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Invited Paper

Fabrication of Functional Nanophotonic Devices by Multi-Photon Lithography

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ABSTRACT

Multi-photon lithography (MPL) is a laser-based method for 3D printing nanoscale devices. Since its introduction in the late 1990's, researchers across many disciplines have made exciting contributions toward its development that include extending the range of material systems available for MPL, improving the achievable resolution, and using it to create functional devices for optics, MEMS, microfluidics, sensing, and bio-engineering. MPL has been used to create conventional micro-optics, like waveguides and micro-lenses. It has also been used to fabricate devices onto novel platforms, such as the tips of optical fibers, which greatly extends the functionality of conventional optics and the range of applications they may serve. MPL is unique among existing fabrication methods in its potential for creating truly 3D structures having arbitrary shape and complexity. This is particularly well illustrated in recent reports of using MPL to create spatially-variant photonic crystals (SVPCs). SVPCs unlock new physical mechanisms to control light, particularly using self-collimation to flow beams through exceptionally sharp bends, which cannot be achieved with waveguides and other technologies based on refraction. MPL and SVPCs open new routes to integrated photonics and opto-electronic circuits.

Keywords: Photonic crystals, metamaterials, nanophotonics, integrated optics, imaging, multi-photon lithography.

1. FABRICATION BY MULTI-PHOTON LITHOGRAPHY

Multi-photon lithography (MPL) grew out of early work pioneered by Watt Webb's group which showed that multi-photon excitation (MPE) could be used to acquire 3D fluorescence images of cells, tissues, and other materials.[1, 2] The key intellectual leap enabling this work was the realization that tightly focused ultrashort laser pulses only activate electronic excitation and subsequent fluorescence efficiently within a volume tightly confined around the geometric focus, where the local irradiance is sufficiently large to generate a high rate of MPE. Longer-wavelength sources can be used to achieve MPE, so excitation can be delivered deep within the volume of the sample without loss due to conventional linear absorption. Working with photopolymers, the team showed that this optical configuration could also be used to activate photochemistry and write digital information encoded as polymerized volume elements, or "voxels," within multiple layers of a volume of photo-responsive material.[3-5] In related work the team showed that the focal spot could be translated within the photopolymer to free-form pattern a structure. A scanning electron microscopy (SEM) image of a simple structure with undercut was shown to illustrate the potential use of the method for creating 3D structures, similar to stereolithography ("SL" or "SLA"), but on the sub-micron length scale.

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Kawata's group followed up with an even more compelling illustration of MPL's potential for creating 3D structures by fabricating a multi-turn cork-screw laying on a substrate.[6] The high degree of under-cut and topological complexity of the example showed that a wide range of previously inaccessible structures could be created in a single serial-exposure by MPL. In the very next year, Borisov et al. showed that MPL could be used to create photonic-crystal structures, like that in Fig. 1, making them among the first to show how MPL could be used to create novel optical devices.[7, 8] Widespread interest in MPL as a practical tool for 3D fabrication was generated by several follow-on works. One by Perry, Marder, and co-workers introduced a strategy for rationally designing molecules that could efficiently activate polymerization through multiphoton absorption.[9] In another, Kawata's team fabricated a free-standing micro-pull and a bead on a spring that could be actuated with optical tweezers. The high fidelity of these structures excited scientists and engineers who then looked to MPL as a practical tool for 3D microfabrication and generated a series of beautiful contributions to the field that introduced improvements in the optical implementations, the materials systems for MPL, and its practical application for creating functional 3D devices.[10] For more details on MPL and its variants, the reader is encouraged to explore several general reviews that have appeared,[11-14] as well as others focused on the opto-mechanical implementation,[15, 16] material systems for MPL,[17-22] novel approaches for improving the resolution of MPL,[23] and the use of MPL to create functional devices.[24]

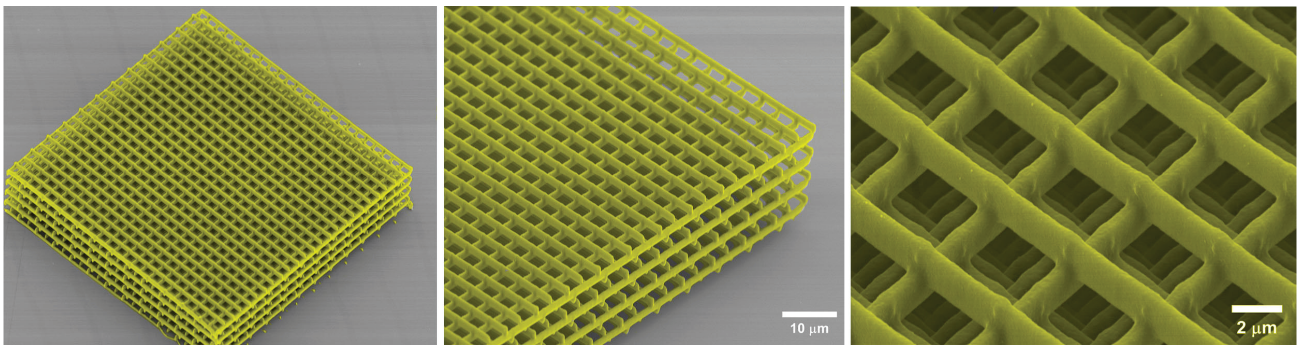

Figure 1. False-color scanning electron microscopy (SEM) images of a face-centered tetragonal "stack-of-logs" photonic crystal fabricated by MPL in SU-8, a cross-linkable epoxide photopolymer. The images show the same structure with the magnification level increasing from left to right.

2. MATERIAL SYSTEMS FOR MULTI-PHOTON LITHOGRAPHY

Polymers and polymer-composites remain the primary material system used for MPL. Multi-functional acrylates are widely used because they are commercially available, easily polymerized, and capable of forming robust cross-linked plastic structures with physical and chemical properties that meet the requirements of many applications. In its most basic form, a photopolymer for MPL, or "resin", consists of an acrylate and a photo-initiator that can be activated by MPE. Other components can be added to imbue the patterned material with targeted properties, like fluorescing dyes,[25] photo-switchable azo dyes,[24] nanoparticles,[26, 27] or magnetic particles.[28] Cross-linkable epoxides have also been widely used to create polymeric structures. Some of these, like SU-8,[29, 30] are cast and baked to remove solvent, leaving behind a glassy solid film that is patterned by MPL.[31] After exposure, the sample holds a latent pattern in a photo-activated species, such as a Brønsted acid. The sample is then baked to activate polymerization in the photo-exposed regions, forming a micro-structure in cross-linked epoxide. Several studies have explored the more complex processing requirements of SU-8 for MPL,[32-36] including the nature of MPE associated with the photo-acid generators formulated with the resist.[37, 38] Now a wide range of chemistries has been employed for MPL. For example, MPE-activated free-radical polymerization has also been used to pattern thiol-enes,[39, 40] and hydrogels,[41, 42] and non-radical step-growth polymerization has been used to pattern disulfides.[43]

Post-fabrication processes have also been used to change the properties or form of a structure created by MPE.[18, 44] Polymers can undergo significant shrinkage during polymerization and post-polymerization processing, which can distort the form and is normally detrimental.[45] Shrinkage has been leveraged, however, to create deeply sub-micron structures, by first patterning a cross-linkable hydrogel, and then dehydrating to shrink the structure by as much as a factor of ten.[42] Silicon- and titanium-rich composites have been formulated so that a pre-form can be fabricated by MPL then sintered to form a 3D ceramic micro-structure.[19] Several approaches have been explored for generating metallic or metallodielectric structures by processing a polymeric scaffold created by MPL, including electroless deposition,[46-52] chemical vapor deposition,[53] and electrodeposition.[54]

Semiconductor 3D micro-structures have been created either by direct patterning or post-exposure processing of a scaffold. Plastic structures doped with thiols have been used to nucleate the growth of cadmium sulfide nanoparticles onto the preform. A multi-step process of atomic layer deposition of silica, etching, chemical vapor deposition of silicon, and multiple etching steps was used to "double invert" a polymeric preform into a silicon nano-photonic structure. Chalcogenide glasses are unique among processes in providing a means to directly patterns a semiconductor structure by MPL, without additional post-exposure deposition.[55, 56] Certain chalcogenide glasses like arsenic sulfide,[57-63] and even germanium doped chalcogenides,[64] can be thermally deposited into glassy films of molecular clusters that are soluble in polar solvents, yet can be photo-crosslinked by MPL back into a network solid. These materials function like a semiconductor analog of cross-linkable polymer and provide a direct route to structures with interesting optical and electronic properties, such as high refractive index and infrared transparency.

3. FABRICATION OF FUNCTIONAL DEVICES

MPL's versatility and relative ease of use has made it the go-to method for fabricating micro- and nano-scale 3D structures with complex form. But because MPL can be applied with the wide range of materials and post-fabrication processes noted above, the technique is increasingly used to create functional 3D devices with applications in optics, photonics, electronics, micro-mechanics, MEMS, and biological function. Numerous groups have shown how MPL can be used to create optical devices, including micro-lenses,[65-67] prisms,[68] and diffractive optical elements.[69-71] The method has been used to create a myriad of photonic devices including waveguides,[40, 72] optical interconnects,[73] and resonators.[74, 75] Some of these devices have even been integrated with optical fibers by fabricating them directly onto the tips of optical fibers.[68, 76-78] The use of MPL to create optical lattices has enabled significant advances in the fields of photonic crystals[7, 62, 79, 80] and electromagnetic metamaterials.[50, 52, 54, 81, 82]

MPL is having high and growing impact as a means to create functional devices well beyond optics. Several teams have used MPL to create MEMS[83] and microfluidic devices,[84] including optically driven paddlewheels[85-87] and pumps.[88]. Structures with novel mechanical function, including negative Poison ratio, have been fabricated and tested, leading to new understanding in mechanics.[89, 90] The ability to pattern 3D structures on the micrometer length scale makes MPL ideal for creating devices that interact with biological cells. Devices have been fabricated for trapping and characterizing cells.[91] Coupling MPL with tailored materials that mimic biological environments, investigators have created surfaces and devices that activate cells[92], mimic the extracellular matrix,[93] and enable growth and characterization of heart cells.[94]

4. SPATIALLY-VARIANT PHOTONIC CRYSTALS

Photonic crystals like those in Fig. 1 are among the most challenging classes of devices to fabricate because they involve high structural complexity and require high resolution and high fidelity over a large area. Other approaches can be used to create some types of periodic 3D photonic crystals. For example, 3D periodic spiral photonic crystals have been created by glancing-angle deposition,[95] and holographic lithography has been widely used to create periodic 3D photonic crystals of various symmetries.[96-99]

The fabrication of spatially-variant photonic crystals (SVPCs) provides an even more compelling illustration of the power of MPL as a fabrication tool. SVPCs are ***a****periodic* photonic crystals that are bent, twisted, or otherwise spatially varied while minimizing deformations to the size and patterns of the unit cells, as this would weaken or erase the optical properties. Spatial variance is incorporated throughout the lattice in one or multiple ways to control the propagation of electromagnetic radiation within the device.[100-103] An example of an SVPC is shown in Fig. 2. SVPCs present even greater challenge for fabrication than conventional *periodic* photonic crystals because the unit cells are purposefully varied to control propagation of electromagnetic radiation, so they are not strictly identical throughout the lattice. As SVPCs are not periodic structures, SVPCs with arbitrary structure cannot yet be fabricated by interference lithography. To date, SVPCs that function at optical wavelengths have only been created by MPL.[104]

SVPCs are designed to control the flow of electromagnetic radiation using the effect of self-collimation.[105-107] Simulations and experiments show that the structure of the unit cells of a photonic crystal can be engineered so that the spatial dispersion of the Bloch waves is anisotropic at a given wavelength. When the Poynting vectors for Bloch waves are parallel over a wide range of momentum vector angles, electromagnetic radiation at that wavelength propagates without divergence and is forced to follow an axis of the lattice, and the device is said to be self-collimating.

Members of our team at the University of Texas at El Paso (UTEP) reported how to design SVPCs based on self-collimation.[101-103, 108, 109] In brief, a map of spatial variation is first constructed to describe how a given optical property should vary throughout the device. In the simplest case, this may be a map of the direction power should flow throughout the lattice. This type of map describes the path along which light is intended to propagate, and thus the orientation that self-collimating unit cells should have at each position within the lattice. Next, a strongly self-collimating unit cell is selected and used to create an infinite lattice. The infinite lattice is then spatially varied according to the map. If an infinite lattice were arbitrarily stretched or distorted to create a spatial variation, then the structure of the individual unit cells would be highly altered and the strength of self-collimation would be decreased or lost altogether. The UTEP-methods for designing SVPCs controllably varies a lattice so that distortions to individual unit cells are minimized and the strong self-collimating properties are maintained along the path of self-collimation.

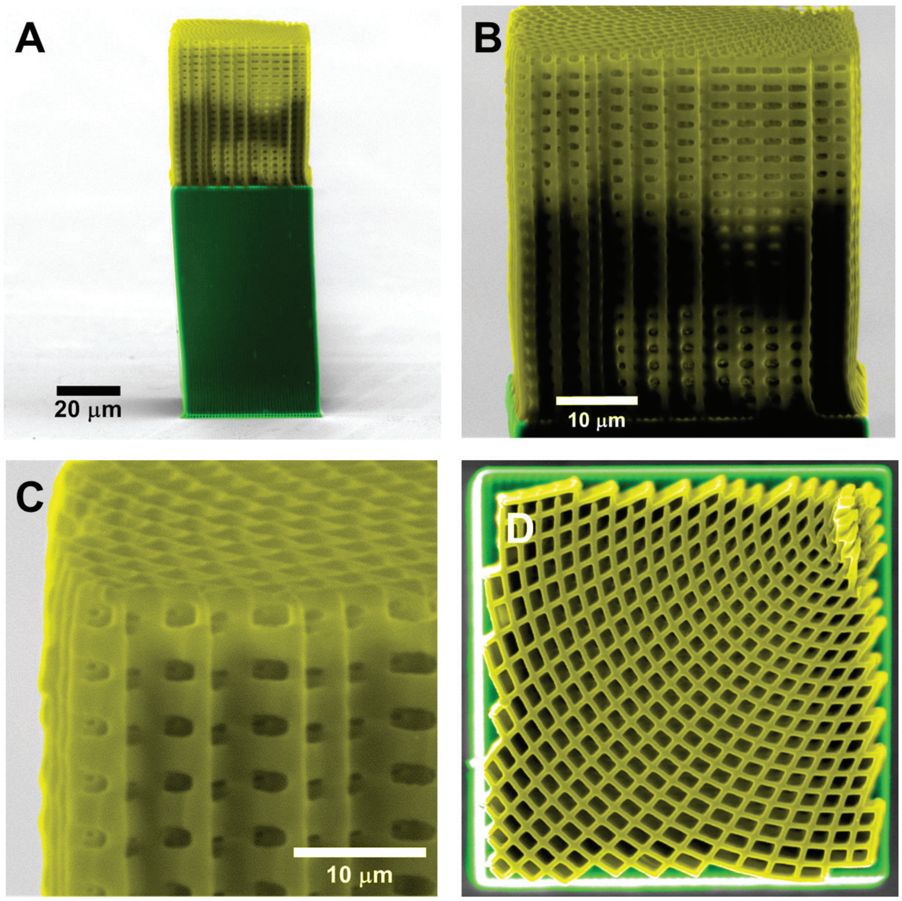

Figure 2. False-color SEM images of spatially photonic crystals (SVPCs) fabricated by MPL in SU-8. (A) Side-view showing the SVPC supported off the substrate by a pedestal. (B and C) Side-views of the SVPC at increasing magnification. (C) Top-down view of the SVPC. Full characterization of devices of this type has been reported elsewhere.[104]

Team members at the University of Central Florida (UCF) work with UTEP to design specific SVPCs.[110] The UCF team then fabricates the structures by MPL, structurally characterizes them by scanning electron microscopy (SEM) and other methods, and optically characterizes their performance using a scanned-optical-fiber system developed in-house. The teams' initial work focused on the beam-bending SVPC shown in Fig. 2. This device is designed to direct light through an extremely abrupt 90-degree turn. Full details on the design, fabrication, characterization, and performance of the device are reported elsewhere.[104] The beam-bending SVPC in Fig. 2 was fabricated using the cross-linkable epoxide SU-8 based on a simple-cubic unit-cell with a spacing of ~2 μm, so that it bends light having a vacuum wavelength of λ_0 = 2.94 μm. The SEM images show that the device is highly regular with a micro-porous interior of a truly 3D spatially-varied lattice. Optical characterization shows that the device can bend light through a turn-radius as small as λ_0, which is much tighter than can be achieved using waveguides, GRIN devices, or other refractive structures.[104]

More recently the team has created beam-bending SVPCs by MPL in the cross-linkable acrylate IP-Dip, with smaller unit-cell spacing of ~1 μm so the device can bend light having λ_0 = 1.5 μm. Figure 3 shows such an SVPC while being optically characterized with scanned-optical fibers that introduce light on the structure and collect light at the output faces. Light scattering within the structure is visible in the image and shows clearly the curved path light takes as it moves through the lattice. This work shows that devices based on SVPCs can be used to steer and control light, even through abrupt turns in 3D, opening new routes to integrated photonics and offering new capabilities for integration with waveguides and other more conventional photonic elements. The work also shows that complex structures that could not be fabricated by any other means are accessible by MPL.

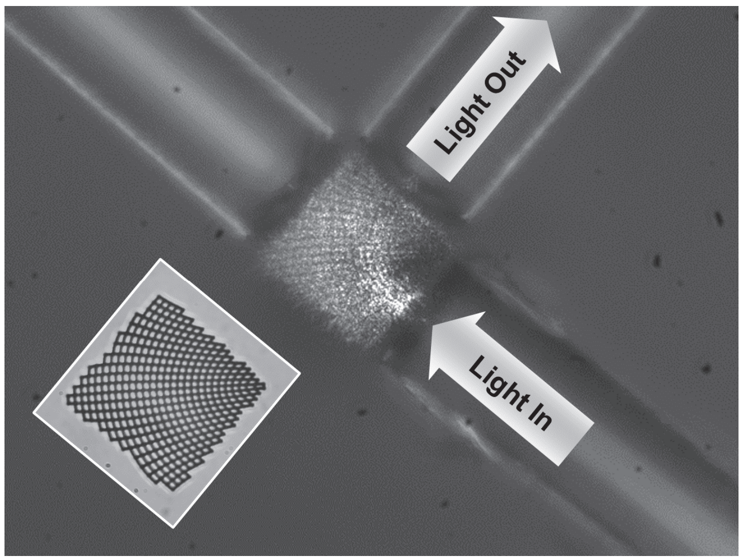

Figure 3. Transmission optical microscopy image of a beam-bending SVPC obtained during characterization with optical fibers positioned adjacent to the input- and output-faces. The device was fabricated by MPL in IP-Dip, a commercial cross-linkable acrylate resin (Nanoscribe[104]). The SVPC is designed with a unit-cell spacing of ~1 μm so it can steer a beam having a vacuum wavelength of λ_0 = 1.55 μm through a 90-degree turn within a footprint of only 20 μm × 20 μm. The bending of the beam through the turn is made visible by light scattering from within the lattice. The inset at lower-left shows a similar SVPC fabricated at an enlarged footprint of 125 μm × 125 μm to enable visualization of the interior of the structure.

5. CONCLUSION

MPL is now an established method for fabricating complex 3D structures of almost limitless form. Scientists and engineers have creatively used available materials and post-fabrication processes to create functional micro-scale 3D devices with applications across a wide range of fields. SVPCs are *aperiodic* photonic crystals that use the effect of self-collimation to control the propagation of radiation. As these devices have highly complex and spatially-variant structure, SVPCs having arbitrary structure do not appear to be feasibly fabricated by any method other than MPL. The fabrication of functional SVPCs illustrates both how this new class of photonic device could greatly extend capabilities in integrated photonics, as well as the tremendous power and versatility of MPL. Going forward, significant opportunities and challenges remain for extending the range of material systems available for MPL. Additionally, further work is needed to improve the speed and throughput of MPL, so that the system becomes more scalable and able to move from the laboratory to the manufacturing floor.

6. ACKNOWLEDGMENTS

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