High-performance optical glass via high-resolution laser direct 3D writing for next generation sensing and imaging (OptoGlass3D)

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ABSTRACT

Glass is one of the oldest materials in optics and key to next-generation devices and applications in sensing and imaging. In terms of its optical properties as well as mechanical, chemical and physical resilience, glass remains unmatched and significantly outperforms polymers in most applications. However, glass is notoriously difficult to shape requiring mostly hazardous etching processes. In this work silica nanocomposites were structured using high-resolution direct laser writing based on two-photon polymerization. Further, an indirect replication process was established allowing the replication of microoptical components with high-throughput from 3D printed mold templates.

Keywords: Nanomaterials; direct laser writing; fused silica glass; Glassomer.

1. INTRODUCTION

Next generation of optical components for sensing and imaging require access to materials with enhanced performance combined with high-resolution three-dimensional shaping capabilities. Transparent fused silica glass is one of the most important materials for high performance optics and photonics, due to its high optical transparency combined with a high thermal and mechanical stability. However, shaping of fused silica glass is notoriously difficult (see section 2 State of the Art). Polymers on the other hand are easily shaped with technologies including high-resolution 3D printing, which enables a number of novel applications such as integrated optics, smart sensors and medical applications.[1] However the advantage in shaping is countered by a wide range of disadvantages like material aging, limited thermal, chemical and physical resilience as well as limited biocompatibility, to name but a few. In many of these applications, glass would have the superior material properties but due to the lack of shaping possibility, polymers are favoured.
A technology, which allows convenient structuring of optical glasses at resolutions of a few micrometers is key for the next generation of optical components for e.g. smartphones, optical data technology and photonics. The aim of *OptoGlass3D* was the development of such an enabling technology, which allows for high-resolution 3D structuring of glass using 2-photon polymerization (2PP). In this work, novel *Glassomer* nanocomposites were developed which have been amplified for structuring using Nanoscribe's 2PP technology for high-resolution printing featuring smooth surfaces. After the printing process, the printed components are converted to high-purity and transparent fused silica glass via thermal debinding and sintering. The process is capable of structuring fused silica glass with tens of microns resolution and a surface roughness of a few nanometers and was used to fabricate refractive optical elements. For the fabrication of microstructures with even higher resolution, an indirect process flow was developed. Here, a master structure was printed using 2PP in a commercial polymeric photoresin, which was subsequently transferred into Glassomer material using UV-casting and converted to transparent fused silica glass via the heat treatment. Using this indirect approach refractive and diffractive fused silica glass components could be fabricated with single micron resolution and a surface roughness of 1 nm.

2. STATE OF THE ART

High-resolution shaping of glasses is still limited in terms of designs and materials. High-purity glasses like fused silica glass are usually structured using grinding and polishing processes, which can only afford simple geometries on the macroscopic scale. Microstructuring of fused silica glass is usually done using wet chemical or dry etching processes, which can only afford very simple geometries, and further require hazardous chemicals like e.g. hydrofluoric acid (HF).[2] Laser assisted etching has been described to microstructure fused silica glass with tens of micron resolution by introducing nanocracks inside the glass, which subsequently show a higher etching rate.[3] However, the process achieves rough surfaces with a surface roughness of 40-200 nm, which require substantial post-processing if optical applications are required.[4,5] Recently, 3D printing methods have been introduced to shape transparent glass either using direct or indirect methods. Direct approaches start with the glass itself and the shaping process is executed at high-temperatures e.g. by melting a glass powder and extruding the melt through a nozzle. These direct 3D printing methods can only be used for the fabrication of macroscopic parts.[6] For high-resolution 3D printing of glass, indirect printing methods are used which print a glass precursor such as a nanocomposite or a sol-gel, which is subsequently converted to a glass in a heat treatment.[7–10] Tab. 1 shows a summary of relevant methods for structuring fused silica glass showing that there is no competitive technology in the state-of-the-art, which would allow for the fabrication of 3D microstructures with optically smooth surfaces.

Tab. 1. Comparison of relevant methods for structuring fused silica glass. Legend: +++ outstanding, ++ very good, + good, - limited; -- very limited.

Technology	3D capability	Resolution	Surface roughness
Etching			
Wet etching	--	++	++
Dry etching	--	+++	+++
Laser assisted etching	+	+	--
Mechanical			
Powder blasting	--	-	--
Additive			
SL	++	+	-
Direct ink writing	+	--	--
DLW	++	++	++

3. BREAKTHROUGH CHARACTER OF THE PROJECT

From a scientific point of view, the project *OptoGlass3D* is a major game changer for the fabrication of novel microstructured glass components, which have so far been inaccessible. As shown in Tab. 1 there was no technology available, which allowed for the fabrication of three-dimensional structures with optically smooth surfaces in transparent glasses. The advent of high-resolution 3D shaping of polymers has enabled a plethora of applications from optic and data communication to life science and medical applications in the last two decades. Many of these applications, especially in the optics and photonics sector, would profit from access to high-performance optical materials with the outstanding material properties of glass.
From a commercial point of view *OptoGlass3D* is a huge success building on the formulation development and fabrication of Glassomer and the high-performance printing capabilities of Nanoscribe. 3D printing at the micrometer scale using the Nanoscribe 2PP technology is already applied in a great variety of fields like microoptics and robotics, photonics, smart materials, medical imaging and various other disciplines. As a global leader in high-precision 3D printing solutions, an entire platform of printer users throughout academia and industry is immediately able to apply the *OptoGlass3D* technology in a straightforward manner. The development within *OptoGlass3D* is fully compatible with the existing Nanoscribe devices and knowledge in the respective scientific disciplines will largely augment. As examples the fields of microoptics for sensing/imaging and photonics will directly benefit from the superior optical properties of glass materials while medical imaging and related life science applications will benefit from improved biocompatibility as well as thermal and chemical stability.
The results within *OptoGlass3D* will further have a major impact on societal challenges. Glass is a material not based on crude oil and which is significantly less critical in disposal and fully recyclable. Given the fact that glass components can undergo harsh cleaning protocols the establishment of reusable components e.g. in a clinical context could become possible reducing polymer waste.

4. PROJECT RESULTS

In this work novel Glassomer nanocomposites for direct 3D printing using 2PP were developed. To achieve this, Glassomer nanocomposites with a high chemical crosslink were fabricated and tailored for two-photon polymerization. The process is shown in Fig. 1. The novel resins were structured using 2PP. After the printing process, residual non-polymerized material was removed in a solvent bath. The resulting polymeric structure is the so-called green part. The green part was subsequently thermally debinded at a temperature of 600 °C where the binder matrix is fully removed (resulting in the so-called brown part). The brown part was finally sintered to a fully dense transparent glass at a temperature of 1300 °C. Exemplary sintered fused silica glass structures printed using 2PP are shown in Figure 3a/b/c, e.g. a hollow glass rook and a microscrew.

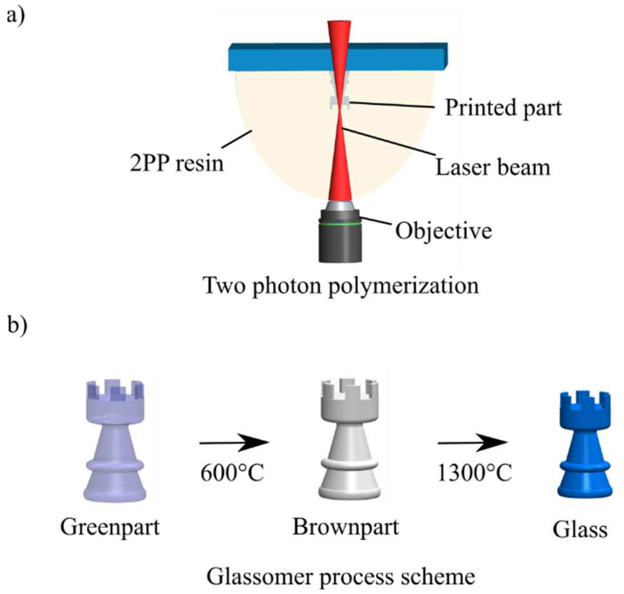

Fig. 1. Process flow: a) Amplified Glassomer nanocomposites are shaped using 2PP (resulting in the so-called green part). b) The green part is thermally debinded at 600 °C resulting in the so-called brown part. The brown part is sintered to a highly transparent fused silica glass at 1300 °C.

Further an indirect replication based process was established to allow for even higher resolution fabrication of microoptical elements. The process is shown in Figure 2. A microoptical polymer master was printed using Nanoscribe's 2PP technology in a polymeric photoresin. The master was then replicated using a soft mold. The Glassomer UV-casting formulations were then replicated from these molds and subsequently converted into transparent fused silica glass via thermal debinding and sintering.

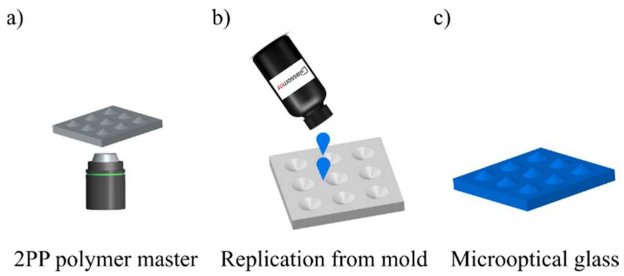

Fig. 2. Indirect shaping of high-resolution microoptical components using 2PP of polymeric photoresins and subsequent replication. a) 2PP printing of microoptical polymer master using a Nanoscribe printer. b) Glassomer replication from silicone mold using subsequent UV-hardening. c) Replicated and sintered fused silica glass part with optical surface quality.

Figure 3d shows the process flow from a polymer master to the final fused silica glass replica for an exemplary microoptical structure. Using this indirect replication process refractive and diffractive optics with single micron resolutions and a surface roughness in the single digit nanometer region could be achieved.

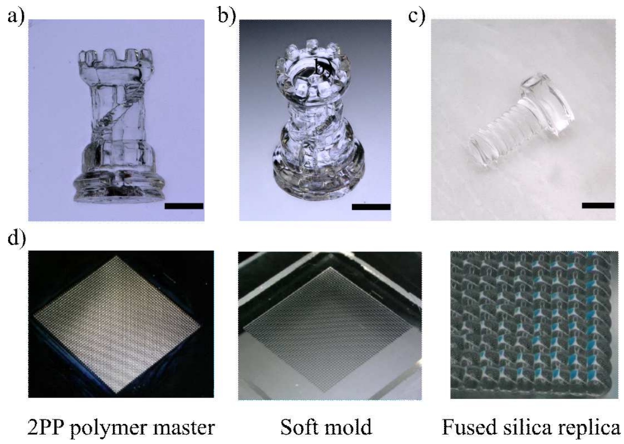

Fig. 3. Exemplarily manufactured high precision fused silica glass parts. a) 2PP printed fused silica glass rook (scale bar: 500 µm). b) Top-side view photograph of fused silica rook from a) (scale bar: 500 µm) c) 2PP printed fused silica glass screw (scale bar: 200 µm). d) Replicated fused silica optical microstructure from 2PP printed polymer master.

5. FUTURE PROJECT VISION

5.1. Technology Scaling

The material formulation will be commercialized. The goal is to make high-resolution glass 3D printing accessible for costumers. Technology Readiness Level (TRL) 5 has been reached in ATTRACT Phase 1 and will be scaled to TRL 9 in a possible ATTRACT Phase 2 thus paving the way for commercializing and selling the material on a large scale as well as identifying suitable minimal viable products. The focus will be on the high-precision optics market as well as applications in the life sciences. Future partnerships with system providers and OEMs will be lined up thus broadening the potential user and customer base.

5.2. Project Synergies and Outreach

Partnerships with worldwide 3D printing material distributors will be set up in order to enlarge the accessibility of the unique glass 3D printing technology. Partnerships with manufacturers of optical imaging devices are planned as well. The results of the first phase ATTRACT will form the basis for this scalability as important milestones have been reached and suitable demonstrators have been designed. Our results will be key in showcasing this technology on industry fairs as well as industrial and academic conferences thus providing a solid communication platform for this technology.

5.3. Technology application and demonstration cases

3D printed optical components will be manufactured using high-resolution 2PP 3D printing of fused silica glass parts. Showcases will include:

- 3D printed fused silica diffractive optical elements (DOE) with nanometer-scale feature sizes
- Highly transparent 3D printed fused silica microlens-arrays
- 3D printed transparent fused silica multi-stack lenses for the application in medical devices.
- High quality fused silica glass optics for optical imaging devices

Further, the 2PP glass process will be even improved by combining of the resin with the newest Nanoscribe printer generation, directly transferring technological improvements in 2PP to glass materials. Using tailored printing consumables by Glassomer and Nanoscribe, the way will be paved to create micrometer glass parts with outstanding shape accuracy.

5.4. Technology commercialization

Glassomer currently offers several different nanocomposites for different applications such as casting and macroscopic printing. Based on the findings of ATTRACT, Glassomer will now be able to produce a resin specially designed for the applications shown in this report and will distribute the resin for customers for microstructuring of glasses. Glassomer, the founders and the technology have already won several prestigious awards like the *Deutsche Studienpreis* and Innovators under 35 by MIT Technology Review as well as several Start Up awards including the Materialica, RapidTech and Formnext award, and has developed a business plan and financing strategy for compounding, packaging and selling of the 2PP resins. Nanoscribe will focus on the commercialisation of a ready-to-use resin for 2PP printing. Thereby, the product portfolio will be extended to glass printing, enabling the 2PP community a facile pathway to glass printing. The novel materials will be presented to potential customers on several fairs including the Formnext, RapidTech and the SPIE Photonics West.

5.5. Envisioned risks

We need a substantial workforce to enable effective compounding, packaging and selling of 2PP *OptoGlass3D* resins, which poses a risk as it is not certain that we will be able to hire enough force in time. We are however confident, that we can overcome this risks, as Glassomer is close to the academic system through one of the founders being a full professor. This will allow us to get in contact with a wide variety of young talents and will ensure a constant availability of work force. We have already detected a large interest in the novel resins for making glass microstructures, so we expect the risk of high-priced resins as a market entry barrier to be low.

5.6. Liaison with Student Teams and Socio-Economic Study

Within Phase 2 of ATTRACT, a student business consulting team will be engaged for developing a market strategy for a wider outreach of the technology developed within the first phase of ATTRACT. Specific application cases outside the classical optical component markets will be targeted with the aim of identifying potential applications of this technology in the life sciences and health market segment highlighting opportunities to specifically contribute to the UN's Sustainable Development Goals (SDG). Focus will be put on applications in water cleaning applications (GOAL 6) and applications in public health (GOAL 3) where first prototypical applications have already been outlined. Within the ATTRACT Initiative expert-driven socio-economic studies will be undertaken to precise these strategies.

6. ACKNOWLEDGEMENT

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