Excimer laser-induced material modification to create nanometer high smooth patterns in glass using mask projection

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Abstract. Laser swelling of borosilicate and soda-lime glass is shown for wavelengths of 193 and 248 nm. Very smooth patterns up to 45 nm high were generated by KrF laser (248 nm) irradiation of borosilicate glass at a fluence of 1.5 J/cm². At 193 nm laser wavelength, lower heights (up to 13 nm) and lower swelling threshold fluences (0.1 J/cm²) were observed due to higher material absorption. For the less absorbing soda-lime glass higher fluences than for the borosilicate glass are needed to establish elevated structures. Gratings in borosilicate glass with sub-micron periodicity demonstrate the high resolution of the method. The results can be explained by a thermo-physical model based on the change of the glass transition temperature due to fast cooling after the pulsed laser irradiation.

1. Introduction

Laser irradiation can be used to shape the surface of various materials. Patterns are generated particularly by laser-induced material removal. But laser irradiation can also cause local heating of materials which can lead, for example, to swelling.

First results of laser texturing of glass, the controlled generation of bumps on the surface, by a pulsed CO₂ laser (λ = 10.6 μm) were published by Teng et al. [1] in 1996. Typically up to 50 nm high elevated structures were observed due to swelling. On hard disk substrates the bumps reduce stiction of the magnetic head in the landing zone [2]. To increase the structure height to several micrometers, glass densified by compression at high temperatures has been used for the CO₂ laser texturing [3].

Thermo-physical models of the bump formation were developed by Bennett et al. [4] and by Shiu et al. [5]. Shape and height of laser-induced bumps were calculated considering the transient temperature field in the glass associated with expansion and incomplete recovery.

Recently, Vanagas et al. [6] demonstrated a non-thermal method to create elevated structures on the surface of borosilicate glass. Bumps of 40 to 70 nm height and diameters between 115 and 155 nm were obtained by femtosecond laser irradiation at a wavelength of 800 nm. According to the authors the bump formation was due to a Coulomb explosion of the exposed material.

In the present work glass surfaces were modified by UV excimer lasers with nanosecond pulse duration and delivered with a mask projection system. In a laser fluence region below the ablation threshold, elevated structures arose for some sorts of glass. The dependence of structure heights and shapes on laser parameters is investigated and high resolution patterns are fabricated.
2. Materials and Methods
In the experiments standard cover glass and microscope slides were used as samples. According to the manufacturers the microscope slides were made of soda-lime glass and the cover glasses were made of borosilicate glass. Laser modification experiments were performed using an excimer laser (Lambda Physik; LPX 220i) with pulse lengths of approximately 20 ns running at $\lambda = 248$ nm (KrF) and at $\lambda = 193$ nm (ArF). The homogenised laser beam illuminates a mask which is projected by a 15x demagnifying Schwarzschild objective onto the sample. Metal contour masks as well as a phase grating mask were used. The surface morphology was investigated by a white light interference microscopy (MicroXAM) and by an AFM in TappingMode™ using standard silicon cantilevers.

3. Results and Discussion
The excimer laser irradiation below the ablation threshold leads to swelling of the glass samples with nanometer high structures remaining permanently. To determine the correlation between laser wavelength, fluence, pulse number, and the height of the surface features, squares of 40 x 40 $\mu$m² were exposed. The laser fluence and the pulse number were varied between 0.1 and 7.5 J/cm² and between 1 and 30 pulses, respectively. The average height and the deviation of four identically exposed squares are shown in figure 1 for the different glass types and wavelengths in comparison.

![Figure 1](image-url)

Figure 1: Height of squares for a borosilicate glass irradiated at a) 248 nm and c) 193 nm and for a soda-lime glass irradiated at b) 248 nm and d) 193 nm; MicroXAM measurements.

At 248 nm the structure heights on the borosilicate glass increase to about 45 nm in the fluence range from 0.7 to 1.65 J/cm², as seen in figure 1a). Further fluence increase leads to ablation associated with pits on the sample. The fluence range for the formation of elevated patterns caused by 193 nm radiation is between 0.1 and 0.35 J/cm². As shown in figure 1c) the heights of the exposed squares are only up to 13 nm for the shorter wavelength. For the soda-lime glass the structures are even shallower at 193 nm, as seen in figure 1d). Additionally, the fluence range of 0.2 to 0.4 J/cm² for bump formation is narrower. In figure 1b) the results for the soda-lime glass at 248 nm are shown. Here the fluence for swelling is very high and ranges from 4.5 to 7.5 J/cm². But in contrast to the modification characteristics of the borosilicate glass the pulse number has a high influence on the
swelling of the soda-lime glass. The highest structures were obtained by single pulse irradiation at high fluences (6.5–7.5 J/cm²). However the standard deviation of the height increases in all cases near the ablation threshold as indicated by the error bars in figure 1a)-d). Higher pulse numbers, already at lower fluences, lead to increasingly jagged features with rounded edges on the basis and also material ablation, as seen in figure 2b). The elevated patterns depicted in figure 2a) that were achieved by single pulse exposure of borosilicate glass feature a flat, smooth top surface and very sharp edges.

Figure 2: Surface topography of laser irradiated glass samples, measured by interference microscopy (a) and b)) and by AFM (c) and d)): a) borosilicate glass, KrF laser, 0.2 J/cm², 1 pulse, b) soda-lime glass, KrF laser, 6.5 J/cm², 3 pulses; c) borosilicate glass, KrF laser, 1.5 J/cm², 1 pulse, and d) same as c) with second exposure at 90° sample rotation using identical parameters.

To examine the resolution of the patterning method, borosilicate glass samples were irradiated using a matched phase grating made of DUV fused silica that suppresses the 0th diffraction order. Figure 2c) shows the resulting surface topography after one laser pulse. The period of the grating is 700 nm with a height of 7 nm. A further sample was irradiated with a second pulse after 90° sample rotation. Figure 2d) shows the resulting array of 10 to 20 nm high bumps at the intersection of the diffraction grating lines of high laser fluence.

The fluence ranges for swelling, values of absorption coefficient, \( \alpha \), and corresponding penetration depths \( (d = 1/\alpha) \) of the samples at the two wavelengths are listed in table 1. The values of absorption coefficient at 248 nm were determined by spectrometric ellipsometry. From UV/VIS spectrometry larger values at 193 nm can be assumed. Obviously higher absorption coefficients lead to lower ablation threshold due to higher volume energy densities and consequently higher temperatures. Also the elevated structures appear at considerably lower laser fluences for 193 nm. Additionally, the heights of the structures are lower because a smaller penetration depth results in less volume heated beyond the glass transition temperature.

In the fluence range of swelling a thermal cycle in the irradiated glass is induced by the pulsed laser energy deposition. During the laser pulse the temperature rises and causes glass expansion and
softening. After the pulse material cooling at high rates occurs and the glass solidifies in disequilibrium [5]. The frozen state is characterised by a lower density and a raised glass transition temperature which is defined by the cooling rate. Because the volume expansion does not recede completely on cooling, elevated patterns remain at irradiated areas. With increasing laser fluence the temperature which is reached during the pulse increases, too, causing higher cooling rates and higher modification depths leading to higher structures. Repeated irradiation of the borosilicate glass at 248 nm or 193 nm does not change the structure heights significantly. Apparently, the thermal cycle does not change dramatically due to material modifications caused by the first pulse. The temperature distribution and the cooling process are presumably reproduced on the following laser pulses. In contrast, the soda-lime glass shows significant incubation effects, i.e. changing response to the laser irradiation for successive pulses. Only ten pulses at fluences above 5.5 J/cm² are sufficient to change the soda-lime glass from swelling to ablation behaviour. With other tested microscope slides, showing an ablation threshold of 10 J/cm², no elevated structures were found and only colour centres were observed in the irradiated areas. In this case the inherent absorption of the material is insufficient to obtain glass swelling.

Table 1: Swelling fluence ranges, \( F \), absorption coefficients, \( \alpha \), and penetration depths \( d \) of the samples.

| Sample             | \( F \), 248 nm [J/cm²] | \( F \), 193 nm [J/cm²] | \( \alpha \) at 248 nm [1/cm] | \( d \) (1/e decay, 248 nm) [μm] |
|--------------------|--------------------------|--------------------------|-------------------------------|---------------------------------|
| Borosilicate glass | 0.7 - 1.65               | 0.1 - 0.35               | 18800                         | 0.53                            |
| Soda-lime glass    | 4.5 - 7.5                | 0.2 – 0.4                | 12800                         | 0.78                            |

The results described in this work can be compared to those obtained with laser texturing performed with a CO₂ laser. The structure heights are in the same range and the fluence range is also similar. Furthermore, the height of the elevated structures depends linearly on the logarithm of the fluence as predicted by the model of Shiu et al. [5].

4. Conclusions

Excimer lasers are capable of inducing the swelling of glass in precise patterns with heights up to 45 nm. The lateral resolution is better than one micron as shown by the generation of gratings in glass with a period of 700 nm. The light absorption of the used glass that depends on glass type and laser wavelength is crucial to the swelling and patterning results. At 193 nm only about 10 nm high patterns were obtained for both glass types whereas at 248 nm for the soda-lime glass up to 80 nm high structures were observed. However, the soda-lime glass shows pronounced incubation effects so that the patterns are less precise in comparison to borosilicate glass and degrade under repeated irradiation.

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