Review Article

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Optical elements from 3D printed polymers

<https://doi.org/10.1515/epoly-2021-0061>
received June 07, 2021; accepted July 08, 2021

Abstract: 3D printing belongs to the emerging technologies of our time. Describing diverse specific techniques, 3D printing enables rapid production of individual objects and creating shapes that would not be produced with other techniques. One of the drawbacks of typical 3D printing processes, however, is the layered structure of the created parts. This is especially problematic in the production of optical elements, which in most cases necessitate highly even surfaces. To meet this challenge, advanced 3D printing techniques as well as other sophisticated solutions can be applied. Here, we give an overview of 3D printed optical elements, such as lenses, mirrors, and waveguides, with a focus on freeform optics and other elements for which 3D printing is especially well suited.

Keywords: additive manufacturing, diffraction, optical splitters, polarizer, whispering-gallery-mode resonators

1 Introduction

3D printing enables preparing objects of nearly unlimited shapes in a relatively fast way, without the necessity to prepare a mold or other tools before (1,2). In the fused deposition modeling (FDM) technique, which is most often used in the low-cost range, typical polymers are poly(lactic acid) (PLA), acrylonitrile butadiene styrene (ABS), polycarbonate (PC), or polyamide (PA) as well as different thermoplastic polyurethane filaments (TPU), while other technologies allow for printing different polymers or metals (3). Besides FDM printing, diverse other techniques exist, which will be presented in Section 2. The broad variety of different technologies allows for

printing quite different materials, e.g., also hydrogels (4,5). They can be used for diverse applications, such as biomedicine and biotechnology (6,7), filters (8,9), orthoses (10–12), recoverable bumpers (13,14), reinforcement of textile fabrics (15–18), or even parts of spaceships and satellites (19,20). All these techniques have in common that objects are produced layer by layer, while nowadays, due to the possibility to use robotic arms, it is even possible to print layers on arbitrarily shaped objects, in different orientations, and on large scales (21–23).

For several applications, the imperfect mechanical properties are problematic (24), while other applications necessitate less wavy surfaces than created with many 3D printing techniques (25). Especially for the creation of optical elements, such as lenses or mirrors, a well-defined surface is of utmost importance. This necessitates in most cases using new 3D printing techniques with small minimum feature sizes. On the other hand, for gratings and other optical elements, the typical waviness of many 3D printed objects may even be useful to reach a certain effect.

Here, we give an overview of recent advances in 3D printing optical elements. Starting with a brief introduction to typical 3D printing techniques used in this area, we present different methods enabling simple and more sophisticated passive and active optical elements.

2 3D printing techniques

In the aforementioned FDM technique, a molten polymer is pressed through a nozzle and deposited on the printing bed or on the previous layer, respectively, to successively build a 3D object from subsequent layers (26). This technique is probably the most well-known one since FDM printers are available in inexpensive versions, affordable also for private people, schools, etc. However, the FDM technique usually results in objects with high waviness due to the production principle.

The first developed 3D printing technique was stereolithography (SLA). Here, the layers of the 3D printed object are built up from a light-sensitive resin that is position-dependent crosslinked by light, typically by a laser. The

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final objects can have diverse mechanical properties, from hard to elastic to hydrogels (27).

Lithographic techniques are also known for the preparation of nanostructures (28). For the preparation of such smaller-scale features, a photomask is applied on a photoresist, so that subsequent UV irradiation only reaches the open areas and either polymerizes (negative photoresist) or dissolves (positive photoresist) the resist at these positions. The better soluble part of the photoresist is afterward washed away. This process is often used to build a master mold (29).

Another possibility to crosslink a UV-curable resin, reaching quite low feature sizes, is given by two-photon or multi-photon polymerization (30,31). In this technique, the resin has to absorb two or more photons in order to reach an excited state, with the process strength being proportional to the squared light intensity and thus limiting it strongly to the desired position, opposite to the common SLA process.

Other techniques, besides resin-based ones, are selective laser sintering (SLS), in which a laser fuses a thermoplastic powder (32), or inkjet printing, which can be used to print hydrogels, etc. on very small scales due to the low viscosities of the ink (33).

A few other highly specialized 3D printing techniques are available, such as direct laser writing or robot dispensing, working with different materials, and reaching different feature sizes. Table 1 gives an overview of typical minimum feature sizes of the aforementioned 3D printing techniques, as reported in the literature (34). These dimensions are essential to choose the optimum 3D printing technique for the optical element that needs to be prepared. Several examples of 3D printed optical elements are given in the following sections.

3 3D printed lenses

Optical lenses are used in many applications nowadays, from glasses for nearsighted people and reading glasses

to microscopes, from lasers to optical systems for lithographic techniques (38,39). The common production steps for preparing glass lenses contain grinding, polishing, and lapping, which can nowadays be performed by computer-controlled machines, in this way increasing reproducibility (40). Besides, precision glass molding techniques can be used especially for irregularly shaped lenses, enabling the production of lenses in a faster way (41,42).

Besides glass lenses, polymer lenses are of increasing importance. Typically, polymer optical lenses differ in optical density, transmittance, and thermal stability from glass lenses (43). Polymer optical lenses can be injection-molded (44), meaning high costs for the mold (45), while microlens arrays can be produced by special inkjet printing methods based on polymeric nanodroplets (46).

3D printed polymer lenses can be found in different dimensions, produced by different techniques from various materials. Since the aforementioned inkjet printing technique is limited to diameters of some millimeters and surface control is low (47), one approach can be based on adding an inkjet-based layer on a larger poly(methyl methacrylate) (PMMA) substrate. Gawedzinski *et al.* tested this approach for lenses of different diameters and focal lengths, prepared by Luxexcel in comparison with glass lenses from large optics producers (48). They found the composite material to exhibit transmission values above 90% for wavelengths of 500–1,100 nm. Excitation in the wavelength range of 350–500 nm resulted in broad-band fluorescence in the visible range, meaning this material should not be used for fluorescent applications. The peak-to-valley roughness was for the glass lenses in the range of 5–10 nm, equivalent to $\lambda/100$ quality, and for the 3D printed lenses in the range of 30–110 nm, which corresponds to often used lenses of $\lambda/10$ to $\lambda/4$ quality. Similarly, the radius of curvature showed slightly higher deviations from the theoretical values for the 3D printed lenses, while astigmatism and coma were significantly higher in the polymer lenses. Thus, increasing the aperture diameters during testing the optical resolution of the lenses clearly increased

Table 1: Resolutions of different 3D printing technologies, reported in the literature, sorted from larger to smaller minimum feature sizes. From ref. (14), originally published under a CC-BY license

Technology	Min. feature size (μm)	Material	Ref.
Selective laser sintering	<400	Diverse polymers	(32,35)
Fused deposition modeling	200	Diverse polymers	(16)
Robot dispensing	200	Hydrogels	(33)
Stereolithography	30–70	Photosensitive polymers	(17)
3D inkjet printing	28	Photoresist	(33)
Resonant direct laser writing	1–4	IP-Dip photoresist	(36)
Multiphoton absorption polymerization	1	SU8 photoresist	(31)
Two-photon polymerization	0.28–1.5	Photoresists	(30)
Direct laser writing	0.085–1.5	Photoresists	(37)

the resolution of the commercial lenses, while the surface roughness rather blurred the images in the case of the 3D printed lenses. This shows that these apparently small roughness values in the range of several 10 nm are sufficient to reduce the image quality significantly.

Another modified inkjet printing technique, called Printoptical[®] technology, was suggested by Assefa et al. (49,50). They used LUX-Opticlear with a refractive index of 1.53 at $\lambda = 588$ nm for printing and established an iterative manufacturing process to correct surface shape deviations from a reference plano-convex lens by subsequent measurements of the output-wavefront error using a Mach-Zehnder interferometer and repeated printing of the optimized lens. The effect of this optimization step is shown in Figure 1 (49). In this way, wavefront errors of the order of magnitude ± 1 wavelength could be achieved. The group also mentioned that since only one material was commercially available that could be used for this process, manufacturing achromatic lens systems still necessitates combinations with silicon molding and vacuum casting.

Instead of optimizing the printing process, Vaidya and Solgaard developed a smoothing technique for optical surfaces and tested it on mirrors, concentrator arrays, and immersion lenses (51). The latter were produced from polydimethylsiloxane (PDMS) in hemispherical shape by filling 3D printed molds with PDMS monomer followed by heat-curing for 24 h. Before molding, the 3D printed molds were smoothed by coating the material with a UV-curable polymer blend of methacrylates, acrylates, and urethane-based polymers, which could be used to prepare smooth top layers, fixed well on the mold surface (52). After molding, atomic force microscopy measurements showed a very low surface roughness of the PDM parts of only 1.4 nm, similar to the mold surface roughness, and focal length deviating less than 1.5% from the nominal values.

Shao et al. as well as Chen et al. again suggested another method to avoid the usually occurring steps in

concave or convex 3D printed surfaces due to the layer-wise printing process (53,54). For this, they combined projection micro-stereolithography (PμSL) with grayscale exposure and meniscus coating. In PμSL, a dynamic mask is applied to control the photopolymerization of each layer, making this process significantly faster than laser-scanning polymerization processes (55). Together with grayscale photopolymerization and meniscus equilibrium post-curing, very low surface roughness of below 7 nm was reached (Figure 2). Besides, to speed up the process further, this technique was combined with micro-continuous liquid interface production (μCLIP) (56) in which 3D printing is performed in a continuous upward movement of the sample stage, without stopping at defined heights, by applying an oxygen-permeable membrane to inhibit photopolymerization reaction near to it. This process only worked with an optimized membrane, here prepared from PDMS, to avoid increased surface roughness.

Two-photon polymerization is another possibility that can be used for high-precision 3D printing. Some groups reported on lenses printed with a commercial microfabrication system from Nanoscribe GmbH. Ristok et al. prepared millimeter-sized spherical and aspherical lenses with the system and compared the first with corresponding glass lenses (57). They found a slightly reduced radius of curvature for the polymer lenses due to shrinking (496 μm instead of 500 μm), only slight differences in the imaging quality of glass and printed lenses, and in general a comparable performance of the 3D printed lenses in comparison with the commercial glass lenses. Similarly, Thiele et al. prepared microlens systems for foveated imaging with the same commercial system (58), and Asadollahbaik et al. used the same technique for the preparation of diffractive Fresnel lenses (59).

The same equipment was used by Weber et al., who developed nano-inks from commercial IP-DIP resin and dielectric nanoparticles as possible lens materials with

Figure 1: (a) 3D printed lens with 25 mm clear aperture; (b) surface profile error before iteration; and (c) surface deviation after five iterations. From ref. (49), originally published under an open-access license.

Figure 2: 3D printing of an optically smooth surface using the PμSL system and post-processing steps. (a) Schematic illustration of the PμSL system. A 3D solid model with smooth surfaces shown in panel (b) is approximated as a set of discrete voxels, resulting in the pixelated rough surface shown in (c). (d–g) Surface roughness optimization and the resulting imaging characteristics of 3D-printed lenses using various methods. (d) Lens printed by binary patterns without post-curing process; (e) lens printed by binary patterns and the following meniscus equilibrium post-curing process. The polymerized meniscus structures are illustrated in yellow; (f) lens printed by grayscale photopolymerization without the meniscus equilibrium post-curing process, with the grayscale polymerization providing a smooth transition from the pixelated roughness (marked yellow); and (g) lens printed by grayscale photopolymerization and the following meniscus equilibrium post-curing process. The first column in panels (d–g) shows SEM images of the surface of the printed lenses. Scale bars: 200 μm for panels (d–g), 1 mm for the inset of panel (g). The second column in panels (d–g) shows the recorded images of the printed “NU” test objects taken by the phone camera with the 3D-printed lenses attached. Scale bars: 1 mm. Reprinted from ref. (54), with permission from Wiley.

modified refractive indices (60). They found slightly hazy images only for the highest nanoparticle concentration of 20%, indicating that the composite with this amount of nanoparticles may no longer be homogeneously blended. Here, investigations of the lens geometries were not in the focus of the study. Similarly, combining high- and low-refractive-index polymers, Campbell *et al.* prepared gradient-index lenses with an inkjet-based process (61).

An SLA system equipped with a digital light processing (DLP) projector was used by Kang *et al.* to fabricate optical elements (62). The projector works with masks for each layer that are subsequently projected onto the printing polymer. The latter can either be a free-radical system, consisting of a monomer and a photoinitiator, or

a cationic system in which a ring-opening process of cyclic ethers, especially epoxides, occurs (63,64). Combining both radical and cationic systems, Kang *et al.* used the material Somos Waterclear Ultra 10122 with a refractive index of 1.52. For thin layers, they are typically cured from bottom to top, allowing for continuous printing without stopping the printing bed, and without an additional membrane, as used in (53). In addition, grayscale masks were again applied here to avoid the usual steps along the sides of the printed samples, and slicing the element into layers of equal thickness, of equal arc length between subsequent layers, and combining both was applied. In this way, especially using the combo slicing method was shown to be very successful in

providing lenses with low staircase effect and high optical performance.

With stereolithography, Kukkonen et al. also managed to prepare nonlinear active optical devices, i.e., devices that were capable of second-harmonic generation, pumped by a femtosecond laser with wavelength 1,195 nm to create a light of 597.5 nm (65). For these special nonlinear lenses, they combined microcrystalline nonlinear active component, urea, or potassium dihydrogen phosphate with a common photopolymerizable polyacrylate-based resin to prepare a resin for SLA printing.

Generally, it can be seen that different approaches can be used to use 3D printing for the preparation of high-quality optical lenses. Most of them are based on inkjet printing, 2-photon polymerization, or sophisticated SLA systems with grayscale masks and continuous printing, while some other approaches concentrate on post-processing of the models themselves or molds from which lenses are prepared.

4 3D printed mirrors

Mirrors are, in their simplest form, flat and relatively easily producible. Nevertheless, there are some approaches in the literature to 3D printed mirrors. One reason to use 3D printing for the production of mirrors is that special curved shapes are necessary. Vaidya and Solgaard, e.g., prepared mirror blanks by the aforementioned surface smoothing technology based on surface coating with a UV-curable polymer mixture (51). Figure 3 shows the parabolic profile directly after printing and the significantly stronger reflecting surface after the smoothing procedure as well as the final metalized mirror.

Mici et al. suggested another application of 3D printed mirrors (66). Mirrors in high-energy lasers need a high

thermal conductivity to allow for cooling the optical surface, in order to reduce thermal expansion. In this case, cooling channels can directly be integrated into the mirror substrates to allow for active cooling.

Other studies include 3D printed electromechanical actuators for large optical telescope mirrors, enabling deformation of several microns (67,68), or 3D printed lightweight mirror bodies from different metals or polymers such as poly(ether ketone ketone) (PEKK) (69,70).

Generally, as long as no special shapes or additional features are necessary, 3D printing mirrors is not investigated in detail since recently no advantages were visible. However, this changes as soon as freeform optics – used as lenses or mirrors – are necessary.

5 3D printed freeform optics

Freeform optics are optical elements without an axis of rotational invariance, with arbitrary shape and possible additional surface structure (71,72). They allow increasing the performance of an optical system, e.g., in biomedical engineering or green energy, building systems with fewer surfaces and thus smaller dimensions and mass with the reduced necessity of assembly (73,74). Such freeform optics can be used in diverse applications, not just imaging, but also in solar energy concentrators (75) or for illumination with increased efficiency and more freedom of design (76). Freeform optics, in form of lenses or mirrors, are natural candidates for 3D printing.

Recently, Li et al. reported on freeform optics, prepared from optical silicones cured by a pulsed infrared laser, i.e., thermally instead of by UV light (77). They investigated the process parameters, i.e., repetition rate and numerical aperture, and applied a wavelength suitable for the PDMS used in the experiments to print

Figure 3: 3D-printed parabolic mirrors (a) as printed, (b) after smoothing, and (c) after Al deposition. From ref. (51), originally published under a CC-BY license.

freeform donut-shaped lenses that were optically clear, without yellowing, as visible in Figure 4.

Hong and Liang used a similar process, followed by a step in which the PDMS is dropped onto the cured lens and cured again to flatten the steps between subsequent layers (78). In this way, they could produce plano-convex and plano-concave lenses and lens arrays with a surface roughness of approx. 15 nm, as compared to approx. 5 nm for the best commercially available glass lenses. Besides, they prepared freeform donut lenses focusing the light onto a ring.

Assefa *et al.* used the Printoptical[®] technology with Opticlear polymer also for freeform optics, similar to the aforementioned conventional lenses (79–81). Partly, they investigated these lenses by white-light interferometry and surface profile macroscopy as well as in comparison with theoretical examinations by ray tracing software. Similarly, a digital twin (82) approach was used by Sieber *et al.*, who used inkjet-printing of optical freeform surfaces and optimized the printed optics by optimizing the difference surfaces (83).

With two-photon polymerization, Li *et al.* added a special freeform micro-optics, a flat-end block with different holes, to single-mode fiber probes, and found low

optical loss for a wavelength range around 1,300 nm (84). For side-viewing probes, specially designed freeform air-photoresist interfaces in the form of off-axis paraboloidal surfaces were used to create total internal reflection. In this way, imaging of biological samples was possible.

Wei *et al.* used two-photon direct laser writing to prepare a freeform polarizing beamsplitter for the near IR (85). They applied an inverse-design algorithm to define the desired structure for a wavelength range of 1.3–1.55 μm and printed it with the necessary resolution of 100 nm (approx. 1/15th of the wavelength λ). The 3D printed polarizing beamsplitter reached extinction ratios of up to 5 at the optimum wavelength.

Diverse freeform shapes were produced by common UV-polymerization of different polymers by Farahani *et al.* (86). They found that for free-standing shapes, such as spirals or also lenses without a plane side, the viscosity of the material strongly influences the printability of the desired shapes, while diverse processing parameters showed a further impact on the result, such as deposition speed and UV irradiation intensity. All parameters had to be optimized fitting to each other to allow for a reproducible production.

For the special application of Raman spectroscopy, Grabe *et al.* developed cost-effective freeform polymer

Figure 4: 3D-printed nonaxially symmetrical PDMS lens. (a) Donut shape lens, (b) donut shape lens showing ray bending, (c) nonaxially symmetry freeform lens, and (d) nonaxially symmetry freeform lens showing ray bending. From ref. (77), originally published under a CC license.

optics by 3D printing (87). These optical elements were 3D printed by MultiJet Modeling, i.e., by UV photopolymerization, and combined focusing of the laser, collection of the Raman scattered light, and also the mount. For the used laser with a wavelength of 785 nm and max. 0.5 W power, they found a Stokes Raman shift resolution of 6.7/cm.

As these examples show, different freeform optics presented in the literature were printed, e.g., by optical silicones cured by an infrared laser, by inkjet printing, common UV polymerization, or two-photon polymerization, depending on the required smoothness and the corresponding optical quality. Slightly different requirements can be defined for 3D printed optical waveguides, as presented in the next section.

6 3D printed optical waveguides

Optical waveguides are often produced from polymers and used in broadband communications, computer systems, and diverse other applications. They guide light beams, e.g., introduced by a laser or LED, and often combine high- and low-index media as step-index or gradient-index waveguides to optimize total internal reflection. While planar

waveguides allow sheet beams to propagate parallel to the surface of a high-index guiding layer, channel waveguides further confine the possible beam orientations (88).

Especially planar and channel waveguides are naturally well-suited to be 3D printed since they do not have to be self-standing, but can be placed on an even substrate. On the other hand, simple optical fibers can just be extruded. Thus, several examples for 3D printed waveguides can be found in the literature.

One possibility to prepare optical fibers is by using a low-cost FDM printer as an extruder. Canning et al. showed that direct drawing of optical fibers from an FDM printer was possible due to the consistent temperature distribution in the nozzle (89). They used this simple method to draw ABS and PETG optical fibers that showed similar propagation losses as standard optical fibers. Besides, they combined ABS and polystyrene, showing losses lower than 1.5 dB/cm at 632 and 1,550 nm and lower than 0.75 dB/cm at 1,064 nm (90). Using a modified nozzle (Figure 5), Talataisong et al. prepared even microstructured polymer optical fibers from a common FDM printer (91). Their fiber showed confinement of light at $\lambda \sim 1,550$ nm in the fiber core with a maximum propagation loss of 1.1 dB/cm.

Other authors report on using 3D printed preforms that are drawn afterward. This approach has the advantage that

Figure 5: (a) Structured nozzle design. Green arrows and green colors represent the direction of filament moving and cross section of extruded polymer from the structured nozzle. (b–d) Micromachined structured nozzle: (b) body, (c) body + cover, and (d) after MPOF drawing. From ref. (91), originally published under a CC 4.0 license.

it is possible to combine two materials with different refractive indices (92). For this case, Toal *et al.* underline the importance of properly choosing the printing direction of an FDM printer (93). They prepared a broad variety of structured and two-material fibers, produced by drawing 3D printed structures, and showed that even very fine cores could transmit green laser light along the whole fiber length of 9 m.

Zhao *et al.* prepared fibers with different core geometries, surrounded by claddings from another material, by simultaneous printing of both materials (94). For the mid-IR, Talataisong *et al.* prepared microstructured hollow fibers from 3D printed PETG preforms and found wave guidance in the wavelength range of 3.5–5 μm inside the hollow fiber core (95).

Besides these drawn waveguides produced by the simple FDM process, there are more complex fabrication methods reported in the literature. Bertoncini and Liberale, *e.g.*, used a two-photon lithography process, applying the commercially available Nanoscribe system to prepare highly complex waveguides from the IP-Dip photoresist (96). With this system, they prepared diverse microstructured optical fibers, *e.g.*, fibers with helically twisted hole arrangements, with photonic bandgap hollow-core, with anti-resonant hollow-core, *etc.*, mostly for a wavelength of the optical mode of 1,060 nm.

Frascella *et al.* modified the common DLP process by using a photoluminescent dye, which enabled 3D printing waveguides and splitters, guiding the luminescence (97). By copolymerizing the dye together with the printing polymer, the dye's solvatochromic properties toward different solvents could be maintained, in this way producing solvents' polarity sensors.

Finally, diverse authors show approaches to use 3D printing for preparing waveguides on substrates, *e.g.*, for optronic sensor networks. Wolfer *et al.* compared inkjet printing with a UV-curable ink with flexographic printing, a typical industrial-scale photopolymer printing process (98). They underlined the additional possibilities offered by inkjet printing, enabling printing after other structures have already been added onto the substrate, while flexographic printing needs to be the first step in a production cycle. Besides, inkjet-printed micro-lenses could be used as coupling structures at the end of a waveguide (99).

A different approach was chosen by Soma and Ishigure, who used a robot-microdispenser to 3D print graded-index fibers (100). With their so-called mosquito method, they first printed the uncured cladding layer, then inserted the needle of a robot dispenser into this layer, and dispensed the core monomer there linearly. By monomer diffusion between both materials, a round core is formed before the whole

system is cured by UV exposure. In this way, they produced a 12-channel polymer parallel multimode optical waveguide with low propagation losses of 0.033 dB/cm at 850 nm, low insertion losses, and low crosstalk. Besides waveguides aligned in one layer, they also showed the possibility to form a 3D waveguide network by this method (101).

A similar approach was chosen by Ishihara *et al.*, who used calixarene, a cyclic phenol resin with lower propagation losses than PMMA, to produce optical waveguides by two-photon polymerization (102). They also inscribed the 3D core into the cladding. While the core was cured by two-photon-assisted polymerization, the residual monomer surrounding the core was afterward polymerized by UV light and built the cladding. In the same way, they also managed to prepare a 1×3 splitter.

Quite a different material was used by Parker *et al.*, who used direct ink writing to prepare optical waveguides from silk (103). They prepared a silk fibroin ink from 28% to 30% silk fibroin in an aqueous solution, which was extruded into a coagulation reservoir containing methanol/water where the continuous rodlike filament was formed rapidly. The optical waveguides showed good optical properties, combined with biocompatibility and biodegradability, and offered the possibility to incorporate dopants to use new ways of photoactivation, making this material interesting for new biophotonic sensing devices.

With stretchable clear ballistic gel and a custom-made microextrusion printer (104), Udofia and Zhou prepared straight and curved waveguides with different nozzle diameters, reaching a minimum diameter of 154 μm . Besides structures located in a 2D area, they also printed 3D stacks of waveguides. Interestingly, a low propagation loss of 0.22 dB/cm was reached with this material as well as high transparency, making this material also interesting for 3D printed fluidic devices (105).

Wang *et al.* used an FDM printer to prepare a 3D stack of waveguides, each prepared from a single printing line, in this way creating an optical faceplate of 20,000 fibers (106). After polishing the ends, they compared four different transparent printing materials and found strong differences in transmission and crosstalk, with limited resolution due to the relatively imprecise printing process.

Besides these pure optical waveguides, several authors introduced special shapes inside the waveguides or at their ends to modify their optical properties. With direct laser writing, Gissibl *et al.* showed diverse sub-micrometer spherical, toric, and freeform lenses as well as polarizing structures that were compared with simulations (107). They found that the internal refractive index variations upon inhomogeneities during polymerization were not problematic for the

optical performance so that the method could be used to prepare new optics for endoscopy or micro-imaging. Direct laser-writing by two-photon polymerization was also suggested by Hadibrata et al. to 3D print a metalens on an optical fiber tip (108). This metalens was inverse-designed and had a focal length of approx. $8\text{ }\mu\text{m}$ at $\lambda = 980\text{ nm}$, resulting in a spot size of approx. 100 nm and could be used for direct laser lithography. Photopolymerization of SU-8 photoresist by UV light patterns, combined with a digital camera for machine vision metrology, was used in a 3D micro-printing platform to prepare suspended mirror devices on the end face of optical fibers (109).

Generally, 3D printing of optical waveguides is possible by extruding in an FDM printer, printing, and extruding afterward, or in the case of highly sophisticated structures, by the aforementioned high-resolution 3D printing techniques. For simple waveguides with round cross sections, the extrusion in an FDM printer offers a fast and inexpensive production method.

Other important optical elements, directly correlated with optical waveguides, are the optical splitters described in the next section.

7 3D printed beam-splitters

When optical data – or light in general – are propagating through an optical waveguide, there is often the necessity to split or to combine these signals. For this, an optical splitter is used, often Y-shaped. Similar to the waveguides themselves, it is necessary to take into account the dimensions and material parameters to prepare single- or multi-mode beam-splitters.

Prajzler et al., e.g., prepared in-plane beam-splitters by a UV-curable photopolymer, which is inkjet-printed to prepare a mold first (110). Commercially available large-core polymer optical fibers (POFs) from PMMA were inserted into the molds before the Y-shaped beam-splitter was filled into the remaining mold, connecting the POFs, and hardened. Finally, the top cover was again 3D printed. They found insertion losses of 5.4 dB at 532 nm and less than 6.8 dB at higher wavelengths of 650 nm and 850 nm , respectively, combined with a well-balanced coupling ratio between both outputs. Even smaller insertion losses were most recently demonstrated by this group, using optical elastomers for core and cladding (111).

Hasan et al. used an FDM printer to prepare a multi-mode planar large-core Y-splitter from ABS, with NOA glue used to fill up the core and found sufficient insertion losses of the splitter (112). NOA UV-curing glues were

already shown before to be suitable as fiber cores for a broad range from visible light to IR (113).

Besides these 1×2 splitters, other groups prepared higher-order beam splitters. Using 3D printing of the UV-resist IP-Dip, Gaso et al. as well as Seyringer et al. prepared 1×4 beam splitters (114,115), while Roggero and Hernández-Figueroa prepared a 1×10 beam splitter with SU-8 as the core (116), and Tao et al. presented even a 1×16 polymeric optical splitter, again with SU-8 as the core polymer (117).

As these few examples show, similar to the preparation of in-plane optical waveguides, optical splitters can also be based on UV-curable polymers or even FDM printers, with the possibility to use the aforementioned NOA glue to avoid too high insertion losses between beam splitters and adjacent waveguides.

8 3D printed whispering-gallery-mode resonators

If an optical field is confined near the surface of a special resonator due to internal reflection, the resonances are called optical whispering-gallery modes (WGM) (118). Such WGMs have an evanescent field that is extended outside the resonator, making them suitable as gas sensors, etc. (119,120).

Several groups investigated possibilities to use 3D printing to prepare such WGM resonators. Wu et al. used a dynamic image projection scheme to develop a SU-8 photoresist (121). They prepared WGM resonators in the form of suspended disks and showed that the WGMs were efficiently excited in the WGM resonator coupled with a tapered optical fiber, as visible in Figure 6. Besides, they measured radius-dependent transmission spectra of the resonators, in good agreement with theoretical calculations.

Similar mushroom-like WGM microcavities were prepared by Ouyang et al. (122,123), while Wu et al. prepared suspended-toroid WGM resonator arrays also by a micro-printing technique based on UV-curing the used resin by a high-speed optical spatial modulator (124).

An interesting application apart from sensing was reported by Tomazio et al. (125), who used a rhodamine-B-doped WGM microcavity as a laser with a very low threshold pump energy of only 12 nJ for free-space pulsed excitation at a wavelength of 532 nm . They prepared a negative-tone photoresist from two acrylate monomers and a photoinitiator to which rhodamine B was added from an ethanol solution. The photoresist was dropped onto

Figure 6: Microscopic images of a WGM resonator coupling with a tapered optical fiber: (a) the tapered optical fiber is far away from the coupling regime and (b) the tapered optical fiber is within the coupled regime. Images were taken applying a 650 nm laser beam into the fiber. From ref. (121), originally published under an open-access license.

a glass substrate, covered by a coverslip with a spacer, and then position-dependent cured with a femtosecond laser. The WGM resonator was found to have high surface quality and low absorption in the wavelength range near 600 nm, making it well suitable as a microlaser.

9 3D printed diffraction elements

3D printed optical diffraction elements are scarcely reported in the literature. Wang *et al.* used a modified two-photon polymerization process to overcome the problem of insufficient precision of the desired microscopic structures (126). By optimizing laser power, beam scan speed, hatching distance, and slicing distance, they could produce millimeter-scale nearly perfect gratings with diffraction efficiencies near to the theoretical limits, in this way enabling precise wave-front shaping.

Using digital light processing (DLP), Vallejo-Melgarejo *et al.* produced diffraction gratings from photocurable resin, followed by smoothing the components by sandpaper with increasing grits and polishing with a polishing cloth and a three-step commercial polishing agent (127). Using gratings with layer thicknesses between 10 and 50 μm , they found that the effective slit width fills the entire volume of the printed part, in this way enabling integration of two or more optical devices in one printed object. Here, the layered polymerization apparently influenced the way in which light was diffracted.

Optical gratings from pillars were produced by two-photon polymerization with different laser powers, resulting in different sizes and optical properties, by Purto *et al.* (128). In this way, defect-free nanopillars down to diameters of 184 nm were created. By tuning the process parameters,

the pillar sizes could be tailored to the desired optical properties.

10 3D printed polarizing optics

Polarizing optics, i.e., optical elements capable of modifying the polarization state of a light beam, are typically polarizers and wave plates (also named retarders), which polarize an unpolarized beam and change the phase of a polarized beam, respectively. Only a few examples for 3D printed polarizing optics can be found in the recent literature.

Polarizers can be produced by integrating dyes by wire-grid polarizers and by using birefringent crystals, such as calcite (129). Apparently, the last type cannot be 3D printed, while especially for wire-grid polarizers, the typical layer structure of 3D printed objects may even be advantageous. In magneto-optical and other measurement applications, however, polarizers necessitate high extinction ratios of 10,000:1 or more (130,131).

Nevertheless, Hahn *et al.* presented a 3D printed polarizing beam splitter at the end of a single-mode optical fiber (132). The element consisted of a refractive prism combined with an elevated and suspended subwavelength diffraction grating and was 3D printed with the Nanoscribe system. They found a polarization purity above 80% for both beams emerging at $+45^\circ$ and -45° . Wei *et al.* used two-photon direct laser writing to prepare a freeform NIR polarizing beamsplitter and found extinction ratios around 2–5, mentioning that this value is limited by recent 3D technology (85).

As a retarding element, Bertoni and Libera prepared a Fresnel Rhomb by 3D printing (133). This rhomb

is actually a rhombohedral prism in which incident light is reflected twice if entering under the right angle, resulting in a phase shift between both incident polarization orientations by 90° . It thus works like a quarter-wave plate, creating circularly polarized light, or if two Fresnel Rhombs are stacked, it can be used as a half-wave plate. Here, a miniaturized Fresnel Rhomb was directly printed on the output face of an optical fiber using direct laser writing by the Nanoscribe system. The authors suggest such miniaturized Fresnel Rhombs for application in circular dichroism or Raman spectroscopy.

Wang et al. used a dielectric geometric phase optical element instead, printed by direct laser writing, to prepare spin-orbit optical vortex generators, of which half-wave plates are a special case, and optical spin splitters (134). Their design consisted of small round dots, split into 16 or more identical parts, in which space-variant gratings were applied in different patterns per part. In this way, different optical vortices could be generated. More recently, Varapnickas et al. prepared dielectric metasurface birefringent optical retarders printed with a similar system and found an even higher polarization conversion efficiency (135). While Liu et al. used two-photon polymerization by femtosecond 3D direct laser writing to prepare common and convex spiral phase plates (Figure 7) (136), Wei et al. prepared spiral phase plates with different topological charges with the same technique (137).

On the other hand, so-called metamaterials can be used to influence reactions in light of different polarization. Hess et al. presented 3D printable plasmonic metamaterial gels, which contain gold nanorods and cellulose nanocrystals in a liquid crystalline colloidal host, showing

polarization-dependent plasmonic properties due to the interaction of all three materials, here by showing different colors for different polarization orientations (138). With pure liquid crystal elastomers, Woska et al. printed flexible substrates for rigid photonic elements as well as tunable photonic structures (139), and He et al. presented an ultra-broadband twisted-nematic diffractive waveplate (140). In order to create metasurfaces for orbital angular momentum multiplexing holography, Ren et al. used two-photon polymerization (141). They produced nanopillars of identical lateral dimensions and 8 different heights having 8 different in-plane rotation angles, leading to a 64-level metasurface which can be used for holographic video displays or optical encryption. Combining SLA printing of mushroom-like and other microstructures with metalizing the surface, Sadeqi et al. prepared diverse metamaterial surfaces with different functionalities for the optical and the Terahertz range (142).

As this short overview shows, in the research area of 3D printed polarization optics, more developments can be expected with increasing printing accuracy.

11 3D printed optical sensors

Among the many possible applications of 3D printed optical elements, sensor applications belong to the most interesting ones. In the simplest form, 3D printed contact lenses, prepared by direct laser printing, can contain built-in microchannels at the edges for diagnostic purposes (143,144). A more sophisticated approach was presented by Park et al., who used 3D printing to prepare a whole photodetector (145).

Figure 7: (a) Spiral phase plate and (b) convex spiral phase plate containing a convex lens and a spiral phase plate. From ref. (136), originally published under a CC-BY license.

They used water-based inks with different functional chemicals or nanoparticles, which were printed layer by layer on a polyethylene terephthalate (PET) film to form a bendable photodetector array in a flat or spherical shape with good performance.

Wei *et al.* prepared an interferometric pressure sensor by two-photon polymerization, based on a miniaturized optical fiber-based Fabry–Perot interferometer (146). For this, they printed an unsealed cylinder column with a suspended polymer diaphragm on a single-mode fiber tip to create a Fabry–Perot cavity. Testing cavities with different lengths, they showed a linear response to pressure changes in different pressure ranges with different sensitivities, making them usable for pressure sensing applications.

Vapor sensing was enabled by a tower-shaped optical waveguide introduced into a transparent photosensitive resin, prepared by digital light processing (147). The surface waviness due to the layered structure here was supportive to enable vapor sensing, implying that optical scattering changed in the presence of vapor due to polymer–vapor interaction, however, on relatively long time scales.

Wang *et al.* produced a 3D printed optical sensor to monitor finger flexion, based on the attenuation of light transmitted through crossed polarizers (148). They found a good accuracy of $\pm 0.5^\circ$ in the whole range from 0° to 90° with high repeatability and stability, together with a fast dynamic response. It must be mentioned, however, that the optical elements here were not 3D printed, but commercially available optics were integrated into 3D printed holders to prepare the whole optical sensor element.

12 Surface improvement for 3D printed optical elements

Generally, improving the surface quality of a 3D printed optical element is only possible to a certain amount since common techniques are more interested in making the surface shiny than in retaining the object's microscopic dimensions at the same time. Nevertheless, some post-treatment techniques are mentioned in the literature. Ogilvie *et al.* presented a solvent vapor treatment that bonds microfluidic chips and at the same time reduces the surface roughness from some hundred nanometers to less than 15 nm (149). Szukalski *et al.* used post-processing by coating the samples with a liquid resin film of thickness 200 μm , followed by UV light curing and washing the uncured residues by isopropyl alcohol, in this way nearly doubling the transmittance (150). Nevertheless, in many

cases, the necessary precision and resolution to produce high-quality optical elements have not yet reached with nowadays 3D printing technologies (151). Low-cost optics, however, can in many cases already be 3D printed (152,153), while in other cases, sophisticated solutions to deal with the available surface roughness and waviness were found by diverse research groups.

It should be mentioned that another well-known problem of 3D printed objects, the shrinkage during cooling down, is only scarcely mentioned in the literature. Ristok *et al.* (57) mentioned a slightly reduced radius of curvature of their 3D printed lenses due to shrinkage. Wang *et al.* discussed methods to reduce shrinkage and deformation of their printed structures in the supplementary information to their paper (126). Gissibl *et al.* mentioned the problem of shrinkage and deformation in general but did not experience such problems in their freeform optics (107). Pearre *et al.* tried to reduce shrinkage by attaching the produced optical elements to larger solid structures (36). Most other papers do not report problems with dimensional stability or shrinkage.

13 Conclusion

Our review shows an emerging number of approaches to use different 3D printing methods to create optical elements. Unexpectedly, even simple techniques such as FDM or SLA can be used in some of these applications, while most optics are produced by more complicated methods such as direct laser writing or two-photon polymerization. In some studies, post-treatment approaches are reported to improve the surface quality, in this way reaching less rough or wavy optical elements than actually possible with a certain 3D printing technique.

Generally, it can be assumed that with further improvements in 3D printing and with new ideas for post-treatment steps, higher-quality optical elements can be produced, in this way enabling producing individual and highly special optics for diverse applications.

Funding information: The study was partly funded by the German Federal Ministry for Economic Affairs and Energy via the AiF, based on a resolution of the German Bundestag, grant number KK5129708TA1, and by the Silesian University of Technology Rector's Grant no. 14/O30/RGJ21/00110.

Author contributions: Tomasz Blachowicz: writing – original draft, writing – review and editing, methodology; Guido Ehrmann: writing – original draft, writing – review

and editing, methodology; Andrea Ehrmann: writing – original draft, writing – review and editing, methodology.

Conflict of interest: The authors state no conflict of interest.

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