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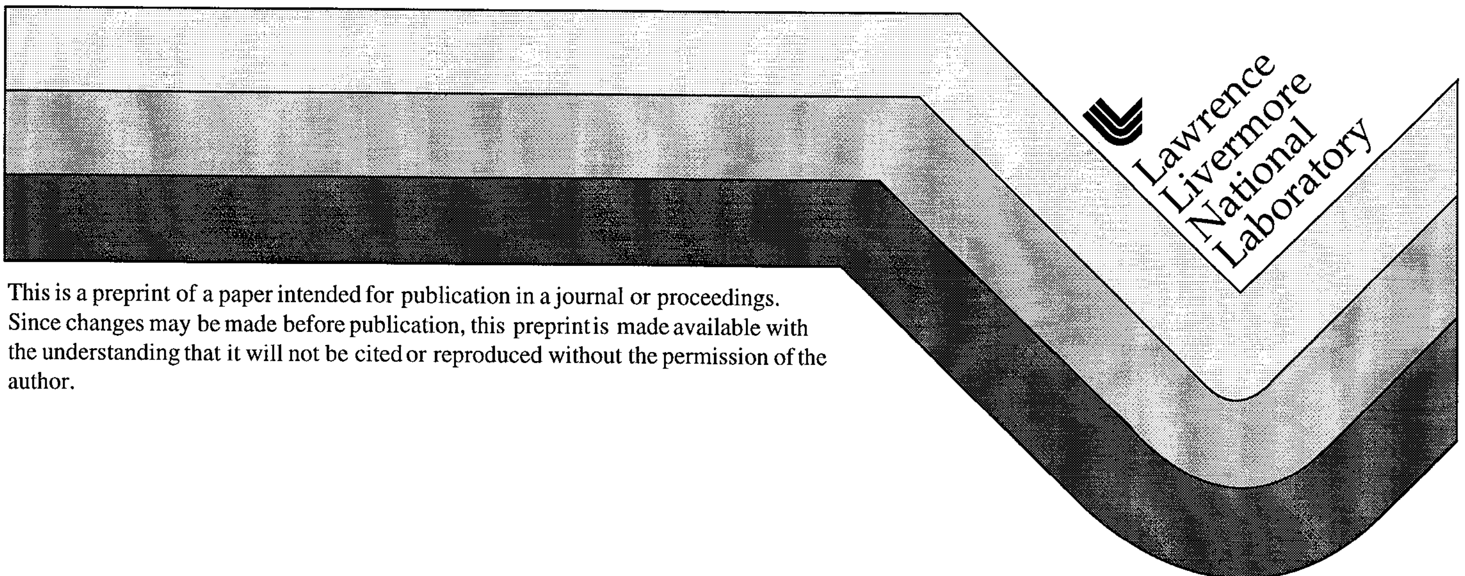

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Lifetime studies of Mo/Si and Mo/Be multilayer coatings for extreme ultraviolet lithography

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ABSTRACT

Extreme Ultraviolet Lithography (EUVL) is a candidate for future application by the semiconductor industry in the production of sub-100 nm feature sizes in integrated circuits. Using multilayer reflective coatings optimized at wavelengths ranging from 11 to 14 nm, EUVL represents a potential successor to currently existing optical lithography techniques. In order to assess lifetimes of the multilayer coatings under realistic conditions, a series of radiation stability tests has been performed. In each run a dose of EUV radiation equivalent to several months of lithographic operation was applied to Mo/Si and Mo/Be multilayer coatings within a few days. Depending on the residual gas concentration in the vacuum environment, surface deposition of carbon during the exposure lead to losses in the multilayer reflectivity. However, in none of the experimental runs was structural damage within the bulk of the multilayers observed. Mo/Si multilayer coatings recovered their full original reflectivity after removal of the carbon layer by an ozone cleaning method. Auger depth profiling on Mo/Be multilayers indicate that carbon penetrated into the Be top layer during illumination with high doses of EUV radiation. Subsequent ozone cleaning fully removed the carbon, but revealed enhanced oxidation of the area illuminated, which led to an irreversible loss in reflectance on the order of 1%.

Keywords: Extreme ultraviolet (EUV) lithography, multilayer reflective coatings, radiation stability, surface contamination

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1. INTRODUCTION

High precision optical surfaces with soft x-ray multilayer reflective coatings are key elements of any extreme ultraviolet lithography (EUVL) imaging system. These thin film coatings are specially designed for optimal performance under illumination with EUV radiation and their optical properties must remain unaltered under the radiation load throughout the lifetime of the system. Small field prototype EUVL systems using 2 mirrors in a Schwarzschild configuration have recently demonstrated the capability of printing sub-100 nm feature sizes with high quality[1], which made EUVL technology a leading candidate for future application by the semiconductor industry[2]. Within the current EUVL program efforts are underway in order to demonstrate the feasibility of full-field wafer exposures at a rate of 10+ wafers per hour using a multi-mirror EUV optical design[3]. These production-like conditions will require unparalleled EUV radiation intensities and doses on the condenser as well as on the projection optics. In-band EUV power of 15 W and integrated doses of several hundred MJ during a full year of operation are projected in order to support production level wafer throughput. The cluster jet laser plasma source delivering these power levels is under development at Sandia National Laboratories[4].

In order to assess stability of Mo/Be and Mo/Si multilayer reflective coatings during the lifetime of an EUVL optical system, several multilayer coatings have been exposed to undulator radiation at the Advanced Light Source (ALS) of the Lawrence Berkeley National Laboratory. Accelerating the experiments using intensities much higher than anticipated in an EUVL environment kept the individual exposure duration within a few days. Dose levels obtained are equivalent to EUVL-realistic conditions on the order of months to years of continuous exposure.

EUVL optical components need to be enclosed in a high vacuum environment in order to minimize absorption of EUV radiation by background gases during EUVL operation. This environment with a minimum pressure of 10^{-6} Torr together with the EUV illumination represents special conditions, which may influence the lifetime of multilayer-coated components. Factors anticipated to have an impact on the multilayer optical performance during EUVL operation are the residual gas composition as well as EUV radiation intensity and dose.

In particular hydrocarbons outgassing from the photoresist during the lithographic process have already been identified as potential sources of carbon deposition on EUV illuminated surfaces. Mitigation techniques using a gas curtain[5] inside the EUVL optical system have been developed in order to prevent the hydrocarbons from reaching the optical surfaces. Other factors, which may influence the lifetime of EUVL optical components, include temperature effects, stress buildup and temporal stability of the multilayer coatings. These effects, which are not directly related to EUV radiation, have been investigated thoroughly[6]. Results are being considered in the design of the EUVL systems in order to minimize risks connected with these factors[7].

2. EXPERIMENTAL

2.1 Overall experimental approach

Although carbon deposition on x-ray optical elements under exposure in general is a well-known effect, little information exists on the radiation hardness of multilayer coatings itself. A single publication reports about controlled exposures of Mo/Si coatings to monochromatic undulator radiation[8]. No negative effect was observed after a 9-hour exposure at an average intensity of 0.75 W/cm^2. At the time of the experiment the corresponding dose was considered to simulate a one-year exposure of a hypothetical EUV component. However, in current EUVL optical designs an intensity of more than 1 W/cm^2 in-band EUV radiation is projected for some of the multilayer coated surfaces during normal operation. Therefore the earlier experiment simulated realistic conditions just for a few hours of EUV operation. As a consequence the main goal for this study is the search for effects possibly occurring at much higher doses. In a first step, several test multilayers were exposed under controlled vacuum and thermal conditions to a focussed spot of narrow-band EUV undulator radiation at the ALS interferometer beamline 12.0.1[9]. In a second step, after the exposure changes in the optical performance of the multilayer coatings were probed at the ALS calibration and standards beamline 6.3.2[10]. Full spatial mapping of the optical properties of multilayer coatings in the area exposed allows detection of variations with a spatial resolution of 0.1 mm.

2.2 Exposures at the ALS interferometry beamline 12.0.1

ALS beamline 12.0.1 utilizes undulator radiation[9] and contains several optical components for spatial and spectral beam shaping. The higher spectral orders of the undulator are filtered to a large extent by grazing incidence reflection on the beamline optical components (Figure 1). The total EUV in-band power available for exposures is on the order of 50 mW.

Third order contamination is expected to be less than 10% with insignificant contributions of other higher orders. A Kirkpatrick-Baez mirror pair is used to focus the radiation near the sample. The spots exposed have a surface area on the order of 10^{-3} cm^2 and therefore an intensity of up to 10 W/cm^2 can be delivered. Controlled vacuum conditions monitored by a residual gas analyzer were maintained by separating the exposure chamber from the rest of the beamline with a 0.1-mm diameter aperture. The temperature of the sample, the sample photoemission current, and the storage ring current were monitored throughout the whole exposure time. Baking temperature of the vacuum chamber did not exceed 100 degrees C in order to reduce the risk of temperature-induced effects on the sample. Temperature gradients occurring on the samples were thoroughly modeled and determined to be negligible for the purpose of the experiment. High thermal conductivity between the test wafer pieces and a copper heat sink was achieved by using an indium foil. The temperature rise observed during the exposure was on the order of a few degrees.

Mo/Si exposures in the current study were performed on the M7 45-degree turning mirror, which is an integral part of end station 12.0.1.2. Therefore, in contrast to the Mo/Be exposures, there was no full control over the experimental parameters and only estimates on the doses and conditions of the Mo/Si exposures can be made. These results may serve as an example for qualitative assessment of the radiation hardness of operational EUV Mo/Si multilayer coated optical components.

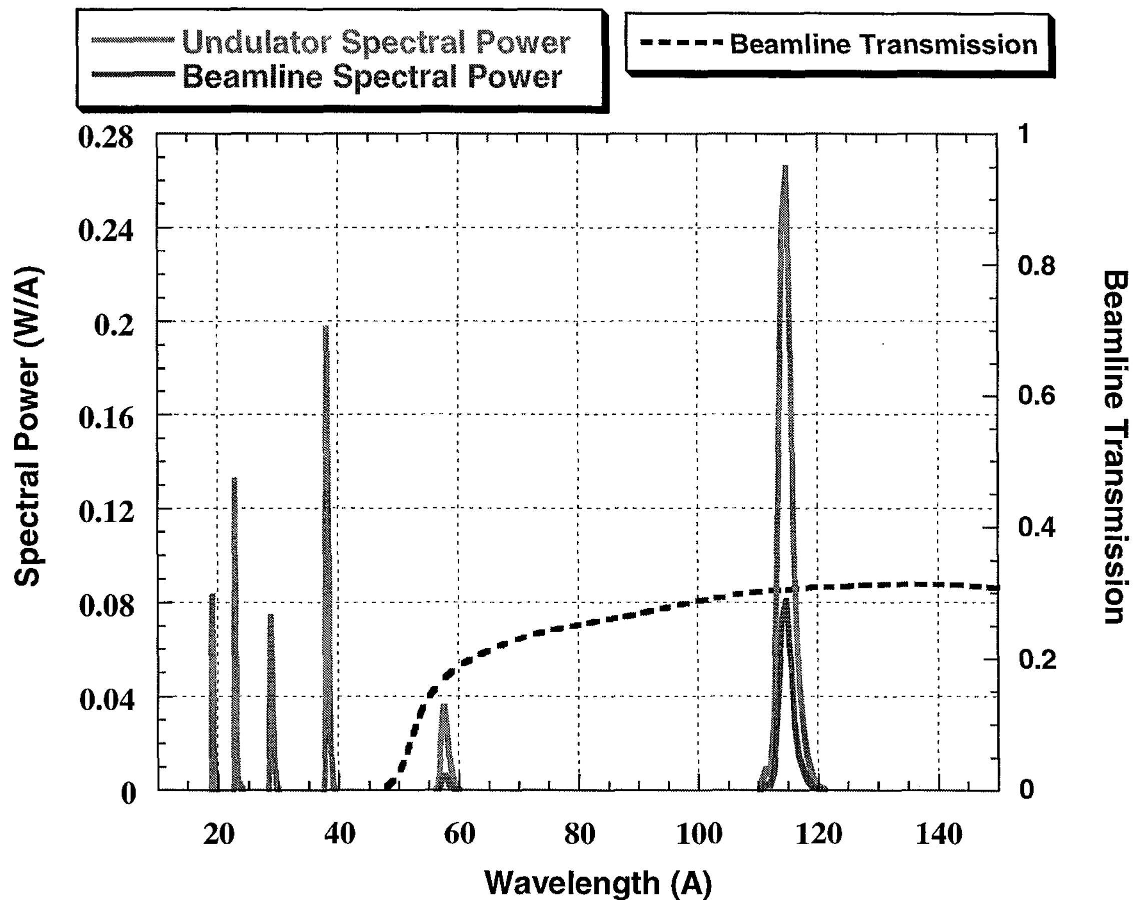

Figure 1: Modeled spectral power of ALS beamline 12.0.1 at the undulator and the beamline exit slit.

2.3 EUV reflectometry at the ALS calibration and standards beamline 6.3.2

ALS beamline 6.3.2 utilizes bending magnet radiation[10] for the characterization of the multilayer coatings after the exposure. The overall set-up includes a permanent high precision reflectometer end station. Experiments are controlled by a UNIX workstation using the LabView graphical programming language. Data evaluation is usually performed directly after the data acquisition using EXCEL and IDL software on a separate beamline PC. Careful selection of appropriate apertures, filters, and

spectral order sorter settings together with full control over the measurement geometry allow high precision measurements of the multilayer reflectivity, wavelength centroid position and bandwidth. The precision limits of the respective parameters are listed in table 1. The parameters peak reflectance, wavelength centroid and bandwidth fully describe the optical properties of a multilayer coating relevant for EUVL purposes. Utilizing automatic procedures all three parameters can be routinely mapped across the surface of any multilayer coating up to 200 mm diameter including curved optics. Samples exposed in this study had diameters ranging from 10 mm to 25 mm and were characterized with high spatial resolution on the order of 0.1-mm step size. Figure 2 shows a typical multilayer reflectance curve measured and evaluated at ALS beamline 6.3.2.

Peak reflectance	**0.2%**
Wavelength centroid	**0.02 Å**
Bandwidth	**0.02 Å**

Table 1: Precision limits (1σ) in the characterization of optical properties of multilayer coatings at ALS beamline 6.3.2.

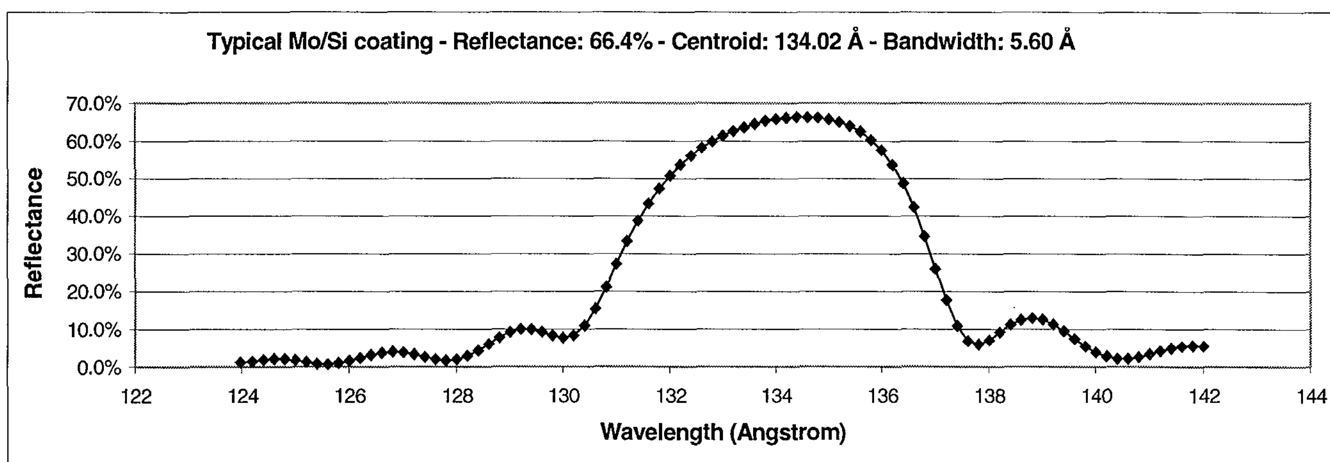

Figure 2: Typical reflectance curve of a Mo/Si multilayer coating obtained at ALS beamline 6.3.2.

2.4 Sputter Auger analysis

Sputter Auger analysis of exposed and unexposed areas of Mo/Si and Mo/Be multilayer coatings has been performed at Sandia National Laboratories. The qualitative chemical composition of contaminants on multilayer surfaces as well as the chemical structure of the bulk of multilayer coatings can be determined with this method. In addition secondary electron emission excited by an electron beam can be utilized for surface imaging of the areas exposed. However, the sputter crater produced during the sputter Auger analysis complicates any subsequent EUV reflectance measurements at the ALS due to partial removal of the multilayer top layer in the test spots exposed. Therefore the precision of EUV reflectance measurements in the remaining portion of the EUV illuminated spots after sputter Auger analysis is estimated to be on the order of 0.5%.

2.5 Ozone cleaning

Ozone cleaning in commercial UV illumination systems, which produce ozone from atmospheric oxygen, is an established method for the removal of hydrocarbon contamination from grazing incidence optical surfaces at the ALS. In the current study ozone cleaning is used, first, for the removal of carbon contamination from multilayer coated surfaces and, second, for the assessment of the chemical reactivity of the multilayer top surface. For chemically reactive surfaces ozone cleaning may fully remove carbon contamination, however, afterwards it is impossible to distinguish between oxidation caused by the EUV illumination, oxidation due to the ozone cleaning process and oxidation due to atmospheric influences on the EUV illuminated spot after the exposure.

3. STRUCTURE OF MO/SI AND MO/BE MULTILAYER COATINGS

Mo/Si and Mo/Be multilayer coatings reveal a very different structure in transmission electron microscope (TEM) cross sectional micrographs. In Mo/Si multilayer coatings interdiffusion at the layer interfaces is more pronounced, while Mo/Be has higher interfacial roughness. Also the chemical structure of the multilayer top layers is different in both systems. One top layer consists of a thin layer of silicon dioxide, while the other top layer consists of a three times thicker layer of beryllium oxide. In this study effects are searched for which may cause reduction of the lifetime of a multilayer coated optical system on the basis of the microscopic structure of the multilayer coating.

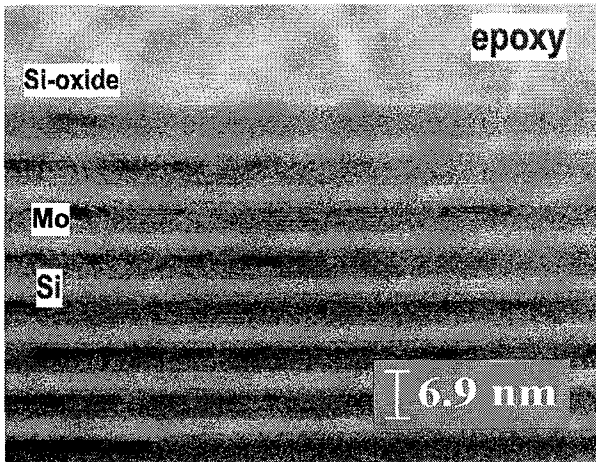

Figure 3: TEM cross section of the top region of a Mo/Si multilayer. A typical coating consists of 40 bilayers. The silicon dioxide top layer is typically 1.3 nm thick.

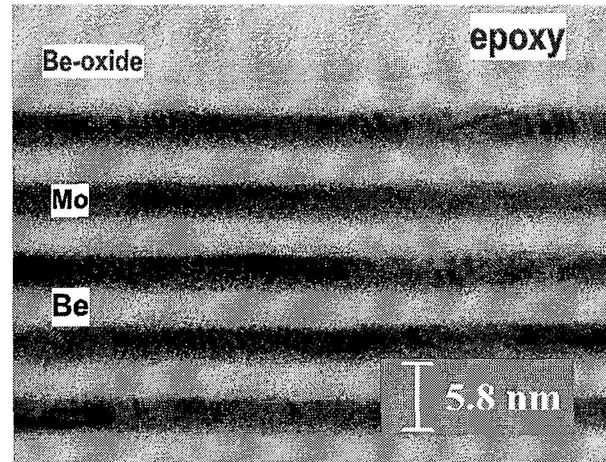

Figure 4: TEM cross section of the top region of a Mo/Be multilayer. A typical coating consists of 70 bilayers. The beryllium oxide top layer is typically 3.5 nm thick.

4. MO/BE MULTILAYER EXPOSURE

4.1 Exposure

At a base pressure of 10^{-9} Torr containing 80% hydrogen, 10% water, small amounts of carbon dioxide and carbon monoxide, a Mo/Be coated silicon wafer piece was exposed to narrow band EUV radiation with an average power of 35 mW for 40 hours. The spot illuminated had a size of 0.6 mm by 0.6 mm with an average intensity of approximately 10 W/cm^2 for a total dose of 1.4 MJ/cm^2. During the exposure the relevant parameters were carefully controlled using methods described in the experimental section. In addition the beam shape and the EUV power were occasionally monitored using a phosphor screen and a calibrated photodiode, respectively.

4.2 Results of the Mo/Be sample analysis after exposure

Visual inspection with a microscope revealed no modification of the area exposed. Auger electron spectroscopy (AES) using a scanning electron beam after the exposure clearly identified increased carbon content near the center of the sample. The beam shape as observed with the phosphor screen coincides in a conclusive manner with a secondary electron emission map, an Auger electron map and an EUV reflectance map of the center portion of the sample. All three methods derive their contrast from modified material properties as compared to the surrounding area. The reflectance in the area exposed dropped from 66.6% to 64.4% without any indication of a shift in the wavelength centroid position or the bandwidth within the instrumental precision as listed in table 2. Ozone cleaning for 4 hours only partially recovered the full original reflectance. Enhanced oxidation of beryllium is probably responsible for this irreversible loss because after ozone cleaning just insignificant amounts of carbon could be detected by AES. On the basis of these observations it is concluded that carbon was deposited on the multilayer surface, but no damage to the bulk of the multilayer has occurred. Doses applied are equivalent to periods of months or years on different components of EUVL optical systems. The risk connected with radiation induced effects in the bulk of Mo/Be multilayers is considered low. However, radiation-induced chemical surface reactions have revealed their potential of decreasing EUV reflectance without damage to the multilayer structure itself. As a consequence multilayer coatings in EUVL optical systems need to be protected against chemically reactive species in the vacuum.

4.3 Radiation induced surface chemistry

Sputter Auger analysis results of the area exposed (Figure 5) indicate the formation of carbide in the beryllium top layer under the influence of EUV illumination. However, we cannot completely rule out that the carbide formation is an artifact of the sputter analysis process itself. Various independent methods support only the evidence of increased amounts of carbon in the exposed area. In any case the occurrence of carbide in the Auger electron spectra can be viewed as a general indication of chemical reactivity of the top layer of Mo/Be multilayer coatings.

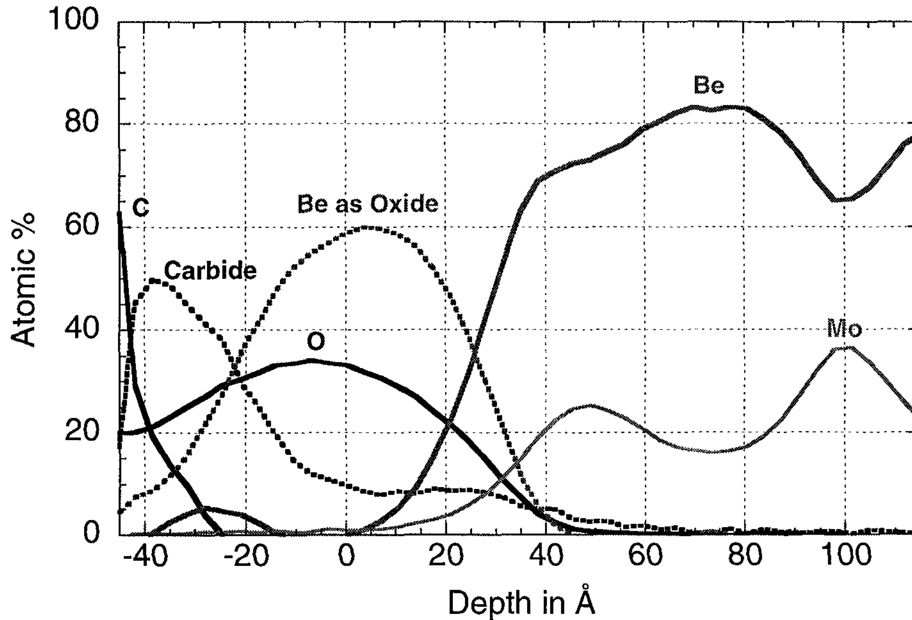

Figure 5: Sputter Auger depth profile of the EUV exposed area of a Mo/Be multilayer. Zero depth corresponds to the original multilayer surface before exposure to atmospheric conditions after multilayer deposition.

5. MO/SI MULTILAYER EXPOSURE

5.1 Exposure

Operation of the EUV interferometer at ALS beamline 12.0.1 requires the use of Mo/Si multilayer coated mirrors. Two such 45-degree "M7" turning mirrors were coated in 1997 and subsequently illuminated with the full EUV intensity at beamline 12.0.1 during operation of the interferometer. Both mirrors showed visible carbon contamination after regular use and were routinely rotated in order to illuminate less contaminated areas. The exposure duration on each of the remaining carbon spots is estimated to be 10 to 100 hours with variable vacuum conditions until the mirrors were replaced and ozone cleaned. Vacuum conditions were determined to be hydrocarbon rich, at a base pressure of approximately 10^{-7} Torr and average EUV intensities on the order of 1 W/cm^2. In summary, the conditions to which the M7 mirrors were exposed represent a worst case scenario for the operation of an EUVL optical system.

5.2 Results of the Mo/Si sample analysis after exposure

Upon ozone cleaning for 4 hours both mirrors recovered their original EUV reflectance of close to 50% uniformly throughout the whole surface without any indication for a shift in the centroid wavelength or bandwidth. Up to 190 Å of carbon build-up had been measured with a profilometer before ozone cleaning.

5.3 Radiation induced surface chemistry

In contrast to Mo/Be multilayer mirrors there is no indication for carbide formation on Mo/Si multilayer mirrors. EUV reflectance losses were observed on Mo/Si multilayers exclusively due to carbon deposition on top of the silicon dioxide top layer.

6. CHEMICAL REACTIVITY OF MO/BE AND MO/SI MULTILAYER COATINGS

The chemical reactivity of Mo/Be and Mo/Si multilayer coatings has been assessed by exposure to ozone for 24 hours and dipping in water for 5 minutes. Results are summarized in table 2.

	water (5 min)	ozone (24 h)
Mo/Be	> 10 % loss	4 % loss
Mo/Si	no change	no change

Table 2: Reflectance loss of Mo/Be and Mo/Si multilayers after ozone exposure and water dipping.

Mo/Si multilayer coatings are very robust systems during exposures to water and ozone. The properties of the top silicon dioxide layer provide sufficient protection against these chemicals under standard conditions. In contrast Mo/Be multilayer coatings are clearly more affected and show detectable degradation of their EUV reflectance.

7. CONCLUSION

No radiation-induced bulk-damage effects were observed on Mo/Si or Mo/Be multilayers at practical doses of EUV radiation. However, contamination of the multilayer top surface may cause EUV reflectance losses depending on the environmental conditions. Contamination on Mo/Be multilayers is partially irreversible due to chemical reactions on the multilayer surface.

8. ACKNOWLEDGMENTS

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