Vilnius University
Faculty of Physics
Laser Research Center

Laboratory assignment No. MNFT-2

FABRICATION OF 3D POLYMERIC MICROSTRUCTURES USING PULSED 3D DIRECT LASER LITHOGRAPHY

For master students of Laser Physics and Optical Technologies and Laser Technology programs

Vilnius 2021

1 The Goal

1. Get acquaintance with 3D Direct Laser Lithography technology.
2. Evaluate a spatial resolution of the technology, depending on the laser irradiation parameters.
3. Fabricate functional microstructures.

2 Exercises

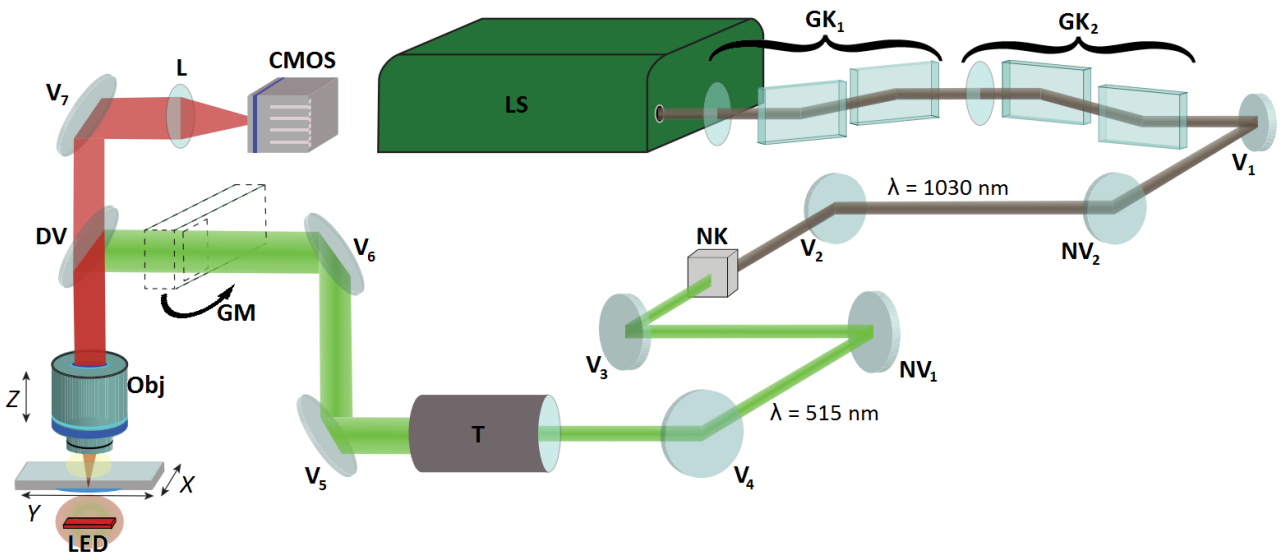
1. Employing 3D Direct Laser Lithography technology, fabricate "resolution bridges" – model for determining spatial resolution.
2. Using scanning electron microscope, experimentally evaluate lateral D and longitudinal L voxel's dimensions and its dependency on the laser irradiation intensity.
3. Measured dependency compare with theoretical model.
4. Manufacture 3 different functional structures: 1 phase element, 2 optical element (lens, prism), 3 3D microporous scaffold.

3 Key Questions

1. Steps of the photopolymerization reaction.
2. Typical parameters of the laser irradiation, used to induce photopolymerization reaction.
3. Lateral D and longitudinal L voxel's dimensions and its dependency on the laser irradiation intensity and objective numerical aperture.
4. Evaluation methods for the lateral D and longitudinal L voxel's dimensions.
5. Application fields of the 3D Direct Laser Lithography technology.
6. Principles of scanning electron microscopy.

4 Equipment and Tools

3D direct laser lithography (3DLL) scheme is depicted in Fig. 1. The main component of the system is femtosecond solid state laser "Pharos" (*Light Conversion, Lithuania*). An active medium is Yb:KGW crystal, central wavelength of the fundamental irradiation is $\lambda_f = 1030$ nm.

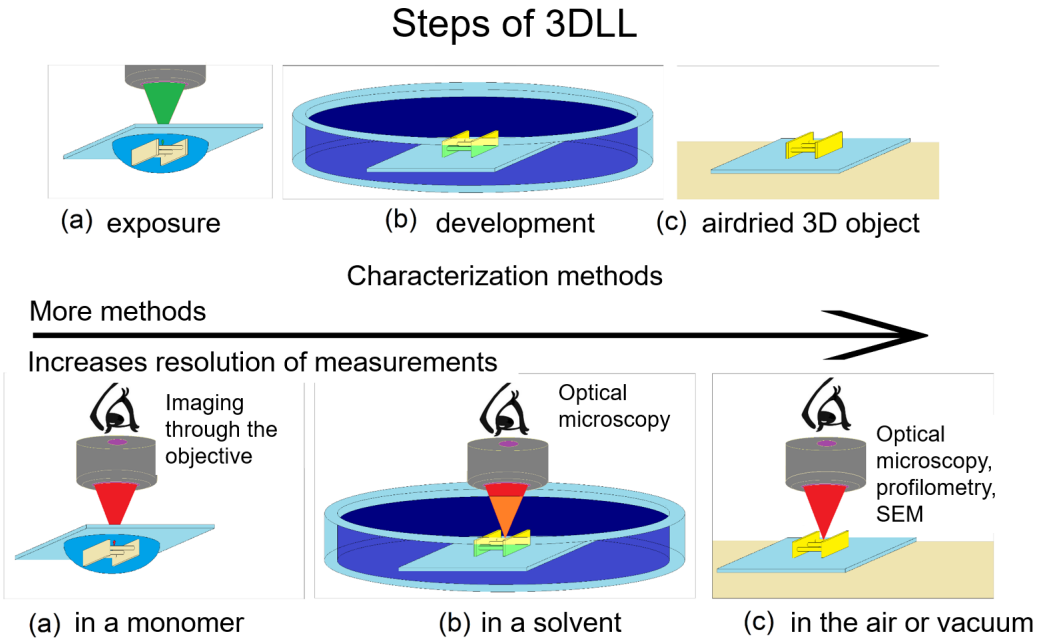


1 Fig. Principal scheme of the DLW. Meanings of the abbreviations: *LS*1 – laser source, *GK*1, *GK*2 – power adjuster, V_1-V_6 – mirrors, NV_1, NV_2 – detachable mirrors, *NK* – non-linear II harmonics crystal, *T* – teleskopas, *GM* – power meter, *DV* – dichroic mirrors, *L* – lens, *CMOS* – camera, *Obj* – immersion objective, *LED* – LED source, *XYZ* sample translation coordinates.

The laser generates pulses of $\tau_{imp} < 300$ fs duration. Repetition rate can be adjusted in order of 1-200 kHz [?]. The experiments are performed using second harmonics ($\lambda_{IIh} = 515$ nm), which is generated in the II harmonics non-linear crystal, placed in the separate arm of the optical system. The irradiation is guided to this arm employing detachable mirrors *NV*.

The average power of the laser used to expose the photopolymers is determined by two-stage power adjusters. The first stage of the power adjuster *GK*1, consisting of a manually rotated $\lambda/2$ phase plate and a Brewster angle polarizer, is used to determine the approximate average power of the beam entering the optical system The second stage of the power adjuster *GK*2, consisting of a $\lambda/2$ phase plate housed in a computer-controlled rotator and a Brewster angle polarizer, is for precise average power adjustment during laser writing. Automatic power calibration is performed by placing a power meter sensor in the path of the laser beam GM. An immersion lens is used to focus the beam in the volume of the photopolymer ($NA = 1,4$, $63x$). An immersion oil is used between the lens and the sample. Its refractive index ($n_{im} = 1,518$) is similar to glass ($n_s = 1,52$) photopolymer ($n_f = 1,504$). A 2x magnifying telescope *T* is installed in the beam path to ensure that the beam fills the aperture of the focusing lens to the maximum. A diode light source (*LED*) is installed below the glass pan with the specimen mounting location. The process is imaged with *CMOS* camera.

Submicrometric precision positioning tables ANT130-110 (*Aerotech, USA*) are used for the translation of the structured sample in the plane of the laser beam *XY*. Translation in the *Z* axis is performed by positioning the focusing lens with ANT130-60 tables. Such positioning



2 Fig. Steps of fabrication of microstructures employing 3DLL. Characterization methods at each step are depicted as well.

systems ensures $+/-75$ nm repeatability in each axles and allows movements up to 300 mm/s velocity [**?**]. "3DPoli" (*Femtika, Lithuania*) software package was used to automate the system.

5 Workflow

Before the laboratory assignment, remember laser safety requirements. In this work you will use 4th class laser, which means that scattered light can cause eye or skin injuries if safety requirements are not fulfilled.

1. Preparation of the sample. Photopolymer SZ2080 + photoinitiator (1 % w/w) is drop-casted on the glass cover slip using a pipette. Then the sample is heated in the oven: 1) for 20 min at 40 °C, 2) for 20 min at 70 °C and 3) for 20 min at 90 °C temperature in order to evaporate the solvent out of polymer. After heating is done, the sample is fixed on the positioning stages. The glass side with drop-casted photopolymer must be faced down, then a drop of immersion oil is placed on the top of cover slip.

2. Under supervision of lecturer, check if the laser system is ready to use.

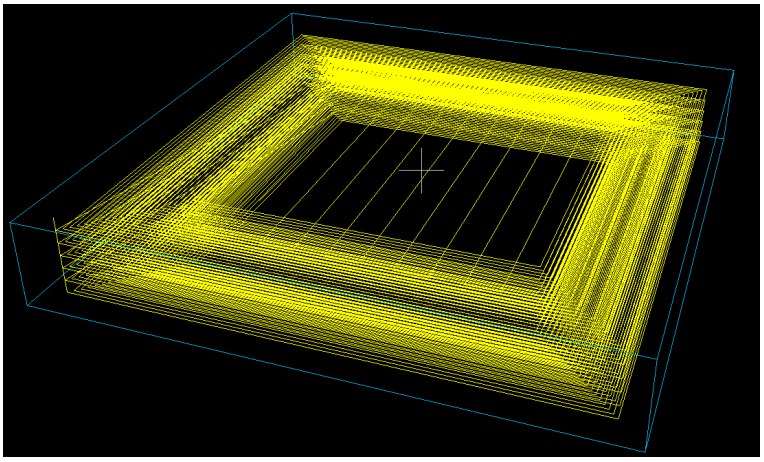
3. Fabrication of 3D polymeric structures.

(a) Turn on „wxPropView“ program for Live observation of fabrication and active it by pressing buttons Use and Live, kad būtų galima tiesiogiai stebėti fotopolimerizacijos procesą.

(b) Turn on *3DPoli 6.12 Compiler* and *3DPoli 6.12 Fabrication* programs. The first one is used to prepare and edit code, which defines the fabrication, the second one controls 3DLL system.

(c) Before starting fabrication process, it is necessary to find a focus position. The focus must be at the interface of the glass substrate and polymer. To implement this, you need to lower the objective changing its position via „3DPoli Fabrication“ program. In the program you can define the step of the stages movements in μm. The objective is lowered till it touches the immersion oil (by movements every 100 μm). Then the stages movement step is reduced to 10 μm and laser Shutter opened. In the program „wxPropView“ appears bright dot. It shows the focus position. Further keep lowering the objective till bright dot disappears. It indicates that the focus is in the glass cover slip. The thickness of the glass cover slip is 170 μm, thus keep moving 15-17 steps further, till the bright dot appears again. It means that the focus is in the photopolymer. Set the stages movement step to 1 μm and find the interface between photopolymer and glass. Now, the fabrication code can be executed. After the fabrication process is done, the objective must be moved away from the glass cover slip around 10-20 mm, then you can remove the sample from the stages.

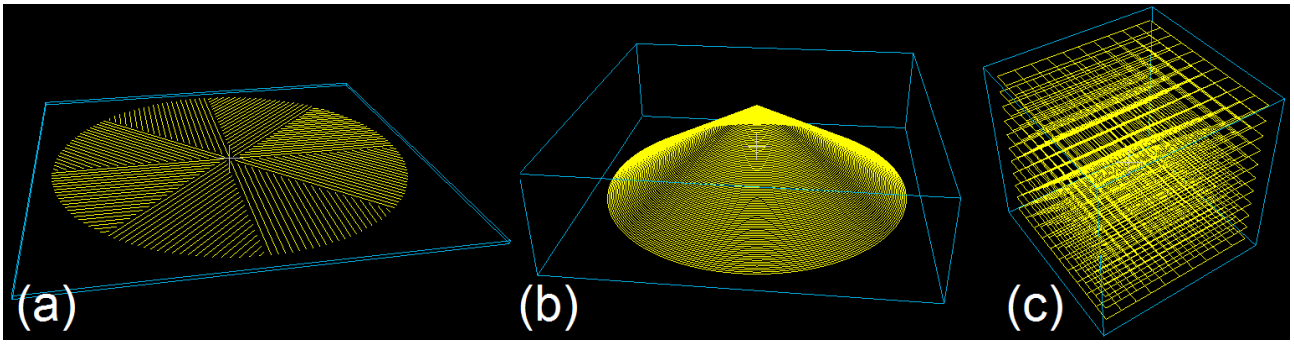
(d) Fabricate „resolution bridges“ when laser scanning velocity is 100 μm/s. Average irradiation power must be change from 20 μW to 200 μW every 20 μW or any other range. The code will be provided by lecturer. Typical CAD model of „resolution bridges“ is provided in 3 fig.



3 Fig. CAD model of "resolution bridges".

(e) Fabricate „resolution bridges“ when average irradiation power is constant, but altering laser scanning velocity: from 5 μm/s to 1000 μm/s.

(f) Fabricate functional microstructures: phase element, 2.5D optical element (lens, prisms) and 3D microporous scaffold. Examples of CAD models of aforementioned objects are presented in 4 fig.



4 Fig. CAD models of functional microstructures: (a) phase optical element, (b) axicon lens, (c) "woodpile" scaffold.

4. Development process. After the sample is removed from the stages, it is placed in Petri dish with solvent 4-methyl-2-pentanone for 30-40 min. During this time unexposed polymer is washed away and exposed remains on the glass cover slip.

5. Developed and dried sample is sputtered with 20 nm of silver.

6. The sample is observed with scanning electron microscope at two positions: top view and angled view (at 45° degrees). Bandinių charakterizavimas skenuojančiu elektroniniu mikroskopu. How to use SEM, you can find in appendix. Of course, the lecturer will give instructions.

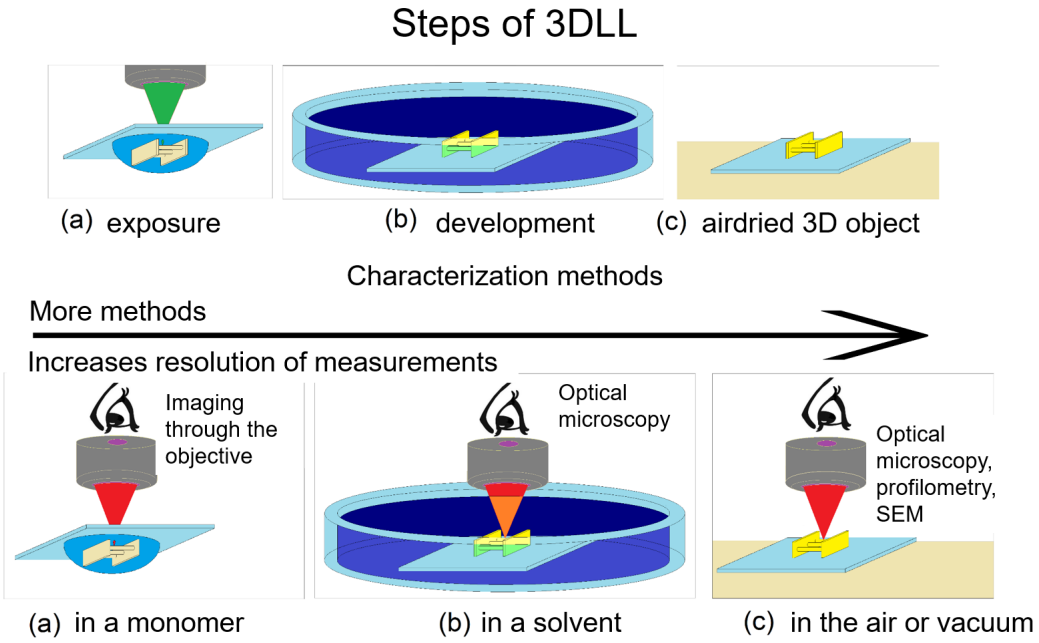
   Scheme of the fabrication and characterization is given in 5 fig.

7. Make a graph, how lateral and longitudinal voxel dimensions depend on the laser intensity: $f(d,l) \sim I$. Abscissa axis is intensity (I, TW/cm^2), ordinate axis – lateral and longitudinal voxel dimensions (d, μm ir l, μm).

   Average laser power can be recalculated to intensity according the formula:

$$I = \frac{2PT}{fw^2\pi\tau}; \tag{1}$$

   where P – average laser power, T – transmission of the objective, f – repetition rate, w – beam waist radius, τ – pulse duration. Beam waist radius can be calculated $w = 0,61M^2\lambda/NA$, when $NA = 1,4$.



5 Fig. Scheme of steps of 3DLL fabrication. Characterization methods of the sample at each fabrication step are depicted as well.

8. Make a graph, how lateral and longitudinal voxel dimensions depend on the scanning velocity: $f(d,l) \sim v$. Abscissa axis is velocity (v, μm/s), ordinate axis – lateral and longitudinal voxel dimensions (d, μm ir l, μm).

9. According equations (8) and (9), evaluate diffraction limit and depict it on the graphs. Compare the obtained dependencies with the theory and explain it.

6 Theory

6.1 Mechanisms of Photopolymerization

Polymerization is a chemical reaction in which low molecular weight molecules combine into high molecular weight compounds of identical chemical composition due to external influences to form three-dimensional networks of polymer chains. [?]. The connection of a monomer molecule to polymer chains can be initiated using external energy. There are two different mechanisms for this reaction (*chain polymerization*) and (*step polymerization*), also known as (*photo-crosslinking*). The chemical reaction, in which solid polymer networks are formed due to the external effects of light, is called photopolymerization. [?].

We will call photopolymers materials consisting of two main components: monomers/oligomers (denoted by – M) and photoinitiator (denoted by – FI). Photoinitiators are materials with low

photo-dissociation energy designed to increase the photosensitivity of a mixture [?]. In the case where the external energy source initiating the polymerization reaction is light, the most common polymerization mechanism is based on chain propagation. This mechanism consists of three stages: initiation, propagation, and termination [?]. Initiation begins when a photoinitiator is excited by interaction with light ($FI^\star$) and free-radicals are generated ($R^\star$) (Equation 2). Further interaction of these radicals with monomers creates a new molecule with a free bond (Equation 3). As the propagation process begins, an increasingly new monomer molecule is attached to the free bond (Equations 4, 5). During the propagation process, the polymer chain elongates rapidly and the excitation energy is no longer required for this process. The propagation process continues until a free radical is attached to the free bond (Equation 6) or another polymer chain with a free linkage is attached. (Equation 7). After such coupling, a chemically inactive polymer chain is obtained [?].

$$FI \rightarrow^{hv} FI^\star \rightarrow R^\star \tag{2}$$

$$R^\star + M_1 = RM_1^\star \tag{3}$$

$$RM_1^\star + M_2 = RM_1M_2^\star \tag{4}$$

$$RM_1...M_n^\star + M_k = RM_{n+k}^\star \tag{5}$$

$$RM_{n+k}^\star + R^\star = RM_{n+k}R \tag{6}$$

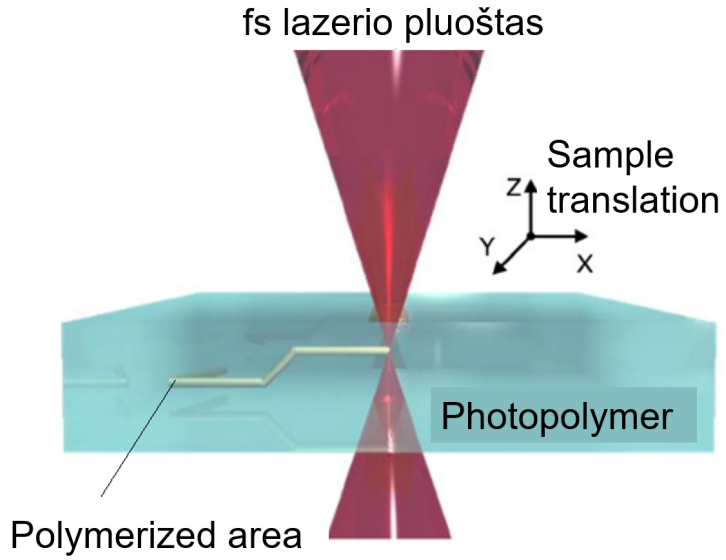
$$RM_n^\star + RM^\star = RM_nM_mR \tag{7}$$

Compared to other polymerization initiation mechanisms, such as thermal, in which thermal energy creates active polymerization centers, photopolymerization has several important advantages [?]. It is the initiation of polymerization with a light source that enables precise control of the polymerization process both in time and space. Depending on the type and concentration of the photoinitiator, commercially available photopolymers generally have strong absorption in the UV range and transmittance in the visible and NIR region. This means that the photoinitiator molecule can be excited by absorbing a photon in the UV region or several photons in the IR region. This phenomenon of non-linear optics is called multiphoton absorption, and the 3D DLW method is based on this phenomenon, enabling the formation of 3D objects in a photopolymer volume [?].

6.2 3D Laser Lithography

3D laser lithography (3DLL) is a DLW method, based on a non-linear absorption of laser irradiation in the photopolymer volume.

Most commercially available photopolymers are optimized for processing by exposure to



6 Fig. Structuring of photosensitive material by 3DLL method. Multiphoton absorption and subsequent polymerization reactions occur only in the focal plane of focused beam [**?**].

UV radiation. TSuch polymers strongly absorb UV radiation, but are relatively transparent to visible and NIR radiation. However, radiation of longer wavelengths can be absorbed by sharply focusing the laser beam and inducing multiphoton absorption in a small volume, which is a non-linear quantum mechanical process [**?**]. Multiphoton absorption can be understood as the excitation of an electron through a virtual energy level in a bandgap. It follows from the Heisenberg uncertainty principle that the lifetime of a virtual energy level is very short (several fs) and that the simultaneous absorption of several photons by an electron in the virtual level is a probabilistic event, so multiphoton absorption is a threshold process and occurs only at high (starting with GW/cm^2) irradiation intensity [**?**].

The schematic diagram of 3DLL is shown in Figure 6. Most of the radiation that is focused from above by a lens with a large numerical aperture propagates through the material without interacting with it. The interaction of the exposed light and the material takes place only in a strictly limited volume - the focal plane, where the achieved light intensity is sufficient for the induction of multiphoton absorption. If the sample is translated in three-dimensional space with respect to the laser beam constriction, we will polymerize a three-dimensional object, the accuracy of which will depend on the accuracy and resolution of the positioning device, and the smallest structured element will depend on the intensity and focusing conditions (numerical aperture). Material that has not been exposed to focused laser irradiation during structuring will be washed out with the appropriate solvent during development, leaving only the polymerized three-dimensional object [**?**, **?**, **?**].

From a technological point of view, 3DLL is performed when light-sensitive material is

exposed by focused beam, following a user-generated computer model (CAD) požiūriu. Three-dimensional exposure of a sample to laser irradiation is accomplished in two ways:

1. In the x and y coordinates, the sample is scanned using a galvanoscanner, and the scan in the z direction is performed by changing the position of the sample itself in step or linear displacement tables.

2. The position of the laser-focusing lens is fixed at all times, and the scanning takes place by changing the position of the sample in the x, y and z directions on the tables referred previously.

Let us also introduce the concept of a polymerization window – it is a ratio $\frac{I_{odt}}{I_{pt}}$, where I_{pt} – the intensity at which the polymerization reaction is initiated, I_{odt} – the intensity at which a bubble forms in the volume of the polymer, in other words, the polymer is optically damaged [**?**]. Such an analysis is accurate in terms of the polymerization reaction initiated by a single laser pulse. In a real 3DLL experiment, the material is structured at a high repetition rate ($10^5 - 10^7$ Hz order) therefore, it is necessary to take into account the influence of thermoaccumulation phenomena on the process window change. Forming 3D derivatives, the photopolymer is translated in space at a finite velocity. The inverse of the material's transfer rate is the pulse overlap, which indicates how many laser pulses affect a unit volume segment of a photopolymer. Since lasers are used with pulse repetition rates of hundreds of kilohertz, we are not talking about single or tens, but rather tens of thousands of pulses affecting a local segment of material. Thus, without changing other parameters, the exposure intensity limits of the polymerization process window will also depend on the translation velocity.

6.3 Spatial Resolution. Theoretical model and empirical measurements

Based on the Rayleigh model, the lateral D and longitudinal L dimensions of the focused laser beam spot are limited by the diffraction phenomenon and are calculated based on (8) and (9) Equations:

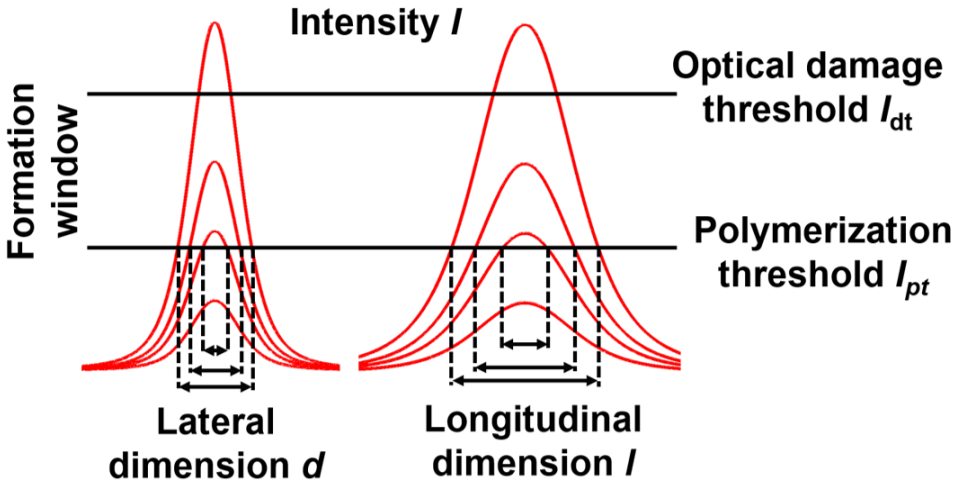
$$D = \frac{1,22\lambda}{NA}, \tag{8}$$

$$L = \frac{2\lambda n}{NA^2}. \tag{9}$$

We see that the dimensions of the focused laser beam can be reduced by using laser irradiation sources of shorter wavelengths or lenses with larger numerical apertures. In the first case, the choice of wavelength is limited by the combination of materials and laser sources suitable for

multiphoton photopolymerization, and in the second case, the numerical aperture of the lens is limited by the possibilities of their production technological processes.

Most practical applications of multiphoton polymerization arise precisely from the ability to form high (up to subdiffraction) spatial resolution 3D objects. The literature describes experiments in which the spatial resolution of 3DLL-formed structures is higher than 100 nm, which is almost one order less than the wavelength of a typical femtosecond laser used in the 3DLL process. [**?**]. Each photosensitive material has a characteristic parameter I_{pt}, above which a polymerization reaction is initiated. It is because of this polymerization threshold that the achievable structuring spatial resolution may be higher than the diffractively limited. In order to adapt the technology to new applications, it is particularly important to understand the fundamental limitations on the minimum size of any object segment (voxel). [**?**].



7 Fig. Dependence of the dimensions of the polymerized segment (voxel) on the intensity of the exposed laser beam in the focal plane and the thresholds of polymerization and polymer optical damage [**?**].

Gaussian beam intensity distributions in the focal plane are shown Figure 7. We see that the smallest possible segments (voxels) of polymerized material will be formed by exposing only the intensity of laser irradiation slightly exceeding the polymerization threshold, and by being able to precisely control the intensity, we can adjust the transverse dimensions of the formed voxel. [**?**].

There are several criteria that determine the principal limitations of the resolution of 3DLL-derived objects. For all multiphoton processes, higher spatial resolution is achieved at a higher degree of non-linearity of the process. If we consider a process with a specific degree of non-linearity, in this case two-photon polymerization, the limitation of the lowest achievable resolution will be determined by the smallest possible molecular structure of the specific material and a factor indicating how close the polymerization threshold can be worked.Finally,

the fundamental resolution limitation is decisive in the intensity distribution of the laser beam, which depends on the wavelength of the radiation and the NA of the focusing lens. Thus, both the structural properties of the material and the properties of the exposing beam determine the resolution of the multiphoton polymerization process. [?].

To estimate the size of the polymerized volume (volumetric pixel (or voxel)), we will use the polymerization threshold parameter. We will assume that a photosensitive material is polymerized when a certain characteristic number of initiator molecules is activated – ρ_{sl}. Density of activated initiator molecules $\rho(r,t)$ is expressed with Equation 10 [?]:

$$\frac{\partial \rho(r,t)}{\partial t} = (\rho_0 - \rho(r,t))\sigma_2 N^2(r,t); \tag{10}$$

where σ_2 – effective cross-section of two-photon initiator molecule activation, N – photons flux, $\rho_0(r,t)$ – initial density of initiator molecules. Approximating the light distribution in the focal plane ($z = 0$) with Gaussian beam: $N(r,t) = N_0(t)\exp(-2r^2/r_0^2)$, assuming, that photons flux $N_0(t) = N_0$ is constant over the entire duration of the laser pulse and regardless of the decrease in initiator between individual laser pulses, we can estimate the voxel width D, formed in the two-photon polymerization mode when the condition is satisfied $\rho \geq \rho_{sl}$:

$$d(N_0,t) = r_0\sqrt{\ln(\frac{\sigma_2 N_0^2 n\tau_L}{C})}, \tag{11}$$

$$C = \ln(\frac{\rho_0}{\rho_0 - \rho_{sl}})$$

where n – number of pulses, t – total exposure duration, τ_L – single laser pulse duration.

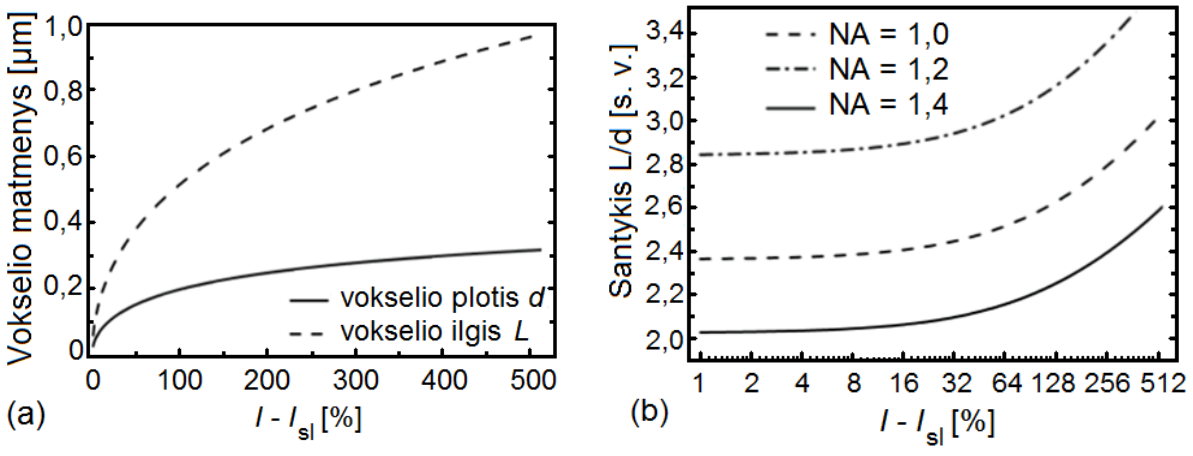
Similarly, for the axial light distribution when $r = 0$, Gaussian beam is $N(z) = N_0/(1+\frac{z^2}{z_R\sqrt{2}})$, and length of voxel L can be calculated:

$$L(N_0,t) = 2z_R\sqrt{\sqrt{\frac{\sigma_2 N_0^2 n\tau_L}{C}} - 1} \tag{12}$$

where z_R – Rayleigh length. To form a voxel whose shape is close to a spherical one ($L/D \approx 1$), it is necessary to use low laser pulse energy and short exposure time, in other words, work close to the polymerization threshold. This mode ensures not only the highest possible polymerization resolution, but also the closest spherical polymerized segment [?].

The dependences of the lateral and longitudinal dimensions of the voxel on the intensity of the laser beam used were calculated ($NA = 1,4$ objective) and depicted graphically (Fig 8 (a)). This model does not take into account any response or polymerization kinetics of the polymerizable material, but it is suitable for the qualitative evaluation of the dimensional change of the voxel formed by the 3DLL method. [?]. We see that as the exposure energy

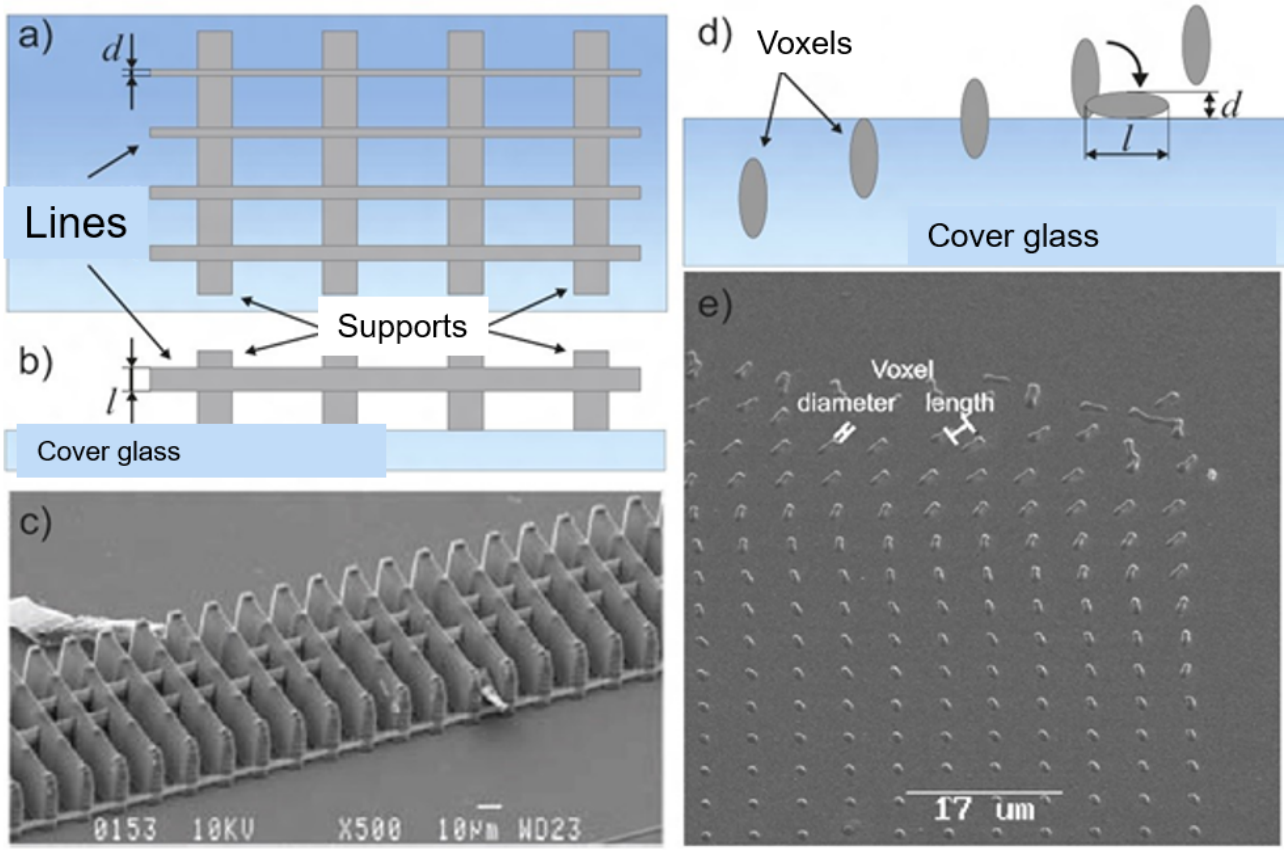
increases, the longitudinal dimension of the voxel increases faster than the lateral dimensions. The dependence of the voxel length-to-width ratio L/d on the exposure energy using focusing lenses with different numerical apertures is shown in Fig. 8 (b). It is noteworthy that the use of larger numerical aperture lenses not only achieves a higher resolution in the lateral coordinates, but also lower values of the voxel length-to-width ratios. [?].



8 Fig. Dependence of voxel dimensions on the energy of the exposing beam: (a) voxel width D and length L, using $NA = 1{,}4$ objective; (b) the ratio of the length and width of the voxel using lenses with different numerical apertures [?].

Still, such a theoretical model, although it well reflects the general regularities of the expression of the formed voxels, the calculated values differ from the experimentally obtained ones. In contrast to the processing of materials by laser ablation, modeling the interaction of multiphoton polymerization requires not only the size of the spot into which the laser beam is focused, but also the exact three-dimensional distribution of the laser beam in the focal plane. [?]. By deriving the equations describing the theoretical dimensions of the formed voxel, we simplified the analysis by approximating the energy distribution by the Gaussian beam. In addition, we completely ignored the irradiation response of the polymerizable material. In the formation of 3D objects in a real multiphoton polymerization system, the polymerization is initiated by long pulse burst, and due to the translation of the sample in 3D space, the number of pulses acting on each unit of volume and their overlap are not constant. For this reason, an analytical description of the energy flow is essentially impossible. In addition, the ultimate energy stability of laser pulses needs to be considered in a real-world 3DLL experiment [?].

Empirical methods are widely used in experimental work to determine the optimal processing conditions. The lateral and longitudinal resolution of the formation of three-dimensional microstructures can be estimated based on two models: „resolution bridges“ [?] and „isolated voxels“ [?]. In both cases, the resolution is assessed by measuring the length and width of the voxel from images taken by a scanning electron microscope (SEM).



9 Fig. Evaluation of the voxel lateral (D) and longitudinal (L) dimensions: (a) top view of „resolution bridges“, (b) side view and (c) SEM images of produced „isolated voxels“ [**?**]; (d) side view of „isolated voxels“ and (e) SEM images of array of „isolated voxels“ [**?**].

Based on the "resolution bridges" model, the resolution is estimated by measuring the height and width of the lines. These lines are formed in a single scan between the supportive walls, which prevents the lines from falling and floating during the development, but allows the lines to avoid contact with the cover glass. (Fig. 9 (a)-(c)). In order to evaluate the formation expression as accurately as possible, the length of the lines must be ∼100 μm and they must be measured in the central part. This avoids errors due to accelerations of the sample positioning system as they accelerate and slowdown. Depending on the dependence being investigated, a different intensity of laser radiation or sample scan rate is selected for each line. Alternative to „resolution bridges“, „isolated voxels“ method can be used. With this method, individual lines are no longer measured, but voxels. They are formed by sharply focusing the laser radiation into the volume of the photopolymer and changing the position of the focal plane of the lens relative to the cover glass. During this voxel formation process, some voxels are formed in a photopolymer volume (when the laser radiation is focused too far from the cover glass), some in contact with the cover glass (focusing near the surface), and some voxel tips are cut off (focusing on the cover glass), Fig. 9 (d). The voxels formed in the volume of the photopolymer

do not adhere to the cover glass and are therefore washed during the development of the sample. oxels that are in contact with the cover glass turn to the side during development and adhere to the surface due to adhesion. It is these voxels that are measured to assess the formation resolution. For unambiguous evaluation of the formation resolution, the exposure duration of each voxel must be the same. If truncated voxels are measured, errors may occur because it is not ensured that at least half of the voxel protrudes above the surface. Based on the „isolated voxels" method, it is possible to estimate not only the formation resolution, but also the shape of the voxel, which is not possible with the "resolution bridges" method. However, this method is not suitable for investigating the dependence of the forming resolution on the scanning speed and for estimating the lateral resolution when it is less than 100 nm. It has been observed that individual voxels of such dimensions do not adhere to the surface and are washed away during development.

Literatūros sąrašas