Materials Overview for 2-Photon 3D Printing Applications

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Interest in microscale 3D lithography continues to grow with the development of new tools and new patterning materials. To date most available materials are rigid, glassy systems derived from stereolithography studies. Soft materials lack the same level of sophistication, but there is a drive to improve this situation with the introduction of new elastomers and hydrogels. A general strategy is lacking for these 3D patterning systems as there is for the production of chemically amplified photoresists. This paper describes both positive and negative tone chemically amplified 3D materials as well and photocured systems based on radical and cationic crosslinking systems.

Keywords: 2-Photon lithography, Photoresist, Photosensitizer, Photoacid, Photoradical generator

1. Introduction

Until recently micro- and nanoscience have been confined to 2 dimensions. This planar paradigm for nanofabrication, developed for silicon microelectronics, has been very successful and has made possible the ongoing microelectronics revolution. However, the world is 3-dimensional and increasingly small 3D structures (sub-micron) are recognized as pivotal aspects of research in many breakthrough areas of science and technology. Availability of 3D printing enables research on and manufacture of both 3D materials and 3D systems and make possible studies at a very small length scale that have been largely the domain of specialists in photochemical processes.

Given the publicity surrounding "maker spaces" and the growth of 3D printers, it would seem that the problem of sub-micron 3D printing is solved. That is, until a close look is given to the capabilities of traditional 3D printers (stereolithography systems) and the needs of new science. Most current 3D printers depend on the millimeter to hundreds of micron scale methods to make 3D structures too large to meet many of the science challenges of interest. The new technology needs are to be found at length scales of several microns and less. Today sufficient advances have been made on both the printing materials and the printing tools based on 2-photon lithography to make this method extremely attractive [1,2]. Derived from confocal microscopy, the printing system makes use of near-IR lasers to write a structure in 3D space. Special 3D photoresists

\[ TPA \propto \delta I^2 \]
\[ I \sim \frac{1}{z^2} \]
\[ \Rightarrow TPA \sim \frac{1}{z^4} \]

Fig. 1. 2-Photon absorbance has a very small reaction volume (red) at the focal point as it depends on the 4\textsuperscript{th} power of length scale and passes through the rest of the film without absorption. In contrast DUV chemistry occurs over the pathlength of the exposing beam.
employ the simultaneous absorbance of 2-photons of near-IR radiation to excite a dye molecule that triggers photochemistry in the ink and enables the creation of 3D printed structures. Since the reaction volume of a 2-photon process can be as small as 0.04 µm³, structures can be made significantly smaller than those of current 3D printers (See Fig. 1) [3].

Only in the last few years have commercial 3D laser 2-photon lithography systems been developed, with sufficiently high speed that they enable the rapid prototyping of nano-, micro- and mesostructures with minimum feature sizes ranging from ~ 200 nanometers up to several micrometers. The tool can print structures with lateral dimensions up to a few cm² and print volumes up to several 10s of mm³. Using tailor-made photoresists, hardware- and software packages, the turn-key system allows high resolution with a previously unavailable freedom of design. Subsequent independent processes will enable the transfer and/or replication of polymeric 3D printed templates into a large choice of materials, including metals and semiconductors [2]. Such tools provide capabilities that not only serve the traditional physics, chemistry and engineering communities for micro- or nanoelectronics fabrication, but afford new capabilities to non-traditional users for microscale additive 3D manufacturing, hybrid hard-soft materials processing, and biological and medical nanotechnology.

The ability to manipulate and produce 3D structures of µm and less is a capability of keen interest to an increasingly broad swath of scientific and engineering disciplines. Until recently only a very complex series of carefully aligned planar fabrication processes could produce a subset of structures on this length scale. Examples of the relevance of sub-micron 3D geometry across scientific disciplines include:

- **Micro/nanophotonics**: Photonics and optics depends on the 3D placement of waveguiding materials and recent work on cloaking and optics on chips has shown that complex 3D structures offer unique possibilities for light guiding.
- **Cell behavior and Nanobiotechnology**: The behavior of cells in tissue has been shown in many instances to depend on 3D placement of cells and cell supports. 2D and 3D culture affects the cell phenotype, can alter the production of extra cellular matrix (ECM), and lead to formation of multi-celled colonies in the 3D case with ECM around and between cells.
- **Microfluidics**: Complex microfluidics can benefit from the ability to shape flow paths in 3-dimensions rather than the conventional 2-dimensional structures derived from the current set of 2D tools available in most fabrication facilities.
- **Neural electronics**: Interfacing electronics with the neural system is a 3D problem, not a 2D problem. 3D microfabrication can provide artificial circuits that can now partner with complex 3D imaging capabilities at Cornell to enable detailed studies of neural function.
- **Heterointegration**: Combining specialized prototype chips such as sensor arrays with high performance signal processors or photonic ICs with VLSI electronics require interconnecting differing form factors, materials, and layouts.

In this report, new materials for 3D 2-photon printing (Fig. 2) will be explored with a special focus on new chemistries. The use of conventional UV curable materials as 2-photon resins will be considered using the capabilities of conventional photoactive compounds (PACs) alone and with the addition of specialty 2-photon sensitizers. In addition, the development of 3D soft materials will be discussed.
described here including: S1) a chemically amplified photoresist, poly(tetrahydropropyran methacrylate-co-methyl methacrylate) with a 2-photon photoacid generator [4], S2) Dow Corning Silgard 182 with (η-5-cyclopentadienyl-methyl)-trimethylplatinum as photoactive material [5], and S3) Norland NOA 63 photocurable resin with a non-ionic 2-photon photoacid generator [6].

2.2. Systems with conventional PACs and a 2-photon sensitizer

We have also explored the use of 2-photon absorbing molecules to enhance the activity of conventional photoactive compounds that alone do not have sufficient 2-photon photosensitivity. These include: S4) hydrogels based on poly(ethylene glycol methacrylate) and hydroxyethyl methacrylate with 2,2-dimethoxy-2-phenyl acetophenone and a 2-photon sensitizer [7], S5) a phenolic molecular glass crosslinked with acid catalyzed TMMGU with a photoacid generator and a 2-photon photosensitizer [8], and S6) SU8 epoxy and thirane analogs with an ionic PAG with a coumarin-7 2-photon photosensitizer [9].

The goal of this work in all cases is to build a robust, 3-dimensional structure with very specific properties and structures in the range of a few microns or less. Mechanical properties, optical characteristics, resistance to solvents including water, surface modification characteristics and the like are all factors in selecting a given photopatterning material. The current commercial 3D tools come with a limited selection of 3D resins that are generally rigid materials. Very little work even today has looked at the creation of low modulus or even hydrogel (water swollen network) materials. The photoactive compounds referred to in this report are shown in Table 1.

3. Results and discussion

All systems share the need to prepare a thick film that has enough mechanical integrity that it can be patterned without worry about flow and associated pattern degradation. The most direct method is to be able to coat a solid film, expose the film and carry out the selected photochemistry and then develop the structure in a manner not unlike the patterning of a 2D photoresist. Materials can be made having a range of properties including acrylate-based polymers, organically-modified ceramic materials, metal oxide sol-gels, and metal-containing hybrid materials.

Of the systems described here, the patterning of a positive tone, base developable chemically amplified photoresist enables 3D pattern formation with high resolution. In this system (S1), the 2-photon PAG enables cleavage to the THP protecting groups and aqueous base developer will remove the exposed regions in the film. Careful thought has to be given to the design of a structure since all remaining parts need to be an integral part of the whole, otherwise a portion of the pattern can be removed during development. Even sub-surface channels can be produced as shown in Fig. 3a.

Table 1. Near IR absorbing molecules useful for 2-photon lithography. In Compound C, R represents the nitrobenzyl or similar group.

![2-Photon Photoactive Compounds](image)

![2-Photon Photosensitizers](image)
In contrast many soft materials begin as viscous liquids and must be handled differently. The PDMS used in S2 is a very viscous oil which contains a photoactive hydrosilylation catalyst. Process challenges come from the mobility of the uncrosslinked polymer and the need to develop and remove the unreacted oligomer in the negative tone process. This aspect of processing can lead to significant swelling and place large mechanical stresses on the materials. Nevertheless, high resolution (single digit micron range) and strong, tough materials well attached to substrates are typical as shown in Fig. 3b.

In contrast, Norland NOA 63 photocurable resin (S3) with a specially synthesized non-ionic 2-photon photoacid generator forms a clear, colorless, liquid photopolymer that will cure when exposed. This resist consists of urethane oligomers with C=C double bonds and mercapto-ester oligomers as cross-linking agents. We assume that the reaction mechanism is radical based even though we are using a 2-photon PAG as photosensitive compound. In this system, the conventional photoactive compound was not effective for curing this material using 2-photon patterning, in contrast to the PDMS system described above.

It can in many cases be convenient to make use of existing photopolymer systems for 3D fabrication, but the photoactive compounds are not sufficiently active in 2-photon conditions as noted above. Addition of a sensitizer that has 2-photon absorbing characteristics at near-IR wavelengths, can in many cases activate DUV absorbing PACs.

Three-dimensional micropatterning of hydrogels can be carried out, but the reactants must be water-soluble. This creates a very complicated situation in which many of the usually water insoluble PACs and sensitizers must be used. In system S4, water-soluble vinyl monomers were combined with benzophenone PAC and a 2-photon sensitizer that was extremely hydrophobic. In order to introduce these aqueous materials, surface-active compounds such as non-ionic surfactants and cyclodextrins were used. Ideally no net change in volume should occur in the patterning of hydrogels. Substantial swelling can occur and this behavior needs to be addressed to make precision patterns in these materials.

Finally, both S5 and S6 are compositions dry film 2-photon resist systems. They both depend on the use of 2-phptoton photosensitizers. S5 makes use of a small molecule molecular glass with an acid catalyzed crosslinker, TMMGU. With a photoacid generator, these materials have been used as high resolution EUV photoresists. With an added sensitizer, they function effectively as dry 3D patternable resins, developed using aqueous base.

S6 is a system based on a material very much like SU8 with either oxirane or thiirane groups, combined with a PAG and a 2-photon sensitizer. The thiirane dry 3D patternable system represents an example of a material with a high refractive index designed for photonic applications.

4. Conclusion

With the development of new 2-photon based 3D patterning tools, the prospects for high speed, manufacturing of 3D microprinting and complex nanostructures becomes increasingly probable. However, the patterning materials lag behind the printing tools at this time. Liquid systems are simpler to create and work with but lack the resolution of dry systems. There are not yet standard 2-photon PACs and patterning materials the way chemically amplified photoresists have consistent standardized strategies and chemistries. As these new materials and concepts develop, 3D microprinting will become much more important than it is today and will become integrated into nanomanufacturing.

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![Fig. 3. Representative examples of 3D patterned materials produced using 2-photon lithography a) PDMS; b) dry poly(hydroxyethyl methacrylate); c) effect of hydration on hydrogel marked with fluorescent dye.](image)
some of the 2-photon photoactive compounds described here. CKO also thanks his many collaborators in this area who are co-authors of the papers referred to.

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