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Reflectivity and surface roughness of multilayer-coated substrate recovery layers for EUV lithographic optics

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Abstract. We investigated the use of separation, or substrate recovery, layers (SRLs), to enable the reuse of optical substrates after the deposition of multilayer reflective coatings, in particular Mo/Si multilayers as used for EUV lithography. An organic material (polyimide), known from other work to reduce the roughness of the substrate, was applied to the optical substrate. It appeared to be possible to remove the multilayer coating, including the SRL, without any damage or roughening of the substrate surface. The SRL was spin-coated at 1500 to 6000 rpm on different substrate types (Si, quartz, Zerodur) with diameters up to 100 mm. For this range of parameters, the multilayer centroid wavelength value remained unchanged, and its reflectivity loss on applying the SRL was limited typically to 0.7%. The latter was shown to be caused by a minor increase of the SRL surface roughness in the high-spatial-frequency domain. The roughness, characterized with an atomic force microscope, remained constant at 0.2 nm during all stages of the substrate recovery process, independent of the initial substrate roughness.
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Subject terms: substrate recovery; spin coating; roughness; multilayer.

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1 Introduction

Presently, Mo/Si multilayers are intensively employed for development and production of optics for extreme ultraviolet lithography (EUVL) projection systems. In the future, when the critical dimensions of line printing need to be in the range of 30 nm and below,[1] this imaging technology will be necessary for the mass production of computer chips.

During EUV lithography tool operation, the performance of reflective mirrors may deteriorate due to surface-chemistry-induced contamination in the presence of background gases.[2] In addition, optics close to the plasma source may suffer during the interaction between the optic and plasma debris. Since the replacement of such optics involves manufacturing expensive, often aspherically curved substrates, a recovery process for the substrates would be beneficial. Recycling of substrates would also greatly reduce the development costs for iterative deposition processes of reflective multilayer coatings.

Although removal of multilayer coatings from substrates can be achieved by a number of methods (wet chemical etching, for example), such methods usually increase the substrate's surface roughness (>0.5 nm). To prevent such roughening, a separation layer can be added between the substrate and the multilayer, as described in Refs. 3 and 4. Although the results of using such layers are promising, their use generally reduces the initial reflectance of the multilayer system deposited on top. Any recovery method should meet strict roughness specifications for the optical surface before and after substrate recovery. A typical value for the high-spatial-frequency roughness required for a high initial reflectance is in the order of 0.2 nm or below. The method explored here meets this requirement.

A different method to reduce the substrate roughness consists in employing spin-on-glass coatings, which can handle temperatures of up to 900 °C. These may have applications in the manufacturing of collector optics for EUVL.[5] In contrast with the use of a polyimide layer, spin-on-glass coatings are not applicable as a substrate recovery process.

The main objective of this paper is to investigate the suitability of using a polyimide layer, known for its ability to reduce initial substrate roughness,[6,7] but here explored as a substrate recovery, or separation, layer (SRL). Our goal was to characterize the processes of repeated deposition and removal of Mo/Si multilayer coatings on single substrates. We present results on how this affected the Mo/Si multilayer surface roughness by comparing atomic force microscopy (AFM) roughness measurements between a reference sample and a test sample. The reference sample consisted of a Mo/Si multilayer on a silicon substrate, which was compared with the roughness of probed test substrates in all phases of its recovery process. We also present results on the EUV reflectivity for multilayers deposited on the

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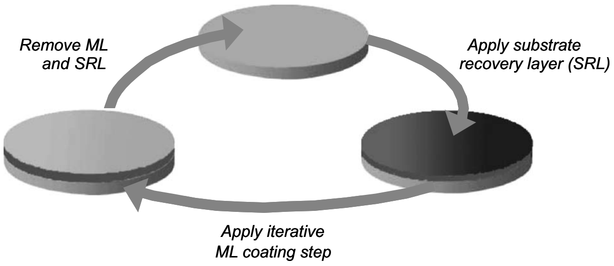

Fig. 1 Schematic representation of the substrate recovery process. The substrate recovery layer (SRL) is deposited on the substrate, followed by deposition of the multilayer (ML). By removing the SRL and the multilayer, the original substrate is recovered.

substrate with and without the polyimide layer, and we investigated possible reflectance losses or wavelength shifts measured at 13.5 nm.

2 Sample Preparation and Analysis

To determine the feasibility of substrate recovery using polyimide layers, we have employed the scheme presented in Fig. 1. The steps of the applied procedure are shown in Table 1. A monocrystalline Si wafer surface, characterized by AFM, was spin-coated with a polyimide layer at the Delft University of Technology (DIMES). Using superpolished Si wafers, various samples were prepared to investigate the polyimide quality resulting from different rotation speeds and thermal posttreatments. Polyimide was also successfully spin-coated on Zerodur substrates. After the polyimide coating was applied, the system was investigated by AFM and then multilayer-coated, applying a 50-period molybdenum/silicon multilayer, using the FOM coating facilities.[8,9] The multilayer period was controlled via an *in situ* x-ray reflectometer to ensure exact tuning to a centroid wavelength of 13.5 nm. To minimize interfacial roughness during deposition, ion beam polishing was applied after the completion of each Si layer. The background vacuum of the system is 10^{-8} mbar, obtained after a 150 °C bakeout procedure. The outgassing behavior of polyimide at enhanced temperatures was characterized in a separate chamber and showed mild outgassing at a 10^{-7}-mbar level, with no serious effect on the base pressure after the bakeout. More details on the multilayer coating process can be found in Refs. 8 and 9.

Table 1 Process steps applied to the EUV mirror substrates.

Sample stage	Process step
a. Substrate	
	↓ Spin coating of SRL
b. Substrate+SRL	
	↓ Coating of Mo/Si multilayer
c. Substrate+SRL+multilayer	
	↓ SRL and multilayer removal
d. Substrate	
	↓ Repeated spin coating of SRL
e. Cleaned substrate+SRL	
	↓ Repeated coating of Mo/Si multilayer
f. Cleaned substrate+SRL +multilayer	

After the multilayer coating, AFM surface characterization was repeated and the near-normal EUV reflectance around 13.5-nm wavelength was measured using beamline SX700 at storage ring Bessy II,[10] at the Physikalisch-Technische Bundesanstalt (PTB). Subsequently, the polyimide was removed in a dissolving bath; then the substrate was rinsed, and a propanol finishing applied. After recovery, the Si substrate was surface-characterized again, and the process of spin-coating the polyimide layer and electron beam deposition of the multilayer system was repeated (including the various analysis steps). As a reference, a 50-period Mo/Si multilayer, deposited onto a Si wafer without an SRL, was also included in the analysis chain. The measurements of the surface roughness were carried out using an AFM (Digital Instruments) at Carl Zeiss SMT AG in Oberkochen. The high-spatial-frequency surface roughness was extracted from 1×1-μm^2 scans at three positions on the wafers, one at the center and two points 6 mm from the center. In addition to the AFM measurements, specular and off-specular x-ray measurements (rocking curves) were performed with a Philips X'Pert double-crystal x-ray diffractometer using Cu Kα radiation (0.154 nm).

3 Results and Discussion

3.1 *AFM Analysis*

Figure 2 shows the atomic force micrographs at selected stages in the substrate recovery cycle described in Table 1. The grayscale for the height, between 0 (black) and 2 nm (white), is the same for all figures. The rms roughness σ was calculated from

$$\sigma^2 = \frac{1}{mn}\sum_{i=0}^{m}\sum_{j=0}^{n} z_{i,j}^2 - \left(\frac{1}{mn}\sum_{i=0}^{m}\sum_{j=0}^{n} z_{i,j}\right)^2, \tag{1}$$

where z_{ij} is the height of the scan point with indices i and j, while m and n are the maximum values of i and j. The calculated experimental roughness values are averaged over the probed area and depicted in Fig. 2.

From Fig. 2 we concluded that the AFM-characterized surface roughness of the Mo/Si multilayers on polyimide-coated silicon substrates remained unchanged during the entire cycle of multilayer deposition, removal, and redeposition. In addition, the surface roughness did not differ significantly (within 0.01 nm) from the reference multilayer deposited without an SRL. This suggests that the application and removal of this type of SRL and multilayer does not influence the substrate quality in the high-spatial-frequency roughness (HSFR) regime, below 1-μm wavelength, as probed by AFM.

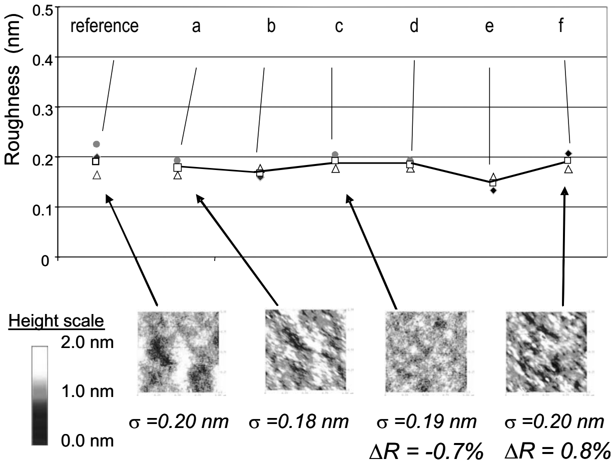

Fig. 2 AFM surface roughness measurements. The grayscale corresponds to roughness and ranges between 0 (black) and 2 nm (white), the same range for all images. AFM images are also displayed for the reference sample, consisting of a multilayer on a silicon substrate, including stages a, c, and f as defined in Table 1. In addition to the three measurements of the roughness per sample (circles, triangles, and diamonds), the mean roughness of all three points per sample is also measured and displayed (solid line).

Additionally, independent of the initial substrate roughness, this 0.2-nm roughness was achieved on all probed substrates. This result shows, at least within the limited process window probed here, that the HSFR value (as determined by AFM) is independent of the investigated spin-coating parameters (rotation speed, sample size, and annealing treatment). The presence of a 0.2-nm limit in all cases, independent of the initial substrate conditions, suggests that it is caused by either a polymerization effect of the SRL material, or a limitation on the frequency range for which the AFM is sensitive. For this purpose, an additional method was employed to characterize the HSFR values (see Sec. 3.2). We note that smoothing of rough substrates by polyimide was also reported in Ref. 7.

Further analysis of the area-averaged AFM measurement data by comparison over the frequency range of the roughness indicated minor differences between the roughness of a bare substrate and the SRL treated samples. To this end we have calculated the power spectral density (PSD) curves from the AFM data (Fig. 3). The PSDs calculated from samples on a monocrystalline Si substrate show higher roughness in parts of the mid spatial frequency (MSF) domain (lateral scale above 1 μm) at stage c (SRL spin-coated and multilayer-coated). However, they also show a lower value in the same range at stage f (i.e., SRL spin-coated and multilayer-coated on removal of the first SRL and multilayer). These PSD curves suggest that the SRL slightly increases the roughness in the MSF domain, but, after removing the SRL and multilayer and recoating with the SRL and multilayer again, a roughness comparable to the bare substrate is obtained. The small multilayer roughness decrease at stage f is in agreement with the small reflectivity increase observed (Fig. 2). Obviously, the area-averaged AFM data do not reveal the differences in different roughness regimes, and the frequency dependence of the smoothing process remains to be investigated. Note that the PSD curves show no difference in HSF domain in the lateral scale range below 0.1 μm, possibly due to the limited resolution of the AFM probing of the surface roughness. This might be caused by the finite dimension of the microscope tip. This limitation leaves room for a small roughness increase in this range when applying the polyimide, which could explain the small reflectivity decrease, observed in Fig. 2 (stage c).

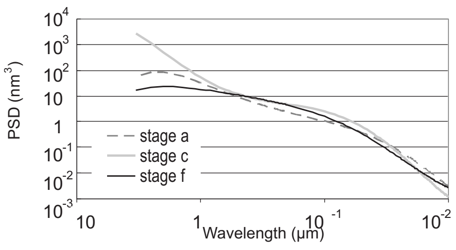

Fig. 3 Power spectral densities of samples in stages a and f, showing a slightly higher roughness at stage f in the frequency range from 0.01 to 1 μm.

3.2 *Hard-X-Ray Scattering*

Besides having a high throughput of the optical system, EUV projection lithography systems also require low flare. In addition to at-wavelength measurements of these quantities, indications for such quantities can readily be obtained from specular- and diffuse-scattering experiments at hard-x-ray facilities.[11] Such measurements can also provide information on roughness in the HSFR domain, especially at the higher frequencies, which are difficult to assess by AFM.

From the unchanged modulation of the Bragg peak's intensity in the specular reflectivity experiments (not shown here), we determined that the layered structure of the multilayer did not change significantly when applying a substrate recovery layer, independent of the investigated spin-coating parameters (i.e., rotation speed and temperature treatment). However, a small decrease of the reflected intensity of the high-order Bragg peaks suggested that the multilayer total roughness increased slightly when the polyimide was applied.

For roughness quantification over an extended range of frequencies, we have carried out diffuse scattering measurements on a reference sample without an SRL and on three samples with SRLs that were applied using different rotation speeds and temperature treatments during spin coating (Fig. 4). This was done to obtain an indication of the parameter dependence of the process, and we selected a rotation speed for samples 1 and 2 that was twice the value used for sample 3. Also, the temperature of the postannealing treatment for sample 1 was half that used for the other two samples.

To analyze the different results, we have used the intensity levels of the side wings of the diffuse-scattering data, and not the main specularly reflected radiation (small differences there might be caused by nonflatness of the samples).

The roughness period Λ for x-ray scattering is given by the formula

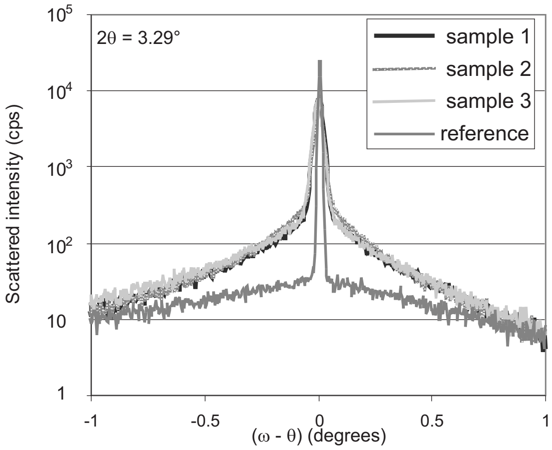

Fig. 4 Diffuse reflectivity at the Cu Kα wavelength versus $\omega - \theta$ around the fifth-order Bragg peak, where ω is the incident angle and $\theta = 1.645$ deg the detection angle. The fifth-order Bragg peak is chosen to obtain a reasonable rocking range at sufficient signal-to-noise ratio. The rotation speed of samples 1 and 2 was twice that of sample 3. The temperature of the post annealing treatment of sample 1 was almost half that of the other two samples.

$$\Lambda = \frac{\lambda}{\cos(2\theta - \omega) - \cos\omega}, \qquad (2)$$

where the detector angle 2θ is fixed at the position of the fifth-order Bragg peak (3.29 deg), and ω is the incident angle. From this, the scattered intensity provides information about the multilayer roughness in the HSF domain (lateral scale below 1 μm).

The increase of the diffuse scattering around the specular peak indicated the presence of a high-spatial-frequency component in the multilayer roughness induced by the polyimide layer under the multilayer. It is noted from these measurements that x-ray diffuse scattering was indeed found to be more sensitive in determining the HSFR of the multilayer structure than was the AFM analysis. This could be caused by the fact that the AFM, having a finite tip radius, probes only the relatively smooth SiO_2 top layer of the multilayer, and not as much of the underlying interfaces. Another factor is that the x-ray wavelength used here rather probes the average interface roughness than the top surface. It seems that the multilayer grows rougher on the polyimide than on a bare substrate, and it is likely that this roughness is more pronounced in the first periods than near the surface. Next to the oxide, this could be an argument why the AFM data do not explain the reflection losses observed.

In conclusion, no difference between the various SRL preparation procedures was observed. However, for even lower rotation speeds (half the rotation speed of sample 3, not shown here) an increase in roughness was observed. This is in agreement with general findings regarding the homogeneity of spin-coated fluids.[12]

3.3 *EUV Reflectivity*

Figure 5(a) shows the difference between the multilayer periods deposited on a substrate without an SRL, and those deposited on SRLs using the same rotation speeds and thermal posttreatments as in the previous section. For all cases, the addition of an SRL did not significantly change the period thickness of the added multilayer, to within an accuracy of 2 pm. This is a critical requirement for the optimization of iterative multilayer coatings using SRLs. The small variations are thought to be caused by tolerances in the deposition and alignment steps of these samples.

Figure 5(b) shows the reflectivity loss for the same samples with respect to the reference multilayer deposited directly on the substrate. The mean reflectivity of the multilayers deposited on an SRL-coated substrate was 0.7% lower than that of the reference sample without an SRL. This reduced reflectivity could be explained by the increased HSF surface roughness, as found by diffuse-scattering measurements (Sec. 3.2). Furthermore, no significant effect on reflectivity was found for the different parameters of polyimide spin coating (i.e., rotation speed, thermal treatment temperature).

After cleaning the silicon substrates, spin coating with polyimide, and again depositing a multilayer, the reflectivity did not decrease any further. This indicates that no further roughening of the substrate occurred during the cleaning procedure. This is confirmed by the AFM analysis presented in Sec. 3.1.

Reflectivity measurements were also performed on multilayers deposited on polyimide-spin-coated Zerodur substrates. The reflectivity loss due to the presence of an SRL layer was found to be similar to the loss using silicon substrates ($<1\%$). Again, this is explained by the increase in

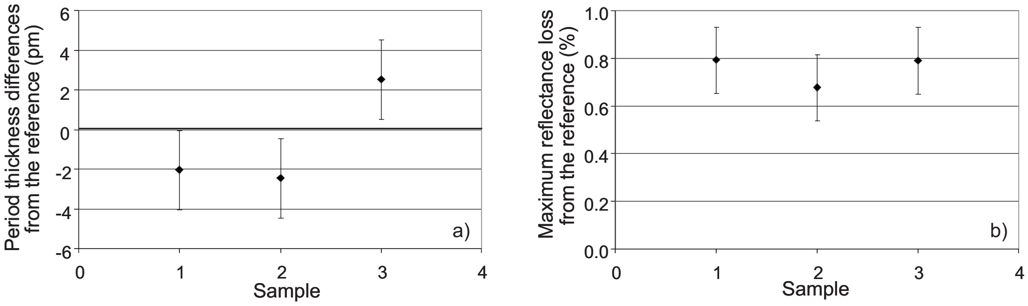

Fig. 5 The period thickness change with respect to a non-SRL reference sample is displayed (a) for three multilayers deposited on polyimide-spin-coated samples with different rotation speeds and temperatures during thermal posttreatment. The reflectivity loss for these samples with respect to the reference multilayer deposited directly on the substrate is illustrated in (b).

HSF surface roughness, as discussed in Sec. 3.2. Although spin coating with polyimide worked, the process of removing the SRL from Zerodur has, so far, resulted in an increased substrate roughness (0.5 to 1 nm). Other cleaning methods are still under investigation.

Since the spin-coating process and removal of polyimide on non-Si substrates is still under investigation, in this work we did not yet consider the additional difficulty of applying uniform polyimide coatings on curved optics. In addition, the effects of possible multilayer delamination due to heat load remain to be investigated. However, due to reflection from and absorption in the multilayer coating, no EUV light will actually reach the polyimide coating, suggesting that delamination in the polyimide, at least due to EUV absorption, is improbable.

4 Summary and Conclusions

The feasibility of applying a polyimide separation, or substrate recovery, layer for the purpose of applying EUV optical substrate recovery was investigated using AFM, hard-x-ray scattering, and at-wavelength reflectometry. On Si wafers, the processes of depositing a multilayer on an SRL layer, cleaning the substrate, and redepositing the SRL and multilayer resulted in a constant 0.2-nm roughness (AFM-characterized). Hard-x-ray diffuse-scattering measurements show that the roughness in the HSF range increased when applying an SRL, resulting in a 0.7% reflectivity loss observed using at-wavelength reflectometry. The cleaning and recoating of an SRL and multilayer did not decrease the reflectivity any further, nor did the centroid wavelength of the multilayer coating change (to within 2 pm). This demonstrates the usefulness of the process for substrate recovery or sample reusage.

On Zerodur substrates, x-ray scattering showed the same small reflectivity loss on applying an SRL, again attributed to the increase in HSF surface roughness observed after spin coating. In addition, the AFM-characterized HSFR, after applying the substrate recovery layer, was 0.2 nm, the same result as obtained after spin-coating silicon wafers.

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Biographies and photographs of the authors not available.