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Improved reflectance and stability of Mo/Si multilayers

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ABSTRACT

Commercial EUV lithographic systems require multilayers with higher reflectance and better stability then that published to date. Interface-engineered Mo/Si multilayers with 70% reflectance at 13.5 nm wavelength (peak width of 0.545 nm) and 71% at 12.7 nm wavelength (peak width of 0.49 nm) were developed. These results were achieved with 50 bilayers. These new multilayers consist of Mo and Si layers separated by thin boron carbide layers. Depositing boron carbide on interfaces leads to reduction in silicide formation on the Mo-on-Si interfaces. Bilayer contraction is reduced by 30% implying that there is less intermixing of Mo and Si to form silicide. As a result the Mo-on-Si interfaces are sharper in interface-engineered multilayers than in standard Mo/Si multilayers. The optimum boron carbide thicknesses have been determined and appear to be different for Mo-on-Si and Si-on-Mo interfaces. The best results were obtained with 0.4 nm thick boron carbide layer on the Mo-on-Si interface and 0.25 nm thick boron carbide layer on the Si-on-Mo interface. Increase in reflectance is consistent with multilayers with sharper and smoother interfaces.

A significant improvement in oxidation resistance of EUV multilayers has been achieved with ruthenium terminated Mo/Si multilayers. The best capping layer design consists of a Ru layer separated from the last Si layer by a boron carbide layer. This design achieves high reflectance and the best oxidation resistance in a water vapor (i.e. oxidation) environment. Electron beam exposures of 4.5 hours in the presence of 5×10^{-7} torr water vapor partial pressure show no measurable reflectance loss and no increase in the oxide thickness of Ru terminated multilayers. Longer exposures in different environments are necessary to test lifetime stability of many years.

KEYWORDS: Multilayers, reflectivity, interfaces, capping layers, oxidation resistance, Extreme ultraviolet (EUV) lithography

1. INTRODUCTION

Extreme ultraviolet lithography (EUVL), a leading next generation lithography technology, is based on all reflective optics operating at a wavelength of 13.4 nm. High quality Mo/Si reflective coatings are the enabling technology for EUVL. In the past few years dramatic improvements in deposition control systems have produced multilayer coatings with unprecedented thickness accuracy and reproducibility, essential to meet the stringent specifications of commercial EUVL tools[1-3]. At Lawrence Livermore National Laboratory (LLNL), accurate multilayer coatings were successfully applied on many large, and often deeply curved, optical substrates including two sets consisting of projection optics and numerous sets of condenser optics. Outstanding levels of wavelength matching and thickness uniformity were achieved, and the added figure error was maintained within specifications, meaning that the multilayer coatings did not contribute any aberrations to the system performance of the Engineering Test Stand (ETS) camera[4-6]. Now that full field EUV imaging has been demonstrated with the ETS tool the emphasis is to make this technology commercially viable. Commercial EUVL tools, planned to be available in 2006, need to have a throughput of 80 300mm wafers per hour. Higher reflectance of the multilayer coatings would have a substantial impact on the throughput and economic viability of EUVL tools. Table 1 shows the EUVL multilayer roadmap that the Virtual National Laboratory (VNL) is pursuing to meet commercial requirements. The first column describes the issues to be solved, the second column shows the current status and the third and the forth column show the requirements for the β-tool in 2004 and for the commercial tools in 2006, respectively. In this paper we will focus on the first four rows that cover peak reflectance and lifetime of these coatings. The requirement for the peak reflectance of the imaging optic is at least 70% with minimal reflectance loss (1.6% absolute) over 5 years. The reflectance loss on condenser optics is allowed to be larger over a shorter lifetime, based on the assumption that condenser optics is cheaper and replaceable.

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Issue	Current status 2001	β-tool 2004	Commercial tool 2006
Peak Reflectance – optics	65%	68%	70%
Lifetime (Imaging Optics)	Unknown	1.6%*/3years	1.6%*/5years
Lifetime (First Condenser Optic)	Unknown	10%*/year	10%*/year
Lifetime (Other Condenser Optics)	Unknown	2.5%*/year	2.5%*/year
Max Operation Temp (Imaging Optics)	25°C	25°C	25°C
Mask Rapid Thermal Cycle	150°C, <2min	200°C, <2min	200°C, <2 min
Max Operation Temp (Mask Plane)	25°C	30°C	35°C
ML Added Figure Error	0.1 nm rms	0.05 nm rms	0.025 nm rms
Relative Optical Throughput**	1.0	1.5	2.0

Table 1: EUVL multilayer roadmap. The numbers labeled with an asterix (*) are relative percents and the relative optical throughput numbers (**) are calculated for a system assuming 10 multilayer-coated surfaces.

In the first part of this paper we present the design of Mo/Si interface-engineered multilayers. The sharper interfaces of these multilayers lead to increased reflectance. The second part of the paper describes different multilayer capping layers and the stability results from electron beam exposures. The multilayer deposition process for all results presented here, and the electron beam exposure procedure are outlined in section 2. The results on interface-engineered multilayers and on capping lyaers presented in section 3 and 4, respectively and the shirt summary is given in section 5.

2. EXPERIMENT

2.1. Deposition system

All the multilayers used in this study were deposited using the DC-magnetron sputtering machine shown in Figure 1. Upgrades of the machine have taken place since it was last described[1]. The deposition system now contains four sputtering guns mounted on the bottom of the chamber and spaced 90 degrees apart. Two of the sputtering guns are rectangular (12.7 x 25.4 cm) placed 180 deg apart and two are circular (100 mm) also placed 180 deg apart. The substrates, which are spun during the depositions, are facing down and are affixed to the platter, which rotates over the sputtering targets. The individual layer thickness is controlled by the platter angular velocity. Two cryo-pumps are used to evacuate the chamber to the operating pressure of at most $2x10^{-7}$ torr. Ultrahigh purity Ar gas at 1 mTorr was used to sputter the Si (360W), Mo (170W), boron carbide (100W) and Ru (50W) targets. A typical deposition run is done in less than 1 hour and up to two deposition

runs per day are easily achieved. Interface engineered multilayers were fabricated utilizing large, rectangular targets (Mo and Si) and two circular boron carbide (B_4C) targets. For the capping layer work we replaced one of the boron carbide targets with a Ru target (Fig. 1). Further upgrades will be carried out so that capped interface-engineered multilayers can be manufactured.

2.2 Electron beam exposures and Auger electron spectroscopy

An Auger microprobe PHI660 was used to test capping layers by exposing them to the electron beam in a controlled environment. The electron beam size on the sample was 1 x 1 mm. The energy of the electrons was kept constant at 2 kV and the current density of incident electrons was 5μA/mm^2. This corresponds to a current density of ≈2.5μA/mm^2 of secondary electrons assuming that each primary electron emits 0.5 secondary electron. To produce the same secondary current from incident EUV photons one would need about 25 mW/mm^2 of EUV irradiance. Our typical exposure time with the electron beam was 4.5 hours and all the exposure experiments were done in 5x10^{-7} Torr of water vapor partial pressure as measured by a SRS200 RGA monitoring mass 18.

Auger electron spectroscopy was used to identify the elemental composition of the multilayers. An additional ion beam gun was used to remove less than a monolayer of material from the surface at a time and to continue to monitor the composition and the chemistry from the surface as this surface moved into the sample. A PHI 660 Scanning Auger microprobe was operated at 5kV and 75nA and the beam was rastered over a 50μm x 50μm area at 30 degrees from normal incidence. A PHI Duoplasmatron ion gun was operated at 2kV and 8.0 nA current and the beam was rastered over a 300μm x 300μm area at a 45 degree angle. Sputter rates within the multilayer of Mo and Si were adjusted for a multilayer rate of 6.9 nm/layer. No attempt was made to adjust sputter rates for the Ru or B_4C capping layers.

2.3 Characterization techniques (X-ray diffraction, reflectometry, TEM)

The sputtering rates were calibrated by varying the velocity of the platter over the sources at a constant power and determining the multilayer periods by fitting the Bragg peaks in the X-ray diffraction spectra. X-ray diffraction measurements were performed using a Rigaku DMAX-IIB diffractometer with a Cu K_α rotating anode source (λ = 0.154 nm). The small angle x-ray diffraction measurements were obtained over the angular range of θ-2θ between 1° - 11°.

Reflectance of the multilayers was measured with a synchrotron-based reflectometer at the Advanced Light Source (ALS), beamline 6.3.2. (Lawrence Berkeley National Laboratory). This reflectometer has been designed for the characterization of multilayer-coated EUVL optics and has high spectral purity, high stability and small beam diameter. The detailed description of the beamline can be found elsewhere[7]. The wavelength precision of this reflectometer is 0.002 nm and the reflectance results are repeatable within ±0.2%.

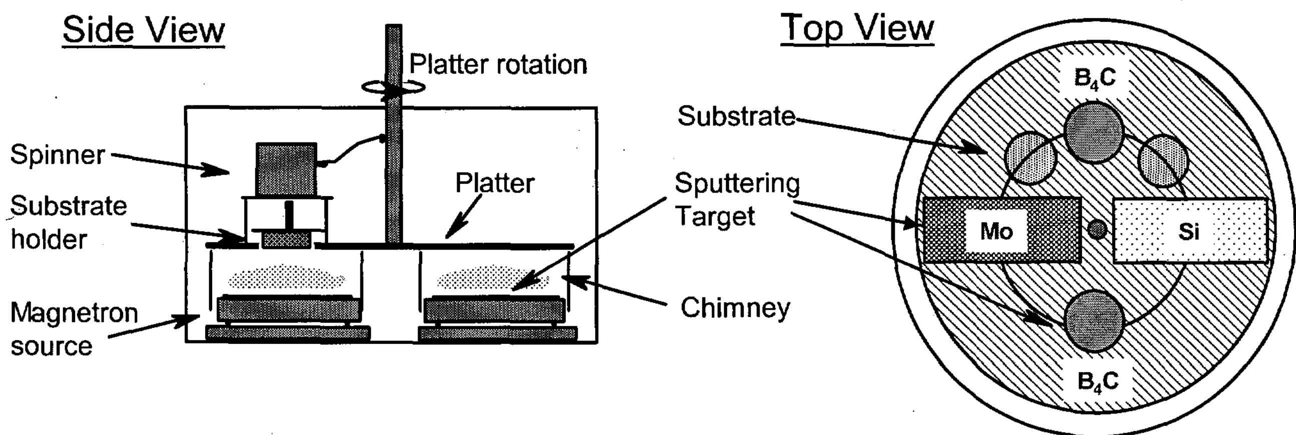

Figure 1: Layout of the DC magnetron sputter system used to deposit multilayer coatings.

Transmission electron microscopy (TEM) was used to verify the quality of the interfaces and the microstructure of the interface-engineered multilayers. High resolution images of the samples were obtained using a Philips CM300 FEG microscope operated at 300 keV with a point-to-point resolution of 0.1 nm. Specimen preparation and operation of the microscope have been reported elsewhere[8].

3. INTERFACE-ENGINEERED MULTILAYERS

In the past few years much work has been done in optimizing the deposition conditions to maximize reflectance of Mo/Si multilayers[4,9]. By optimizing Γ (Mo thickness/period thickness) and increasing the number of bilayers to 60 we can achieve reflectivity up to 68.8% at 13.4 nm. However, increasing the reflectance even further requires a major change in the multilayer design or in the deposition process. For example, introduction of low Z material barriers[10], ion beam etching[11], substrate heating[12] and pulsed laser deposition[13] are just few techniques that are currently being pursued to achieve this goal.

What are the major imperfections in the multilayer that reduce the reflectance? One of them is the formation of surface oxide. This is impossible to avoid completely because the multilayers get exposed to air, but choosing a material to terminate the multilayer that forms a thinner, less absorbing surface oxide than Si may mitigate this effect. Another source of imperfections is the quality of the interfaces between the Mo and Si layers. In standard Mo/Si multilayers the interfaces are not abrupt at all. Polycrystalline Mo layers and amorphous Si layers are separated by asymmetric silicide layers. The exact silicide composition and its compositional gradient across the layer thickness are still subjects of debate. However, the silicide formation is accompanied by a multilayer period contraction. It is well known that to achieve a certain period thickness one needs to add about an extra 0.52 nm per bilayer of bulk material in the deposition process to compensate for contraction due to silicide formation. Interestingly, the silicide layer thicknesses are interface dependent. For example, the silicide thickness on the Mo-on-Si interface is at least two times thicker than the silicide thickness on the Si-on-Mo interface. The appearance of the asymmetry in the silicide thickness is associated with a phase transition from amorphous to crystalline structure in Mo layers[14]. Roughness of interfaces is yet another source of imperfections that lowers the multilayer reflectance. However, some studies suggest that interfacial roughness is negligible for optimized sputtering conditions[15]. We have identified a parameter space where the roughness increases dramatically due to amorphous to crystalline transition in Mo layers[14]. Fortunately in an optimized EUV multilayer the Mo thickness is well above that transition.

The approach we took to improve the reflectance of EUV multilayers was to engineer the interfaces to minimize silicide formation at interfaces. The idea is to limit the inter-diffusion of Mo and Si by using a third material as a diffusion barrier and which is EUV transparent (Fig. 2). This idea was recently used by other authors to improve thermal stability of the

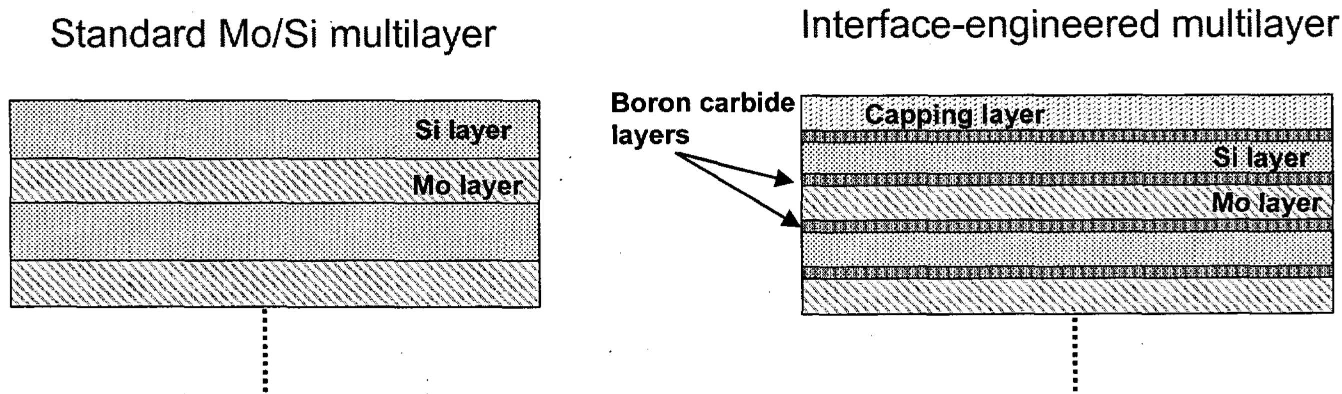

Figure 2: Ideal standard Mo/Si multilayers (a) consist of alternating Mo and Si layers and are terminated with Si layer. Ideal interface-engineered multilayers (b) consist of Mo and Si layers separated with thin boron carbide interfaces. They are terminated with an oxidation resistant capping layer such as ruthenium. However, the interface-engineered multilayers in this paper are terminated with Si layer.

multilayers but always on the expense of slightly lower reflectivity[3,10]. In our study we used boron carbide as diffusion barrier material. Boron carbide is a low Z material that reduces the silicide formation and increases the reflectance but also improves heat resistance of the multilayers. Figure 2 shows a Mo/Si multilayer that consists of Mo and Si layers and is terminated with Si layer. In the following we will call such multilayers standard Mo/Si multilayers. The multilayers with Mo and Si layers separated with thin boron carbide layers will be called interface-engineered multilayers.

3.1. Experimental results

To optimize the thickness of boron carbide on each interface we made a series of deposition runs. By varying boron carbide thickness on selected interface (either Mo-on-Si or Si-on-Mo or both) we could directly monitor its effect on silicide formation by measuring the total contraction of the multilayer period thickness. We define the contraction, $\Delta\Lambda$, as:

$$\Delta\Lambda = \Lambda_{calc} - \Lambda_{meas} \tag{1}$$

where Λ_{calc} is the calculated multilayer period thickness based on the bulk sputtering rates and Λ_{meas} is the measured multilayer period thickness using small angle x-ray diffraction data. The thickness of the silicide interlayer can be measured directly via the contraction:

$$\Delta\Lambda = \alpha \cdot t \tag{2}$$

if the parameter α is known. This parameter α was deduced from experimental data. The most likely silicide that forms on the interfaces is the silicide with the lowest heat of formation ($MoSi_2$) and for which $\alpha = 0.38$ [16].

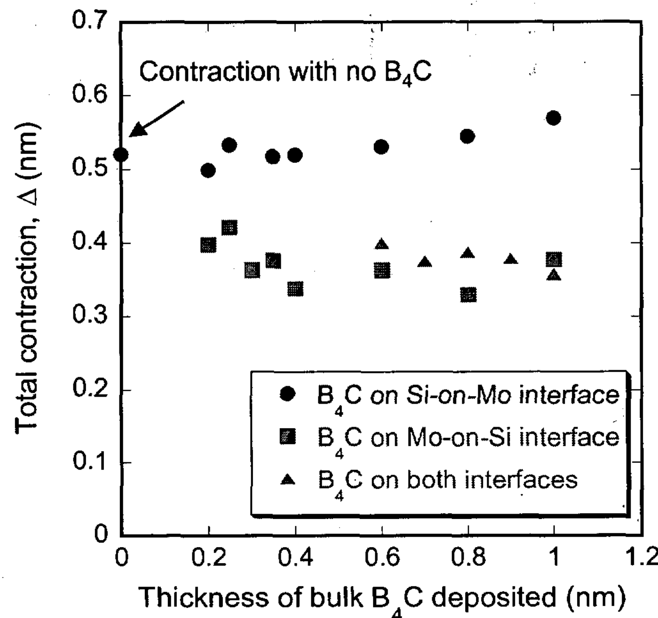

Figure 3: The contraction of the multilayer period is about 0.52 nm per bilayer for a Mo/Si multilayer with no boron carbide on the interfaces. Boron carbide on the Mo-on-Si interface reduces the contraction of the multilayer to about 0.36 nm per bilayer for a range of boron carbide thicknesses (squares). No change in the contraction of the multilayer period is observed for boron carbide deposited on the Si-on-Mo interface when compared to the Mo/Si multilayer with no boron carbide interfaces. The contraction of the multilayer period for multilayers with boron carbide deposited on both interfaces (triangles) is the same as for boron carbide on the Mo-on-Si interface.

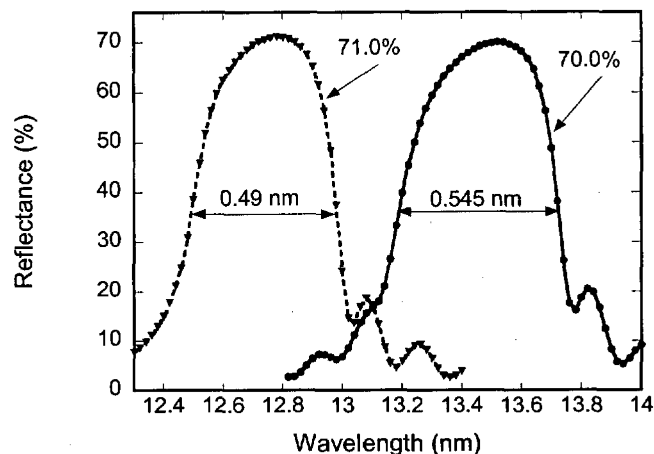

Figure 4: Measured reflectance of interface-engineered multilayers reflecting at 13.5 nm and at 12.7 nm, respectively. Measurements were done at 5 degrees off normal. Both multilayers consist of 50 bilayers Mo/Si multilayer with boron carbide interfaces. The thickness of boron carbide on the Mo-on-Si interface is 0.4 nm and on the Si-on-Mo interface is 0.25 nm. The reflectance curve of one multilayer has a peak value of 70.0% at 13.5 nm and of the other multilayer has a peak value of 71.0% at 12.7 nm, respectively. The spectral bandwidth of these mirrors, measured at full width at half-maximum (FWHM) is 0.545 nm and 0.49 nm, respectively.

In Figure 3 we plot the total contraction as a function of the thickness of bulk boron carbide thickness. Also shown is the contraction in standard Mo/Si multilayer with no boron carbide on interfaces. Application of boron carbide on Mo-on-Si interface substantially decreased the contraction, especially for boron carbide thickness of 0.4 nm and higher. The contraction was reduced from 0.52 nm/bilayer to about 0.36 nm/bilayer. This implies that the deposition of boron carbide on Mo-on-Si interface reduced the formation of silicide but did not completely prevent it. However, when we applied boron carbide on Si-on-Mo interface no change in contraction was observed. When we deposited boron carbide on both interfaces the contraction was reduced by the same amount as for Mo-on-Si interface. Therefore, a 0.36 nm/bilayer contraction was used in interface-engineered multilayer design.

Knowing bulk sputtering rates of Mo, Si, boron carbide and the total contraction we were able to design multilayers for a particular wavelength. The optimum thicknesses for 13.4 nm wavelength multilayer are the following: [Si(4.37 nm)/B_4C(0.4 nm)/Mo(2.25 nm)/B_4C(0.25 nm)]$_{50}$ + Si (4.2nm). Seventy percent multilayers at 13.5 nm and FWHM of 0.545 nm were achieved with 50 bilayers using this design. For a EUV optical system with 9 reflective surfaces this new multilayer would increase the optical throughput by more than 50% compared to our best standard Mo/Si multilayers (68.2% at 13.4 nm with 0.533 nm FWHM). The optical throughput is proportional to:

$$\int R(\lambda)^n d\lambda \quad (3)$$

with R being a reflectance curve of the multilayer in the EUV wavelength region and n the number of reflective mirrors in the system.

High reflectance multilayers have been achieved reproducibly on superpolished Si (100) wafers and on 2.5cm diameter flat silica substrates. However, the EUV multilayer roadmap calls for 70% reflectance multilayer coatings at 13.4 nm on optics for commercial tools. These optical substrates will consist of either Zerodur or ULE, both low expansion materials that should prevent aberrations due to thermal load. It is currently a considerable challenge to polish optical substrates that meet the roughness specifications in the low, middle and high frequency range simultaneously. The reflectance is especially sensitive to the roughness in the high frequency range (0.001 – 0.05 nm^{-1}). Studies in which Zerodur substrates were measured for their high frequency roughness before and after the standard Mo/Si multilayer coating showed that the peak

reflectance decreases by about 2% (absolute) for each additional 0.1 nm high frequency roughness[17]. Ideally the substrate should have 0.1 nm rms high frequency roughness or less to achieve 70% reflectance.

4. CAPPING LAYERS

High reflectance multilayers are of no use to commercial tools if their performance is not stable as a function of EUV exposure. Hence, reflectance stability of EUV multilayers exposed to EUV radiation in the presence of environmental contaminants is of great concern. Many environmental factors contribute to the loss in the multilayer reflectance over time. The most important ones are oxidation due to water vapor and EUV light or molecular oxygen and EUV light, carbon contamination from outgassing, debris from the source and increased interdiffusion in the multilayers at elevated temperatures. In this paper we propose a solution that addresses the reflectance loss due to oxidation. The solution is a capping layer that acts as an effective oxidation barrier when the multilayer is exposed to the EUV light in the presence of water vapor. So far, most of the studies done on EUV multilayer stability involved multilayers that were terminated with Si[1,4,18-20]. These studies on Si capped multilayers show good reflectance stability for multilayers exposed to EUV light in vacuum[19,20], however, in the presence of EUV light and water vapor the reflectance decreases due to increase in the surface oxide layer thickness[21]. It is believed that upon the irradiation of the mirror with the EUV light the low energy secondary electrons are created and that these secondary electrons are the causing the major damage to the surface of the multilayers. The mechanism on how these electrons interact with water molecules from the environment and what exactly is happening on the surface of the multilayer is not understood yet. However, so far all the existing experimental data suggest that Si capping layer is not an adequate protection against oxidation. Therefore, the lifetime of the multilayers is probably the highest risk item for the EUVL multilayer coatings (Table 1). It is crucial to find a capping layer material that is oxidation resistant, forms a sharp and stable interface with the material underneath and has good optical properties in the EUV region. Little or no experimental work has been published on alternative capping layer materials even though many have been proposed based on their optical properties[22]. Once a good capping layer material has been found the challenge is to test it and project its stability for continuous exposure for long periods of time based on accelerated, short time experiments. The study presented here is based on accelerated electron beam exposures.

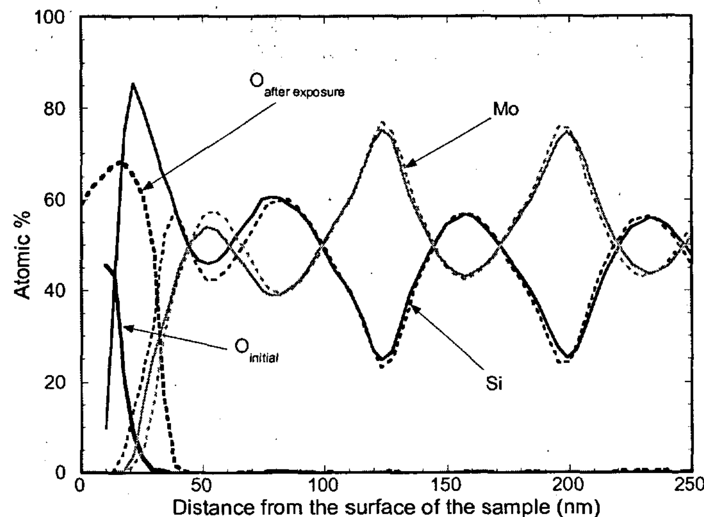

Figure 5: Auger depth profile of Si capped multilayer before (solid lines) and after the exposure to the electron beam (dashed lines)

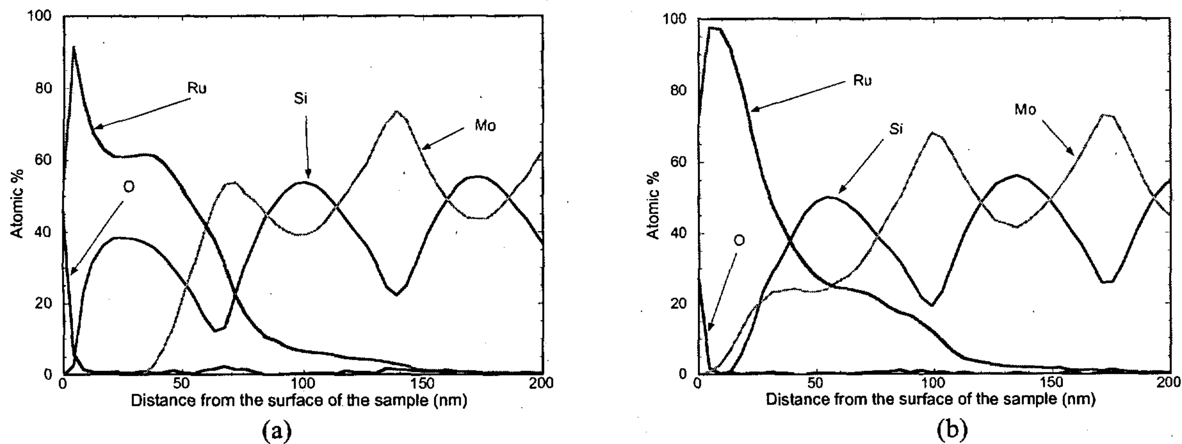

Figure 6: Depth profiles obtained with Auger spectroscopy on Ru capped multilayers. Ruthenium was deposited directly on the top of the last Si layer in (a) and separated with a thin Mo layer in case (b).

4.1. Experimental results

The electron beam experiments were done in the Auger electron microprobe as described in section 2.2. All multilayers in this study were exposed to the same dose. The 4.5 hour exposure with the electron beam corresponds to about 48 hours of EUV exposure on imaging optic for full power EUVL commercial tool with the throughput of 80 300mm wafers per hour. These exposures were done at a constant water vapor partial pressure of 5 x 10^{-7} Torr. This was the highest water vapor pressure at which we could operate the electron gun with sufficient stability.

All the multilayers in this study consisted of a standard 40 bilayer Mo/Si multilayer but had different capping layers. Ruthenium was selected as the most promising candidate for oxidation barrier. Preliminary studies on single, thick Ru films showed thin oxide layer formation on the surface of this metal whose thickness remained unchanged if exposed to the electron beam in the presence of water vapor[23]. We studied stability of Ru capped multilayers by measuring the reflectance before and after the electron beam exposure and by analyzing the depth profiles with Auger spectroscopy. Three different capping layer designs have been proposed and tested. A Si capped multilayer was used as a reference.

3.2.1. Si cap

A standard Mo/Si multilayer with 40 bilayers, a period thickness of 6.9 nm and Γ of 0.42 was capped with a 4.2 nm thick Si layer. The initial reflectance was 66.6% at 13.4 nm. After the exposure the reflectance dropped to 64.9%. No change in the peak wavelength was detected. Auger spectroscopy was used to measure depth profile of different elements (Fig. 5) before and after the exposure. Based on the periodicity of Mo and Si peaks, which remains constant, we can measure the change in thickness of the surface oxide and monitor oxygen diffusion into the multilayer. Before the exposure the oxygen could be detected about 1 nm deep into the sample. After the exposure the oxygen layer is much thicker. Part of it is due to the growth of an additional surface oxide (about 1 nm) and part of it is diffusion of oxygen into the silicon layer (about 2 nm).

3.2.2. Ru on Si

A standard Mo/Si multilayer was terminated with a Si layer on the top of which we deposited 2.3 nm Ru. The initial reflectance was 65.5% at 13.45 nm. The reflectance of one month-old multilayer was 65.2% at 13.45 nm. The reflectance in the exposed area decreased to 64.53% and no peak wavelength change was observed. Auger spectra of the multilayer show less than 1 nm thick Ru oxide (Fig. 6a). Most of the Ru seems to react with the last Si layer to form a ruthenium silicide.

3.2.3 Ru on Mo

To control the interdiffusion between Ru and Si we deposited a thin layer of Mo between these two layers. The standard Mo/Si multilayer was terminated with Si on the top of which we deposited 1.3 nm thick Mo layer and 2.3 nm thick Ru layer. The initial reflectance was relatively low (62.0% at 13.34 nm) because the last absorber layer, which consists of Mo and Ru, is too thick for positive interference with the multilayer underneath. However, the Auger spectra of the multilayer before the exposure shows that the interdiffusion between Ru and Si is largely suppressed (Fig. 6b). Also, the reflectance after the

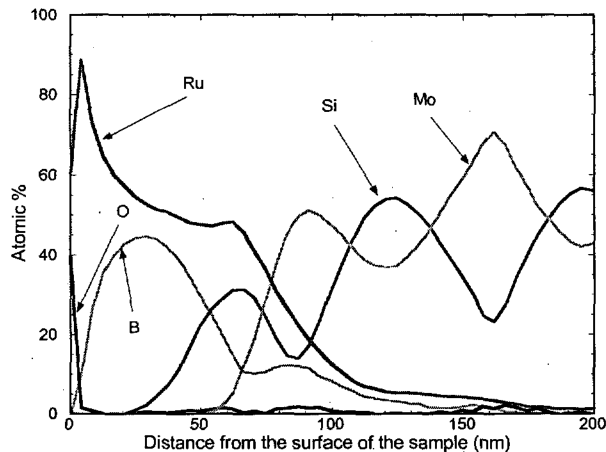

Figure 7: Ru on B4C on Si capping layer

exposure is less (0.6%) than in Ru on Si capped multilayer. No change in the peak wavelength was detected. Multilayers with initial reflectance of up to 66% were achieved with 1.3 nm Mo and 0.6 nm thick Ru. This Ru thickness is believed to be too thin for oxidation protection. Ru on Mo capping layer design is a better oxidation barrier than Si cap, however it is not practical because of its low initial reflectivity.

3.2.4 Ru on B4C

So far the best results were achieved with Ru capped multilayer in which B_4C was used as a diffusion barrier between Ru and Si. The best oxidation protection was obtained on multilayers that consisted of a standard 40 bilayer Mo/Si multilayer terminated with a thinner, 2.0 nm Si layer on the top of which we deposited 2.0 nm B_4C and 2.3 nm Ru. The initial reflectance of so capped multilayers was 65.88% at 13.31 nm but the reflectance measured one month after the deposition decreased to 65.34% at 13.31 nm. Depth profile shows a very thin Ru oxide (Fig. 7). The reason why we were not able to plot carbon depth profile is that the electron binding energy for carbon and ruthenium peaks almost overlaps. After the exposure the reflectance of this sample was still 65.88% at 13.31 nm. However, the reflectance in the non-exposed area is lower (65.34%). We do not have enough data to understand this but one possible explanation is that the ruthenium oxide is volatile. Additional experiments are being planned to study this further.

5. SUMMARY

The success of Extreme Ultraviolet Lithography (EUVL) is greatly dependent on the performance and stability of Mo/Si multilayer coatings. These multilayers need to maintain high reflectance in realistic lithography tool environment in order to commercially viable.

In this paper we outlined the requirements for high performance EUV multilayers and presented EUVL roadmap for multilayer coatings. We developed above 70% reflectance multilayers using interface-engineering. Instead of using a simple, two layer multilayer we developed a more sophisticated multilayer system in which Mo and Si layers are separated with low Z material interlayers (boron carbide). In addition we studied different capping layers for their reflectance stability in the presence of EUV light and water vapor. The exposures were actually done with electron beam exposures assuming that the low energy secondary electrons are causing the damage and that their spectrum is somewhat similar to the spectrum of low energy secondary electrons created by EUV light. In this study we addressed only the reflectance loss to oxidation and the best protection was observed on Ru capped multilayers with boron carbide diffusion barrier between Ru and last Si layer.

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