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Recovery of EUVL substrates

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Abstract

Mo/Si multilayers were removed from superpolished zerodur and fused silica substrates with a dry etching process that, under suitable processing conditions, produces negligible change in either the substrate surface figure or surface roughness. Full recovery of the initial normal incidence extreme ultra-violet (EUV) reflectance response has been demonstrated on reprocessed substrates.

Introduction

Extreme ultra-violet lithography (EUVL) technology requires the development of imaging systems capable of diffraction limited performance at photon energies near 100 eV. The proposed imaging systems use Mo/Si multilayer (ML) reflective coatings at near normal incidence and four reflective surfaces to achieve diffraction limited performance at 13 nm wavelengths. Diffraction limited performance implies a total wavefront error of 3 nm for the composite imaging system and requires that the optical figure of each surface be maintained within an accuracy of 0.8 nm. This exceeds the current state of the art in optical fabrication; however, it is reasonable to expect that continued advances in lithographic technology will drive the optical fabrication industry to meet these specifications. These EUVL optics will be, literally, one of a kind imaging systems. As such they will be very expensive with estimated pricing in the 500K$ - 1000K$ range. For EUVL the figured optics require deposition of optically matched Mo/Si ML reflective coatings to provide an imaging system with high resolution and good wafer throughput. Tolerances on the ML coatings are extremely tight and a failure in the ML deposition process will result in degraded imaging performance. Other likely failure modes involve deterioration of the ML coatings due to long term radiation dose effects, corrosion and surface contamination. Consequently there is a need to identify an effective process for removing the ML coatings without degrading the surface figure and finish of the precision substrates. Any roughening of the substrate surface or change in the optical figure produced in the removal process will adversely effect the performance of the imaging system.

Previous attempts to remove Mo/Si MLs from superpolished optical substrates have met with marginal success. Wet etching of Mo/Si MLs utilizing both potassium ferrocyanide/alkali hydroxide and hydrofluoric/nitric etchants has been reported[1]. In both cases the etchant solutions had poor selectivity to the SiO_2 substrates and the authors were forced to resort to sputter depositing an etch resistant amorphous carbon (αC) barrier layer between the substrate and the Mo/Si ML. Pinhole free αC films >100 nm thick were required to eliminate substrate attack; unfortunately, the surface roughness of the αC barrier layer increases with film thickness and reduces the Mo/Si ML EUV reflectance. Reactive ion etching (RIE) of Mo/Si ML using an SF_6 plasma has been studied for both SiO_2 and zerodur substrates[2]. The process has an etch rate selectivity of only ~ 20:1 for SiO_2 which is problematic when loading effects produce non-uniform removal of the Mo/Si ML, but in the most favorable case a 95% recovery of the initial EUV reflectance was demonstrated. For zerodur no figure modification was observed, but only 40% of the initial soft x-ray reflectance was recovered indicating significant roughening of the substrate. The roughening was attributed to the differential etch rates of zerodur's multi-component matrix. Below a two stage RIE process for Mo/Si ML removal that permits full recovery of the initial EUV reflectance for both zerodur and SiO_2 substrates is reported.

Experiment

A series of measurements were performed to quantify changes in surface figure, surface roughness and normal incidence reflectance (NIR) produced by RIE removal of Mo/Si MLs from superpolished fused silica and zerodur optical flats. Substrates were 1" diameter by 0.25" thick and flat to λ/10, at 633 nm, with a surface roughness of < 1Å RMS, as determined by optical methods. The following experimental protocols and procedures were employed: First, the substrate surface profile was measured using an optical heterodyne interferometer. Subsequently, N = 40 1/2 bilayer Mo/Si ML coatings (the Si layer is uppermost) with ML periods of $\Lambda \approx 70$Å were deposited using dc magnetron sputter deposition in an Ar plasma[3]. The ML coatings were removed with a two stage RIE process in an rf diode configuration with the substrate located on the powered electrode. Complete removal of the ML coating required 25 minute etch times. In order to quantify the process latitude associated with RIE removal of Mo/Si MLs, etching experiments were conducted with durations between 25 and 200 minutes.

The surface profile of the etched specimens was measured using the same optical heterodyne interferometer. The change in surface figure resulting from deposition and removal of the MLs was determined by comparing the measured surface profiles of the pre and post etched substrates. Atomic force microscopy was used to measure the RMS surface roughness of selected specimens derived from the areal power spectral density (PSD) of surface height variations over the spatial frequency region between 1 and 1000 μm^{-1}. Following these measurements, the substrates received new Mo/Si ML coatings with the same characteristics describe above, i.e. N = 40 1/2 and $\Lambda \approx 70$Å. For comparison purposes an unprocessed control specimen was coated in each magnetron sputter deposition process. The normal incidence EUV reflectance of all specimens was measured and compared to that of the control sample.

Results

Mo/Si ML coatings react with atmospheric gases. The temporal stability of the EUV reflectance of ML coatings with Si uppermost is greatest, and this is the favored design for

EUV MLs operating at 13 nm. High performance near-normal incidence EUVL optical elements properly consist of a substrate, a Mo/Si ML and an overlayer of SiO_2 formed in the oxidation of the uppermost Si layer upon exposure to the atmosphere. The Mo/Si ML was removed in a chlorine RIE, typical process parameters were 10 Watts of rf power at 13.56 MHz, at a pressure of 15 mTorr and gas flow rates of order 50 sccm. However, the surface oxide is resistant to the chlorine etch, and ML removal will not occur unless the surface oxide has been stripped in a separate process. A three minute RIE process using SF_6, at 15 mTorr and 40 sccm with 10 Watts of rf power at 13.56 MHz effectively cut the surface oxide. With the surface oxide removed, the time required to completely remove the ML coating is of order 20 minutes; this corresponds to a Mo/Si etching rate of order 10 nm/min.

The surface height variation after a 200 minute chlorine RIE process for both zerodur and SiO_2 substrates is illustrated in Figure 1. Difference curves were calculated from a Zernike polynomial analysis of the measured surface height distributions of the pre- and post-etched substrates correct to 16^{th} order. The measurements were made over a 20 mm diameter clear aperture centered on the 25 mm diameter substrates. Within the measurement accuracy (3 nm), the chlorine RIE process produces no detectable change in the surface figure of either substrate material.

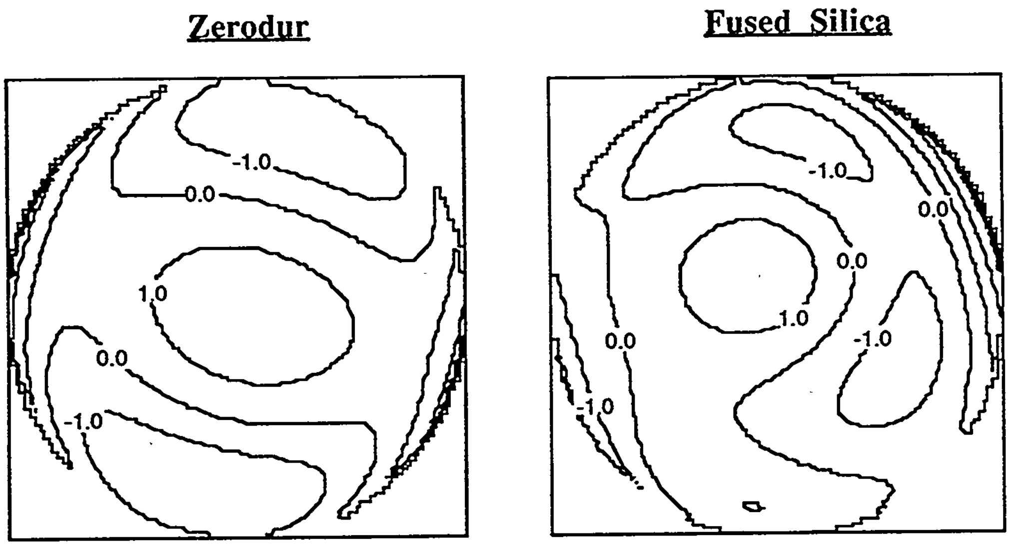

Figure 1. Change in surface figure after a 200 min Cl etch. Contour intervals are 1 nm.

Measurement of the EUV normal incidence reflectance of the recoated substrates provides a more detailed probe of the substrate surface condition. In Fig. 2 the recovered reflectance is illustrated vs. etching time for both fused silica and zerodur substrates. In each case, the reflectance has been normalized to the measured NIR of the control sample. The recoated substrates exhibit a gradual degradation in reflectance with increased etch time which is more severe for zerodur than fused silica. For the longest etching times recoated zerodur substrates exhibit approximately twice the reflectivity loss of fused silica substrates; however, for the longest etching time investigated (200 minutes), this corresponds to 60% recovery of the initial NIR. For SiO_2, worst case behavior corresponds to greater than 80% recovery of the initial NIR. Note that a 200 minute etch corresponds to an eight-fold increase in the time required to completely remove the ML. For shorter processing times ≤ 50 minutes $> 95\%$ of the initial reflectance is recovered for both substrate materials.

In Fig. 3, we illustrate the relationship between ML reflectance and substrate surface finish as derived from scanning probe microscopy measurements of RIE processed SiO_2 optical flats. The variation in substrate surface condition was produced by altering the duration of the chlorine etch. The ML reflectance is well correlated with surface roughness

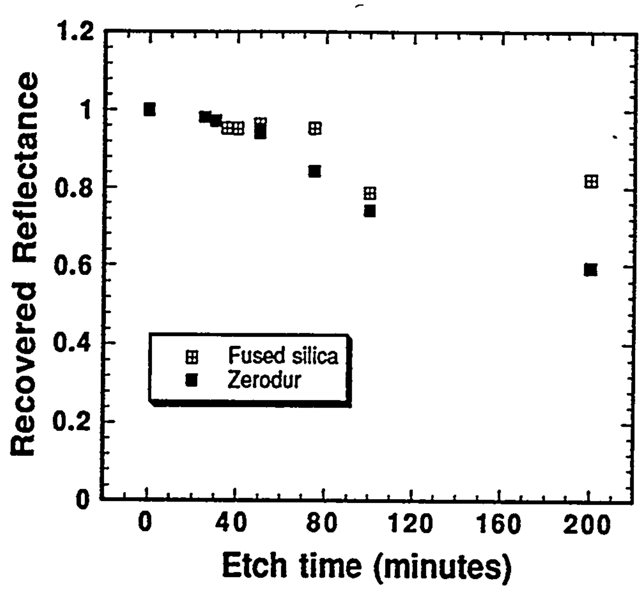

Figure 2. Recovered normal incidence reflectance vs. etch time.

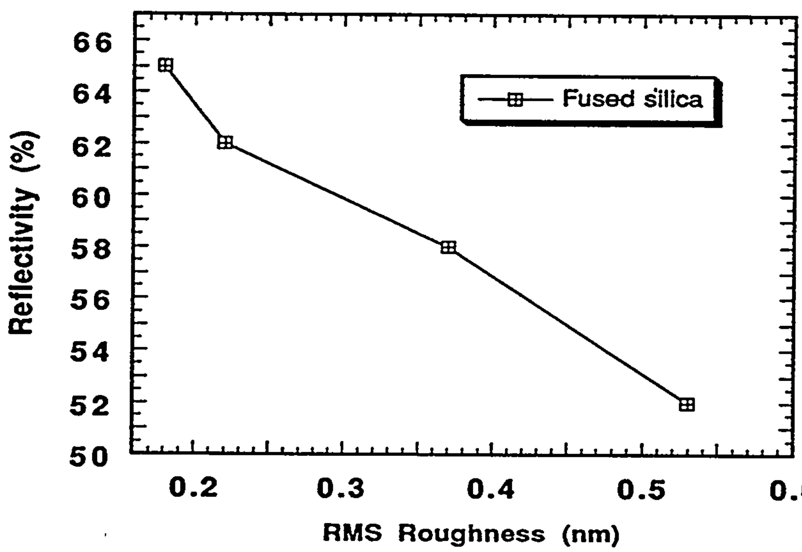

Figure 3. Reflectance vs. substrate surface roughness for SiO_2 substrates.

and decreases from a maximum of 65%, typical of high reflectance Mo/Si ML coatings on superpolished optical flats[4], to 50% as the substrate surface roughness increases from 0.1 to 0.55 nm.

Conclusions

A method for the removal of high reflectance Mo/Si ML coatings from superpolished EUV substrates which permits substrate re utilization and the full recovery of the initial EUV reflectance of the ML coated optic has been demonstrated. The method is successful for both zerodur and fused silica substrates. For optical flats, within the experimental accuracies, the process produces no detectable modification to the surface figure; however, the substrate surface roughness is increased for substrates subjected to the reactive environment for excessive periods. The method offers significant process latitude in that an eight fold over etch on SiO_2 substrates still enabled 80% recovery of the initial normal incidence reflectance. The technique has been successfully used to recover highly curved spherical surrogate optics utilized in calibration of the ML deposition process for the Lawrence Livermore National Laboratory (LLNL) front-end test bed imaging system[5]. Extensions of the technique to the recovery of precisely figured EUVL substrates are in progress.

Acknowledgments

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