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Surface micromachining of UV transparent materials

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Abstract

A method which utilizes XeCl excimer laser and an absorbing liquid in contact with the material for precise structuring of UV transparent materials is presented. This *one step* micromachining process enables the fabrication of micro-optical elements with continuous profiles such as Fresnel micro-lenses in CaF_2 and quartz with fluences well below the damage threshold of these materials. The roughness of the etched features varies from 10 nm to 3 μm depending on the laser fluence and material. The etch rates of different UV transparent materials (such as CaF_2, BaF_2, sapphire and quartz) at various laser fluences suggest that several different parameters influence the etching process.

Keywords: Wet etching; Micro lens; Laser ablation; CaF_2; BaF_2; Sapphire

1. Introduction

UV transparent materials, e.g. quartz, CaF_2, BaF_2, or sapphire are widely used in optics. Arrays of micro-optical elements, e.g. Fresnel lenses in quartz, are applied as beam homogenizers for a high power excimer and Nd:YAG lasers. Quartz is a suitable optical material at the wavelengths ≥248 nm, but for shorter wavelengths, absorption of quartz strongly increases. Therefore CaF_2, BaF_2 and sapphire are most favorable optical materials in the vacuum UV region. However, micromachining of these dielectrics is restricted due to their high transparency and great mechanical stability. The conventional method for fabrication of microstructures with continuous profiles in quartz and CaF_2 is photolithography followed by the subsequent transfer of the resist profile into the substrate surface by reactive ion etching [1]. This technique requires high vacuum conditions, an excellent control of the exposure dose, the resist characteristics, and the proportional etching process. Other alternative methods of machining UV transparent dielectrics are direct writing with ultrafast (femtosecond) lasers [2,3], or structuring (only quartz) by VUV excimer lasers [4]. The VUV lasers are complicated to use, as they require vacuum or at least a transparent inert gas for the beam path and VUV transparent optics. However, the complex patterning of UV transparent glasses by femtosecond lasers is a slow sequential scanning process [5]. The fast and efficient structuring of sapphire with a copper vapor laser and aqueous Cr_2O_3 solution as 'etchant' was reported by Dolgaev et al. [6]. Yabe and coworkers investigated the etching of quartz and CaF_2 in contact with an organic solution using KrF and XeCl excimer lasers. The UV light passes through the quartz or CaF_2 samples and is strongly absorbed by the pyrene in the acetone solution. The vibrational relaxation of pyrene molecules generates a temperature and pressure jump at the substrate–liquid interface, which results in etching of the UV transparent materials. This technique was named Laser Induced Backside Wet Etching (LIBWE) [7–9]. Until now mainly proof of principle experiments, i.e. hole and line structures prepared in quartz and CaF_2 by applying a slit mask [7–9] or interference grating projection [10] were reported. A simpler method for the fabrication of three-dimensional structures with continuous profiles in polymers was demonstrated by David et al. [11]. Here, a diffractive gray tone phase mask (DGTPM) is used to modulate the incoming laser beam intensity, which is projected onto the polymer surface. The one step microfabrication method, which combines DGTPM and LIB-

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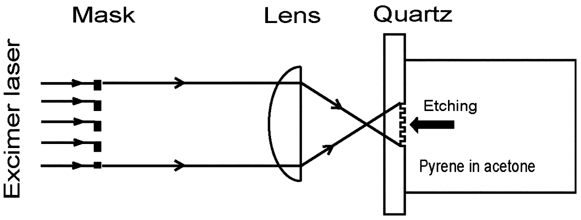

Fig. 1. Scheme of the experimental setup for fabrication of micro optics in UV transparent dielectrics.

WE allows the fabrication of optical elements with continuous profiles, e.g. Fresnel lenses in quartz [12]. First result for the creation of complex patterns in very brittle materials, such as a Fresnel micro-lens in CaF_2 is shown. The etch rates and the roughness of the etched features for the different dielectrics are discussed in this paper.

2. Experimental

Four different UV transparent materials, CaF_2, BaF_2, sapphire and quartz, were chosen for this study. The samples thickness was 2 mm for CaF_2, BaF_2, and sapphire, while the thickness of the quartz substrates was 0.5 mm. A surface roughness of ≈4 nm was obtained by profilometer scans for all samples. The intensity of the laser was varied by a dielectric plate. A solution of pyrene in acetone with a concentration of 0.4 M was used as 'etchant'. One side of the substrate was in contact with the solution, while the irradiation was performed through the other side, as shown in Fig. 1. Diffractive gray tone phase masks (DGTPM's) were fabricated by e-beam lithography and reactive ion etching [11]. DGTPM's are utilized to modulate the intensity of the incoming beam from a XeCl excimer laser (Lambda Physics, Compex 205, 308 nm, 25 ns (FWHM)). The laser repetition rate was 4 Hz in all experiments.

A refractive doublet lens system (10× demagnification) was used for transferring the image of the DGTPM onto the sample backside. The etching of microstructures with continuous profiles in CaF_2 was carried out with a laser fluence of 2 J cm^{-2} and 70 pulses. The depth profiles of the etched features were analyzed with a profilometer (DEKTAK 8000).

3. Results and discussion

The etching of UV transparent dielectrics by LIBWE reveals the same features as laser ablation, where a threshold fluence exists below which no etching is observed. The threshold fluences for quartz, BaF_2, CaF_2, and sapphire were determined experimentally by measuring the etch rates at various laser fluences (shown in Fig. 2a,b). The experimentally obtained threshold fluences for etching different UV transparent materials by LIBWE are summarized in the Table 1 together with some selected thermodynamic properties. The similar etch rates of quartz and BaF_2 at the low fluence range cannot be explained by the thermodynamic properties of these materials. Mechanical or optical properties may be another important parameter in the LIBWE process. This can be also the reason for the much higher etch rates of the BaF_2 compared to CaF_2. The efficient etching of UV transparent materials with etch rates of up to 100 nm pro pulse (Fig. 2b) is due to the deposition of the laser energy in a thin pyrene–acetone layer above the sample surface. The non-radiative relaxation of excited states of pyrene molecules generates a temperature jump at the substrate–liquid interface, resulting in

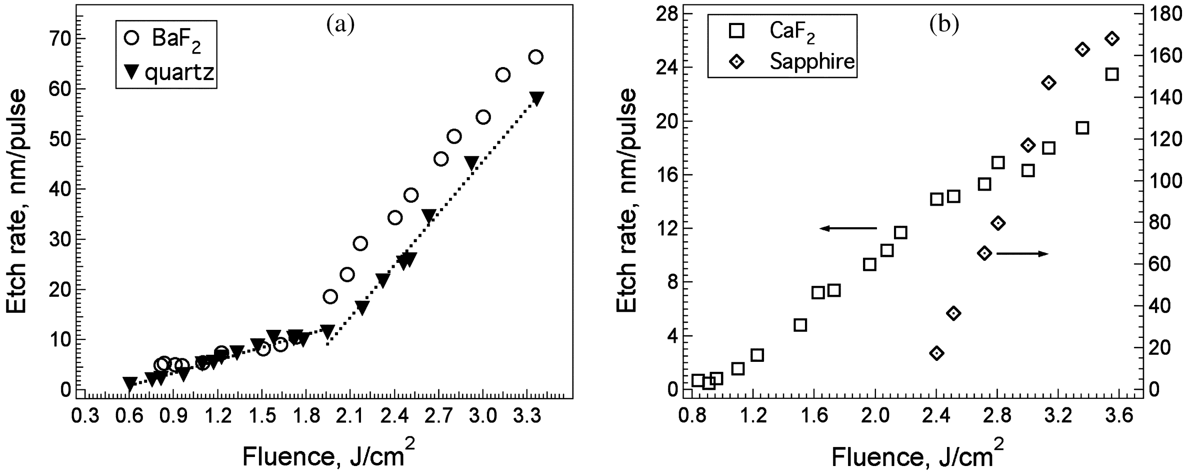

Fig. 2. Etch rates vs. laser fluences (a) for BaF_2 and quartz, (b) for CaF_2 and sapphire.

Table 1
Threshold fluence of UV transparent dielectric materials structured by LIBWE and thermodynamic properties of dielectrics

	Quartz	BaF_2	CaF_2	Sapphire
Threshold fluence, J/cm^2	0.5	0.4	0.8	2.3
Softening point, K	1850	1550	1630	2310
Thermal conductivity, W/m K	1.38	11.72	9.71	22.20
Heat capacity, J/g K	0.74	0.41	0.76	0.85
Hardness (Knoop), (kg/mm^2)	530	82	158	1370
Threshold fluence for dry ablation-damage, J/cm^2	20*	>20	>20	$\gg 20$

*Ihlemann J., Wolf B., Simon P., Appl. Phys A, 54 (1992) 386.

softening of the material [7]. The reason why melting/softening of the studied dielectrics results in etching is not clear, as the molten materials are also not soluble in acetone. One possible explanation is that the laser-induced temperature in the solution exceeds the critical temperature of acetone (60 °C), which leads to vaporizing of the solvent (acetone) and formation of bubbles (cavitation) [13]. The rapidly expanding or collapsing bubbles create a pressure jump, which interacts with the surface of the molten samples and removes the material by a mechanical force. The etch rates of the studied dielectrics (Fig. 2a,b) reveal two distinct different behaviors over the complete fluence range.

The etch rate increases slowly with the fluence at low fluences (above the threshold) while at high fluences the slope of the etch curves is several times higher. This indicates that several different etching processes are active, which are difficult to understand in terms of the removal molten quartz by an acoustic waves or collapsing bubbles alone. These two different etch rates have not been reported previously [7–10] due to the smaller fluence range that has been applied in these studies. However, for sapphire only one slope is observed, most probably also due to the limited fluence range. In the low fluence range (below 1.2 J/cm^2) the etching of the UV transparent materials may be influenced by the formation of surface color centers, which increase the absorption of the incoming radiation inside the dielectric materials. The formation of defects (color centers) in various dielectric materials caused by femtosecond laser irradiation has been reported in Ref. [2] and was termed 'incubation' analogues to polymer ablation [14]. Another possible process, which may influence the etching of quartz is the chemical decomposition of the solvent or pyrene molecules. However, at higher fluences the exposure dose is high enough to initiate the etching process with a single laser pulse. The relation between the etch rate vs. pulse numbers [shown, e.g. for quartz in Fig. 3a] in the case of LIBWE experiments resembles the behavior detected for femtosecond irradiation. At low fluences (just above the threshold) the etching of quartz by LIBWE occurs after ≈150 laser shots, while in the high fluence range the etch depth increases linearly with the pulse number. The incubation effect in dielectric materials is closely related to the excitation and generation of conduction-band electrons, which will eventu-

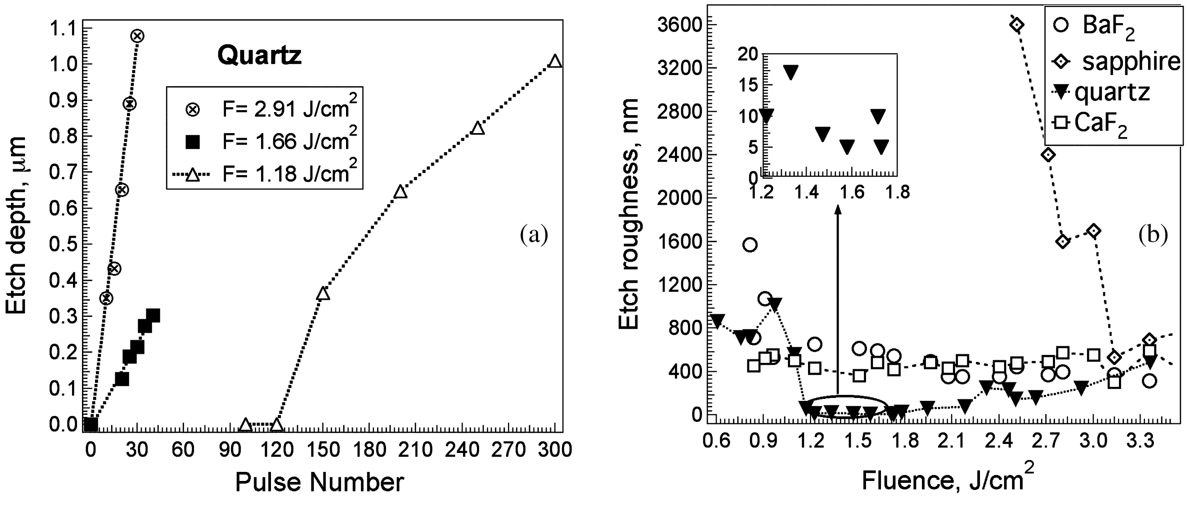

Fig. 3. Dependence of the etch depth on the laser pulse numbers for quartz (a), and etch roughness vs. laser fluence for different dielectrics structured by LIBWE (b).

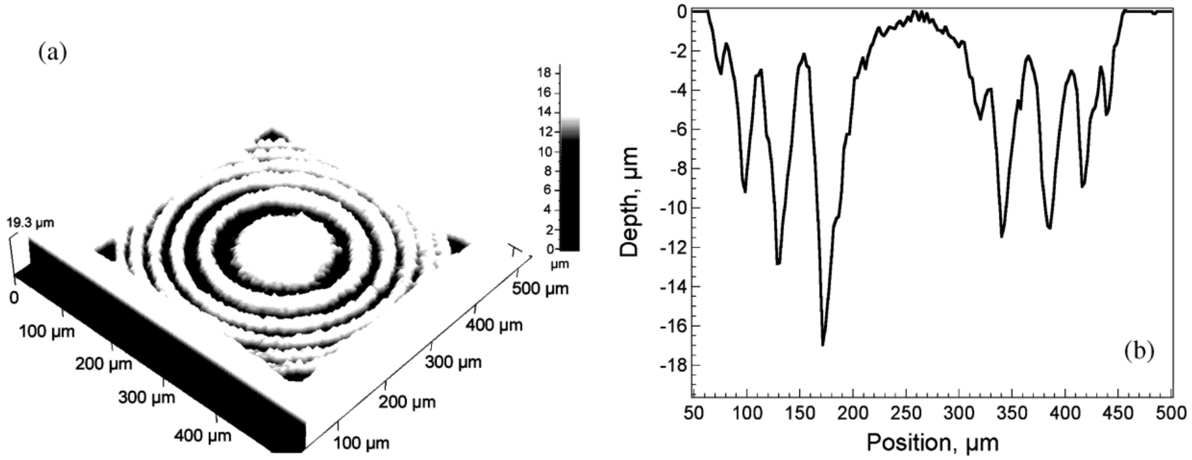

Fig. 4. (a) Three-dimensional profilometer scan of a Fresnel lens etched in CaF_2 by LIBWE using a XeCl excimer laser and (b) line scan of etched profile.

ally result in an accumulation of defects. The microroughness of studied dielectric materials (shown in Fig. 3b) in the low fluence range is probably due to the fact that ablation-damage can occur through the defects, the chemical modification of the surface of material, or by cooling (hardening) in the time periods until the bubble collapse might remove the material. The efficient heat transfer from a liquid to the solid, however, can smoothen the surface roughness at those fluences where an etch roughness of several nanometers is observed, e.g. for quartz [shown in the insert of Fig. 3b]. At the high fluence range the etch roughness for quartz increases again with increasing fluence, but remains constant for CaF_2, BaF_2. The roughness of the etched features in sapphire decrease also with increasing fluences, probably due to the high temperature obtained with higher fluence. The higher threshold fluence for sapphire compared to quartz or CaF_2 is most probably due to the higher melting point (see Table 1) and hardness of this material.

Microstructures in CaF_2 and BaF_2, as discussed above, are very important for VUV optics. Various three-dimensional structures, such as Fresnel lenses with continuous profiles, were etched in CaF_2 to test the potential of LIBWE as a new method for micromachining of dielectric materials. A three-dimensional scan of a Fresnel lens, etched in CaF_2 with a fluence of 2 J cm^{-2}, is shown in Fig. 4a. The line scan of this lens (shown in Fig. 4b) presents the typical features of a Fresnel lens, i.e. the parabolic depth profile in the center and a triangular structure on the sides. The size of the microlens is 500×500 μm^2 and the etch roughness is approximately 400 nm. The focal length is 0.8 mm at 632 nm wavelength. The optimization, e.g. with respect to roughness, and the characterization of Fresnel lenses in various UV transparent dielectric materials is currently studied.

4. Conclusion

Laser-induced backside wet etching is a suitable technique for fast microstructuring of UV transparent dielectric materials using a relatively simple experimental setup. The roughness of the etched features varies between 5 nm and several micrometers and depends on the material and laser fluence. The application of diffractive gray tone masks allows the creation of complex three-dimensional patterns, such as Fresnel lenses, in very brittle materials, e.g. in CaF_2, which is difficult to structure with other techniques.

Acknowledgments

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