Laser induced nanogratings beyond fused silica - periodic nanostructures in borosilicate glasses and ULE™

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Abstract: We report on the ultrashort pulse laser induced formation of birefringent structures in the volume of different glasses: Borofloat 33, BK7 and ULE™. Using polarization contrast and scanning electron microscopy we could prove that this birefringence is induced by nanogratings. We were able to identify the pulse duration as a crucial process parameter for the generation of nanogratings in these glasses. The achieved birefringence in ULE is comparable to fused silica, while borosilicate glasses show much less birefringence (only about 12%). Remarkably, the period of the nanogratings is also dependent on the type of the glass, being 250 nm for ULE and only 60 nm in case of Borofloat 33.

OCIS codes: (220.4241) Nanostructure fabrication; (320.2250) Femtosecond phenomena.

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1. Introduction

One of the most fascinating effects of the irradiation of glasses with ultrashort laser pulses is the formation of birefringent domains [1–3]. This birefringence is due to periodic nanostructures, so-called nanogratings, whose orientation is perpendicular to the laser polarization. All reports so far demonstrated, that nanogratings in fused silica consist of small cavities with a size of several tens of nm [3,4] surrounded by a nanoporous structure [5], which form a grating structure with a period around $\lambda/2$n, with n the refractive index of the material and λ the wavelength of the incident laser pulses. Raman measurements suggested that these cavities are filled with oxygen [6]. This periodic change of the density leads to a modulation of the refractive index and results in form birefringence of the modified material [3,7]. The retardation of such a birefringent structure can be used to realize polarization sensitive optical devices as waveplates, zone plates or polarization converters [7,8].

Although ultrashort pulse laser induced structures with sub-wavelength periodicity occur on the surface (laser induced periodic surface structures - LIPSS) of various materials like dielectrics, semiconductors, or metals [9], the formation of nanogratings in the volume of transparent materials was mainly reported for fused silica or slightly doped fused silica glasses, respectively [1,10]. Thus, it was presumed that nanogratings in glasses are a special feature of fused silica [11]. However, the formation of nanostructures in crystals such as tellurium dioxide single crystal and sapphire has been reported, too [12,13]. In this paper, we report on the inscription of nanogratings into different glasses other than fused silica.

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2. Experimental procedure

The samples tested included two different borosilicate glasses: BK7 (Schott) and Borofloat 33 (Schott) and ULE™(Corning), which is a silica glass with a high fraction of TiO_2 to obtain a low thermal expansion. We specifically focused on the influence of the pulse duration, as it determines the threshold for nanograting formation in fused silica [14]. Thus, we used a tunable ultrashort pulse oscillator (Femtosource XL 50, Femtolasers GmbH) delivering pulses at a wavelength λ of 800 nm, a repetition rate of 5.1 MHz and a pulse energy E_P of 500 nJ. By tuning the position of the compressor prisms the pulse duration can be varied from 40 fs to 400 fs. The pulse duration was measured by a FROG (Grenouille, Swamp Optics). After the laser output we used a Pockels cell and polarization optics to change the repetition rate and pulse energy, respectively. The laser pulses were focused 150 µm below the sample surface by an aspheric lens with a focal length of 4.51 mm (Thorlabs 230 TME-B). For the inscription of extended lines of modifications we moved the sample with respect to the focal spot. For most experiments we used a translation velocity of 10 mm/min and a repetition rate of 100 kHz, which results in an exposure of about 800 pulses for each irradiated focal spot (diameter of about 1.3 µm). To analyze the structure of the laser induced modifications, we exposed them by polishing. Afterwards we etched ULE for 15 s and Borofloat for 20 s with 2% hydrofluoric acid.

In a next step, we analyzed the retardation of laser induced nanogratings in fused silica, ULE, Borofloat and BK7 for different processing parameters. Therefore, we used polarization contrast microscopy to measure the form birefringence of the gratings. The transmission T of a birefringent element between two crossed polarizers, is given by [15]:

$$T = \frac{1}{2}\sin^2(2\vartheta)\,[1-\cos(\delta)] \tag{1}$$

where δ is the retardation of the birefringent structure and ϑ is the angle between its fast axis and the transmission axis of the first polarizer. The orientation of nanogratings and hence the orientation of their fast axis is parallel to the polarization of the writing laser beam [16]. Thus, equation. (1) allows simple measurements of the retardation of the birefringent structures. In addition, it allows to distinguish between form birefringence and stress induced birefringence as stress induced birefringence is independent of the orientation of the laser polarization and occurs mainly at both sides of an inscribed line. We measured the transmission of the inscribed modifications, for a fixed ϑ of 45° and used equation 1 to calculate the retardation of these samples. For illumination, we used a helium-neon laser at 633 nm. The measured retardation values are given in radiant.

3. Results and discussion

3.1. SEM images

The modifications in ULE and Borofloat exhibit a grating structure which is much smaller than the laser wavelength (λ = 800 nm), as can be seen in Fig. 1. The grating period in ULE is about 250 nm, which fits to the expected value of about $\lambda/2n$ (n = 1.48). Remarkably, for Borofloat the grating period is significantly smaller, only about 60 nm. In addition, the width of the cavities (dark vertical lines) is also much smaller than in ULE. However, this might also be partially effected by the etching process. For BK7 we could not find any structures after the HF etching, although the modifications showed birefringence in a polarization contrast microscope. A possible explanation for this failure may be the small structure size or an unusual etching rate of BK7 for modified and unmodified material, in comparison to fused silica.

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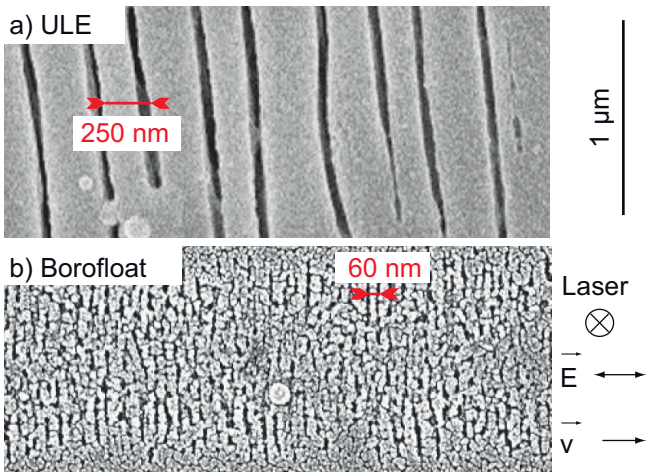

Fig. 1. SEM images of periodic nanostructures of laser induced birefringent structures in: a) ULE (E_P = 200 nJ; τ = 120 fs) b) Borofloat (E_P = 400 nJ; τ = 400 fs). A thin gold coating was used to prevent charge accumulation.

3.2. Birefringence of nanogratings in different glasses

For almost all processing parameters, we could measure a birefringent signal, which was especially weak for the borosilicate glasses, however. Remarkably, our investigations yield the pulse duration as a the crucial parameter for the inscription of birefringent structures. Figure 2 shows the retardation of induced nanogratings as a function of the pulse duration for fixed translation velocity (10 mm/min) and pulse energy (400 nJ). The writing polarization was parallel to the translation direction of the sample. The given error-bars are the standard deviations of the measurements of different birefringent lines inscribed with identical processing parameters. For fused silica (red points in Fig. 2), we measured an increasing retardation with increasing pulse duration, which fits to the results in [11, 14]. ULE (black points in Fig. 2) shows almost no dependence on the pulse duration in the investigated range. However, there is a slightly increased retardation for a pulse duration of about 130 fs.

The retardation obtained in ULE is comparable to that of fused silica for long pulse duration ($\geq$ 150 fs), which also allows the application of ULE for various birefringent devices. The nanogratings inscribed in fused silica and ULE yield a maximal retardation of almost $\pi/3$ ($\lambda/6$). In contrast, the retardation of Borofloat 33 and BK7 is much weaker for all pulse durations than in ULE or fused silica. However, both glasses show a comparable behavior, which we attribute to their similar composition as borosilicate glasses. In addition, the retardation curve of the borosilicate glasses shows a much more complex distribution. For pulse durations above 250 fs the retardation is about fifty times smaller than fused silica, which explains the previous opinion that nanogratings do not exist in borosilicate glasses.

The induced retardation of a nanograting depends on the length of the birefringent region times the birefringence $\Delta n \equiv n_o - n_e$ of the structures, where n_e and n_o are the extraordinary and ordinary refractive indices of the birefringent modification [15]. If we assume that the length of the birefringent region is comparable for all investigated glasses, the individual birefringence has to be different. The birefringence Δn depends on the dimensions of the grating structure and the index contrast between the modified and unmodified material [3]. We know for fused silica, that a grating plane, which exhibits a low density, consist to about 50% of hollow cavities [4]. The sheet-like arrangement of these low-density planes forms the periodicity of the nanograt-

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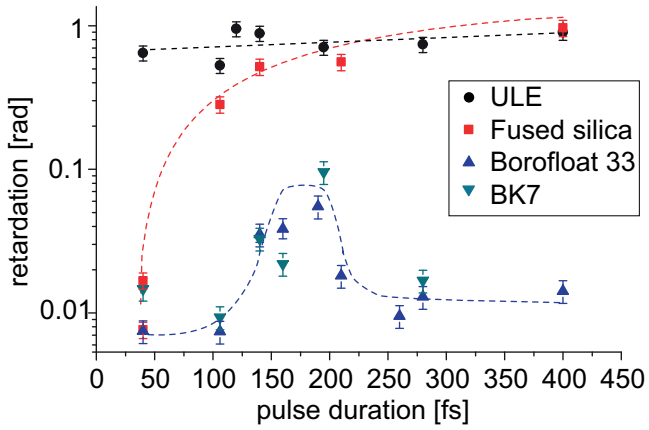

Fig. 2. Dependence of the retardation on the pulse duration for different glasses for an illumination wavelength of 633 nm. For the inscription we used a pulse energy of 400 nJ. The dashed lines are a guide to the eye.

ings. From Fig.1 we estimate the grating period in Borofloat (about 60 nm) and the width of the cavities to a few nm. Taking these dimensions and the low value of the retardation into account, we can conclude that the cavities in Borofloat are either not completely hollow or that a low density grating plane consists only to about 10% of cavities and to 90% of unmodified material. This low number of pores within a grating plane might explain our difficulties to find nanogratings in BK7. However, for a pulse duration between 140 and 220 fs the retardation is increased by almost a factor of 10 and reaches a maximal value of 0.12 (π/27). This increased retardation might be due to a higher number of cavities of about 20% within a low density grating plane. Both borosilicate glasses show this trend, which expose a distinct parameter window for the effective inscription of nanogratings in these glasses.

3.3. Absorption spectra of induced structures

So far, we have seen that the inscription of nanogratings in various gratings is possible. One remaining question is the mediating mechanism between the individual laser pulses, which allows the formation of nanogratings under irradiation of several hundred of laser pulses. For fused silica, the formation of nanogratings is a cumulative process of numerous laser pulses, mediated by dangling bond type defects [17]. The initial laser pulses induce defects in the processed material, which enhance the absorption of the following laser pulses. Thus, temporally isolated pulses may modify the glass collectively and form nanogratings. The complete formation of nanogratings requires several hundred pulses in fused silica [18]. For all the glasses investigated, we measured an increasing retardation with increasing number of laser pulses, finally reaching a maximal value after about 800 laser pulses. In order to determine the mediating effect of nanogratings in the different glasses investigated, we measured their absorption spectra with a spectrometer (Perkin Elmer Lambda 950). For the inscription of a large modified area (3×3 mm^2 with a line separation of 1 µm) we used a pulse energy of 400 nJ and a pulse duration of 165 fs (Borofloat) and 120 fs (ULE), respectively.

The resulting spectra are shown in Fig. 3. ULE (red lines) shows an increased absorption over the whole measured spectral range. Consequently, the sample appears slightly dark (inset of Fig. 3) which is due to the reduction of the TiO_2 content of ULE induced by the laser irradiation [19]. This darkening increases the absorption and hence the cumulative action of the laser pulses. Birefringent structures in borosilicate glasses induce only a small difference in the absorption

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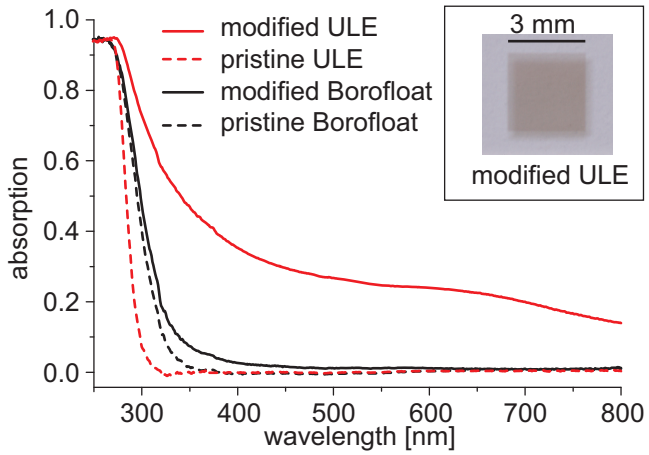

Fig. 3. Absorption spectra of Borofloat and ULE containing nanogratings and untreated glasses as reference (dashed lines). The inset shows an image of the inscribed modification in ULE.

spectra (black lines). However, the time between inscription and measurement of the absorption spectra was several days, thus additional features of the absorption spectra might have already decayed. The observed slight increase of the absorption for short wavelengths may be caused by the remnants of laser induced color centers [20]. These color centers may significantly enhance the absorption at short time scales and consequently mediate the formation of nanogratings.

The complex formation mechanism of nanogratings in fused silica is still not fully understood, although their discovery was more than one decade ago. In addition, the properties of nanogratings in ULE and borosilicate differ from those in fused silica. Thus, a general model of nanograting formation has to consider all the different nanograting properties of various glasses. An important factor for the formation is the chemical composition. In contrast to pure fused silica, ULE consists of approximately 7.5% TiO_2 and 92.5% SiO_2 [21], whereas borosilicate contains large quantities of Na_2O, B_2O_3, K_2O and even other components. These additional components might hinder the inscription of a nanoporous grating structure.

4. Conclusion

We have shown that is possible to inscribe nanogratings in borosilicate glasses and ULE using ultrashort laser pulses. ULE depicts strong birefringent structures, which are comparable to fused silica. Retardation in borosilicate glasses is much weaker, yet a distinct parameter window for the inscription of stronger birefringent structures could be found for a pulse duration between 140 and 220 fs. Period of these gratings is about 60 nm, which is much smaller than in any previous reports of nanogratings.

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