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UV-assisted selective chemical etching of relief gratings in Er/Yb-codoped IOG1 phosphate glass

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Abstract. The patterning of sub-micron periodicity Bragg reflectors in Er/Yb-codoped IOG1, phosphate glass is demonstrated. A high yield patterning technique is presented, wherein high volume damage is induced into the glass matrix by exposure to intense UV radiation, and subsequently a chemical development in a strong acid selectively etches the exposed areas. The grating reflectors were fabricated by employing an elliptical Talbot interferometer and the output of a 213nm, 150ps frequency quintupled Nd:YAG laser. The grating depth of the etched relief pattern in time was measured at fixed time intervals and the dependence is presented in upon the etching time and exposure conditions. The gratings fabricated are examined by atomic and scanning electron microscopy for revealing the topology of the relief structure. Gratings with period of the order of 500nm were fabricated, having a maximum depth of 60nm.

1. Introduction
Phosphate glasses are excellent host materials for the development of high-power, integrated lasing and amplification devices, for optical communications [1], and waveguides for bio-sensing applications [2]. These glasses exhibit unique spectroscopic and material properties such as high solubility of rare-earth ions and long emission lifetime. Nonetheless, they suffer from low-chemical stability, hygro-sensitivity and low transformation temperature. The last drawbacks pose restrictions in terms of fabrication methods used for structuring such glasses, towards the development of functional integrated optical devices. Relief diffractive, fluidic or guiding structures, fabricated in phosphate glasses using low-damage, straightforward etching methods, can constitute the basic optical elements in the design and development of novel and functional integrated optical devices. Thus, the micro-/nano-structuring of phosphate glasses by means of Bragg grating reflectors or rib channel fabrication is of high importance for the realisation of the aforementioned optical devices.

We are presenting a wet etching laser assisted method for patterning arbitrary shape relief structures in phosphate glasses, however, the method is demonstrated for the patterning of sub-micron periodicity Bragg reflectors. A high yield patterning technique is adopted, wherein high damage is induced into the glass volume by exposure to intense ultraviolet (UV) radiation and subsequently, the exposed areas are selectively etched in a strong acid. As it will be shown later, the presented method produces relief structures of high smoothness, free of debris or defects, and without extensive optical damage, compared to other approaches [3]. Additional advantages of the presented method are the mask-less process, and the elimination of undercutting, a detrimental process observed for typical wet etching methods using protective masks.
The Er/Yb-codoped IOG1 phosphate glass fabricated by Schott-USA is a hybrid sodium-aluminum-phosphate glass [4] that can be heavily doped with rare earth ions. IOG1 glass is optimized for ion-exchange using silver or potassium ions, for fabricating high-contrast, low-loss waveguides [4]. Moreover, the imprinted Bragg gratings, that are tuned for reflection in the 1.5\mu m band, have periodicities of the order of 500nm.

2. Experimental
The laser used for grating exposures was a 213nm, 150ps frequency quintupled Nd:YAG laser, delivering pulses of 13mJ energy over a beam size of 8mm. The periodic pattern was created by employing an elliptical Talbot interferometer (see figure 1) being optimized for 213nm operation and having a fused silica diffraction phase mask for beam splitting [5]. The laser beam exhibited a “gaussian-like” profile, while it was scanned onto the sample surface by employing an oscillating mirror placed outside the interferometric cavity for averaging beam irregularities, thus, for producing gratings of improved spatial uniformity. During UV exposure the formation of volume damage and colour centers in the glass samples [6] was monitored in real-time by diffraction efficiency measurements, using a 635nm laser diode and probing the 1\st diffraction order of the grating at the Bragg angle.

![Figure 1 Experimental setup for exposing Bragg gratings in phosphate glass slabs using a 213nm Nd:YAG laser. RA: rectangular aperture. OM: oscillating mirror. CL: cylindrical lens. PM: phase mask. M1, M2: 45° beam folding mirrors. GS: glass sample.](image)

The glass slabs were 1mm thick, and doped with 2.3% wt. Er2O3 and 3.6% wt. Yb2O3. The samples exhibit a Class 3 acid resistance [4], denoting the dissolution time for a glass layer of 100nm thickness, which lies between 10 and 100h when 0.5M HNO3 acid is used at 25°C. The samples were exposed to different energy densities using 36000 pulses at 10Hz repetition rate. After the exposure the samples were chemically etched in aqueous solution of HNO3 of 3M concentration [7]. The temperature of the etching solution was kept stable at 40°C. The growth of the relief grating was measured at fixed time intervals using a simple diffraction efficiency measurement setup similar to that used for the real-time monitoring. The grating depth was estimated from diffraction efficiency measurements by employing standard coupled mode theory formulas for low-loss, thin gratings [8]. Moreover, atomic force microscopy (AFM) and scanning electron microscopy (SEM) were used in the investigation of the morphological characteristics of the relief gratings fabricated.

3. Results and Discussion
Several wide area and grating exposures were performed for quantifying the colour centres and structural modifications induced by UV radiation in the examined glasses by employing spectrophotometric measurements and real-time colour centre and diffraction efficiency probing. These spectrophotometric measurements are used for identifying colour centres induced in the material, which are expected to predominantly contribute to the selective etching mechanism. Briefly, exposure of the IOG1 glass to intense 213nm radiation induces strongly absorbing colour centres, located at the visible and near ultraviolet spectral bands (from 650nm to 240nm), as well as, shifts the
short wavelength Urbach slope. The last observation constitutes an indication of significant structural changes induced by the UV radiation in the exposed glass [11]. The results refer to volume damage effects and the photosensitivity of the bulk material will be presented and analysed elsewhere [10][12].

Figure 2 (a) Saturated grating depth vs. etching time in acidic solution for gratings exposed to different energy densities. The grating exposed to 64 mJ/cm² energy density reaches saturation after 40 hours developing time in the acid. (b) Saturated depth of the wet-etched gratings vs. energy density of the UV exposure, for exposures of 36000 pulses.

Depth evolution graphs of gratings exposed with different energy densities and developed until etch saturation level is reached and saturated grating depth versus energy density, are presented in figures 2a, b. The results presented refer to glass samples exposed to 63, 93 and 161 mJ/cm² energy densities and developed in acidic solution until saturation in diffraction efficiency is observed. As it is shown in figure 2a, exposures of greater energy densities result in deeper gratings and in shorter developing times. However, grating depth growth reaches saturation, with the differences in depth between gratings that have been exposed to 161 mJ/cm² and 93 mJ/cm² energy densities being rather small (see figure 2b). Prolonged exposures at high energy densities can result in extensive formation of absorbing centers that are accumulated close to the sample surface which in turn reduce the absorption depth of the incident radiation, limiting the induced damage at shallower depths. The maximum grating depth estimated from diffraction efficiency measurements is ~60 nm, however, this corresponds to average values.

Figure 3 (a) SEM scan of grating exposed with 36000 pulses and energy density of 161 mJ/cm² after 6 hours of chemical etching. The wavy pattern observed is attributed to an apparatus artefact, related to poor vibration isolation. (b) AFM scan of grating sample exposed and developed using the above conditions. Grating period ≈528 nm.
For prolonged immersion in the acidic solution and after etching saturation has been reached, the relief structures start to degrade, since the etchant starts to attack the dark fringes (unexposed areas) of the gratings, reducing their maximum depth modulation.

SEM and 3-D AFM scans of the relief gratings are presented in figure 3a, b. In both scans the surface of the etched gratings appears to be of high smoothness (RMS roughness $\approx 2$nm). No debris deposition is observed; a parasitic feature that is common for gratings patterned using direct ablation methods [3]. The groove profile of the gratings is “sinusoidal-like”, with deep sharp notches observed in the bright fringes of interference. Results presented elsewhere [10][12], describing the nature of the light-glass interaction, confirmed a single photon dependence between the colour centre and volume damage formation and the laser fluence of the exposure. Therefore, if one considers Beer law for describing the modified volume depth and chemical etching taking place only over the heavily exposed areas, a “notch-like” grating profile is obtained. Furthermore, before chemical etching the exposed glass samples were examined using AFM for investigating shallow relief structures attributed to extensive material amorphisation. However, the AFM scan shows that the exposed areas were kept intact (flat) after exposure, thus, only volume damage effects have taken place.

4. Conclusions
An ultraviolet laser radiation assisted selective chemical etching method for micro-/nano-patterning of hybrid phosphate glasses was presented here. The capabilities of the method were demonstrated for the patterning of sub-micron period Bragg reflectors in Er/Yb-codoped Schott IOG1 phosphate glass. The radiation of a 213nm, 150ps Nd:YAG laser, in combination with a modified Talbot interferometer were used for grating exposing; while a 3M HNO$_3$ aqueous acidic solution was used for selective etching of the modified material. High surface quality gratings with an average depth of 60nm were inscribed in the glass, for wet etching developing time of the order of 3.5 hours. The method presented here is currently applied in the patterning of 2-D reflectors on Er/Yb-codoped Schott IOG1 glass slabs, for the development of high-brightness planar lasing devices, emitting at the 1.5$\mu$m band.

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