Optimizing a Cleaning Process for Multilayer Dielectric (MLD) Diffraction Gratings

Introduction

The OMEGA EP Laser System consists of four beamlines, two of which will provide 1054-nm pulses having multikilojoule energies, picosecond pulse widths, petawatt powers, and ultrahigh intensities exceeding 10^{20} W/cm^2 (Ref. 1). These two beams can be directed into the existing OMEGA laser's target chamber for (1) fast-ignition experiments, which use a pulse of energetic electrons to heat the compressed fuel, thus igniting the fusion reaction,[2] and for (2) production of short pulses of x rays to "backlight" imploding fusion targets for diagnostic purposes.

The picosecond pulses are created by chirped-pulse amplification (CPA),[3] as shown in Fig. 112.24. To amplify the laser pulse without damaging the amplifier, a short pulse from the source is first chirped, or stretched into a longer, lower-power pulse in which the longer wavelengths travel at the front. The pulse is expanded in diameter, amplified, and then compressed by a series of four diffraction gratings. The compression occurs as the longer (red) wavelengths at the front of the amplified pulse are diffracted more and, therefore, forced to travel longer paths than the shorter (blue) ones. As a result, all wavelengths in the pulse arrive at the fourth grating at the same time. The fourth grating in the series experiences the shortest pulse length and is subjected to the highest fluence. The damage resistance of this last grating is the limiting element on the amount of energy that can be obtained in the compressed laser pulse. The last grating must be of a very high optical quality and have a high laser-damage threshold. The primary requirements for these large-aperture (43 cm × 47 cm) gratings are a high diffraction efficiency greater than 95%, peak-to-valley wavefront quality of less than $\lambda/10$ waves, and a high laser-induced-damage threshold greater than 2.7 J/cm^2 at 10-ps measured beam normal.

The multilayer dielectric (MLD) grating consists of a film of SiO_2, etched to form a grating structure with 1740 lines per millimeter. This structure resides on top of a multilayer dielectric high-reflector stack composed of alternating layers of SiO_2 and HfO_2. It is the cleanliness of this structure that is of paramount importance to survivability. Previous work at LLE has evaluated several candidate MLD cleaning protocols.[4] This article describes the results of an investigation to further optimize a final MLD-diffraction-grating cleaning process called "piranha clean" to increase laser-damage resistance.

Piranha Clean

Piranha solution is a mixture of sulfuric acid and hydrogen peroxide. This chemically aggressive agent has been used in the semiconductor industry for many years as the primary means of removing heavy organics like photoresist from wafers and photomasks. Typically, mixtures of H_2SO_4 (>95 wt%) and H_2O_2 (30 wt%) in volume ratios of 2 to 4:1 are used at temperatures of 80°C and higher. When hydrogen peroxide and sulfuric acid are mixed, "Caro's acid" [i.e., monopersulfuric acid (H_2SO_5)] is formed [Eq. (1)]. Caro's acid is the active etchant in a piranha bath.[5]

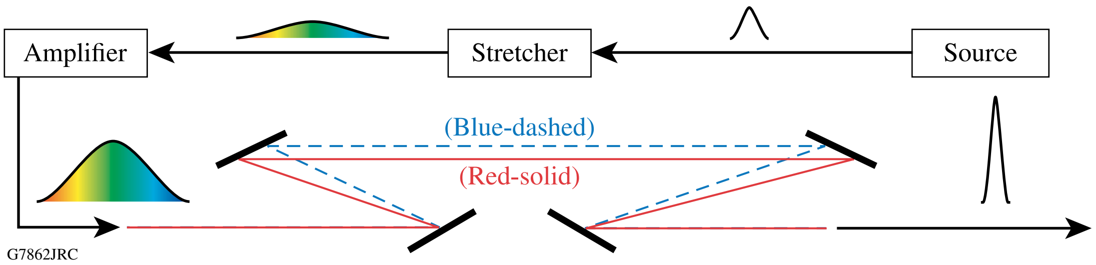


Figure 112.24
Diagram of chirped-pulse amplification. The pulse is amplified and then compressed by a series of four tiled-grating assemblies.

$$\begin{aligned}&H_2O_2+\left[HO-\left(SO_2\right)-OH\right] \rightleftarrows\\&\left[HO-\left(SO_2\right)-O-OH\right]+H_2O.\end{aligned} \tag{1}$$

As shown in Eq. (1), water is produced in the reaction between hydrogen peroxide and sulfuric acid. The presence of excess water in the mixture shifts the equilibrium toward the reactants, minimizing the production of Caro's acid. Therefore, using highly concentrated hydrogen peroxide (85 to 90 wt%) optimizes the production of Caro's acid; however, the use of highly concentrated hydrogen peroxide is extremely dangerous. For safety reasons, a lower concentration (30 wt%) is used. The excess water in 30-wt% H_2O_2 shifts the reaction away from the formation of H_2SO_5. The use of H_2O_2 in a low concentration also leads to significant heating of the piranha solution when the reactants are mixed. Caro's acid, which is heat sensitive, subsequently breaks down, resulting in a low-equilibrium concentration of this oxidizing acid. So, the mixture of H_2SO_4 and H_2O_2 requires higher temperatures to be effective in removing heavy organic materials like photoresist.

Experimental

Small (100-mm-diam) MLD diffraction gratings were fabricated at Plymouth Grating Laboratories (Fig. 112.25) by the following process steps:

1. *E*-beam deposit a 1053-nm, high-reflectivity multilayer coating of hafnium dioxide (HfO_2) and silicon dioxide (SiO_2) on a BK7 substrate.

2. Meniscus-coat a bottom organic antireflective coating (BARC) to the multilayer stack to eliminate standing wave effects; then meniscus-coat a PFI 88 (Sumitomo) positive photoresist layer.

3. Expose (pattern) the photoresist layer using a scanning-beam interference-lithography (Nanoruler) method. (The Nanoruler was developed by Dr. Mark Schattenburg at MIT. This exposure system moves a small UV laser beam over the substrate in overlapping scans to create a pattern of parallel lines in the photoresist. The gratings were patterned for 1740 lines/mm.)

4. Develop the patterned photoresist layer using an OPD262 developer.

5. Selectively remove the BARC layer with an O_2 reactive ion-beam-etch (RIBE) process.

6. Etch the SiO_2 grating layer using an $Ar/O_2/CHF_3$ RIBE process.

After step 6 above, gratings were shipped to LLE to evaluate the piranha clean process for removing (e.g., stripping) all photoresist and cleaning the grating surface. Two variables were examined: the ratio of H_2SO_4 to H_2O_2 and the treatment temperature.

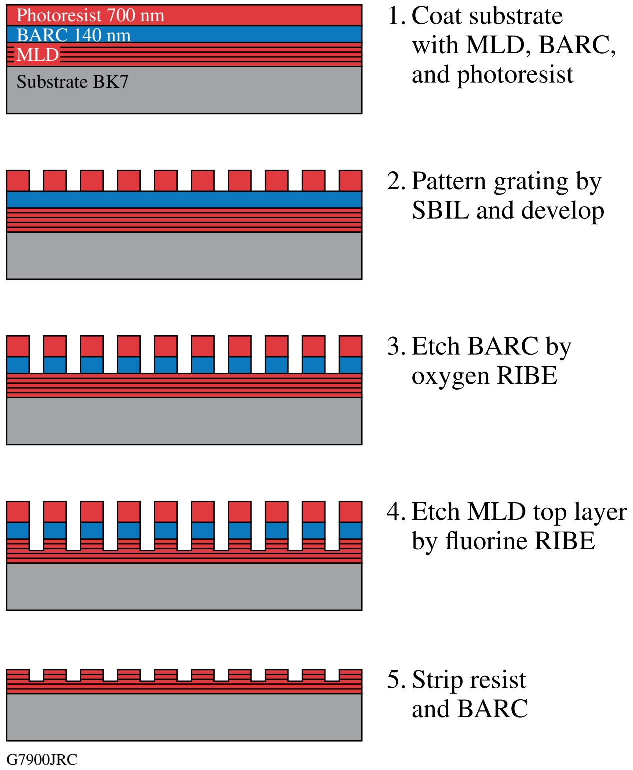


Figure 112.25
MLD grating fabrication process (figure not drawn to scale).

A sufficient number of gratings were cut into quarters to generate nine parts. A design-of-experiments (DOE) test was conducted with these parts to evaluate the influence of piranha solution composition and temperature on laser-damage threshold. The piranha clean process is shown schematically in Fig. 112.26. At a given treatment temperature, a part was immersed in a piranha bath of a given concentration and stirred for 20 min to strip the resist (step 1), subjected to a piranha rinse for less than 1 min (step 2), cleaned again for 10 min (step 3), rinsed in de-ionized water for approximately 3 min (step 4), then cooled to ~22°C and blown dry with filtered N_2 gas (step 5). Dried parts were evaluated for cleanliness by determining their laser-damage thresholds.

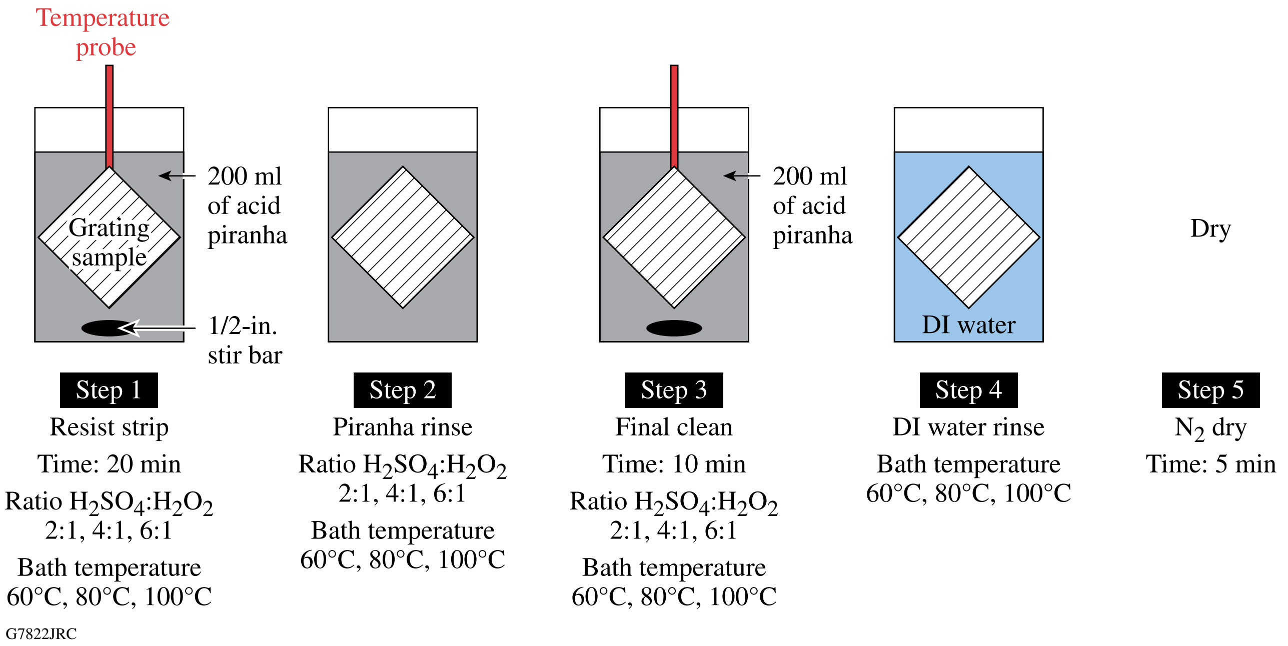


Figure 112.26
Piranha process. The variables within the experiment were the ratio of H_2SO_4 to H_2O_2 and the temperature of the piranha mixture.

Results

1. Laser-Damage Threshold

Laser-damage testing was conducted using a 10-ps-pulse, *s*-polarized laser operating at 1053 nm with an incident beam angle of 61° (diffracted beam of 72°). Both 1-on-1 and *N*-on-1 laser-induced-damage tests were performed. For 1-on-1 testing, individual sites on the grating are irradiated once with increasing energies until visible damage is observed. For *N*-on-1 testing, a single site is irradiated at increasing energies until damage is observed. The LLE specification for the damage threshold of our MLD gratings is >2.7 J/cm^2 at a 10-ps pulse length (for both 1-on-1 and *N*-on-1).

Figures 112.27 and 112.28 show the results of the damage-threshold tests that were measured for the different piranha clean processes. These results indicate that the temperature of the piranha mixture was the main variable, while the ratio of H_2SO_4 to H_2O_2 had a lesser effect. For both 1-on-1 and *N*-on-1

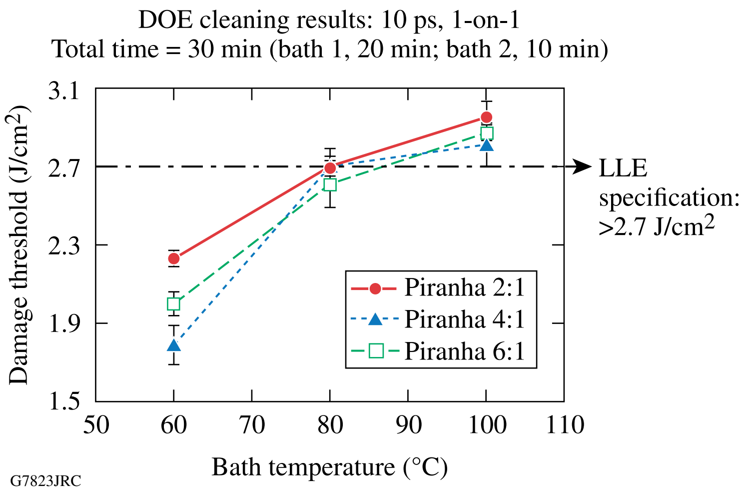


Figure 112.27
10-ps, 1-on-1 damage threshold at 1053 nm.

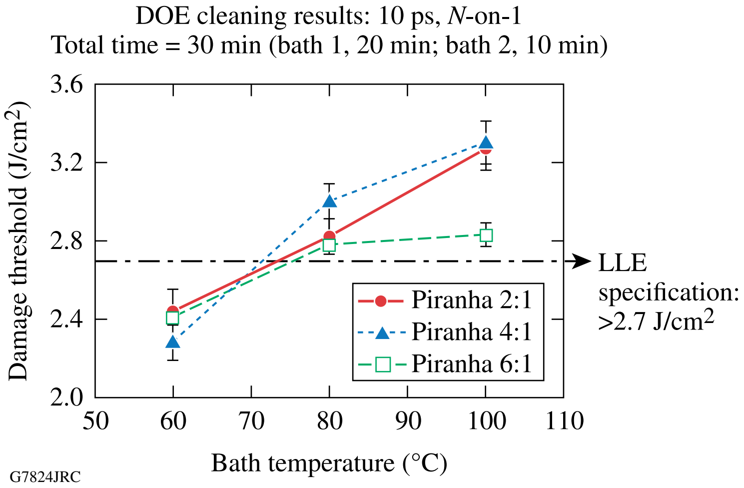


Figure 112.28
10-ps, *N*-on-1 damage threshold at 1053 nm.

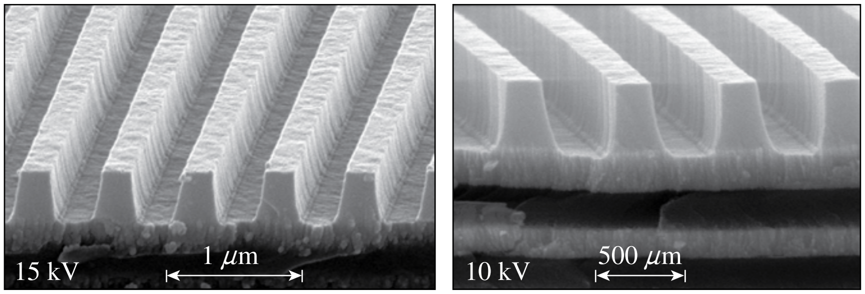
tests, increasing the piranha temperature caused the grating laser-damage threshold to increase. This observation supports the discussion earlier in this article regarding the need to generate sufficient Caro's acid for efficient etch-cleaning. One could expect that further increases in bath temperatures would lead to even more enhanced laser-damage thresholds. Other work (not described here) has shown that higher process temperatures create thermal shock issues for small test gratings. The full-size grating elements used in OMEGA EP, consisting of 10-cm-thick plates of BK-7 glass, will not be subjected to cleaning process temperatures greater than 100°C. (Preliminary work to model this issue is reported elsewhere.[6])

2. SEM Analysis

Scanning electron microscopy (SEM) images were collected and analyzed for the highest (2:1, 100°C) and lowest (4:1, 60°C) damage-threshold MLD gratings that were cleaned in this study. The SEM images of the piranha 2:1, 100°C and piranha 4:1, 60°C processes indicate there is no visual residual contamination within either of the grating trenches. The SEM images, along with the associated laser-damage-threshold data for these gratings, are shown in Fig. 112.29. Since neither sample had visual contamination, SEM analysis is not useful in determining the root cause for the differences in damage-threshold values.

3. ToF-SIMS Analysis

The ToF-SIMS analysis was performed at Surface Science Western, University of Western Ontario. The instrument used was an ION-TOF (GmbH), TOF-SIMS IV, with a mass range of 1 to 1000 amu. To acquire positive and negative "shallow" depth profiles (i.e., meaning probing a few tens of nanometers into the surface), a 3-keV Cs^+ sputter ion beam was used for the negative secondary-ion profiles, while a 3-keV O_2^+ sputter ion beam was used for the positive secondary-ion profiles. The sputter-beam raster area was 500×500 μm². Each sputter beam



Piranha 2:1, 100°C, 30 min
Damage threshold:
10 ps, *N*-on-1: 3.27 J/cm²
10 ps, 1-on-1: 2.95 J/cm²

Piranha 4:1, 60°C, 30 min
Damage threshold:
10 ps, *N*-on-1: 2.29 J/cm²
10 ps, 1-on-1: 1.79 J/cm²

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Figure 112.29
SEM images of the highest- and lowest-damage-threshold samples (piranha 2:1, 100°C; piranha 4:1, 60°C process). Laser-damage-threshold standard deviation for these samples is ±5%.

enhanced the secondary-ion yield through a reactive-ion effect for the given secondary-ion polarity. The Bi_3^+ analysis area was centered within this sputter crater, with a raster size of 200 × 200 μm^2. (Using a smaller raster size for analysis rather than the sputter crater size allows one to avoid edge effects during depth profiling.) By alternating the Bi_3^+ analysis and Cs^+/O_2^+ sputter beams, and inserting an electron flood-gun pulse in between for charge neutralization, a depth profile into the surface was acquired.[7]

A ToF-SIMS "shallow"-depth-profile analysis was conducted on the highest (piranha 2:1, 100°C) and lowest (piranha 4:1, 60°C) damage-threshold samples to determine if there was a correlation between higher contaminant ions and lower damage-threshold values. The relative intensities of the positive and negative ions detected versus the sputter time for the two samples were plotted to examine the differences between the two samples.

The data (see Fig. 112.30) indicate that there were significant levels of salt ions remaining within the lowest-damage-threshold samples (piranha 4:1, 60°C). The potassium (K^+) and sodium (Na^+) ions were the most abundant at the surface and into the grating. These salt ions are thought to have come from multiple contamination sources, including, possibly, the rinse water, developer, materials used during cleaning (beakers), and general handling.

Piranha process	10-ps, 1-on-1 (J/cm^2)	10-ps, *N*-on-1 (J/cm^2)
— 2:1 at 100°C	2.95	3.27
···· 4:1 at 60°C	1.79	2.29

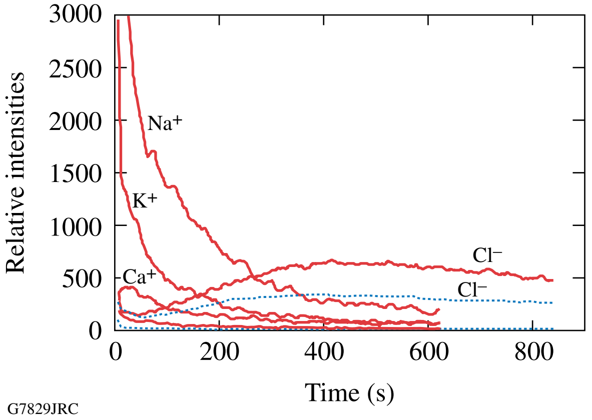

Figure 112.30
Salt-containing species. Piranha 4:1, 100°C has significant levels of salt remaining after clean. Laser-damage-threshold standard deviation for these samples is ±5%.

The carbon-ion species are shown in Fig. 112.31. The carbon ions are associated with the photoresist that was used in the fabrication process. This graph indicates that there were carbon (i.e., photoresist) species remaining at the surface and within the grating. The 4:1, 60°C sample had a much higher level of carbon ions than the 2:1, 100°C sample. There was also a high level of carbon implanted within the gratings. Since the top SiO_2 grating layer is amorphous, the resist was being driven into this surface. This correlates well with the damage-threshold values measured on these samples. Low-temperature piranha (with lower ratio) creates less Caro's acid and is ultimately less effective in removing organic contamination. This temperature effect can be seen clearly within our ToF-SIMS results.

Piranha process	10-ps, 1-on-1 (J/cm^2)	10-ps, *N*-on-1 (J/cm^2)
— 2:1 at 100°C	2.95	3.27
···· 4:1 at 60°C	1.79	2.29

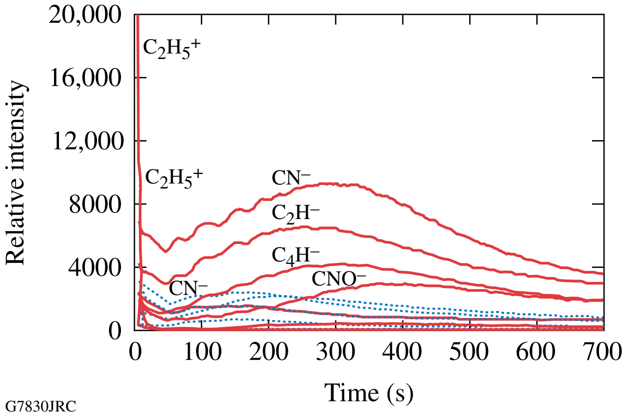

Figure 112.31
Carbon-containing species. Piranha 4:1, 100°C has significant levels of carbon (photoresist species) remaining after clean. Laser-damage-threshold standard deviation for these samples is ±5%.

Poor rinsing and neutralization of the piranha chemistry can over time cause problems at the grating surface. Residual sulfur-containing ions on or within the surface can cause surface haze (a common soft defect in the photomask industry). Figure 112.32 indicates that we did not completely rinse the piranha chemistry from the surface of the grating. The 4:1, 60°C sample had a much higher level of remaining sulfur ions than the 2:1, 100°C sample. This may be due to the lower-temperature piranha mixture not reacting completely with the carbon-resist species on the surface. The final rinse step to remove all of the piranha mixture will be very important in our final clean process to prevent the growth of sulfur-type haze.

Piranha process	10-ps, 1-on-1 (J/cm^2)	10-ps, *N*-on-1 (J/cm^2)
— 2:1 at 100°C	2.95	3.27
····· 4:1 at 60°C	1.79	2.29

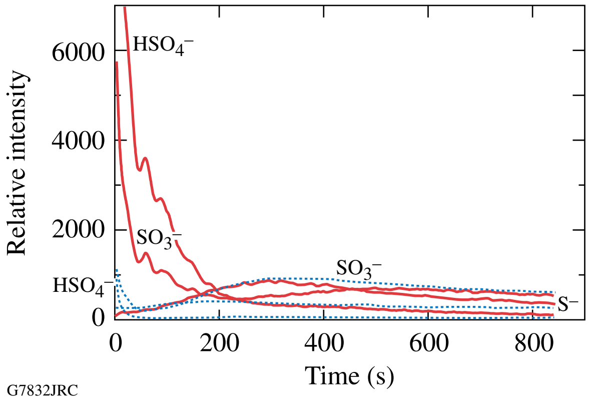

Figure 112.32
Sulfuric-containing species from incomplete rinse of the piranha mixture. Laser-damage-threshold standard deviation for these samples is ±5%.

Conclusions

The final clean removes any resist or particle contaminants that remain on the MLD diffraction grating after patterning and etch. Contaminant-removal efficiency in this step is critical to the performance of the grating within the laser system. The final clean employs a piranha mixture and DI water rinse to remove residual organic and other particulate and molecular contaminants. This final clean process must leave the surface free of unwanted contaminants and be able to produce high-damage-threshold gratings.

Using the 100-mm-diam MLD gratings fabricated at Plymouth Grating Laboratories, the final piranha cleaning process was optimized to achieve the OMEGA EP specification of >95% optical-diffraction efficiency and >2.7-J/cm^2 laser-damage threshold. The two main variables in the piranha process were the ratio of H_2SO_4 and H_2O_2 and the temperature of the mixture. Post-clean laser-damage threshold was measured for each cleaned sample. Additionally, scanning electron microscopy (SEM) and time-of-flight secondary ion-mass spectrometry (ToF-SIMS) "shallow"-depth-profile analysis was used to evaluate what type of contamination remained after the final clean process.

The laser-damage-threshold results indicate that as the ratio of H_2SO_4 to H_2O_2 increases within the piranha mixture, the damage threshold increases. Additionally, as the temperature is increased, the laser-damage threshold increases. From our data, there is a stronger correlation with the temperature of the piranha mixture.

ToF-SIMS shallow-depth-profile analysis provides an understanding of the contaminants on the surface as well as how far these contaminants are implanted into the grating surface. The analysis determined that the lowest-damage-threshold sample (4:1, 60°C) had considerably more contaminants on the surface and implanted into the grating. The low ratio and temperature piranha mixture was also unable to effectively rid the surface of the organic (i.e., photoresist) material and left considerable amounts of salts on the surface. Incomplete rinse and removal of the piranha mixture will leave sulfur-containing groups on the grating that may cause haze defects. LLE will use the information obtained in this study to scale up the piranha clean process to full-size gratings (43 × 47 × 10 cm).

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