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CRADA SC94-1259 Final Report Dielectric Mirror Masks for Laser Processing of Microelectronics

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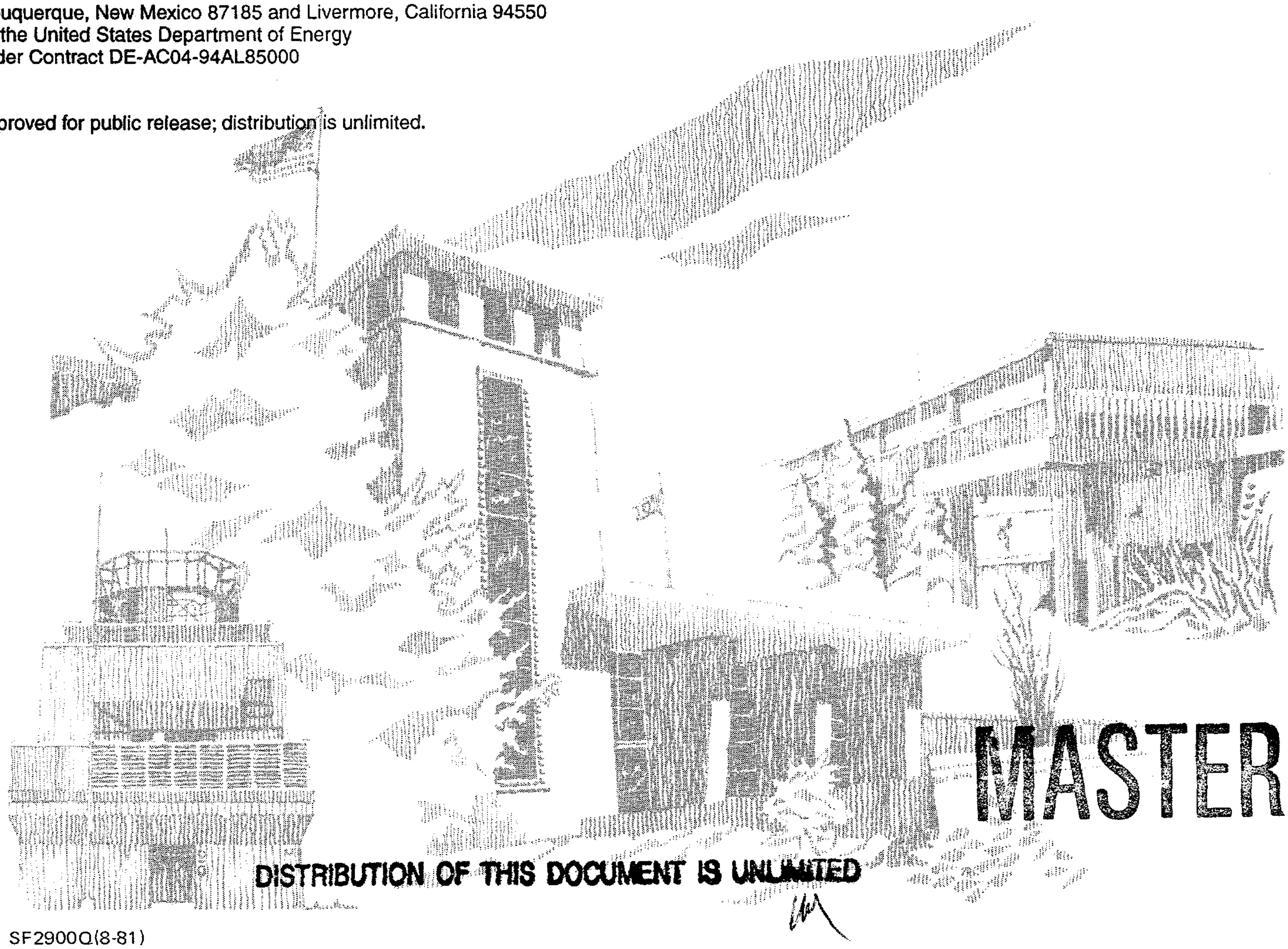

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CRADA SC94-1259 Final Report
Dielectric Mirror Masks for Laser Processing of Microelectronics

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Abstract

Two methods were examined for the fabrication of dielectric mirror masks. In the first method, a commercial laser mirror was patterned with photoresist and the dielectric film etched with ammonium bifluoride. The ammonium bifluoride etch showed strong kinetic anisotropy with the fastest etch rate in the vertical direction. However, horizontal etching still resulted in significant undercutting of the photomask. In the second method, a photoresist coated laser mirror was etched with an argon plasma. The argon plasma caused significant damage to the photoresist and underlying dielectric layer without adequate removal of the dielectric film in the open areas of the mask. Neither of the two methods examined were able to produce usable dielectric masks.

During the course of this project, it was discovered that a foreign company, Balzers AG of Liechtenstein, had recently developed successful fabrication procedures for dielectric mirror masks. A mask purchased from Balzers for testing showed distinguishable pattern features down to 2 μm in size. This mask was used in ablative projection etching experiments to form microstructures in Mylar polymer films. A thin film resistor pattern with 7.0 μm wide lines was etched 5.4 μm deep into a Mylar substrate. The etch pattern showed uniform linewidths but exhibited some thinning of the lines in areas where U-turns occurred. The ablative projection etching technique shows promise as a method for the rapid fabrication of contact masks in microstructuring applications.

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1.0 Introduction

Ablative laser etching processes utilize high photon fluxes that can quickly degrade metal film masks. These masks, which are easily produced using standard photolithography techniques, exhibit thresholds for laser damage typically less than 0.1 J/cm^2 under long term exposure conditions. Because irradiances of this magnitude or larger are required for direct laser etching of even the most easily ablated materials, the problem of mask damage has prohibited the use of ablative projection laser etching in many microstructuring applications. Dielectric mirror films, which have been in commercial production for many years, can exhibit laser damage thresholds up to 10 J/cm^2. These mirrors are constructed of alternating layers of two dielectric materials with different refractive indices. The layer thickness of each material is such that light transmission through the film at a specific wavelength is extinguished by destructive interference while light reflection from the film is enhanced by constructive interference. Because reflection from the film is based on interference effects, materials can be employed with very low absorption coefficients at the laser operating wavelength resulting in very high laser damage thresholds. These mirrors appear ideal for use as a mask system for laser etching. However, at the time this project was initiated in 1994, no technology was known to exist for the patterning of dielectric mirror films to form a mask. Under CRADA SC94-1259, a partnership was established between Sandia National Laboratories and Microphase Laboratories of Colorado Springs, Colorado for the expressed purpose of developing a patterning process for dielectric mirror films and evaluating the suitability of masks produced by this process in laser ablative projection etching applications. CRADA SC94-1259 was a modest effort to accomplish these tasks, budgeted at $70,000 split equally between Microphase and Sandia. Under the terms of the partnership Microphase evaluated the feasibility of two different approaches for the formation of dielectric mirror masks. In the first approach, a photoresist contact mask was applied to the surface of a commercial dielectric laser mirror using standard photolithography techniques. The dielectric film on the surface of the mirror was wet etched with aqueous ammonium bifluoride through the contact mask. The contact mask was then stripped from the mirror surface, leaving the patterned dielectric mirror film. The second approach was similar to the first but used an argon plasma etch to remove the dielectric layers. A third approach, discussed in the original proposal, involved deposition of the dielectric mirror layers through a photoresist contact mask applied directly to the mirror substrate. This was to be followed by removal of the photoresist with the intent of lifting off the dielectric layers which were deposited on top of the photoresist. However, this approached was judged to be unworkable by Microphase and was not attempted. Sandia inspected all dielectric mask samples produced by Microphase for etch depth and geometric accuracy of the patterned dielectric film, and tested a dielectric mirror mask fabricated by Balzers AG for suitability in laser ablative projection etching of Mylar polymer films. This report documents the results of this work.

2.0 Experimental Procedures

The commercial front surface dielectric mirrors used in this study were obtained from Litton Airtron. The mirrors were composed of UV grade fused silica optical flats coated for maximum reflectivity at a wavelength of 248 nm using alternating layers of SiO_2 and Al_2O_3. The total thickness of the dielectric mirror film was 2.7 μm. The breakdown threshold of this film was quoted by the manufacturer to be greater than 1 J/cm^2 at 248 nm. The dielectric mirrors were spin coated with 0.5 μm of AZ1450 photoresist and air baked for 30 minutes at 90°C. A chrome sodalime mask was placed in contact with the resist and given a 100 unit flood exposure from an Olite AL9 light source at an approximate distance of 36 inches. The exposed resist was then developed with a 3% solution of sodium hydroxide at room temperature for 30 seconds, rinsed with deionized water and allowed to air dry. Chemical etching of the dielectric mirror film through the photoresist mask was performed by immersion of the mirrors in a 5% solution of ammonium bifluoride at 20° C with mild agitation followed by an immediate rinse in deionized water to stop the reaction. The mirrors were then treated with a 5% solution of sodium hydroxide to strip off the photoresist, cleaned in a CA40 soap solution, rinsed in deionized water, and air dried. Depth profiles of the etched mirrors were measured by mechanical profilometry using a Dektak 8000 profilometer with a 2.5 μm radius tip and a normal force of 30 milligrams. Scans speeds were less than 20 μm/sec. The measurement interval of all contour maps presented in this study was 0.2 μm in the Y direction and 5 μm in the X direction. Mechanical profilometry of initial ammonium bifluoride etching tests run for 6 and 18 minutes resulted in a measured etch rate of 59 nm/min. The plasma etched dielectric mirror mask evaluated in this report was coated with photoresist, developed, and etched with an argon plasma by Yield Engineering Systems under contract to Microphase.

Ablative projection etching tests were performed using the optical system diagrammed schematically in Figure 1. The laser used in these tests was a Questek Model 2940 excimer laser operated on the KrF line at a wavelength of 248 nm. The average pulse energy of the laser was 238 mJ at a pulse length of 29 nsec and a pulse frequency of 1.0 Hz. The pulse to pulse energy of the laser varied by ± 5 % (reported as 2 times the standard deviation) over the course of these experiments. The laser beam had a rectangular flat top output profile with full width at half maximum intensity dimensions of 7.5 mm X 18.4 mm. The divergence of the laser beam was 1 X 3 milliradians. The laser beam was decollimated using a fused silica plano-convex lens with a focal length of 250 mm place between the laser and the dielectric mask. This lens allowed adjustment of the laser irradiance incident on the mask by varying the distance between the lens and the mask. The dielectric mask was placed 70 mm beyond the focal point of the 250 mm lens for all of the etching experiments reported here. The laser irradiance incident on the mask at this position was 170 mJ/cm^2 for each laser pulse. This optical arrangement did not result in air breakdown at the focal point of the 250 mm lens in these experiments due to the low laser pulse energies used and the high divergence of the laser beam. Laser radiation passing through the mask was focused by a fused silica bi-convex lens with a focal length of 150 mm onto a Mylar target film attached to a planar substrate. The magnification of the mask image on the target film could be continuously adjusted by varying the position of the 150 mm lens and the target film along the optical axis. Pulse exposures to the Mylar film were controlled with a mechanical shutter attached to the output aperture of the laser. The optical system shown in Figure 1 is not corrected for spherical aberrations. Consequently, the sharp focus field on the surface of the target was only 3 mm in diameter. Nevertheless, this optical performance was sufficient to demonstrate proof-of-concept for mask function within the limited scope of this project. The polymer films etched in this study were 35 μm thick free standing Mylar films.

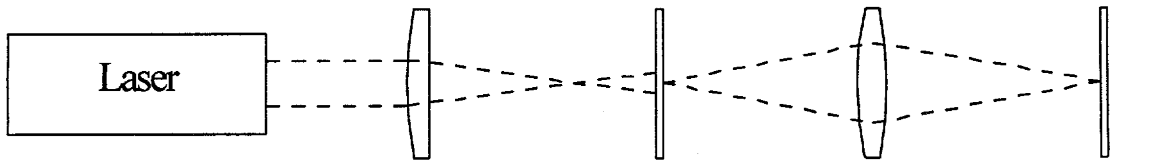


Figure 1. Schematic diagram of the optical system used for ablative projection etching. All transmissive optical components are UV grade fused silica. The laser emission wavelength is 248 nm.

3.0 Results

A diagram of the mask pattern used in the ammonium bifluoride etching studies is given in Figure 2(a). This pattern is a radio frequency power splitter used in radar applications. The power splitter consists of interlocking arms 203 μm wide with 20 μm gaps between adjacent arms. Bond pads are provided at the four corners of the power splitter for electrical connectivity. The dark areas in this figure were covered by photoresist during the etching process and represent regions where the etched dielectric mirror film should exhibit high reflectivity. The white areas in the figure represent regions were the dielectric film was etched by the ammonium bifluoride solution. Laser radiation incident in these regions should be transmitted through the mask. Figure 2(b) shows a micrograph of a dielectric mirror film etched in the ammonium bifluoride solution for 60 minutes. Note the high density of lightly colored defects in the regions of the pattern previously covered with photoresist during the etching process. These defects are pits and scratches in the surface of the dielectric film indicating that the photoresist did not adequately protect the underlying film from the ammonium bifluoride etchant. A high density of pits is also observed in the chemically etched plane on the upper left corner of the photograph. Figure 3(a) is a contour map of the central arms of the power splitter obtained by mechanical profilometry. Note in the contour map that undercutting of the photoresist has occurred at each exposed edge of the dielectric film. This is shown more clearly in the topographic cross section given in Figure 3(b). This cross section was taken along the dashed line shown in Figure 3(a). The dotted line in Figure 3(b) shows the intended contour of the dielectric film. The ammonium bifluoride etch shows strong kinetic anisotropy in the dielectric film with the fastest etch rate proceeding vertically downward. This resulted in the formation of the desired contour in the lower region of the etched structure. However, horizontal etching, while proceeding much more slowly, has still resulted in severe undercutting of the photoresist. The total etch depth in this experiment is 3.7 μm, which corresponds to complete penetration of the 2.7 μm thickness of the dielectric film and 1.0 μm penetration into the underlying fused silica substrate. Due to the high defect density observed, this mask was judged unsuitable for further testing. Two additional

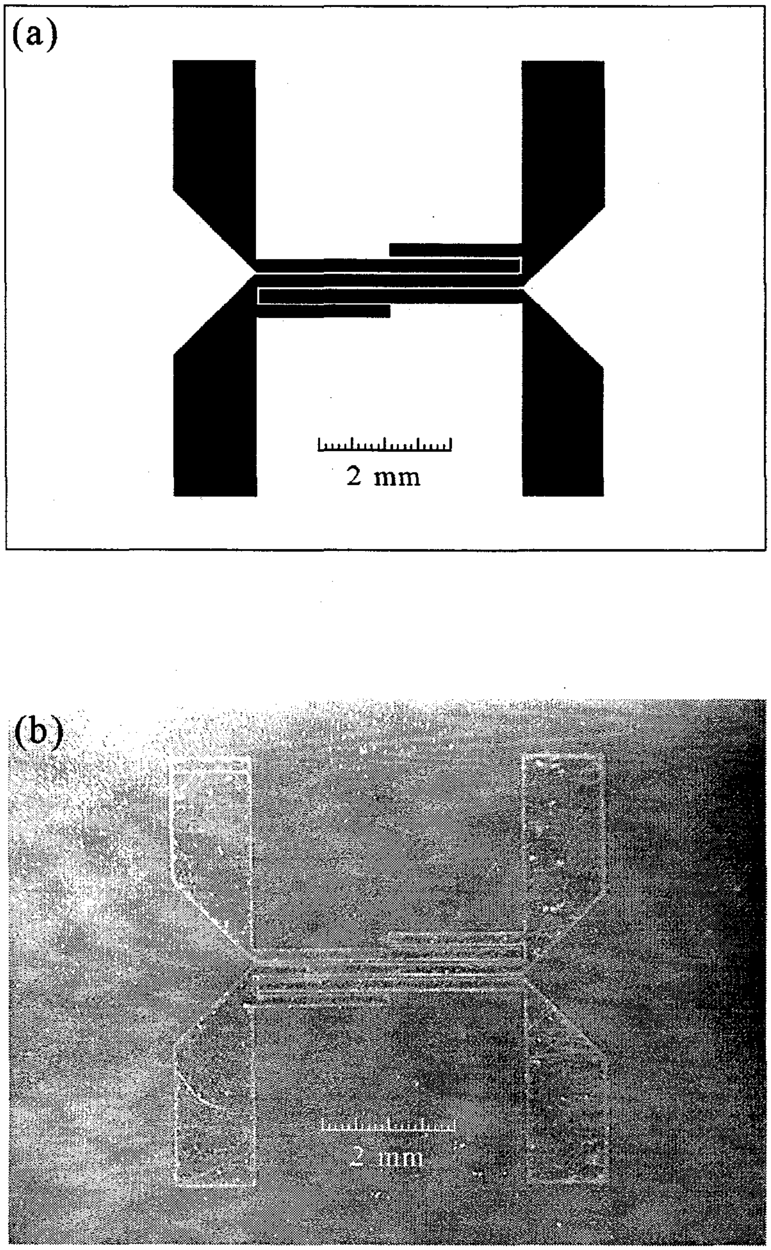


Figure 2. (a) Diagram of the power splitter mask pattern used in the ammonium bifluoride etching studies. The power splitter consists of interlocking arms 203 μm wide with 20 μm gaps between adjacent arms. (b) Micrograph of the dielectric mirror film etched with ammonium bifluoride for 60 min.

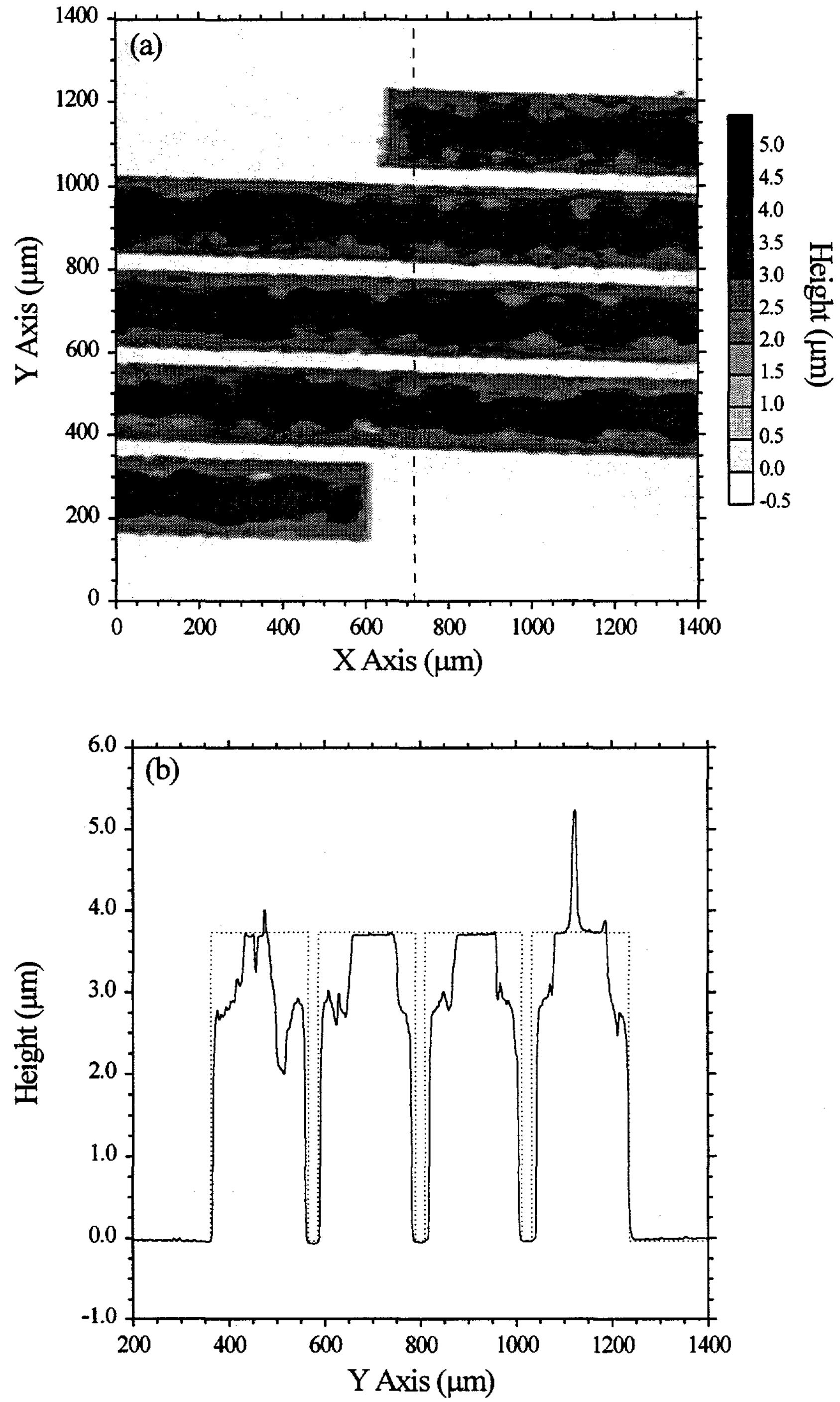


Figure 3. (a) Contour map of the central arms of the power splitter pattern etched into the dielectric mirror film using ammonium bifluoride. (b) Topographic cross section of the etched dielectric film taken along the dashed line in Figure 3(a). The dotted line in Figure 3(b) represents the intended contour of the etched dielectric film.

attempts to form dielectric mirror masks using the ammonium bifluoride etchant under these conditions produced similar results.

Micrographs of two pattern features on the dielectric mirror etched by Yield Engineering using the argon plasma process are shown in Figure 4. The pattern used in the plasma etching study was developed by Microphase and contains a wide variety of structures including large circles, squares, and rectangles with dimensions between 0.5 and 3.5 millimeters, a series of dot patterns with diameters of 25 and 125 μm, thin film resistor patterns with linewidths down to 5.0 μm, and resolution measurement patterns with feature sizes down to 1 μm. The pattern shown in Figure 4(a) is a thin film resistor pattern with a linewidth of 5.0 μm. Part of a larger resistor pattern with critical dimensions exactly two times those of the smaller pattern can be observed on the right hand side of the figure. Figure 4(b) shows a 125 μm diameter dot located in a region near the center of the mask. All of these patterns were formed as negative images. The lines and bond pads of each resistor and the interior of the dot represent open areas of the mask which were directly etched by the plasma. The adjacent fields were covered with photoresist and should have been protected from the plasma. However, partial removal of the photoresist by the plasma was observed on this mask leading to surface damage on the underlying dielectric film. This surface damage has resulted in the speckled appearance observed in Figure 4 in the fields previously covered by photoresist during the etching process. In addition, many lightly colored defect sites were observed on the mask which appear to be deeply etched regions. Examples of these defect sites can be seen on the upper bond pad of the small resistor pattern in Figure 4(a). Finally, material of unknown origin was deposited in many of the larger etched regions of the mask. Examples of these deposits appear as dark areas on the two lower bond pads in Figure 4(a) and as the dark area in the interior of the dot in Figure 4(b). A contour map of the 125 μm diameter dot in Figure 4(b) is presented in Figure 5(a). A cross sectional plot of the surface profile of the dot taken along the dashed line in Figure 5(a) is given in Figure 5(b). The dot, which should be an etched circular well, actually has the appearance of an etched annulus due to the presence of the central deposit. The deposit is irregular in shape with a flat top extending 23 nm above the surface plane of the mask. The deposit most likely results from the lateral redeposition of photoresist sputtered from adjacent areas. This sputtered polymeric material appears to have been altered by the ion irradiation such that it could no longer be removed by the stripping agent. The apparent etch depth of the dielectric film measured from the bottom of the annulus to the surface plane of the mask is 75 nm. This dimension is only 3 % of the original thickness of the dielectric film on the mirror. For reasons of incomplete etching and high defect density, this mask was also judged unsuitable for further testing.

During the course of this project, it was discovered that a foreign company, Balzers AG of Liechtenstein, had recently developed methods for the production of an ultraviolet mask using a dielectric mirror coating on a quartz substrate. A sample mask was obtained from Balzers containing the Microphase pattern. The patterned dielectric film was Balzers Type UV-Spiegel with a maximum reflectivity of 99.9% at 245 nm. Inspection of the mask using an optical microscope revealed critical dimensions in agreement with all mask specifications and only 3 small defect sites originating from the manufacturing process. A micrograph of the resolution pattern placed on the mask to determine the minimum feature size is shown in Figure 6(a). The

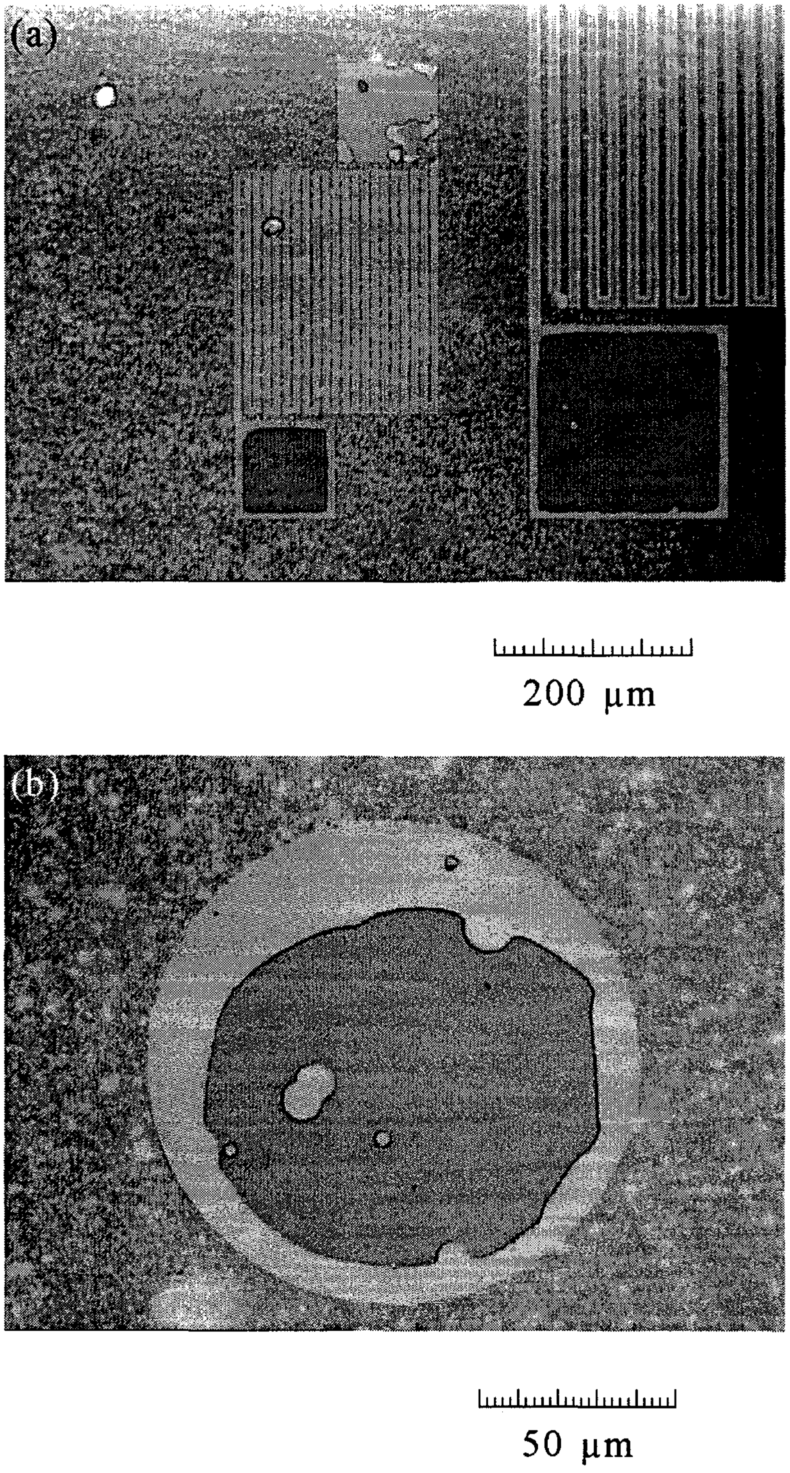
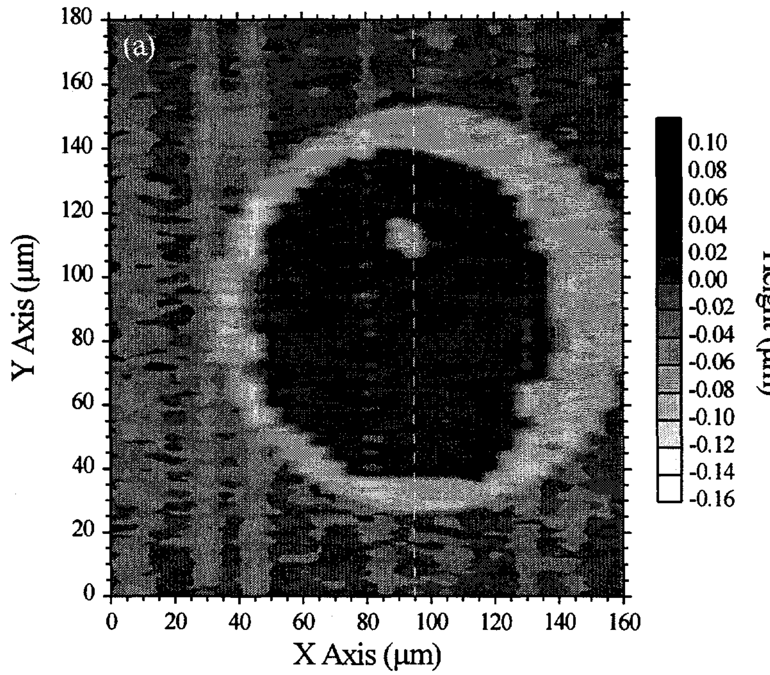


Figure 4. Micrographs of selected pattern features etched into a dielectric mirror films by Yield Engineering Systems using an argon plasma. (a) A thin film resistor pattern. (b) A 125 μm diameter dot.



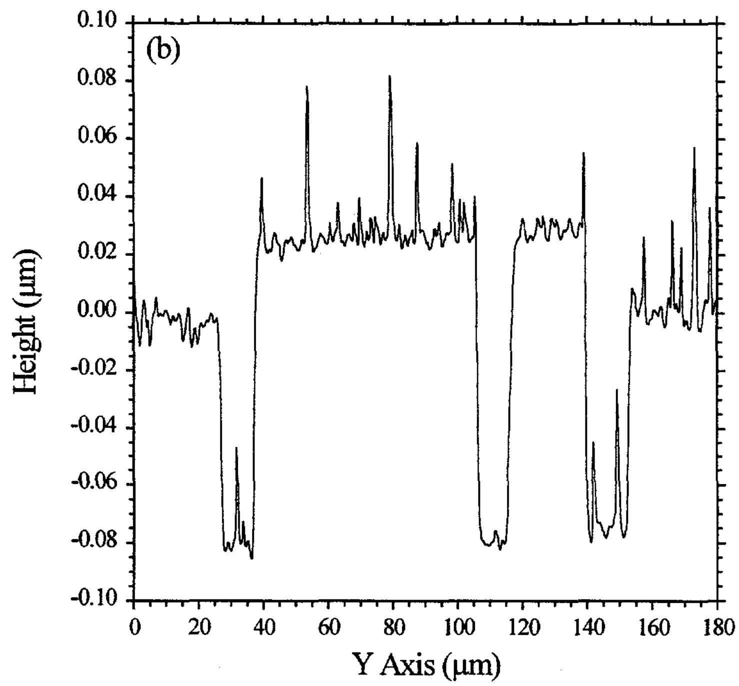


Figure 5. (a) Contour map of the 125 µm diameter dot shown etched into the dielectric mirror film in Figure 4(b). (b) Topographic cross section of the etched 125 µm diameter dot taken along the dashed line in Figure 5(a).

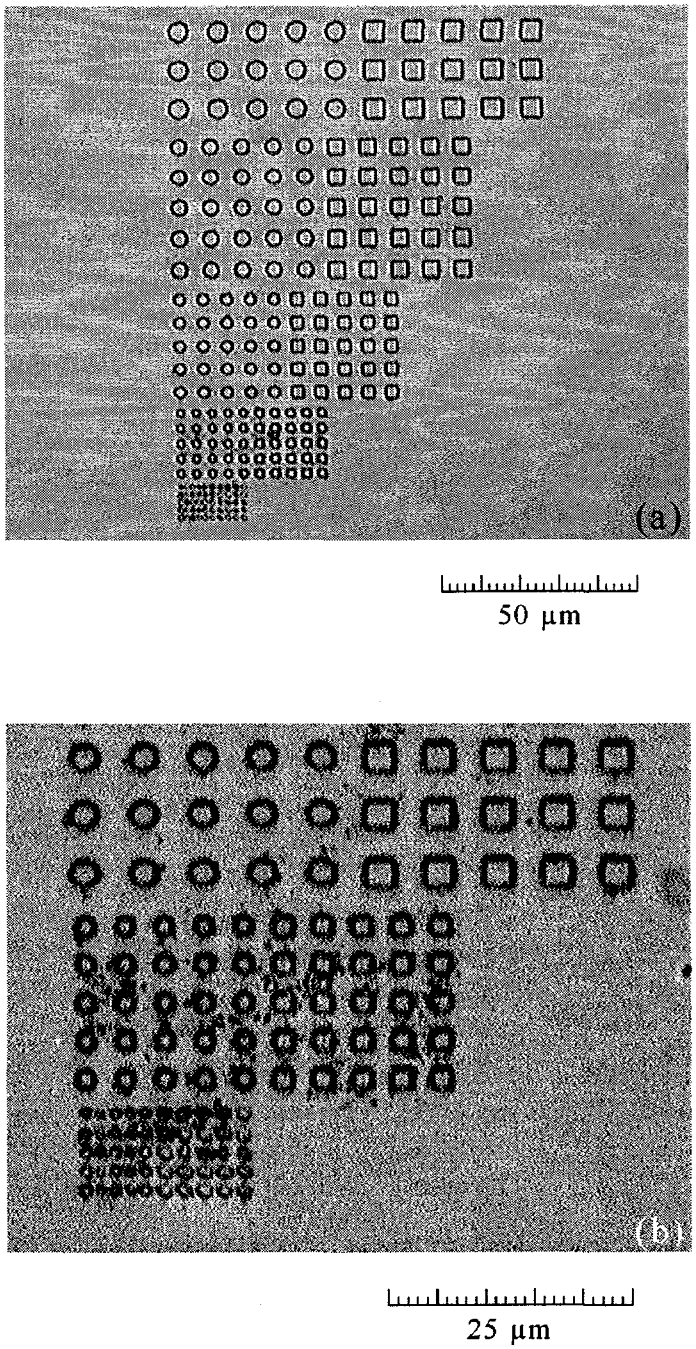


Figure 6. (a) Micrograph of the high resolution pattern on the Balzers dielectric mirror mask. The circles and squares vary in size by 1 μm steps from 5.0 μm at the top of the pattern to 1.0 μm at the bottom of the pattern. (b) Micrograph of the 1, 2, and 3 μm features in the high resolution pattern taken at 2.5 X higher magnification.

pattern consists of a series of circles and squares decreasing in size by 1 μm steps from 5.0 μm down to 1.0 μm. The 1, 2 and 3 μm features are shown at 2.5 X higher magnification in Figure 6(b). Note that the squares in the resolution pattern are easily identifiable down to 2.0 μm but show significant rounding of the corners between 3.0 μm and 2.0 μm. At 1.0 μm the corners of the squares are rounded to the point where the squares and circles are indistinguishable except for a slight difference in size. In addition, many of the 1 μm features are irregular in shape. The pattern shown in Figure 6 demonstrates that the minimum distinguishable feature size possible with the Balzers mask fabrication process is approximately 2 μm. The debris observed around the 2.0 and 1.0 μm size features in Figure 6(a) was deposited during mask handling. We were unable to remove this material from the mask using normal solvent cleaning techniques.

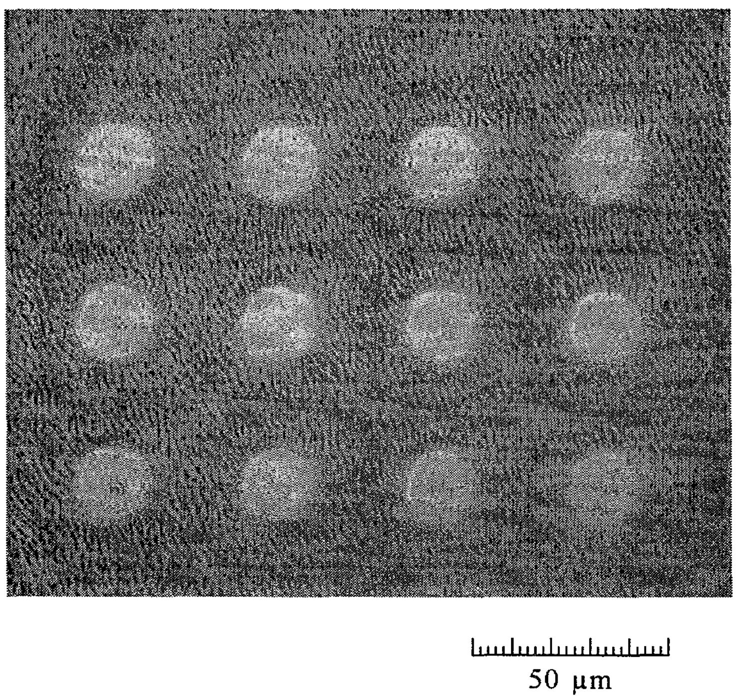


Figure 7. Micrograph of an array of 19.5 μm diameter pedestals etched 1.1 μm deep into a Mylar polymer film by ablative projection etching with an excimer laser.

The results of ablative projection etching tests on Mylar films using the Balzers mask are presented in Figures 7 through 10. These etching tests were performed at a projection magnification of 0.82 and an incident laser irradiance of 253 mJ/cm^2 per laser pulse at the surface of the Mylar films. Figure 7 shows an array of 19.5 μm diameter pedestals etched 1.1 μm deep into a Mylar film using an exposure of 8 laser pulses. The pedestals show good circular symmetry with nearly vertical side walls. Figure 8 shows a thin film resistor pattern etched 5.4 μm deep into a Mylar film using a laser exposure of 40 pulses. The pattern shows good edge

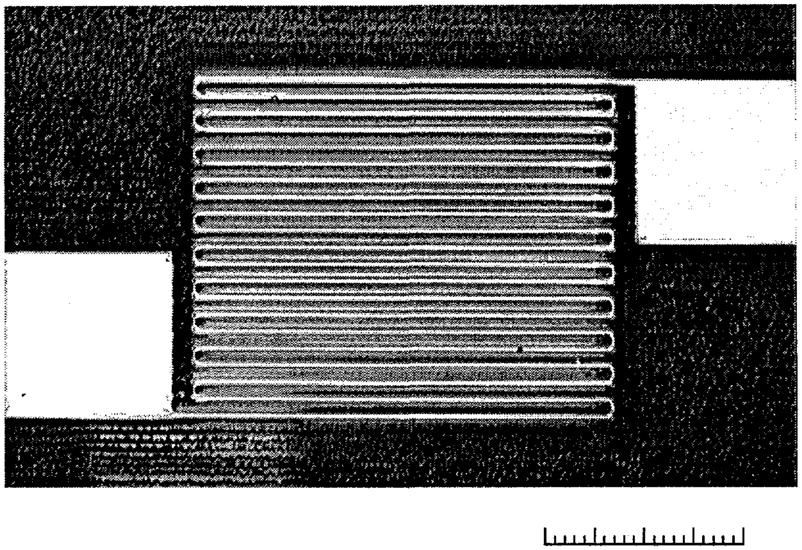


Figure 8. Micrograph of a thin film resistor pattern etched 5.4 μm deep into a Mylar polymer film by ablative projection etching with an excimer laser.

definition with uniform line thickness over almost the entire resistor path. The measured 165 μm width of the bond pads matches exactly the width expected based on the 0.82 magnification of the projection optics. Figures 9(a) and 9(b) show the lower left and upper right edges of the resistor lines at 4X higher magnification. The measured width of the resistor lines is 7.0 μm, which is only 85% of the expected width. Measurement of the second line from the bottom of Figure 9(a) gives an apparent base width of 7.9 μm and a top width of 5.7 μm. Given the 5.4 μm etch depth of the trench between the lines, this yields a calculated wall slope for the etched lines of 7° off vertical. The line width is uniform along the horizontal dimension of the resistor pattern but thins considerably in the U-turns. This thinning effect is more much pronounced on the left side of the conductor pattern than on the right side of the pattern. The dimpled regions observed in the pattern are most likely due to thermal damage in the unetched regions of the polymer surface. The laser etch depth was measured as a function of the number of incident laser pulses in the open area adjacent to the upper left bond pad in Figure 8. The results of these measurements are shown graphically in Figure 10. The observed etch depth of the Mylar film at the incident irradiance of 253 mJ/cm^2 appears to be a linear function of laser pulse exposure, at least over the measured range of 1 to 40 laser pulses. The measured etch rate taken from the slope of the least squares line in Figure 10 is 135 nm per laser pulse.

Laser etching tests were also conducted on silicon, alumina, and pyrex glass substrates. No measurable etching could be detected on any of these substrates at an incident irradiance of 253 mJ/cm^2, even after an exposure of 300 laser pulses.

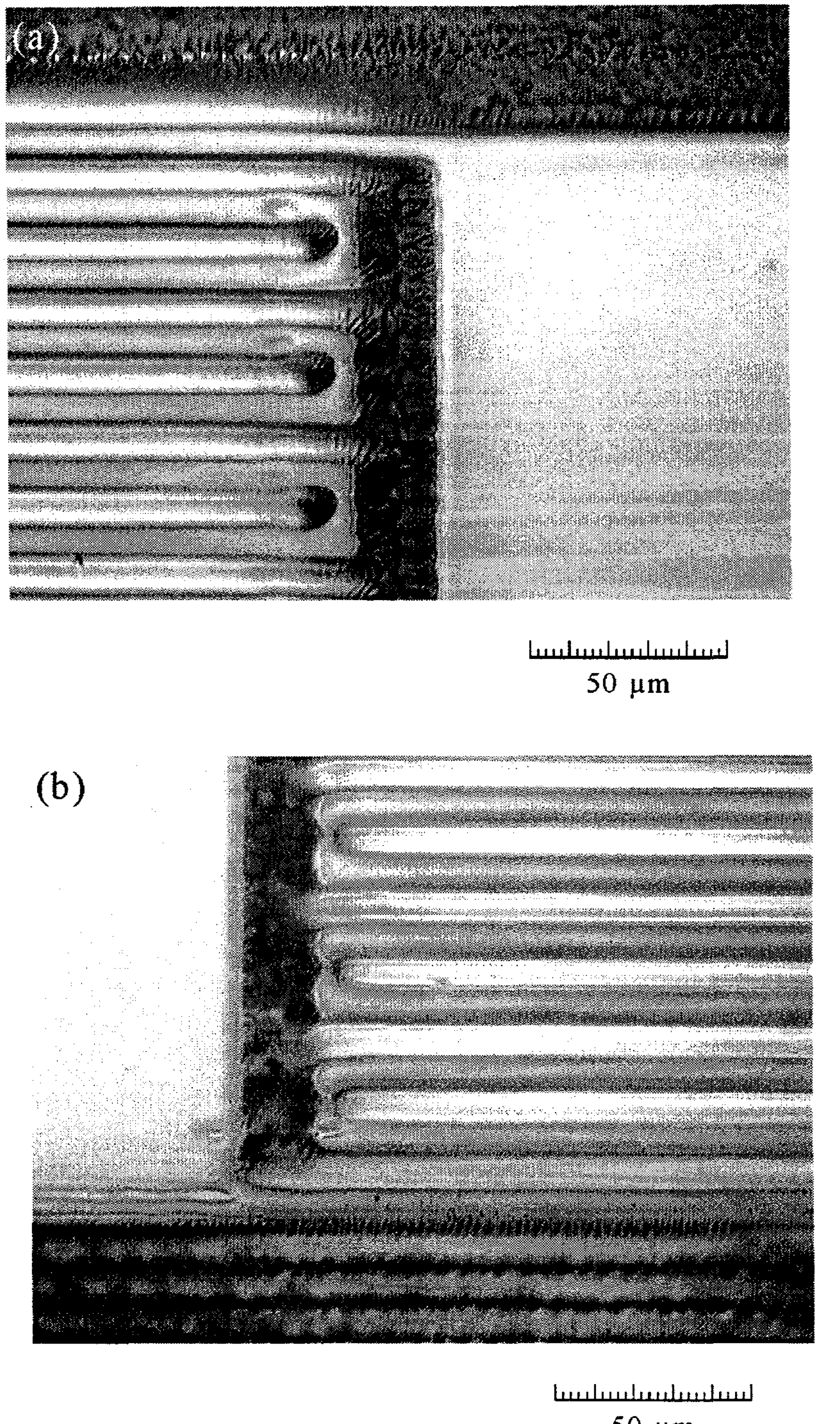


Figure 9. Micrographs of the thin film resistor pattern shown in Figure 8 at 4 X higher magnification. (a) Right top edge of the line pattern. (b) Left bottom edge of the line pattern.

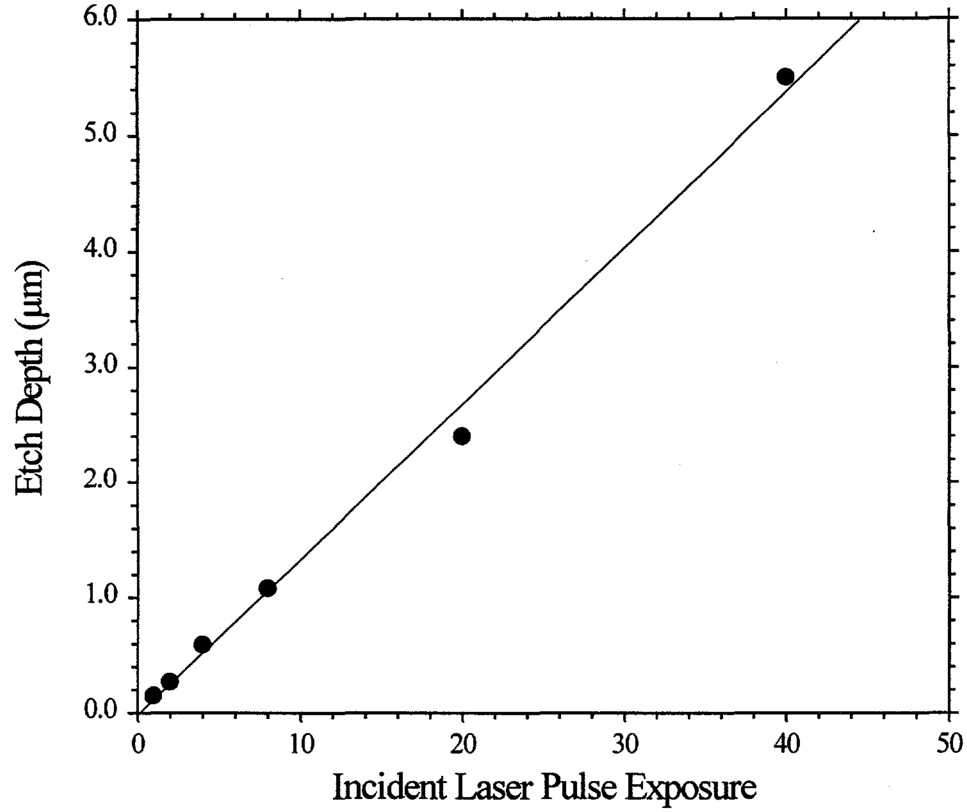


Figure 10. Laser etch depth in Mylar as a function of incident laser exposure for an incident pulse irradiance of 253 mJ/cm^2.

Following completion of the ablative projection etching tests, the reflective film on the mask was subjected to laser breakdown threshold testing by exposing the unpatterned areas near the edge of the mask to successively higher pulse irradiances until laser damage to the dielectric film was observed. A logarithmic plot of the number of laser pulses required to induce breakdown as a function of incident pulse irradiance is given in Figure 11. The equation of the least squares line calculated from the data is:

$$\log(y) = 24.050 - 7.413 \cdot \log(x) \quad (1)$$

At 1 J/cm^2, the Balzers dielectric films shows limited resistance to laser damage. Most commercial ultraviolet dielectric mirrors are stable at this irradiance value. However, at the 170 mJ/cm^2 irradiance incident on the mask in this study, the Balzers film should show excellent stability. By extrapolation using equation 1, the film is predicted to be capable of withstanding a minimum exposure of 3 X 10^7 laser pulses at an incident irradiance of 170 mJ/cm^2 per pulse. This is the equivalence of 24 hr continuous operation in the laser beam under the conditions used in this study for 1 year. Microscopic inspection of the patterned surface on the Balzers mask

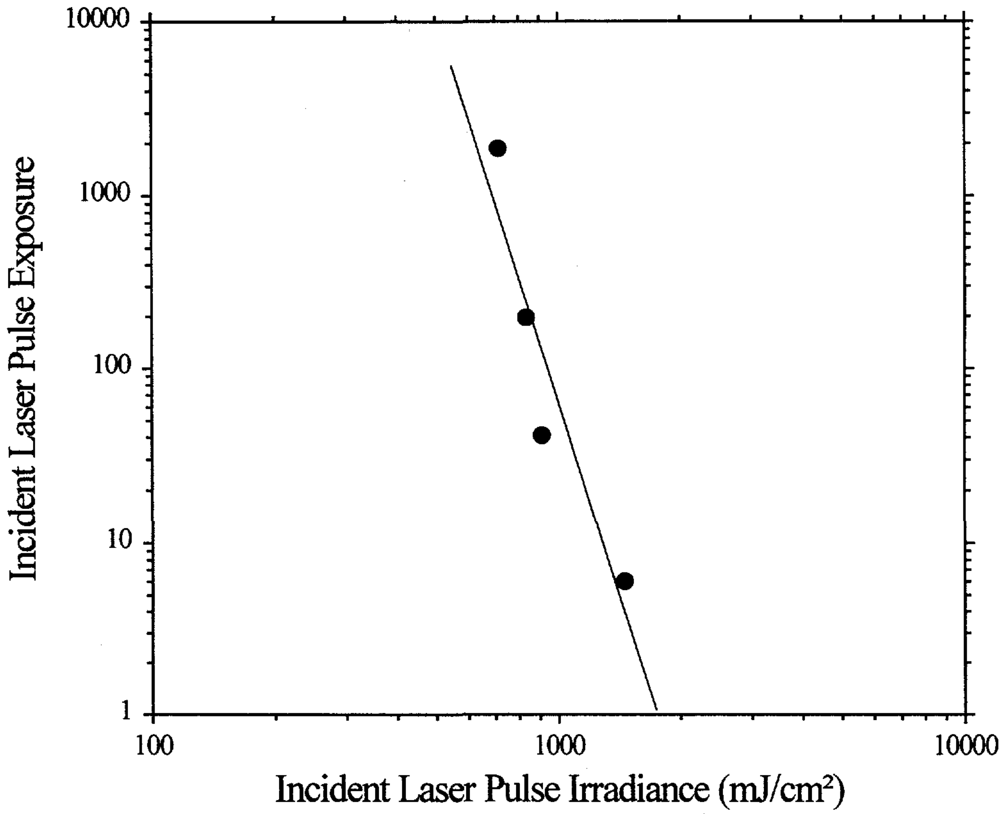


Figure 11. Logarithmic plot of the number of laser pulses required to induce breakdown of the Balzers dielectric mirror film as a function of incident pulse irradiance.

following completion of this study revealed no laser induced damage after an estimated laser exposure of 10^5 laser pulses.

4.0 Conclusions

Two methods were examined in this study for the fabrication of dielectric mirror masks from commercial laser mirrors. In the first method, a laser mirror was patterned with photoresist and the dielectric film wet etched with an ammonium bifluoride solution. In the second method, an argon plasma was used to etch the dielectric mirror film. The argon plasma caused significant damage to the photoresist contact mask and the underlying dielectric layer without adequate removal of the dielectric film in the open areas of the mask. A contaminating deposit was formed by the plasma in the open areas of mask that could not be removed by the photoresist stripping agent. Further use of this plasma process appears unlikely to produce any usable results. The ammonium bifluoride etchant exhibited a strong kinetic anisotropy for the removal of the dielectric film with the fastest etch rate occurring in the vertical direction. However, horizontal etching was still observed causing severe undercutting of the photoresist mask. Nevertheless, this etchant still shows promise provided that the undercutting problem can be acceptably minimized. A detailed study of the Arrhenius parameters for the etching reaction in the vertical and horizontal directions could reveal conditions where the vertical etch rate is significantly enhanced relative to the horizontal rate. Furthermore, the thickness of the dielectric film could be reduced to minimize exposure time to the etchant. This latter step would result in an increase in the ultraviolet transmission of the reflecting film due to a decrease in the number of alternating dielectric layers in the film but could still produce a mask with sufficient contrast for laser ablative etching.

During the course of this project, it was discovered that Balzers AG of Liechtenstein had recently developed methods for the production of an ultraviolet mask using a dielectric mirror coating on a quartz substrate. A mask purchased from Balzers for testing showed distinguishable pattern features down to 2 μm in size. This mask was used in ablative projection etching experiments to form microstructures in Mylar polymer films. A thin film resistor pattern with 7.0 μm wide lines was etched 5.4 μm deep into a Mylar substrate. The etched pattern showed uniform linewidths over most of its length but exhibited some thinning of the lines in areas where U-turns occurred. The apparent wall slope of the lines was 7° off vertical. The ablative projection etching technique shows promise as a method for the rapid production of contact masks in microstructuring applications. For example, a Mylar film could be spin coated on a silicon substrate. Ablative projection etching could then be employed to pattern the film to form a contact mask. This mask could be used in other etching or deposition processes to form microstructures. Assuming the substrate will not ablate at the irradiance used to etch the Mylar, the etching process will be self terminating at the Mylar substrate interface. The use of ablative etching to form a contact mask has several potential advantages over photoresist contact masks, including elimination of the development step in photomask fabrication, the ability to re-etch new vias in the mask following a previous etching or deposition step, the potential ability to use thick masks for the formation of deep trenches and wells for additive deposition of tall microstructures, and the potential ability to form a contact mask on non-planar surfaces with large surface steps.

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