$d_{21}$</td>
</tr>
</tbody>
</table>

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{figure5-15.png}
\caption{Four layer representation of one multilayer period.}
\end{figure}

Using a least squares fitting procedure the refractive index and the multilayer period are readily obtained from a plot of $[m \lambda / 2 \sin(\theta)]^2$ as a function of $[1 / \sin^2 (\theta)]$.\textsuperscript{38} The points fall on a straight line that intersects the y-axis at $d^2$ and has the slope $2\delta_{\text{eff}}^2$.

\textsuperscript{36} IMD, version 4.1.1, august 2000, written by David L. Windt.
\textsuperscript{37} T. Feigl, S. Yulin, N. Kaiser, R. Thielsch. "Magnetron sputtered EUV mirrors with high thermal stability"
An example of a plot obtained via this method is given in the next figure.

Figure 5-16. Plot of \([m \lambda / 2 \sin(\theta)]^2\) as a function of \(1/ \sin^2(\theta)\). The angles are determined from GIXR.

A summary of the values found from GIXR data of all samples having a \(\Gamma\)-ratio of 0.4 is given in Table 5-5, using the simplifications:

\[\delta_u \ll \delta_{\text{mo}}, \delta_{\text{ai}} \ll \delta_{\text{ai}}, d_i / d \ll 1.\]  

Eq. 5-3 can than be rewritten as

\[
\delta_{\text{eff}} = (d_{\text{mo}} / d) \delta_{\text{mo}} + (d_{\text{ai}} / d) (\delta_{\text{ai}} - \delta_{\text{ai}}) + (d_i / d) (\delta_i)
\]

Where \(d_{\text{mo}}\) is substituted for \(d_{\text{i}}, d_{\text{ai}}\) for \(d_{\text{ai}}, d_{\text{ai}}\) referring to the carbon implanted interlayer, for \(d_{\text{ai}}, d\) is substituted for \(d_{\text{ai}}\).

The value of \(\delta_{\text{eff}}\) found from experiment is plotted as a function of the \(\Gamma\)-ratio in Figure 5-17.
Figure 5-17. Average refractive index obtained at different molybdenum fractions. Both a lower gamma and a lower etching energy result in a lower value $\delta_{\text{eff}}$.

The values found for $\delta_{\text{eff}}$ are of the same magnitude as values calculated using Eq. 5-3. A molybdenum layer thickness of 1.64 nm is assumed and a silicon layer thickness of 3.66 nm. Both the carbon and the silicide interlayer thickness is 0.6 nm. From these values an average refractive index of $1.2 \times 10^{-5}$ is found.

<table>
<thead>
<tr>
<th>element</th>
<th>Average refractive index, $\delta_{\text{eff}}$ ($x10^{-5}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si</td>
<td>7.59</td>
</tr>
<tr>
<td>C</td>
<td>7.27</td>
</tr>
<tr>
<td>Mo</td>
<td>28.8</td>
</tr>
<tr>
<td>SiC</td>
<td>14.0</td>
</tr>
</tbody>
</table>

Table 5-4. Refractive index of elements for $\lambda = 0.154$ nm.
Table 5-5. Average refractive indices obtained from analysis of the carbon-implanted multilayers, having a $\Gamma$-ratio of 0.4. The etching energies are indicated.

The refractive index of the carbon-implanted multilayer matches the refractive index for Mo/Si multilayers. Figure 5-17 shows an increasing refractive index as a function of increasing $\Gamma$-ratio of the multilayer. This increase is explained by the higher value of $\delta$ of molybdenum, yielding a higher multilayer refractive index. Figure 5-17 also shows that $\delta_{\text{eff}}$ increases for higher implantation energies. This can be explained using Eq. 5-3, because the refractive index of the silicon carbide is higher than that of carbon. This increase is therefore explained by carbide forming at the interlayers.

<table>
<thead>
<tr>
<th>Etch energy (eV)</th>
<th>Average refractive index, $\delta_{\text{eff}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>500</td>
<td>1.3e-6</td>
</tr>
<tr>
<td>1000</td>
<td>1.5e-5</td>
</tr>
<tr>
<td>1500</td>
<td>1.6e-5</td>
</tr>
</tbody>
</table>
6. Conclusions

Annealing experiments have been performed on Mo/Si multilayers with and without barrier layers. Without protection the multilayer reflectivity decreases significantly on annealing above 375 K. The wavelength of maximal reflectivity also shifts on annealing, indicating a decrease of the multilayer period. Annealing at temperatures higher than 375 K results in a decrease in reflectivity of more than 1%. The annealing effects on reflectivity and period are largely independent of annealing time. Upon repetitive annealing no significant changes in multilayer period and reflectivity are found. To observe repetitive annealing effects, three samples have been measured. After the first annealing step the data points show a trend towards lower reflectivity and decreasing period. No decisive trend has been observed after the first annealing session.

From Auger measurements it is concluded that a Kaufman gun can be used successfully to implant carbon in electron beam deposited molybdenum/silicon multilayers. The presence of the carbon KLL peak was clearly observed after the etching step with the neon/methane mixture. Implantation of the molybdenum layers results in a much lower yield, than the silicon layers. This is attributed to the higher mass (factor three) of the molybdenum atoms relative to the silicon atom. After etching of the molybdenum layers, a fast decrease of the reflected in-situ x-ray signal was observed. This decrease in reflected intensity is explained by the fact that at the molybdenum layer the standing wave x-ray field reaches a maximum, whereas at the silicon layer a minimum is situated. Therefore the absorption of the carbon layer situated on the molybdenum interface results in a much higher absorption than the layer situated on the Si layer. It is therefore preferred that only the silicon layer is implanted.

Mo/Si multilayers with carbon at the Mo-on-Si interface show sufficient increase in thermal stability. At annealing of the carbon implanted Mo/Si multilayers at 425 K no GIXR peak shift was observed, whilst for the non-injected multilayers a shift of more than 2% was observed. The carbon content is strongly dependant on the implantation energy. A change in energy from 500eV to 1500eV results in an increase of the refractive index by 50%. This change in $\delta$ is tentatively explained by compound formation, since only the high value of $\delta$ of the SiC component can account for the observed high value of the multilayer refractive index.