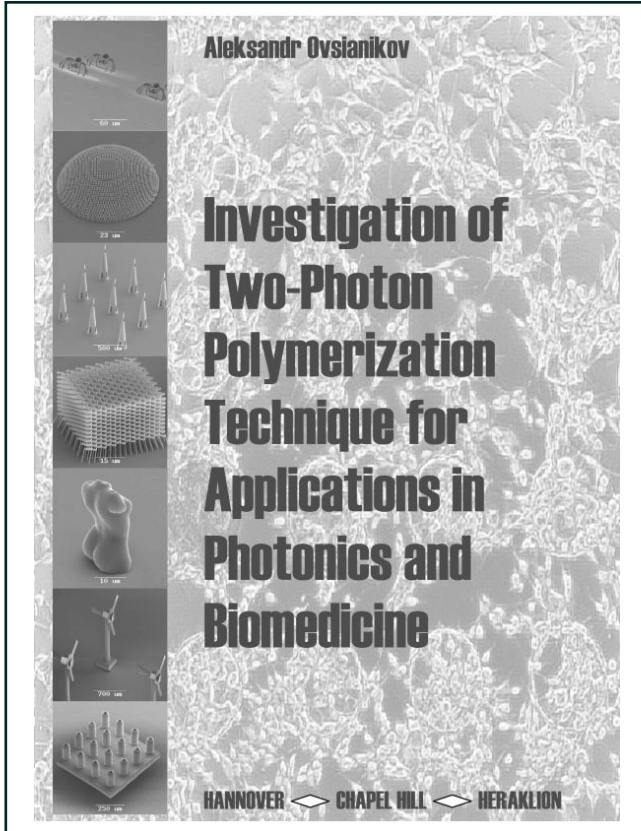




Aleksandr Ovsianikov (Autor)

Investigation of Two-Photon Polymerization Technique for Applications in Photonics and Biomedicine



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Telefon: +49 (0)551 54724-0, E-Mail: info@cuvillier.de, Website: <https://cuvillier.de>

1 Introduction

1.1 Multiphoton Absorption

Multiphoton absorption (MPA) is a quantum mechanical process, where an atom/molecule absorbs few photons simultaneously and can therefore surmount the energy gap, which is exceeds the energy of a single photon, in a single excitation event [Boy92, She84]. Multiphoton absorption was predicted in 1929 by Maria Göppert-Meyer [MGP29]. Three decades prior to the experimental observation of this process, her work described theoretical model gathering the principles of multiphoton interaction between light and matter. The publications main thesis was that an atom might absorb two or more photons, this way allowing electron transition to states which cannot be acquired by single photon absorption. Furthermore the probability of n -photon absorption is proportional to the n^{th} power of the photon flux density; consequently high photon flux densities are required in order to observe this phenomenon. In fact, MPA was one of the first effects demonstrated with the help of lasers, since intensities much higher than provided by other light sources could be achieved [KG61].

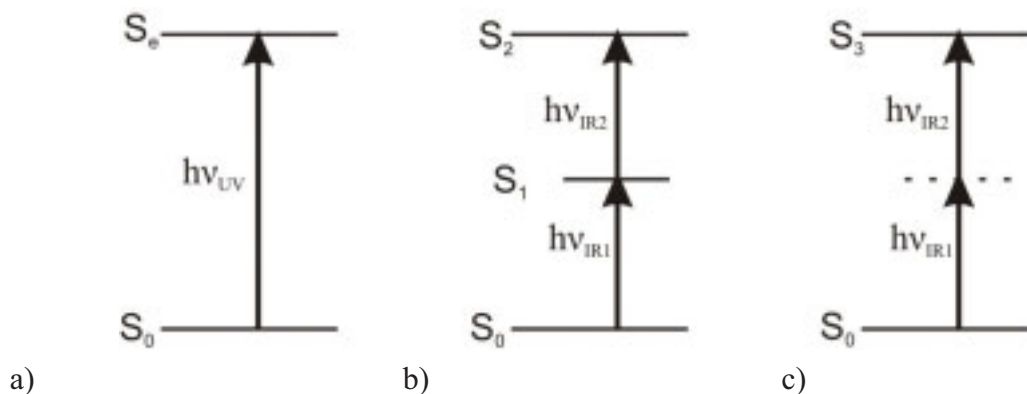


Figure 1.1 Schematic illustration of an atom excitation process with: a) single-photon absorption; b) stepwise absorption of two photons; c) two-photon absorption (TPA).

Figure 1.1 illustrates atom excitation processes through single-photon absorption, stepwise absorption of two photons and two-photon absorption (TPA). In conventional linear absorption process, an atom is excited via single photon absorption process. An excitation of an atom through absorption of single UV photon is illustrated in figure 1.1a. The excited state is characterized by the energy level S_e , the absorption rate scales linearly with the light intensity [Sve98]. An atom can also be excited by absorption of two photons. If a real intermediate state is present, the atom is excited through sequential absorption of photons. After the first photon ($h\nu_{IR1}$) is absorbed, the atom in the excited state can be characterised by a relaxation time or a certain lifetime of the energy level (S_1 in figure 1.1b). Before the decay of this excited state such atom can be promoted to another excited state (S_2 in figure 1.1b) by absorption of a further photon ($h\nu_{IR2}$). Therefore, the absorption of two photons here is

stepwise and is mediated by a “real” energy level. The energies of both photons do not have to be equal and depend on the position of the intermediate level (S_I). The important fact is that the energy level of this intermediate state, and therefore the energy of both photons ($h\nu_{IRI}$ and $h\nu_{IRI}$) are well defined. TPA is in turn mediated by a so called “virtual” state (dashed line in figure 1.1c). TPA is only possible if a second photon is absorbed before the decay of this virtual state. In analogue to sequential absorption, an equivalent description of this process, defining the lifetime of such excited state or virtual energy level, exists. In accordance to Heisenberg’s uncertainty principle a lifetime of such virtual state is on the order of a few femtoseconds (fs), which is very short when compared to lifetime of real energy level. A further important difference here is that the energy level of such excited state is not defined. Therefore any two photons, whose energy sum equals to the gap between the atoms ground and the excited state can participate in the process. In contrast to stepwise absorption of two photons, for TPA process coherence of the incident light is required.

The excited energy levels S_e and S_3 , shown in figure 1a and c are not exactly the same, since the selection rules for single photon and two-photon absorption are different [She84]. This fact implies that MPA can reveal information about transitions not accessible by single photon processes. The first applications of MPA process were as spectroscopic tool, for identifying the energy states which are not linked to the ground state via single photon absorption [HWP63].

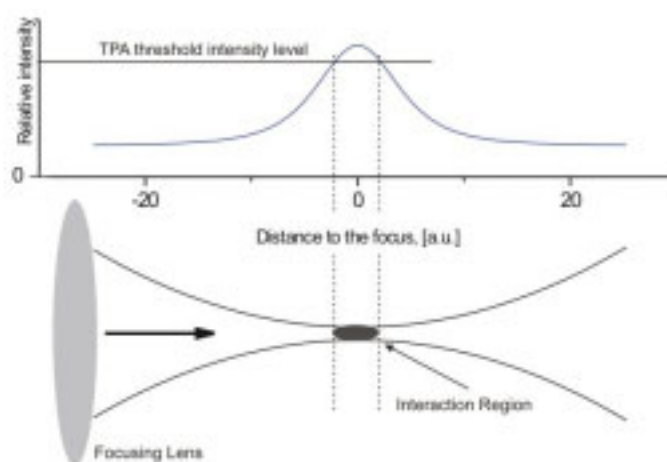


Figure 1.2 Schematic illustration to TPA interaction confinement. Top image shows intensity distribution along a focused laser beam. Lower image shows according interaction TPA region (dark ellipsoid), whose size is defined by the TPA threshold intensity.

Since the probability of the TPA is proportional to the square of the intensity of the laser radiation, favourable conditions for TPA in the first place are created in the waist of the focused laser beam (see figure 1.2). Thus, the multiphoton interaction region is strongly confined. This advantage, widely applied in multi-photon microscopy, leads to high spatial resolution and the ability to selectively excite specific molecules [DSW90]. Using multi-photon microscopy one can, for example, observe the spatial distribution of one specific molecule inside a living cell, and create 3D images with submicrometer resolution. Since the

availability of fs laser systems, multiphoton microscopy gained widespread popularity and currently presents a “must have” tool of any life science laboratory.

1.2 Principles of Photopolymerization

Currently photopolymerization presents an indispensable part of industrial processing for our everyday products. The demand of raw materials for radiation curing in a segment of specialty chemicals market is a constantly growing. Recent findings show that photopolymerization of resins has been applied in mummification procedure in ancient Egypt as early as 1900 BC [BE01]. Nevertheless, the history of modern applications of photopolymerization on the industrial scale is comparatively short. First commercial applications of this technique in coatings started in early 1960s. By the end of 1960s many new material systems, fitting a wide variety of possible industrial applications, were developed. Appropriate equipment allowing fast curing and providing control over the process on the industrial scale was developed. Photopolymerization for industrial applications is very competitive and presents many advantages over many conventional approaches, it allows reducing energy consumption, it is ecological, and finally it is economical due to its high productivity at lower costs. Combination of these factors made photopolymerization a choice of process for evermore new applications areas in the industry throughout the years, this growth continues to present days.

In mid 1980s knowledge gained in this field and its wide acceptance in the industry paved way for rapid prototyping technologies based photopolymerization. Stereolithography, also known as 3D printing, solid free-form fabrication or solid imaging, is a technique allowing to create complex 3D models from photosensitive materials in accordance to provided CAD design. Since this method is very economic for prototype manufacturing it is now widely applied in automotive, aerospace, and many other major industries. By looking at the history and fields of application of radiation-curing it becomes clear that the main driving force is its high potential for innovation.

In general, polymerization is defined as a process of reacting monomer molecules together in a chemical reaction to form three-dimensional networks or polymer chains [You87]. In case of photopolymerization this process is initiated by light. Most often addition polymerization is meant when talking about photopolymerization. Here, photopolymerization is defined as the light-induced chemical reaction of monomers or oligomers that results in a solid polymeric network [Dec94]. Modern materials systems for photopolymerization contain at least two main components a photoinitiator and a monomer or an oligomer. Apart from that, additives, whose function is to impart desired material properties, are often used. Photoinitiators - molecules which have low photo dissociation energy – are added in order to increase the material photosensitivity and so to improve the efficiency of the process.

Photopolymerization reactions that form a cross-linked network follow the characteristic steps of any chain polymerization mechanism: photoinitiation, propagation and termination. Figure 1.3 provides a detailed illustration of a free-radical photopolymerization

reaction on the example of methacryloxypropyltrimethoxysilane (MAPTMS) and photoinitiator 2-benzyl-2-dimethylamino-4'-morpholinobutyro-phenone (Irgacure 369). In the first step, two free-radicals are produced through light-induced bond cleavage in the photoinitiator molecule (photolysis), as a result of absorption of a UV photon (figure 1.3a). By definition radicals are atomic or molecular species having unpaired electrons on an otherwise open shell configuration, and therefore exhibiting extremely high reactivity [Dec98]. When produced radical comes into close proximity with an oligomer molecule (MAPTMS in this case) they can react by breaking a methacrylic bond (an arrow in figure 1.3b indicates which bond radical is able to break). As a result of this reaction a larger radical molecule is created (figure 1.3c). If this newly formed radical appears in proximity of another oligomer molecule it can react by once again breaking the methacrylic bond (figure 1.3d) and forming an even larger radical (figure 1.3e). Hence produced radicals serve as propagating active centers of a chain reaction. Reaction continues in this manner until it is terminated by a reaction between two radicals, which can be either photoinitiator fragments or larger radicals.

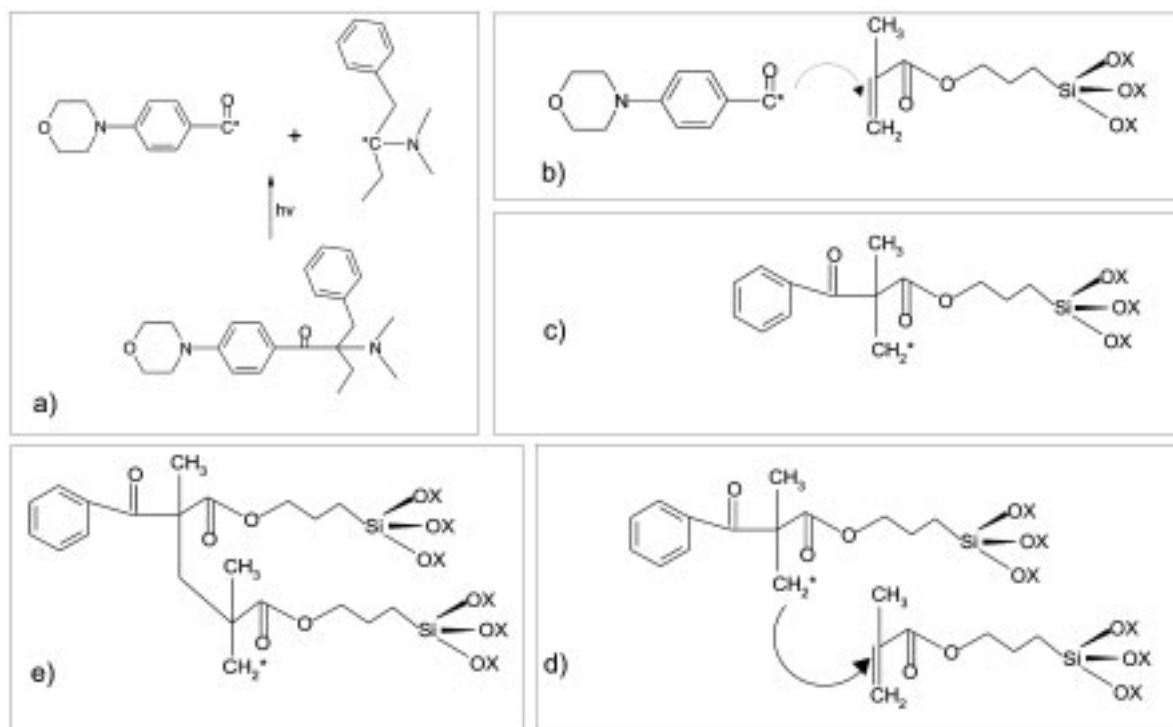


Figure 1.3 Illustration to photoinduced free-radical polymerization process on the example of MAPTMS: a) absorption of a UV photon by photoinitiator Irgacure 369 results in bond-cleavage and production of two radicals; b) radical reacts with MAPTMS molecule by breaking a methacrylic bond (indicated by arrow); c) a larger radical molecule is created as a result of this reaction; d) it can further react with another MAPTMS molecule by breaking a methacrylic bond (indicated by arrow); e) an even larger radical molecule is created as a result of this reaction.

Compared to other initiation routes, e.g. thermal in which heat is used to produce active centers, light-induced polymerization offers certain advantages. Most importantly in the context of this thesis, it provides both spatial and temporal control of the initiation reaction through control of illumination conditions. Linear polymer chains are obtained by

reacting monomer species that contain a single double bond, while a cross-linked network of polymer chains can be formed using multifunctional monomers. The resulting solid polymers are used in many applications due to their insolubility in organic solvents and resistance to heat and mechanical treatments [Rof82].

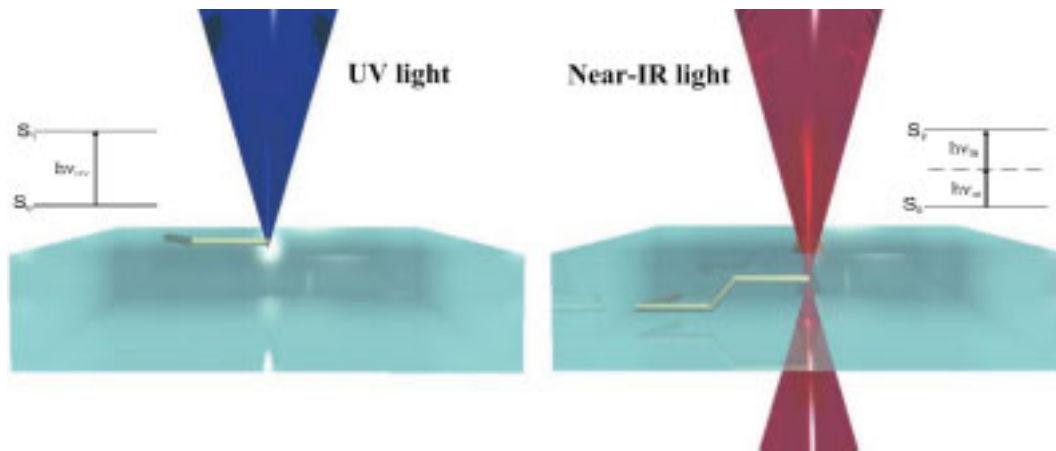
Main drawbacks of free-radical polymerization are oxygen quenching and polymer shrinkage [FR93, KS02]. At normal conditions some atmospheric oxygen is always dissolved in the material. During free-radical polymerization it can deactivate the intermediate states by producing oxygenated radicals and so slowing down or disturbing the polymerization reaction. In thick films oxygen quenching is mostly expressed in the upper layers of the material, which are in direct contact with the atmosphere. Shrinkage is a result of increased density of the final polymer state compared to the density of original material formulation before polymerization. Since the amount of material before and after polymerization does not change, this density change will result in volume reduction i.e. shrinkage. Recent efforts in the material synthesis field brought about some novel materials that exhibit very little shrinkage even when polymerized via free-radical route.

An alternative material system often applied in photopolymerization is based on ionic polymerization. Here ions play role of active propagating centers. The advantages of ionic polymerization are the absence of oxygen quenching and substantially lesser shrinkage. A prominent example of such material is commercially available SU8, also widely applied in multiphoton processing. Here, photoacid generators can be interpreted as photoinitiators, since acid, generated during light exposure, acts as polymerization reaction catalyst and spacially defines the produced pattern. Polymerization reaction itself is induced by cations, and requires addition of heat, i.e. sample postbaking. This implies that in contrast to free-radical polymerization mechanism, here the exposure and the polymerization steps are separated. Compared to free-radical route, disadvantages of cationic material systems are longer sample processing time and often less temporal and spatial control over the reaction.

1.3 Two-photon Polymerization Technique

Two-photon polymerization (2PP) is a novel direct laser writing technique based on the two-photon absorption (TPA) of laser radiation in photosensitive polymers. The mechanism of this technique is best explained in comparison to another widely known rapid prototyping technique - stereolithography. In stereolithography UV laser radiation is applied to scan the surface of the photosensitive material (in the UV range). This radiation induces photopolymerization through single photon absorption, and is therefore confined to the surface of the material. Single surface irradiation step is producing 2D patterns of polymerized material (Figure 1.4a). Another liquid photopolymer layer is then deposited/flown onto such pattern in order to create a new surface. The steps are repeated until the complete 3D structure is produced. Finally, in a so-called developing step, the unpolymerized material is washed out and the fabricated structure is revealed. Due to linear absorption nature of the process, with stereolithography it is only possible to fabricate 3D

structures using a layer-by-layer approach. The liquid polymer reflow step requires high precision, it is relatively slow and constitutes the largest part of the fabrication duration.



a) b)
 Figure 1.4 Photosensitive material processing by: a) a single photon absorption with UV light. Light is absorbed at the surface of the photosensitive material. 2D patterns can be produced by photopolymerization; b) two-photon absorption with near-infrared light. TPA and following chemical reactions are confined in the focal volume, and the rest of the laser radiation is passing through the material without interaction. According to insets in the figures illustrate: a) single photon absorption; b) two-photon absorption processes.

Majority of available photosensitive materials are designed to be structured using UV radiation sources. They are transparent in the near-infrared and highly absorptive in the UV spectral range. 2PP approach is based on the nonlinear interaction between the materials and laser radiation through TPA. One can initiate two-photon polymerization with near-infrared laser pulses within the small volume of UV-sensitive material using tightly focused femtosecond laser pulses. Figure 1.4 provides a simplified illustration of the difference between single photon and two-photon activated processing. In 2PP most of the laser light focused into the sample from the top is passing through the material without interaction and exits at the bottom. The laser-material interaction is strictly limited to the waist of the focused laser beam, where the intensity is high enough to induce the TPA (see Figure 1.2 in section 1.1). The material is polymerized along the trace of the moving laser focus. This way fabrication of any desired polymeric 3D pattern by direct “recording” into the volume of photosensitive material is possible (figure 1.4 b). In a subsequent processing step the material, which was not exposed to the laser radiation, and therefore, stayed unpolymerized, is removed by an appropriate solvent and the fabricated structure is revealed. The material sensitive in the UV range (λ_{UV}) can be polymerized by irradiation with the near-infrared laser light at approximately double wavelength ($\lambda_{IR}=2\lambda_{UV}$), under the condition that the intensity of the radiation is high enough to initiate TPA. Since femtosecond lasers provide very high peak intensities at the moderate average laser power, they present a very suitable light source creating favourable conditions for TPA and are commonly used in 2PP microfabrication.

In stereolithography the structural resolution depends on the size of the focal spot and is limited by diffraction, thus the minimum feature size can not be smaller than the half of the applied laser wavelength. In reality, due to the technical reasons, inherent to this technology,

the best lateral resolution of stereolithography is in the range of a few micrometers [BJB⁺03]. Since 2PP is a nonlinear process displaying threshold behaviour, the structural resolution beyond the diffraction limit can be realized. Structures with feature size less than 100 nm have been realised experimentally, which is almost an order of magnitude smaller than the laser wavelength used for microstructuring (usually a Ti:Sapphire laser at 800 nm).

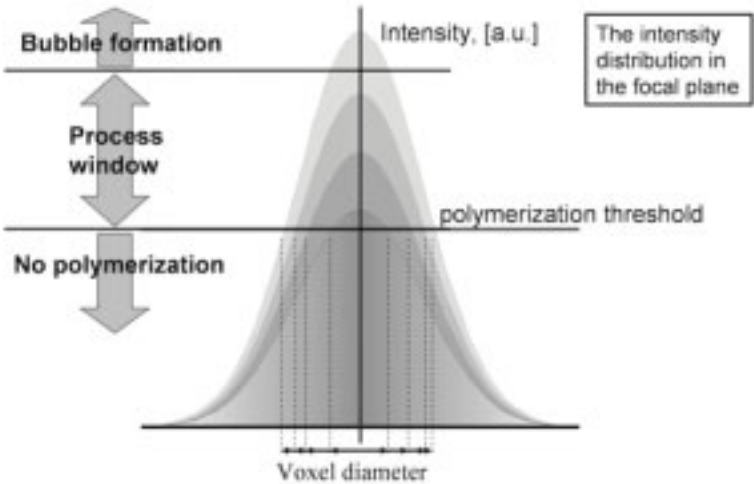


Figure 1.5 Effect of intensity on the volume pixel (voxel) size i.e. structural resolution of 2PP process.

For all photosensitive materials, a threshold irradiation fluence (and/or irradiation time) exists which has to be overcome to initiate polymerization. Due to this well-defined polymerization threshold, one can reach a resolution far beyond the diffraction limit as is schematically illustrated in figure 1.5 for a Gaussian intensity distribution in the laser focus plane. Precise control over the applied irradiation dose is used to tune the obtained structure size.

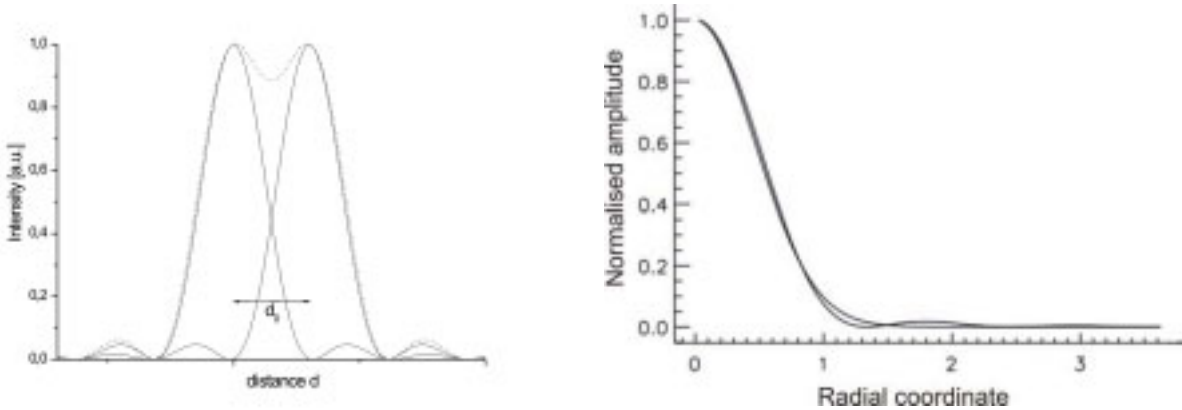


Figure 1.6 a) Rayleigh criterion for resolution of an optical system; b) Airy pattern approximation by a Gaussian distribution.

There are several factors determining the structural resolution limits of 2PP microfabrication. In general for multiphoton processing, the higher the order of process nonlinearity, the better the spatial resolution. For a fixed process order, for example 2PP, two further factors are of great importance. One is set by the material composition, i.e. the lowest limit for the structure size for a certain material is set by the size of the molecules composing this material. Another factor is related to how close one can approach the 2PP process threshold. Here both laser characteristic and material composition play an important role. Finally, the classical resolution limit is set by the intensity distribution in the waist of the diffracted laser beam, which is in direct relation with the wavelength of the laser and the numerical aperture (NA) of the imaging optics.

Intensity distribution in the focal plane of a microscope objective is governed by the theory of Fraunhofer diffraction. For a microscope objective with a round aperture a point source forms a so-called Airy pattern in the image plane. The intensity distribution here is given by a Bessel function of the first order. The central peak exhibits a maximum intensity, the amplitude oscillates and gradually decreases away from the centre. In accordance to the Rayleigh criterion two equally bright point sources can be resolved by a microscope if in the image plain the intensity maximum of the Airy pattern formed by one source coincides with the first minimum of an Airy pattern formed by the second source (see figure 1.6a). Therefore, in accordance to this criterion, the lateral and axial values of diffraction-limited resolution of a microscope objective are given accordingly by [Ino95]:

$$D_{xy} = 0.61 \frac{\lambda}{NA} \quad \text{and} \quad D_z = 2 \frac{\lambda n}{NA^2} \quad (1)$$

where λ is the exposure wavelength, NA is the numerical aperture of the objective ($NA \cong r/f$ where r is the radius of the lens and f is the focal length), and ' n ' is the refractive index of the sample material.

The amplitudes of side peaks of this intensity distribution are small compared to the amplitude of the central peak. Due to the threshold behaviour of a TPA interaction, in most cases side peaks do not contribute to the 2PP microstructuring process. The central peak of intensity distribution in turn can be well approximated by a Gaussian distribution (see figure 1.6 b). In order to deduce relation for a volume pixel (voxel) width and height one has to find isophotes of light intensity. In accordance to (1) for intensity drop to $1/e=0.37$ times the peak intensity the Gaussian beam width in the focal plane is given by $d_{xy}=0.21\lambda/NA$. According size along the axial direction is given by $d_z=0.66 \lambda n/NA^2$ [TRS⁺02]. The size of the interaction region or polymerized volume (volume pixel or voxel) depends on the polymerization threshold. The spatial intensity distribution of a Gaussian beam as a function of the axial and radial distances ' z ' and ' r ' is described by a following function:

$$I(r, z) = I_0 \frac{\omega_0^2}{\omega(z)^2} e^{-2\left(\frac{r}{\omega(z)}\right)^2}$$

here ' ω_0 ' and ' $\omega(z)$ ' are the size of the beam waist ($z=0$) and the beam radius in the plane at distance ' z ' from the waist position. I_0 is photon flux at the center of the beam waist ($r=0, z=0$). By solving this equation for a fixed threshold intensity ' I_{th} ', one can obtain the width ' ω ' and the height ' h ' of the polymerized voxel. For a second order process following relations are obtained:

$$\omega = \omega_0 \sqrt{\ln\left(\frac{I}{I_{th}}\right)} \quad \text{and} \quad h = 2z_R \sqrt{\left(\frac{I}{I_{th}}\right)^{\frac{1}{2}} - 1} \quad (2)$$

here z_R and ' I ' represent the Rayleigh range and the applied intensity accordingly. The calculated dependency of these parameters on the applied laser intensity for objective with NA=1.4 is shown in the figure 1.7a. Presented relation does not take any material influence on a molecular level or polymerization kinetics into account. Nevertheless, it provides a general idea about the voxel size dependencies in 2PP microstructuring. According to these calculations, for ideal material system, if the intensity is set at 2% above the threshold value voxel width and length of around $\omega = 33$ nm and $h = 80$ nm are obtained. At 5% over the threshold level these values are already $\omega = 52$ nm; $h=125$ nm. For 8% the values are doubled.

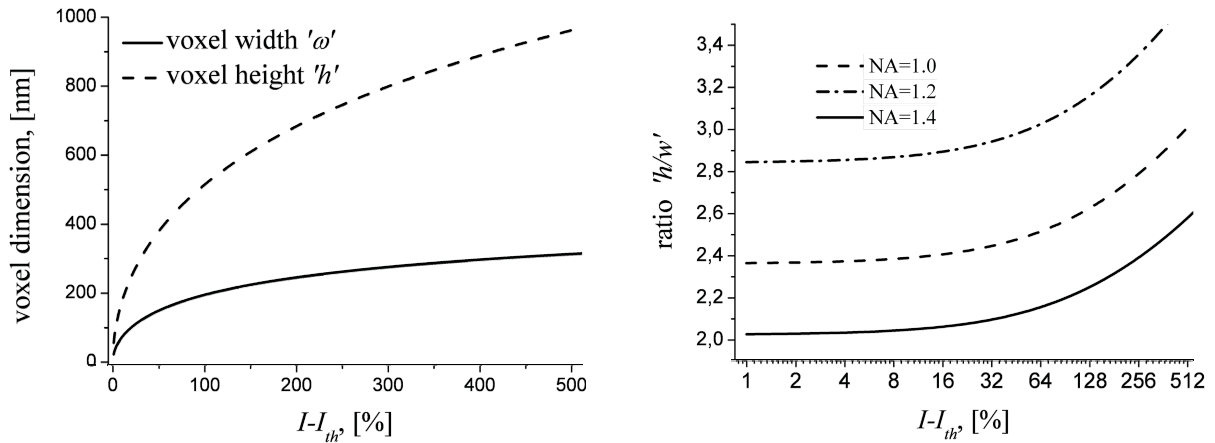


Figure 1.7 Voxel dimension dependence on applied laser intensity: a) voxel width ' ω ' and height ' h ' for a NA=1.4; b) voxel ' h/ω ' aspect ratio for different objective NA values, presented on a logarithmic scale.

It is therefore important to provide precise control over the intensity level of applied laser radiation. In a realistic system the pointing stability and the energy stability of the laser have biggest influence. For many practical applications, relying on the high structural resolution of the 2PP technique, it is important to know the form of the structures primitive building block - the voxel. Figure 1.7b presents voxel aspect ratio ' h/ω ' dependence on applied laser intensity for different NA values. It is observed that with increasing intensity the voxel becomes elongated along the axial direction. For objectives with higher NA not only the

better lateral resolution, but generally smaller aspect ratios can be realised. The NA of the objective used in work presented here is 1.4. Therefore, diffraction in the optical system sets a lower limit on the values of aspect ratios of voxel dimensions.

1.4 Materials for 2PP Processing

Early reports on 2PP microstructuring employed commercially available photoresists originally developed for UV lithography [MNK97, CAB⁺99]. Over the years a lot of effort has been devoted towards development of specialised photoinitiators (see next section for details), which are used with available materials or material blends. From the polymer side, little has been done. While the applied material spectrum has been significantly expanded, still mostly standard lithographic resins are currently used for 2PP microfabrication.

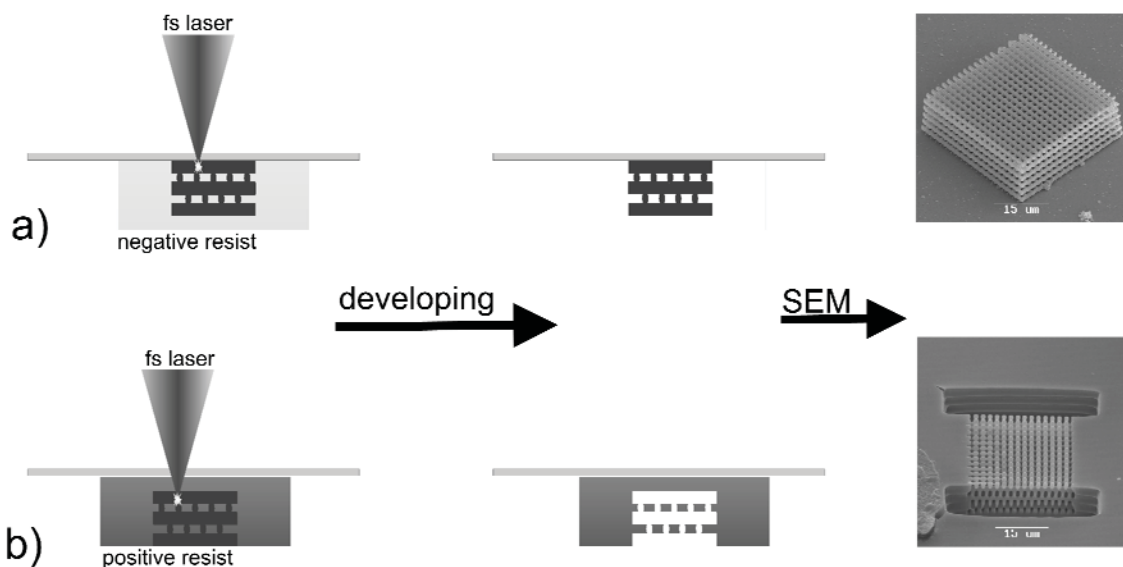


Figure 1.8 Schematics of two-photon activated (a) negative and (b) positive tone resist processing. According insets on the right show the SEM images of fabricated woodpile structures.

Conventionally, photosensitive resist materials are divided in two classes - negative and positive tone. The illuminated volume of negative resists undergoes cross-linking or polymerization, and becomes insoluble in developer. Unexposed material is removed during the sample development step (figure 1.8a), revealing the inscribed pattern/structure. In positive resists situation is exactly inverse - light induces dissociation of the molecules in the irradiated area. Here exposed material is removed during the development step (figure 1.8b), while the rest stays [ZKB⁺02]. Therefore, one obtains a hollow pattern. Most positive resists are developed for the fabrication of integrated circuits by photolithography, where they are patterned in 2D and are used as a sacrificial layer in a lift-off process. Therefore, these resists are designed for an easy chemical or thermal removal. By applying femtosecond laser pulses one can write 3D structures in positive resists, in this case we are talking about two-photon activated processing, since no polymerization is actually taking place. Conventional negative resists are most often acrylate- or epoxy-based resins, i.e. pure organic materials. Although