APPLICATION NOTE

Three-Dimensional Microfabrication by Two-Photon Polymerization

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Technology and Applications Center
Newport Corporation

Three-Dimensional Microfabrication by Two-Photon Polymerization

Introduction

For many technologies, smaller is synonymous with better. Shrinking the size of devices brings many advantages: more components per unit area, lower power consumption, lower cost, faster response, and higher performance. An area of research that has affected almost every aspect of society because of device downsizing is microelectronics. Staggering examples of these changes can be found across diverse fields including automotive, computers, communications and medicine. The successful story of microelectronics is based on the development of a set of tools that goes under the name of Integrated Chip (IC) technology and comprises processes such as photolithography and electron beam lithography.[1] By means of IC technology, microprocessors with millions of transistors can be routinely fabricated and launched in enormous numbers of calculations per second.

With the increasing complexity of micro/nano-devices needed in most modern applications though, IC technology presents significant limitations.[2] In particular these techniques are incompatible with many chemical and biological environments, features smaller than 100 nm are difficult to create, they are not capable of fabricating structures with complex three-dimensional shapes, cannot fabricate features on a curved or uneven substrate and generally require expensive facilities. For these reasons, in recent years there has been a tremendous effort from the research community to develop unconventional micro/nano-fabrication techniques. Nanoimprint lithography, proximity probe lithography, and soft lithography were born from the desire to break free from the constraints of conventional lithography.[3-5]

Two-photon polymerization (TPP) is a serial process for the fabrication of three-dimensional microstructures.[6,7] Because of its ability to produce geometries with no topological constraints with a resolution smaller than 100 nm, TPP is a unique tool in the arsenal of unconventional microfabrication methods now available to scientists. Although the first report in the scientific literature of photopolymerization induced by a multiphoton absorption process appeared more than forty years ago,[8] it was a paper of Kawata and coworkers published in 1997 that established TPP as a technique for the fabrication of three-dimensional microstructures.[9] Since then the number of works based on TPP has grown rapidly, allowing researchers in diverse fields such as nanophotonics, microelectronics, and bioengineering to create and use devices previously impossible to manufacture with conventional microfabrication procedures.

Two-photon polymerization principles

The excited state of a molecule can be reached by the absorption of one photon of an appropriate wavelength or by the simultaneous absorption of two photons, each having half the energy required for the transition. In this case, two-photon absorption is said to be degenerate. When the photons promoting the transition are of different energies (wavelengths), the process is said to be nondegenerate. Because of the simplicity of the experimental setup for degenerate TPA, most of the applications have used this technique. Two-photon cross-sections of most molecules are very small; usually on the order of 1 GM or less, where 1 GM corresponds to 10^{-50} cm^4 sec photon^{-1} (GM stands for Göppert-Mayer in honor to the scientist who theoretically predicted multiphoton absorption). As a result, high local photon fluxes are needed to promote two-photon absorption. Commercially available Ti:sapphire lasers emitting at wavelengths in the near-infrared region of the spectrum and producing pulses shorter than 100 fs can meet this requirement. Each pulse has a peak power on the order of a kilowatt, while at a typical repetition rate of 80 MHz the average power is on the order of milliwatts. When focused into tight spots, these lasers allow reaching the photon densities needed for two-photon absorption to occur.

Since the probability of a two-photon absorption event is proportional to the second power of the light intensity, excitation can be spatially localized. Figure 1 illustrates the total one-photon (dashed line) and two-photon (continuous line) absorption per transverse section of a focused laser beam. While the absorption probability is the same along the optical axis for a one-photon process, a maximum coinciding with the focal point is present for the two-photon process. Researchers have used the ability to confine excitation in a volume as small as a femtoliter by two-photon absorption in several applications, including photolysis,[10] optical data storage,[11] photochromism,[12] and photodynamic therapy.[13] Among these areas of research, the one that has experienced the most explosive growth is two-photon fluorescence microscopy. (www.newport.com/TAC/AppsNote32).
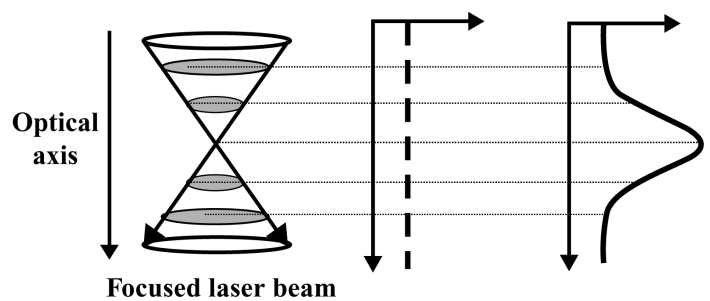

Figure 1 - Integration of the intensity (- - -) and the intensity square (——) in each transverse section of the focused laser beam along the optical axis. While the probability of one-photon absorption is always the same, the probability of two-photon absorption is highest at the focal point.

In polymerization induced by a one-photon process, the excitation beam is usually greatly attenuated by linear absorption before reaching the focal point. Consequently, only the first layer of the photoresist (photosensitive material) is polymerized. If the intensity of the laser is

increased, all the material along the optical axis may polymerize (Fig. 2a), or worse the energy dumped into the system is high enough to boil the material away. In either case the lack of polymerization control forbids the use of one-photon absorption for the fabrication of three-dimensional microstructures. Conversely, polymerization is confined to the focal point when excitation occurs via two-photon absorption (Fig. 2b).
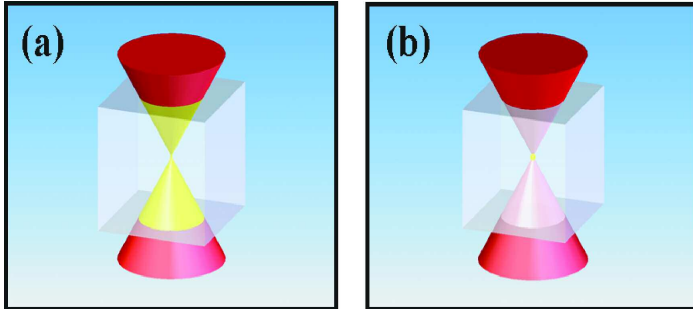

Figure 2 – One-photon (a) and two-photon (b) polymerization. Only when non-linear excitation occurs (2b), spatial confinement of the chemical reaction is observed.

In TPP the selective excitation of molecules within the focal volume of a tightly focused beam allows for a spatial confinement of matter transformation. If the photoresist can be solidified by two-photon absorption, then three-dimensional microstructures with sub-micron resolution can be fabricated by means of accurate positioning of the laser focal point. As long as the solubility properties of the solidified and unsolidified photoresist are different, the non-polymerized material can be washed away to leave the freestanding structures. A diagram representing the three main steps of TPP are shown in Figure 3 where the proportions of the objects depicted have been exaggerated for viewing clarity.

Since the index of refraction of the photoresist changes upon polymerization, TPP can be monitored in real time by the aid of white light microscopy. Any failures of the process can be detected and corrected in real time, though fine details of the microstructures cannot be observed. Furthermore, a three-dimensional view is impossible. Hence, prior to being employed in experiments, microstructures fabricated by TPP are carefully investigated by scanning electron microscopy (SEM) in order to check if the desired geometry and surface roughness were obtained. Figure 4 is a SEM image of a microstructure fabricated by TPP in the Technology and Applications Center at Newport Corp. (www.newport.com/TAC). The sample was positioned at a 45° tilt in order to reveal the complex topology.
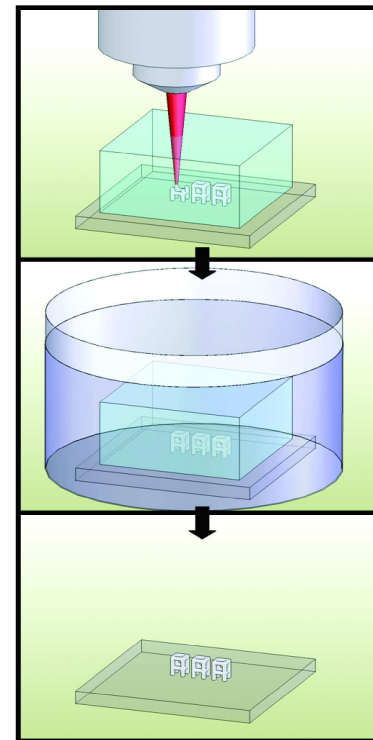

Figure 3 – Free-standing three-dimensional microstructures can be fabricated by TPP. First the desired pattern is "written" by precise positioning of the laser focal point in the photoresist. Then, the unsolidified remainder of the photoresist is washed away by means of an organic solvent, leaving only the newly fabricated microstructures on the substrate.
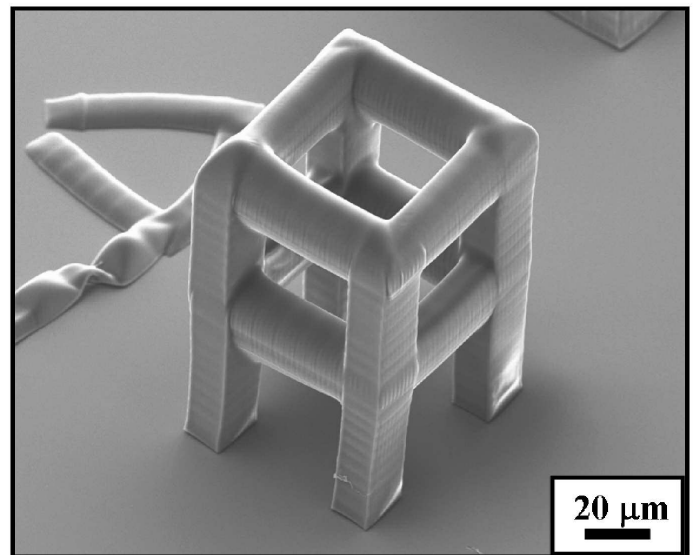

Figure 4 – SEM image of a three-dimensional microstructure fabricated by TPP.

This fabrication process offers a unique combination of advantages. First, no topological constraints are present in the fabrication of three-dimensional structures. Second, sub-diffraction-limited resolution can be attained by employing laser intensities just above the intensity threshold at which

polymerization will occur. Third, the optical penetration depth is greatly increased with the use of near-IR light. Fourth, movable components can easily be created without the use of sacrificial layers. Finally, the carbon-based nature of the materials can be used as a chemical handle to fabricate structures with tunable physical and chemical properties such as hardness, shrinkage, index of refraction and chemical specificity, depending upon their application.

Materials

The photoresists used in TPP are made mainly of two molecular components. One set of molecules are the ones capable of undergoing excitation by two-photon absorption and of generating active species that start the polymerization process. They are named photoinitiators. Monomers are the second set of molecules and in the presence of excited photoinitiators can form a complex linked network, a polymer. Monomers are present in much large numbers than photoinitiators in photoresists.

Photoresists can be used for TPP in their original state (highly viscous liquid), or they can be casted by means of filler polymer in order to create gels. Other components can be combined with the photoresist, such as dyes and nanoparticles, which can add new functionality to the polymerized structures. In one interesting area of research of TPP, photochromic materials are embedded in the photoresist prior to polymerization. The microstructures fabricated with these materials offer the possibility to prepare active devices, where the shape or the optical properties of the microstructures can be reversibly changed.[14,15]

TPP has been successfully applied to radical polymerization. This process follows a chain growth mechanism where active species (i.e. free radicals) react with monomers to form high molecular weight materials. Several reactions with different rates for initiation, propagation, chain transfer, and termination occur at the same time. In chain polymerization, monomers react only with the propagating reactive center, not with other monomers, and chain addition ceases when the active species are depleted by a number of termination reactions. The molecular weight of chain polymers increases rapidly during polymerization and typical monomer to polymer conversion rates range between 70% and 90%.

In radical polymerization an initiator molecule plays a fundamental role. Its properties, such as the non-linear absorption at the wavelength used, the initiation efficiency of the active species formed upon absorption, and the quantum yield for the generation of the active species all influence the fabrication process. Commercially available radical photoinitiators used in TPP are Lucirin® TPO-L, Irgacure® 369, and Irgacure® 184.[16,17] In these cases, a molecular bond breaks homolitically after excitation generating two radicals, one of which is capable of initiating the polymerization reaction. In Lucirin® TPO-L, for example, there is a carbon-phosphorus bond that can be easily cleaved by using 350nm light. One of

the newly formed radicals has a tetrahedral structure with a single electron at one corner, which allows it to attack efficiently many substrates with no steric hindrance. It has been shown that Lucirin® TPO-L can be easily excited by two-photon absorption at 750nm making it suitable for TPP.

Molecular oxygen is a diradical species, so radical photoinitiators are strongly inhibited by its presence. Although this represents a limitation to their use in curing thin films, it is an advantage in TPP. By quenching the triplet state of the photoinitiator and by efficiently scavenging primary radicals, oxygen contributes to the formation of a laser intensity threshold below which fabrication is not possible. It is the presence of this threshold that allows for the breaking of the diffraction limit, permitting fabrication with sub-micron resolution.

The properties of commercially available photoinitiators, such as radical generation quantum yield and initiation efficiency, have been optimized only for linear absorption. For this reason some research groups have chosen a different approach, in which molecules with large two-photon-absorption cross-sections (δ) are rationally designed and synthesized.[18,19] It has been shown that molecules having electron-donating and electron-withdrawing groups separated by π-conjugated systems have large δ values. An example of this class of molecules is 4,4′-bis(N,N-di-*n*-butylamino)-*E*-stilbene. Starting with this structural motif, Perry and co-workers were able to synthesize molecules with δ values as large as 4400 GM, at least three orders of magnitude greater than those of most commercially available photoinitiators. Upon excitation by two-photon absorption, these molecules go through a large electronic reorganization. The excited molecule can efficiently transfer electrons to many substrates that upon their reduction can initiate polymerization reaction.[20] An appealing characteristic of this approach is the ability to shift the λ_{max} of the two-photon absorption by small modifications in the molecular structure of the photoinitiator. Furthermore, photoinitiators with large δ values have allowed for fabrication with a low intensity threshold and wide dynamic range, which is defined as the ratio between the threshold and the damage intensities.[21] Although these are desirable properties in TPP, the scarce availability of these initiators makes their widespread use limited.

The materials most widely used in TPP are based on acrylate monomers. Since acrylates are used extensively in several industries, a large variety is commercially available in a wide collection of functionalities, sizes, and compositions.[22] Another reason that makes acrylate monomers attractive for TPP is their high rate of polymerization via radical mechanism. Fast polymerization is essential in a serial microfabrication technique such as TPP in order to decrease processing times.

In order to give the required stiffness to the microstructures fabricated by TPP, highly branched monomers incorporating cyclic structures are generally used. These kinds of monomers produce highly cross-linked solid polymers that can easily

withstand the development step after fabrication without swelling and therefore losing mechanical structure.[23]

Most of the formulations used in TPP are negative photoresists, in that the regions exposed to light harden, becoming insoluble in a post-exposure development solvent. For applications in which empty volumes are required such as in microfluidics, it would be more appealing to use TPP on positive photoresists where regions exposed to light can be washed away in the development step. Some work in this direction has appeared in the literature where the authors use molecules capable of producing acidic environments when excited by two-photon absorption.[24] The local generation of acid induces an ester-cleavage reaction in a solid polymer. The newly formed polar groups make the volume in which they are present soluble in an aqueous base developer, thus allowing for their removal.

Experimental setup

Microfabrication by TPP can be performed by either moving the laser beam inside the photoresist or by moving the photoresist across the fixed laser beam. In the first case a set of Galvano-mirrors are used to scan the excitation beam in the x and y dimensions and a piezo stage to move the sample or the objective up and down. In the second scheme, the sample is moved in all three dimensions with the aid of a three-axis stage. Although both techniques have proven to be effective in the fabrication of three-dimensional microstructures, they have complementary advantages that have to be taken into considerations when choosing one system over the other. While galvos enable using greater scanning speeds than a stage, the area they can pattern is limited by the objective's back aperture. On the other hand, the stage total travel distance is the only boundary that determines the maximum area of the sample that can be patterned, allowing a stage to microstructure a larger section of the sample than with a set of galvos.

A typical setup used in TPP is described schematically in Figure 5. The source of light is a mode-locked Ti:sapphire laser capable of producing pulses with a duration of tens to hundreds of femtoseconds at a repetition rate on the order of 80 MHz. An excellent choice for this application is the Mai Tai® from Spectra-Physics, a compact single-box femtosecond oscillator (www.newport.com/MaiTai).[25] Even though output average power is maximum at 800nm, more than enough power is emitted to induce TPP across the tuning range of 690 nm to 1020 nm.
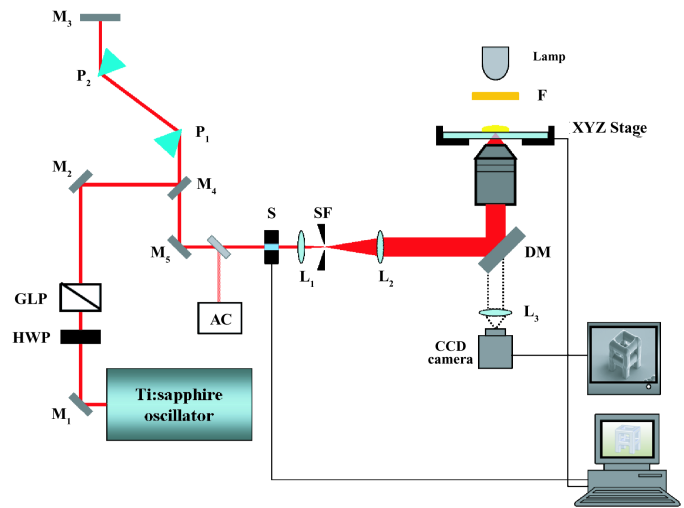

Figure 5 – TPP experimental setup. HWP, *half-wave plate*: GLP, *Glan-laser polarizer*; M, *mirror*; P, *prism*; AC, *autocorrelator*; S, *shutter*; L, *lens*; SF, *spatial filter*; DM, *dichroic mirror*; F, *filter*.

A half-wave plate and a polarizer are positioned after the oscillator and are used to variably attenuate the laser output power to the desired input required by specific experiments. The laser beam is then steered into a prism compressor assembly that introduces enough dispersion compensation to ensure that the shortest pulses arrive at the sample. For more details on how to assemble and setup a variable power attenuator and a prism compressor, please see Application Notes 26 and 29 respectively (www.newport.com/appnotes).

A small portion of the laser beam is then directed to a beam diagnostic unit. In this setup, the laser pulse is characterized both in the time and frequency domain by employing an autocorrelator and a spectrometer (www.newport.com/pulsescout).

The laser beam is then expanded by means of two lenses to match or overfill the back aperture of the objective. This is done in order to take full advantage of its numerical aperture. At the focal point of the first lens, a pinhole is carefully positioned to spatially filter the beam. A mechanical shutter used to control exposure times in the photoresist is usually placed before this assembly.

A dichroic mirror, which is reflective for near-IR and transparent for visible radiation, deflects the laser beam into an infinity corrected objective that focuses the excitation light into the sample. The sample's position in the objective field of view is adjusted by the aid of a three axis computer-controlled stage.

TPP is monitored in real time by the aid of white light illumination, a CCD camera, and a video screen. It is important to remember to cover the light source with a low-pass optical filter in order to prevent the blue part of the lamp emission spectrum from causing any undesired polymerization to occur in the photoresist. The ability to

image the sample while performing TPP is an important feature for a successful fabrication process. It is of utmost importance to anchor the microstructures to the substrates if they are to survive the washing step of the unsolidified photoresist. The way to ensure this is to start TPP exactly at the interface between the substrate and the photoresist, a task easily achieved with the above described real time monitoring.

The coordinates of the desired structure together with the velocities that have to be maintained are fed to the shutter and stage via a computer workstation that accurately synchronizes their activities. The software utilized to control the stage and the shutter can use two strategies for three-dimensional microfabrication. In one method, a cube element is scanned into the photoresist and the structure is formed inside the cube by opening and closing the shutter only where the volume of the structure intersects the one of the cube. This is called raster-scan mode and the entire volume of the object is hardened. In the second method, the shutter remains open while the focused laser traces the profile of the microstructure. This second method of fabrication is called vector-scan mode and only the surface of the object is fabricated. The inside remains liquid until after development when it can be cured with a UV source of light. Depending on the geometry of the structure, the vector scan method can lead to shorter processing time and higher precision, but requires higher software sophistication. Examples of microstructures fabricated in our lab by TPP with an experimental setup similar to the one described earlier are presented in Figure 6.
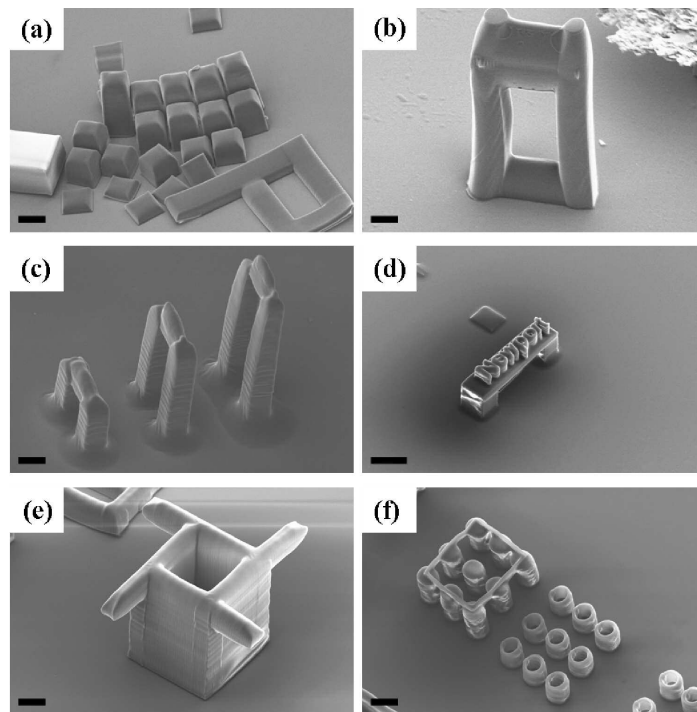

Figure 6 – Scanning electron microscopy images of structures fabricated by TPP. *All the samples were tilted 45º in order to reveal the three-dimensional nature of the microstructures.* T*he scale bars are* 20 μ*m in* (*a*), (*c*), (*d*), (*e*)*, and* 10 μ*m in* (*b*) *and* (*f*).

Resolution in TPP

The ultimate resolution and complexity of 3-D microstructures fabricated by TPP depends upon factors influencing the shape and size of the smallest polymerized volume element or voxel. It is the accurate overlapping of these voxels that produces the desired surface topology of the final structure.

The modification of the photoresist state from liquid to solid occurs in the region with the highest concentration of radicals. In TPP this corresponds to the central part of the square light intensity distribution at the focal plane. As a consequence, the shape of the polymerized voxels resemble ellipsoids with the two minor axes equal to each other and lying in the geometric focal plane.

The volume of the polymerized voxel is proportional to λ^3, where λ is the wavelength of the laser beam used to induce two-photon absorption. Although shorter wavelengths will form smaller voxels, the choice of the excitation energy is dictated mainly by the photoinitiator efficiency. In general, the working wavelength of choice optimizes the product of the photoinitiator two-photon cross-section area and quantum yield for radical generation.

By assuming a Gaussian distribution of light intensity at the focal volume and a constant photon flux during a laser pulse, an equation predicting the voxel dimensions as a function of experimental parameters can be found.[26] As expected, both voxel diameter and length increase with increasing values of exposure times and average powers. The relationships though are not intuitive. For example the voxel diameter is proportional to the square root of the natural logarithm of the product between the exposure time and the average power squared.

When the conditions for TPP are optimized to achieve the best resolution, the ratio of the axial and lateral dimensions of the polymerized voxel (μ) varies from three to five. By increasing either exposure time or average power, this ratio becomes larger implying that the length of the voxel grows more rapidly than its diameter. Furthermore, it has been measured, that μ is affected in larger degree by the average power than by the exposure time and that it saturates at long exposure times. Although these behaviors are not fully understood, it is believed that radical diffusion plays an important role during the polymerization of a voxel.[27]

One of the most important parameters that determine the size of the polymerized voxel is the objective numerical aperture (NA). The resolving power of an objective scales laterally as the inverse of its NA and axially as the inverse of its NA squared. Hence, in order to achieve the maximum resolution in TPP, high numerical aperture (NA) objectives are used.

The smallest voxel fabricated to date by TPP is only 100 nm in diameter.[28] Even by using the highest numerical aperture objective commercially available, this number is three times smaller than the one calculated by adopting the Raleigh criterion. Thus, diffraction limit can be broken in TPP.

The ability to fabricate with sub-diffraction-limited resolution by TPP arises from the presence of an intensity threshold below which no polymerization occurs. For example, by adjusting the laser intensity to a value just slightly higher than the intensity threshold, one can harden regions in the focused laser spot only 100 nm wide. A diagram on how the presence of an intensity threshold can be used to "cheat" the spatial limit imposed by diffraction is illustrated in Figure 7.

In radical polymerization, the growth of macromolecular chains depends greatly on delicate ratios of the rate constants among different processes that occur at the same time. These are initiation, propagation, recombination, and termination. If radicals are not continuously generated during the initial stages of the polymerization reaction, no chains will be formed. In polymerization induced by light absorption, this mechanism results in the presence of an intensity threshold. As mentioned in the materials section, in TPP no attempt is made to eliminate molecular oxygen from the photoresist, and this greatly adds to the presence of an intensity threshold. Besides quenching the active state of the photoinitiator, oxygen interacts with propagating radicals slowing their growth.
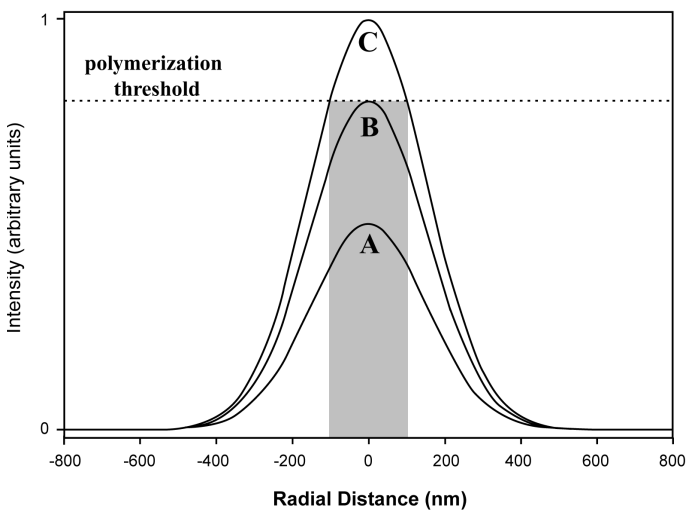
Figure 7 – Light intensity distribution at the focal point. A, B, and C are, respectively, the intensities below, at and above the intensity threshold (dotted line) for TPP. C shows the achievement of sub-diffraction-limited resolution.

Applications

Although the first communication reporting the fabrication of three-dimensional microstructures by TPP appeared only ten years ago, this technique has already been applied to address several problems. While most of the work has been done in the field of optics, applications in medical devices and microelectronics are rapidly emerging.

TPP was used successfully for the fabrication of both active and passive optical elements. For example by doping the photoresist with fluorescent dyes, microstructures with lasing capabilities were fabricated and their operation demonstrated.[29] Planar and nonplanar waveguides, Fresnel lenses, Mach-Zehnder interferometers, and microring resonators were all also manufactured by TPP.[30, 31] Perhaps the application in optics most developed by TPP is the microfabrication of three-dimensional photonic crystals.[32, 33]

Photonic crystals are structures that present periodic alternation of materials with different indices of refraction. The most common photonic crystal is the one with a log–pile geometry that consists of layers of parallel rods in which the rod orientation in each layer is perpendicular to that of the adjoining layers. Photonic crystals have the interesting property of forbidding the propagation of certain modes of the electromagnetic spectrum. It turns out that this photonic band gap phenomenon occurs at wavelengths corresponding approximately to the distance between the rods. Thus, TPP is the preferred technique for the fabrication of photonic crystals that operate in the visible and near-IR regions of the spectrum. Furthermore, TPP allows researchers to investigate the effect that geometries differing from the log-pile stacks have on the performance of photonic crystals.

In biology, TPP has been used for cross-linking proteins on artificial substrates and inside living cells.[34] Since these patterns retain enzymatic activity after laser processing, TPP is being considered for the fabrication of drug delivery devices on the micrometer scale. Other applications of TPP in the area of medical devices are the fabrication of three-dimensional scaffolds for tissue engineering by employing biocompatible materials as photoresists, and the fabrication of tools for cell manipulation.[35] Microtweezers and microneedles were fabricated by TPP and remotely controlled via optical trapping with far greater precision than standard electrostatic devices.[36, 37]

The surface of the microstructures fabricated by TPP can be chemically modified to enhance affinity toward metallic nanoparticles.[38] Once assembled on the microstructure's surface, the nanoparticles are used as catalytic centers for electroless plating. This methodology led to the formation of conductive three-dimensional structures. Devices almost impossible to fabricate by standard microelectronics techniques can now be attained by TPP. For example, true three-dimensional microinductors were fabricated with resonance frequencies in the GHz range, making them interesting for communications.[39]

Conclusion

Although TPP is almost ready to be implemented in a complimentary fashion to other microfabrication methods at an industrial level, there is still an obstacle to its widespread use. Being a serial process it can produce one device at a time slowing the manufacturing process and increasing its cost. Several methods for increasing TPP productivity have been implemented such as the use of microlens arrays for multipoint fabrication,[40] interference lithography,[41] and microtransfer molding with a suitable elastomer.[42] Even though it requires further development before being used on a large scale, the solution that seems most promising is the replication method.

TPP is a unique technique in that it can create three-dimensional microstructures with arbitrary geometries at sub-micron resolution. In this Application Note, the basic principles and the current state of TPP were briefly described.

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