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Surface relief gratings with submicrometer periods have been fabricated in silica by ion implantation with a focused ion beam, followed by etching in diluted hydrofluoric acid. Implanted silica etches three times faster than unimplanted silica and groove depths of the order of 300 nm have been achieved. The method does not require photolithography or masking layers, allows arbitrary patterns to be defined, and may be used to fabricate diffractive optical elements or grating filters in optical waveguides.

Phase masks or diffractive optical elements are finding increasingly important applications in optical systems and in microfabrication technologies.[1] The use of high quality synthetic fused silica for the fabrication of these devices has several advantages in terms of thermal stability, capability to tolerate high power laser light, and overall durability over competing technologies, based mainly on organic materials. The standard techniques used for writing grooved patterns in silica involve multilayer masks patterned with optical or electron beam lithography, followed by reactive ion etching to transfer the pattern to the silica surface (see Ref. 2, for instance). We demonstrate a novel method in which we use the differential wet etch characteristics of ion implanted silica to write submicrometer sized grooves directly on the surface of the silica substrate with a focused ion beam (FIB). The advantages of our method are that no intermediate masking process is needed and that the wet etch step is a much simpler process to implement than a reactive ion etch. Furthermore, the FIB can define arbitrary patterns of implanted spots or lines with linear dimensions as small as 50 nm, and the depth can be varied (as will be discussed below). In the experimental conditions used for our work, we show that the etch rate enhancement obtained with the FIB is quite uniform across the penetration range of the ions and that the width of the etched grooves can be predicted accurately from the ion beam size and lateral straggle. The use of silica implies that this method can be used to define grating patterns in silica optical waveguides and fibers for the fabrication of wavelength selective devices.[2]

It has been known for some time that the etch rate of silica damaged by implantation of ions[3] or electrons[4] is different from that of unimplanted silica. This property has been used to define patterns in silica substrates or in deposited silica layers in the following instances. Stengl *et al.*[5] and Speidel and You[6] used uniform proton and lithium ion beams going through photolithographically fabricated free standing metal masks to define grooves as narrow as 300–500 nm in silica films. The implanted lines etched 3–5 times faster in NH_4F/HF solutions and groove depths reached the 200–400 nm range. On the other hand, using the same technique (uniform ion beam through a mask) Znamirowski and Martan[7] found that high doses (greater than 2×10^{15} ions/cm^2) of nitrogen in silica prevented any etching to occur in HF solutions! With this method, silica ridges (instead of grooves) are fabricated by etching the unexposed material. The same effect has been reported with implanted silicon doses larger than 2×10^{16} ions/cm^2 using a FIB system with the same parameters as those used in our experiments.[8] Again, a complete resistance of the implanted silica to a standard buffered HF etching solution was observed. In this case, silica ridges were defined with linewidths as narrow as 50 nm. It is very interesting to note that silicon implantation in silica enhances or reduces the etch rate in HF solutions, depending on the dose. This may be due to the formation of atomic silicon at high doses, since silicon is less sensitive to this type of wet etch. In the case of electron irradiations,[9,10] relatively large energies (300 keV) are used so that the lateral scattering of the electrons, which widens the irradiated area to several micrometers near the stopping range, occurs well below the film to be patterned. Large currents are also required because of the relative insensitivity of silica to electron damage. With an electron beam of 0.4 nm in diameter, 10 nm wide grooves have been defined in thin films of silica. It is not obvious that this technique would work on bulk fused silica substrates because chemical vapor deposition (CVD) deposited silica, in contrast with thermally grown SiO_2 on silicon, needs to be preimplanted uniformly with oxygen ions for the electron damage to result in a differential etch rate.[10] For ion induced damage, however, there does not appear to be any fundamental difference between bulk silica and deposited or grown silica layers.[11]

In our work, we used 0.5-mm-thick substrates made of SUPRASIL 2 synthetic fused silica (available from Heraeus Amersil). A thin layer of 20 nm of aluminum was deposited on the top surface and grounded to dissipate the charge from the incoming ions. The FIB system is a 100

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kV JEOL 104UHV with a Au-Si-Be liquid metal ion source. For the experiments, Si^{++} (200 keV) ions were selected by a E×B filter. In order that the implantation time should not be excessively long, a relatively large aperture was used, giving a beam current of 54 pA with a beam diameter (full width at half-maximum) estimated at 100 nm. A single pass scan rate of 0.56 mm/s gives a nominal dose of 3×10^{14} ions/cm^2 at the center of the beam. The total writing time for a 1×1 mm grating with a period of 0.72 μm is about 40 min. Apart from the other advantages of the FIB, these process durations compare well with currently used submicrometer techniques: E-beam writing in resist followed by reactive ion etching, or gratings defined in photoresist by interference of two laser beams (for periodic patterns only).

A Monte Carlo simulation (using the TRIM code[12]) of ion trajectories indicates that collisional spreading of the ions widens the implanted single lines to 300 nm and that the average depth (range plus straggling) is 410 nm. The energy deposited into atomic collisions determines the level of damage in the material. It has been shown that most physical effects of such damage from ion implantation in silica (including the enhancement in the etch rate) saturate at an atomic energy density near 2×10^{20} keV/cm^3.[11] In our case this corresponds to a dose of 10^{14} ions/cm^2. By implanting three times the saturation dose, we ensure that the central portion of the implanted area will etch uniformly. Also, since the differential etch rate depends on the dose, a pattern of variable depth would result from changing the local dose along the writing path.

For the wet etch process, we follow Arnold *et al.*[13] and use a stirred 0.5% solution of hydrofluoric acid (HF) in water at room temperature. The etch depth as a function of time for implanted and unimplanted silica has been determined in a separate experiment where a uniform ion beam of germanium ions was implanted in a substrate partially masked with a 2.5-μm-thick layer of gold. The dose (10^{14} ions/cm^2) and energy (3 MeV) of the germanium beam were adjusted to yield approximately the same level of damage as the 200 keV silicon beam over the first half-micrometer of depth in the silica. It turns out that most of the stopping of the high-energy germanium beam is electronic, which explains why the nuclear damage density near the surface is almost the same in the two cases. At the relatively small doses used, chemical effects due to doping by the implanted ions can be ruled out and the etch rate enhancement should depend only on damage, regardless of the ion species used. After removing the gold, the surface was scanned with a profilometer to measure the height difference at the boundary of the implanted area after several stages of wet etch. The results are shown in Fig. 1: Straight line fits to the data give etch rates of 3.8 and 1.3 nm/min, respectively, for implanted and unimplanted material. Therefore, the implanted silica etches three times faster in our experimental conditions. Returning to the parameters available with the focused ion beam, the maximum groove depth achievable theoretically is 275 nm if the implanted layer is totally etched, and the groove deepening rate about 2.5 nm/min. Of course, the use of lighter ions

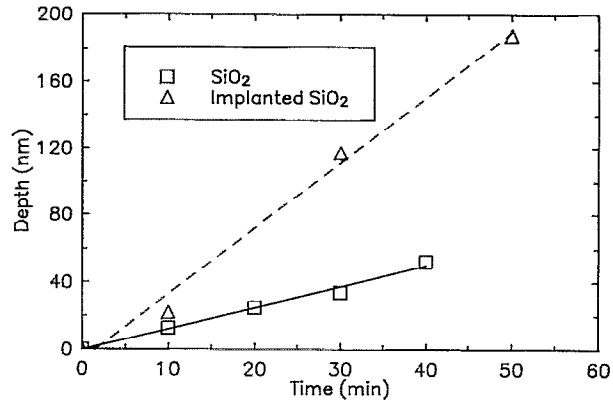

FIG. 1. Etching characteristics of unimplanted silica and of silica implanted with 10^{14} Ge ions/cm^2 at 3 MeV, in a water solution of 0.5% HF. The magnitude of the experimental error equals the symbol height.

(or higher energies, if available) would increase the thickness of the implanted layer and the eventual groove depth, at the cost of higher doses to reach the same damage level and, more importantly, larger lateral straggle which would limit the spatial resolution of written lines.

Several grating patterns were written with periods ranging from 0.45 to 1.06 μm. The gratings were slowly etched in several steps in a 0.5% HF solution and the groove depth was calculated at each step from a measurement of the diffraction efficiency of a 632.8 nm helium-neon laser beam. Figure 2 shows the time evolution of the groove depth for a 1.06 μm period grating. The discontinuity in the curve results from an interruption in the process for the purpose of taking a scanning electron micrograph to view the groove pattern. This required an aluminum coating for charge dissipation under the electron beam, and the removal of this coating in a 25% potassium hydroxide solution for a few minutes. The jump in the groove depth measured immediately after is most likely due to a strong differential etching in the potassium hydroxide. A maximum depth of 330 nm is reached after 130

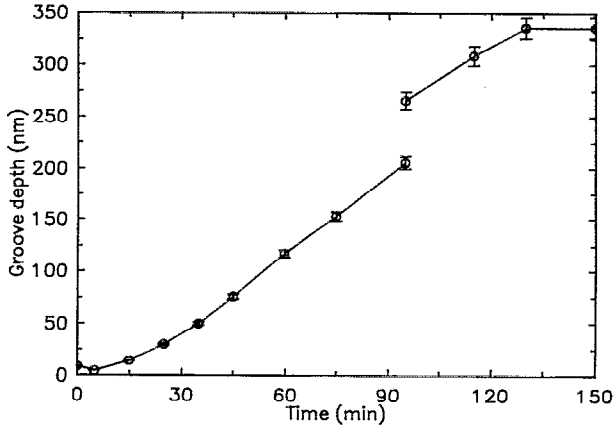

FIG. 2. Groove depth for a 1.06 μm period diffraction grating as a function of etch time in a 0.5% hydrofluoric acid solution in water. The discontinuity arises from an interruption of the process to take a scanning electron micrograph (see text).

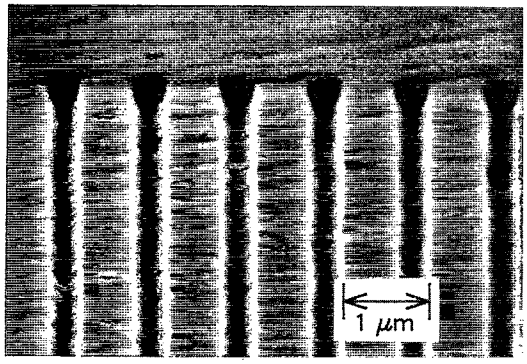

FIG. 3. Scanning electron micrograph of the grating used for Fig. 2, taken after the final etch.

min, and the rate of groove deepening in the uniform portions of the graph is 2.7 nm/min. Both these numbers are in reasonably good agreement with the high-energy results of Fig. 1 and show that the damage profile is fairly uniform.

Figure 3 shows a scanning electron micrograph of the grating pattern after the final etch. The width of the groove is about 300 nm, almost exactly equal to the width of the FIB beam plus twice the lateral straggle of the ion beam obtained from TRIM. In calculating the groove depth from the diffraction efficiency, the groove shape was approximated by a truncated sinusoidal function of width equal to 300 nm.

In another test, a 0.45 μm period grating was written with the same implantation parameters to study the regime where the implanted zone is wider than half the period. In spite of the overlap, useful diffraction efficiencies as high as 20% at 632.8 nm have been reached.

In summary, we have presented the results of what we believe is a new method to define useful grooved patterns in silica flats. The method involves simpler processing steps than existing techniques (provided one has access to a focused ion beam machine) and may be used to write arbitrary patterns under computer control. We have shown that the grooves have sufficient depth to yield useful diffractive optical elements and that spatial features of the order of 0.3 μm are possible. At a dose close to the saturation level for nuclear damage density, the etch rate enhancement is very uniform across the depth of the implanted layer and the groove width can be accurately predicted from the ion beam size and lateral straggle. Furthermore, the use of the FIB allows for writing lines of varying depth in the same pattern by changing the ion dose at each point. Such variable depth gratings have applications in the beam shaping properties of diffractive optics and optical waveguide taps.[14] While it is unlikely that this process would be used for mass production, some of its unique features make it attractive when complex diffractive elements are needed. We have used these FIB written diffraction gratings to photoimprint Bragg gratings in optical fibers with the method described in Ref. 1.

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