Towards ultra-fast femtosecond-laser-assisted chemical etching of mid-IR transmitting Barium Germano-Gallate (BGG) glass

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The development of very-high-intensity femtosecond laser pulses in the 1980s has led to significant advancements in the field of laser micro/nanostructuring of materials [1]. The Direct Laser Writing (DLW) process, which involves creating 3D structures by focusing a laser beam within transparent materials, stands apart from UV photolithography due to its ability to shape complex three-dimensional geometries. However, the high surface roughness associated with this process prevents the achievement of optical-quality inscriptions.

To overcome these challenges, FLICE (Femtosecond Laser Irradiation-assisted Chemical Etching) was introduced about twenty years ago [2]. FLICE combines DLW with a subsequent chemical etching step to achieve finer structuring. This two-step process first involves creating arbitrarily shaped patterns through femtosecond laser irradiation within the glass volume, followed by immersing the substrate in a chemical etching bath (acidic or basic) which preferentially dissolves the laser-exposed areas. This allows the creation of high-resolution functional negative structures.

The key parameters required to achieve optimal selective etching have already been investigated in fused silica by many research groups [3,4]. In 2021, Casamenti et al. showed that type I modifications in fused silica etched in a 5 wt% NaOH solution (before nanogratings formation) allowed much higher etching rates and selectivity compared to a 2.5 v% HF solution [3]. By 2023, we had achieved state-of-the-art etching rates of more than 300 μm/h in fused silica using a Yb-doped fiber laser emitting 250 fs pulses at 1030 nm. Even though other groups have since demonstrated structures with higher selectivity and etching rate in fused silica [4], this glass still has a major drawback. Despite its excellent thermal and chemical resistance properties, as well as outstanding optical transparency, its transmission remains limited to the SWIR (< 2.3 μm). However, the demand for miniaturized photonic devices operating in the mid-IR range is increasing, particularly for gas sensing in the 3-4 μm range.

One way to overcome this issue is by using a Heavy Metal Oxide (HMO) glass matrix such as Barium Germano-Gallate (BGG) which offers good mechanical and chemical resistance, but most importantly, transmission in the mid-IR up to 6 μm. Based on the work of T. Guérineau et al. [5], we have identified suitable etching regimes (type I / type II) in a BGG glass composition. We have then investigated chemical etching and, for the first time in a BGG glass, report on a maximum etching rate of 2270 μm/h with an aspect ratio of 5.3 after 5 min of immersion in a 1 mol/L HCl bath. Although the current aspect ratio is not yet comparable to that of fused silica, the achievable etching rate is very promising and allows for ultra-fast micro-structuring. An in-depth parametric study is underway and could lead to potentially better aspect ratios. This work paves the way for the creation of miniaturized and functional optical devices in the mid-IR.

References

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