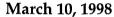
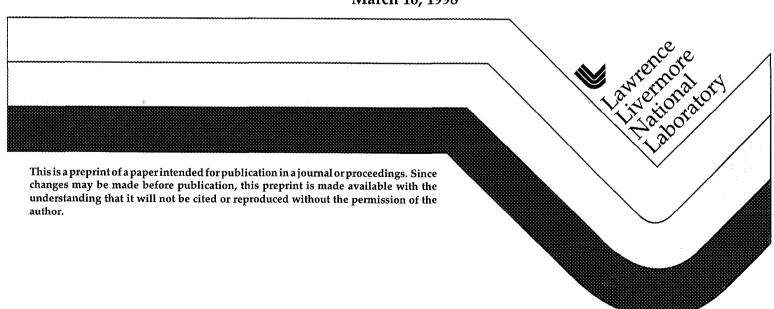
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Multilayer reflective coatings for extreme-ultraviolet lithography

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ABSTRACT

Multilayer mirror coatings which reflect extreme ultraviolet (EUV) radiation are a key enabling technology for EUV lithography. Mo/Si multilayers with reflectances of 67.5% at 13.4 nm are now routinely achieved and reflectances of 70.2% at 11.4 nm were obtained with Mo/Be multilayers. High reflectance is achieved with careful control of substrate quality, layer thicknesses, multilayer materials, interface quality, and surface termination. Reflectance and film stress were found to be stable relative to the requirements for application to EUV lithography. The run-to-run reproducibility of the reflectance peak position was characterized to be better than 0.2%, providing the required wavelength matching among the seven multilayer-coated mirrors used in the present lithography system design. Uniformity of coating was improved to better than 0.5% across 150 mm diameter substrates. These improvements in EUV multilayer mirror technology will enable us to meet the stringent specifications for coating the large optical substrates for our next-generation EUV lithography system.

Keywords: Extreme ultraviolet (EUV) lithography, reflective coatings, multilayers, reflectance, stress, radiation stability, sputtering deposition, uniformity, reproducibility.

1. INTRODUCTION

The present consensus design for an industrially viable extreme-ultraviolet (EUV) projection lithography system incorporates multiple reflective optics: (1) four condenser optics to collect EUV radiation from the source and illuminate the mask; (2) a reflective mask consisting of an integrated circuit metalization pattern on a multilayer mirror; and (3) four precision projection optics to project a reduced image of the mask onto a resist-coated wafer. Seven of the nine surfaces operate at near-normal incidence and require coatings with EUV multilayer mirrors. The EUV projection lithography system throughput is therefore a strong function of the multilayer reflectance because of the seven reflection design.

The multilayer coatings typically consist of alternating layers of molybdenum and silicon (Mo/Si) or molybdenum and beryllium (Mo/Be), where the thicknesses of each layer are determined by the trade-off between maximizing the constructive interference of the beams reflected at each interface and minimizing the overall absorption to enable more interfaces to contribute to the reflectance.² The resulting multilayer structures resemble a quarter-wave stack in which the relative thickness of the Mo layers in the bilayer has been slightly reduced. This results in individual thicknesses of 2.8 nm for Mo and 4.1 nm for Si in the Mo/Si case, or 2.3 nm for Mo and 3.4 nm for Be in the Mo/Be case.

The multilayer mirrors must meet stringent requirements for a production EUV projection lithography system to be practical in terms of performance and throughput. Initial lithography system throughput analysis and cost-of-ownership estimates have led us to set goals for multilayer mirrors with 70% or higher reflectance which is stable for 3–5 years.³ Five years ago, the Mo/Si multilayers had already proven to be effective reflective coatings for normal incidence in the 13.0–13.5 nm wavelength region with reflectances around 65.5% being achieved routinely.⁴ Mo/Be multilayers had been much less investigated but reflectances around 68% at normal incidence were reported in the 11.1–11.5 wavelength region.⁵ With

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the likelihood of better reflectances in the near future, it is no exaggeration to claim that these developments in reflective multilayer technology have enabled EUV lithography.

However, several issues other than the multilayer reflectance were then raised. The precision projection optics must be fabricated with aspheric surface figures that are accurate to within 0.25 nm to maintain diffraction-limited performance. This dictates a rigorous control on the thickness distribution of the deposited multilayers and an accurate knowledge of the multilayer stress since they both affect the final figure of the optics. Also, since these multilayers mirrors have fairly narrow bandpasses, about 0.56 nm for Mo/Si, the reflectance peak positions of the mirrors must be all aligned to within 0.05 nm to preserve at least 90% of the optimum throughput. This means that the multilayer coating on each element must have the same bilayer thickness to within an accuracy of 0.025 nm. This imposes an unprecedented control on the run-to-run reproducibility of the deposition system and an accurate knowledge of the multilayer stability as a function of temperature and radiation since the mirrors are not all exposed to the same environment.

This manuscript describes our current status of knowledge on the reflectivity, the stress and the stability of the Mo/Si and Mo/Be multilayer mirrors (Section 2). It also discusses some of the recent developments in multilayer mirror technology which make the realization of advanced optical designs for the EUV projection lithography system possible (Section 3). Finally, it reviews remaining issues of the multilayer technology that must be solved to enable fabrication of EUV lithography production tools (Section 4).

2. MULTILAYER DEVELOPMENT

The three key issues related to the material properties of EUV multilayer mirrors are reflectance, stress and stability; with reflectance having the most importance. In the following sections we treat each of these issues for both the Mo/Si and the Mo/Be multilayer mirrors.

2.1 Normal incidence reflectance

The EUV projection lithography system throughput is a strong function of the multilayer reflectance because of the seven reflection design. It is therefore critical that the multilayer mirrors have the highest possible normal incidence reflectance. Mo/Si and Mo/Be are today's material pairs of choice due to both their superior optical properties in the EUV wavelength region and their structural properties on the sub-nanometer scale. They are the only material pairs for which multilayer mirrors with normal incidence reflectances higher than 60% were achieved in the EUV spectral region. 7,8

Figure 1 shows the reflectance versus wavelength curves of the best Mo/Si and Mo/Be multilayer mirrors produced to date in our laboratory. The measurements were made at 5° from normal incidence using the EUV reflectometer at the Lawrence Berkeley National Laboratory (LBNL) which is attached to beamline 6.3.2 of the Advanced Light Source (ALS).⁹ The reflectance curve of the Mo/Si multilayer reaches a peak value of 67.5% at 13.42 nm while the Mo/Be multilayer has a peak reflectance of 70.2% at 11.34 nm. The spectral bandwidth of these mirrors, measured at full width at half-maximum (FWHM), is 0.56 nm and 0.27 nm for the Mo/Si and Mo/Be multilayer mirrors, respectively. These multilayers were both deposited on standard Si<100> substrates with DC-magnetron sputtering using the deposition systems described in Section 3.1. The Mo/Si multilayer consists of 40 bilayers with a period thickness of 6.89 nm and a thickness ratio, i.e., the relative Mo layer thickness, of 0.37. The Mo/Be multilayer consists of 70 bilayers with a period thickness of 5.74 nm and a thickness ratio of 0.42. The Mo/Si multilayer has a Si layer as the top-most layer on the surface while the Mo/Be multilayer has a Be top layer.

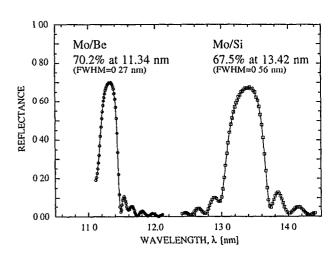


Figure 1. Reflectance response of typical Mo/Si and Mo/Be multilayer mirror coatings measured at 5° from normal incidence. Peak reflectances of 70.2% and 67.5% are routinely achieved for Mo/Be and Mo/Si, respectively.

It is possible to simulate these reflectance curves and extract information concerning the limitations that prevent higher peak reflectances from being achieved. For example, Fig. 2 shows the measured reflectance curve of the Mo/Si multilayer mirror shown in the previous figure (circles), together with the best theoretical fit to the data (solid line) and the theoretical reflectance of an ideal or perfect multilayer structure (dotted curve). Also shown in this figure is the calculated reflectance curve taking only the interface roughness into account (dash-dotted curve). The reflectance calculations were made using a standard recursive method 10,11 with optical constants derived from scattering factors taken from the literature. 12 The best fit to the data was obtained assuming linear interface width parameters¹³ (roughness) of 0.6 nm and 0.3 nm for the Mo-on-Si and Si-on-Mo interfaces, respectively, and a 4.5 nm thick oxide layer (SiO₂) on the surface of the multilayer. A similar fit to the Mo/Be multilayer reflectance curve of Fig. 1 can be obtained using interface widths of 0.4 nm and 0.2 nm for the Mo-on-Be and Be-on-Mo interfaces, respectively, and a 3.0 nm thick oxide layer (BeO) on the surface of the multilayer.

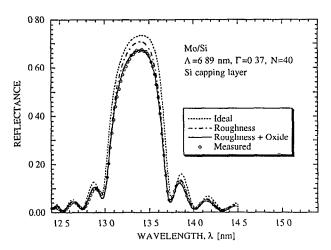
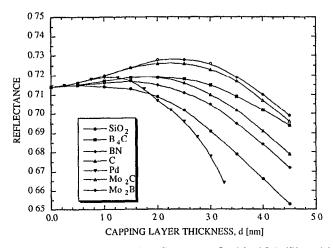


Figure 2. Measured reflectance of a typical Mo/Si multilayer compared to the calculated reflectances for an ideal multilayer, a multilayer with rough interfaces, and a multilayer with rough interfaces and an oxidized surface.

The model identifies the two major limitations to achieving the highest possible peak reflectances in a Mo/Si or a Mo/Be multilayer mirror. The theoretical peak reflectance of an ideal multilayer is ~75% for the Mo/Si multilayer mirrors and ~80% for the Mo/Be multilayer mirrors. However, the existence of diffuse interlayers of mixed composition at the layer boundaries limits the reflectance of each interface^{4,14} and the existence of a contamination or corrosion layer on the surface of the multilayer¹⁵ also significantly reduces the reflectance. For the Mo/Si multilayers, not much can be done with magnetron sputtering to further minimize the formation of the interlayer at the Mo-Si interfaces since the deposition conditions have been optimized exhaustively. Improvements may be possible, however, if the multilayers are deposited with ion beam sputtering since this technique offers more control on the energetics of the layer growth. For the Mo/Be multilayers, significant improvement can still be expected since research in Mo/Be multilayer is relatively new.

Concerning the second limitation, the formation of a contamination layer at the surface of the multilayer, there is definitely room for improvement. The problem was first reported by Underwood et al. 15 where the reflectance drop versus exposure time to air was measured for two Mo/Si multilayer mirrors, one with a Mo layer as the top layer and the other with a top Si layer. Although the sample with the top Si layer had a lower peak reflectance at the beginning, its performance remained unchanged after several months of exposure to air while the performance of the sample with the top Mo layer significantly decreased. When the Mo layer was exposed directly to air, it eventually became completely oxidized to MoO₃ and MoO2 and contaminated with carbonaceous materials causing a 10 to 12% decrease in absolute reflectance. The oxidation of Si is not as severe but still forms approximately 3 to 5 nm thick SiO₂ which causes a 4 to 5% decrease in reflectance. For the Mo/Be multilayers, we have found that it is preferable to have Be as the capping layer rather than Mo, showing once again that Mo strongly oxidizes. This suggests that reflectance increases (>2%) should be possible if a thin passivating layer of a non-reactive material (e.g., carbon) is deposited on the surface of the multilayer before exposure to air. The mechanical modifications necessary to deposit such an overcoat layer have been implemented in our magnetron sputtering deposition systems. Also, a theoretical investigation of candidate capping materials has recently been performed. Figure 3 shows the predicted reflectance improvements for different capping layers on an ideal Mo/Si multilayer with Si as the layer underneath the capping layer. Note, however, that the calculated curves shown in Fig. 3 are optimistic since they neglect the fact that these materials may also get contaminated or adsorb water vapor to some extent.

Finally, multilayer reflectance strongly depends on the high-spatial-frequency (HSF) roughness of the optical substrate. HSF substrate roughness not only degrades the smoothness of the multilayer interfaces, but more importantly, it causes high angle scatter of the EUV radiation. ^{16,17} Figure 4 shows the decreasing reflectance of Mo/Si multilayers deposited on zerodur substrates with increasing HSF roughness. The roughness was determined from 2 µm square atomic force microscopy (AFM) scans. Our typical substrates used for multilayer development—both fused silica optical flats and prime grade Si<100> wafers—have surface finishes which are routinely better than 0.1 nm rms. Advanced EUV lithography system designs



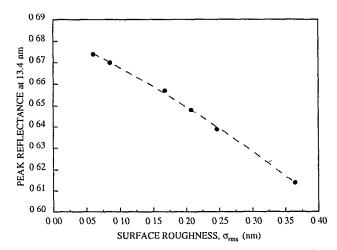


Figure 3. Calculated peak reflectances for ideal Mo/Si multilayers with a variety of increasingly thicker capping layer materials on top of the last Si layer.

Figure 4. The effect of substrate roughness upon multilayer peak reflectance. Substrates were Zerodur flats with varying levels of surface roughness. Roughness values shown correspond to the high spatial frequency component as measured by atomic force microscopy on $2 \, \mu m$ square scans.

require aspheric optical substrates with extremely tight specifications on aspheric figure and both mid- and high- spatial frequency roughness. However much recent progress has been achieved in fabricating ultra-polished aspheric optics and a clear development path for the required substrates has been identified.⁶

2.2 Residual stress

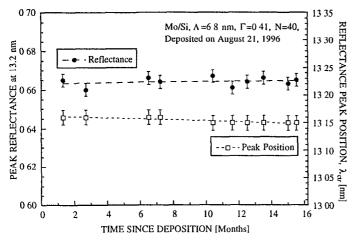
The EUV multilayers optimized for reflectance typically have a stress of -420 MPa (compressive) for Mo/Si and +330 MPa (tensile) for Mo/Be. This level of film stress is large enough to deform the figure of the projection optics in an EUV lithography system. Due to the stringent surface figure requirements for these optics, it is desirable to minimize deformation, and in particular non-spherical deformation, of the optics due to the multilayer film stress. Except near the edges, most of the deformation due to film stress should be spherical. It is expected that the spherical component of the deformation will be compensated by adjustment of the position of the optics during alignment; however, such methods may not compensate for some of the non-spherical component of the deformation. 19

Previous techniques for reducing stress in Mo/Si multilayer films included varying the composition, varying the base pressure, and post-deposition annealing. ²⁰⁻²⁸ However, any technique used to reduce the effects of multilayer film stress must do so without incurring a significant loss in reflectance, since the reflectance has a strong impact on the throughput of an EUV lithography tool. We have tested these methods and found that post-deposition annealing yields the greatest stress reduction at the lowest cost in reflectance. ¹⁸ For example, the stress can be reduced by 75% with only a 1.3% (absolute) drop in reflectance at annealing temperatures near 200 °C. However, since it has not been determined if the precisely figured substrates can withstand a 200 °C anneal, it was decided that to reduce risk a viable non-thermal (athermal) technique for stress reduction should also be developed.

Using an athermal buffer-layer technique with amorphous silicon and Mo/Be buffer-layers it was possible to obtain Mo/Be and Mo/Si multilayers with a near-zero net film stress and less than a 1% loss in reflectance. ¹⁸ For example a Mo/Be multilayer with 68.7% reflectance at 11.4 nm and a Mo/Si multilayer with 66.5% reflectance at 13.3 nm were produced with net stress values of less than 30 MPa.

2.3 Temporal and radiation stability

It is important that the EUV reflectance be stable over time and under EUV irradiation. The temporal stability of the reflectance and peak wavelength of a Mo/Si multilayer with a reflectance of approximately 66.4% was monitored over a period of 18 months (Fig. 5). The reflectance (circles) remained stable and the fluctuation in the measured value indicates a relative uncertainty of 0.5% in the measurements. The reflectance peak position slightly shifted, however, from 13.16 nm to



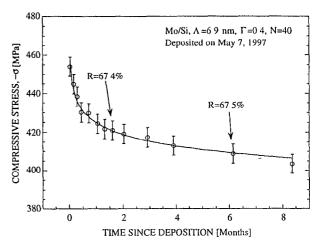


Figure 5. Temporal stability of peak reflectance and peak wavelength for a typical Mo/Si multilayer.

Figure 6. Temporal stability of stress for a typical Mo/Si multilayer. After the initial relaxation period of about 10 days, subsequent stress changes are not expected to affect the performance of an EUV lithography system.

13.15 nm. This small shift is indicative of a bilayer thickness contraction which can most likely be attributed to a slow silicide formation at the interfaces.²⁹ We recently began monitoring the stress (and reflectance) of another Mo/Si multilayer which had as-deposited stress of -455 MPa. As shown in Fig. 6, the stress was observed to decrease significantly (7%) during the first month, but changed by only 4% thereafter, which is not a problem for EUV lithography systems.¹⁹

It is also important that the multilayer mirrors maintain high reflectance after exposure to radiation typical of an EUV lithography system. The stability of high reflectance Mo/Si multilayers under exposure to EUV radiation has been studied by several researchers. However, the study undertaken in 1992 by Gaines *et al.*³⁰ is the only reported work where the incident spectrum and dose were carefully matched to the spectrum and dose incident on the first imaging optic of an EUV lithography camera system. In addition, this was the only reported work where the temperature was carefully controlled to eliminate effects due to thermal annealing. No measurable degradation in reflectance was measured; hence there is some assurance that radiation damage should not affect the first imaging mirror in an EUV lithography camera system after one year of operation. However the report did not examine the radiation damage susceptibility of the first stage condenser optics which receive not only much higher doses of EUV radiation, but also high doses of UV, visible, and IR radiation.

Although we believe the multilayers are stable against the radiation flux present in EUV lithography systems, we are currently performing more exhaustive radiation stability experiments in which we increase the exposure dose by a factor of 10 to 100x over previous experiments.

3. DEPOSITION TECHNOLOGIES

As shown in the previous sections, the current state-of-the-art EUV multilayer mirrors are of sufficient quality to be used in a commercial EUV lithography system. However, several challenges must be overcome in deposition technology for these coatings to be deposited with the thickness control necessary to meet the stringent specifications over the large substrates required.

3.1 Deposition system and procedure

Our Mo/Si and Mo/Be multilayers are currently deposited in two similar DC-magnetron sputtering systems (Fig. 7).³¹ The primary difference between the Mo/Si and Mo/Be deposition systems is that the Mo/Be system is housed in an exhausted enclosure to prevent exposure to toxic Be dust. The systems contain two 12.7 x 25.4 cm rectangular sputter sources placed 180° apart, i.e., at diametrically opposite sides of a circular chamber, with chimneys that limit the deposition region to the area directly above them. Two substrates located 90° apart are held face down on a rotating table (platter) at a distance of 6 cm above the sources in a "sputter-up" configuration. The sputter chamber is typically cryo-pumped until the pressure is in

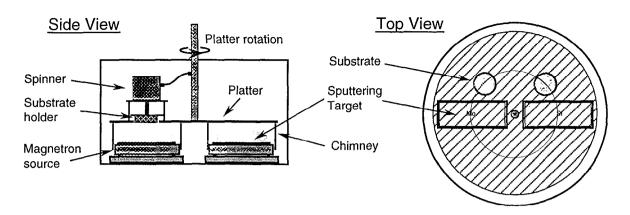


Figure 7. Layout of the DC magnetron sputter system used to deposit multilayer coatings.

the 10^{-8} Torr range. Ultrahigh purity Ar at pressure of 0.50–2.00 mTorr is used to sputter the Si, Mo and Be targets at source powers of 100–400 W.

The multilayers are deposited by sweeping the substrates above the sources with a controlled rotation of the platter. A bilayer is deposited with each complete revolution of the platter. The layer thicknesses are determined by the time the substrate is exposed to the source which, in turn, depends on the substrate transit velocity. Additionally, the substrates are spun around their axis of symmetry which provides better azimuthal uniformity by averaging out the spatial variation of the deposition rates. The arrangement of the substrates and the sputter sources is such that at any given time only one substrate is over a source and being coated. Therefore, the two substrates can be coated with identical or completely different (and independent) multilayer structures, which is very useful in several comparative studies.

3.2 Uniform multilayer coatings

To preserve the figure of the projection optics, thickness control to within 0.5% will be necessary across an optical substrate 150 mm in diameter. This imposes a rigorous control on the uniformity of the multilayer period thickness over the surface of the substrate.

The relative thickness variation of our Mo/Si multilayers is about 6% over a 150 mm diameter region when the deposition is made by rotating the platter at constant velocity (Fig. 8). We can improve the uniformity of multilayer thickness by use of a platter velocity profiling technique in which the platter revolution speed is varied as a function of its position relative to the sources. The optimum velocity profile is determined by an iterative approach. In our case, the peripheral coating thickness obtained from a constant velocity rotation is too thin. Therefore, the substrate is moved more slowly while the periphery is entering and leaving the deposition zones. In this manner, variation in coating thickness was reduced from 5.2% to 0.4% peak-to-valley over a 140 mm diameter region on flat Si substrates.

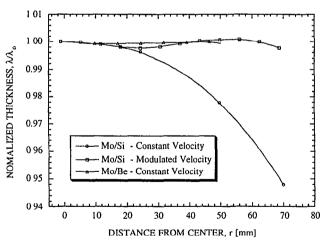


Figure 8. Spatial uniformity of Mo/Si multilayer film thickness has been improved from 5.2% peak-to-valley to better than 0.4% over a 140 mm diameter region on flat Si substrates. Mo/Be multilayers have 0.1% uniformity over 100 mm diameter.

Also shown in Fig. 8 is the thickness uniformity of our Mo/Be multilayers when deposited with a constant platter rotation velocity. In this case, the uniformity is much better, within 0.1% peak-to-valley, due to an improved design of the sputtering sources. Indeed, with these sources the magnetic field is such that the erosion profile on the sputtering target is much more uniform resulting in a more uniform flux distribution of the deposition.

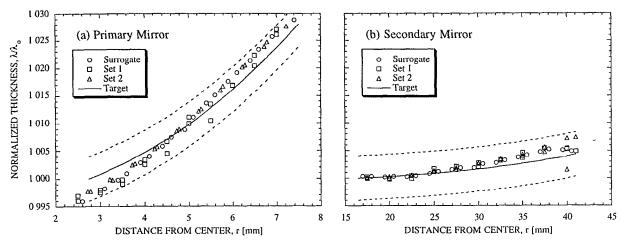


Figure 9. Thickness gradient of multilayers deposited on a 10x Schwarzschild camera for a prototype EUV lithography system. Figures 9a and 9b represent the primary and secondary mirrors of the Schwarzschild system, respectively. The solid line is the target value, the dashed lines represent the boundaries of the specifications, and the symbols are the measured values for three subsequent depositions.

3.3 Graded multilayer coatings

Some optics require multilayer coatings with a thickness gradient in order to accommodate a variation in angle of incidence of the EUV radiation. A prime example is the first condenser optic which must collect a large solid angle of the radiation from the laser plasma source. Other examples are the optics of the EUV 10x microstepper system, i.e., the two Schwarzschild projection optics and the ellipsoidal condenser optic. 32

We have coated the mirrors for two sets of Schwarzschild projection and condenser optics for the 10x microstepper system. The tolerances for these optics were about ± 0.1 nm, which represent $\pm 0.75\%$ of the EUV reflectance peak position (13.4 nm). We obtained the desired thickness gradient by using a shadow mask in front of each of the spinning optics, while the absolute value of the thickness was adjusted with the rotation speed of the platter. The shape of each shadow mask was obtained in several (2 to 3) iterations using data from a previous mask to derive the required change in mask shape. The mask-making iterations were stopped when the deviations from the desired profile were less than $\pm 0.4\%$ peak. Figures 9a

and 9b show the resulting thickness profiles for the two projection optics for three consecutive deposition runs. The three sets of data in each plot show that we can reproduce the thickness profile from one deposition run to another within a 0.1% error when the same mask is used. This is about a factor of 8 better than the present specifications. The absolute value of the multilayer thickness, however, showed larger variations from run-to-run with a standard deviation of 0.08 nm, just within the allowed tolerances. It will be necessary to reduce these variations if we want to make use of the excellent reproducibility of the profile data.

3.4 Wavelength matching

Run-to-run repeatability of deposition rate is critical to insure that multiple optics in a system operate at the same peak wavelength. Wavelength-mismatched optics reduce the optical throughput of a system with multiple reflections. Figure 10 shows how the throughput of a 7 reflection system is reduced as the standard deviation of the optic-to-optic mismatch increases. The reflectance-wavelength response curves were assumed to have a gaussian distribution. We

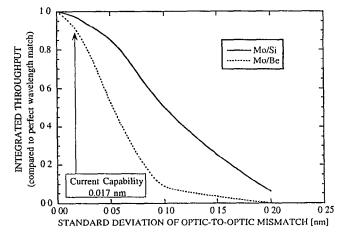


Figure 10. Optical throughput loss expected from optic-to-optic mismatch of peak wavelength for an optical system with 7 multilayer mirrors. The narrower bandpass of Mo/Be mirrors (0.27 nm FWHM) results in higher loss than for Mo/Si (0.54 nm FWHM). We currently achieve wavelength matching of 0.017 nm at 1 standard deviation.

have measured the standard deviation of our run-to-run repeatability of peak wavelength to be 0.017 nm, or 0.13% on flat Si wafers. According to Fig. 10, this results in an optical throughput loss of 4% for Mo/Si and 10% for Mo/Be. Mo/Be suffers a greater throughput loss for the same level of process repeatability because the narrower bandpass of Mo/Be (FWHM = 0.27 nm vs. 0.56 nm for Mo/Si) amplifies the effect of mismatching.

4. REMAINING ISSUES

An increasing part of our work is in the multilayer coating of relatively large optics to demonstrate the commercial viability of high throughput EUV lithography. These optics will be aspherical, some will be deeply concave, and will require either highly uniform or accurately graded coatings. We are retrofitting our existing deposition system as well as designing new deposition systems to meet the challenges of coating large optics—for both existing and future advanced designs of EUV lithography systems.

The high cost of the optical substrates makes it desirable to have techniques available for substrate recovery—that is, the ability to either remove or overcoat a multilayer which does not meet performance specifications. Multiple approaches for substrate recovery are possible, including wet etching, dry etching and simply coating over the original multilayer.

5. CONCLUSION

Multilayer mirror technology has advanced to meet most of the stringent requirements of extreme-ultraviolet (EUV) lithography. Near-normal incidence (5°) reflectances of 67.5% at 13.4 nm are now routinely achieved with Mo/Si multilayers; while a reflectance of 70.2% at 11.4 nm was obtained with Mo/Be multilayers. Methods to reduce or counteract the stress of these two multilayer systems with minimal loss of reflectance were developed. The reflectance and stress of the as-deposited multilayers were also found to be relatively stable after initial time periods of 10 days to 40 days for the reflectance or the stress, respectively.

In addition to these material science related multilayer developments, several improvements in the deposition technology were made. High reflectance coatings can now be deposited with layer thickness control better than 0.5% across substrates up to 150 mm in diameter. The run-to-run reproducibility of our deposition system, which is essential to obtain near-perfect wavelength matching among the different elements of the EUV lithography camera, was characterized to be better than 0.2%. The primary remaining challenge lies in applying our high performance coatings to the large optics (up to 270 mm diameter) needed to demonstrate EUV lithography.

6. ACKNOWLEDGMENTS

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