Single step self-enclosed fluidic channels via two photon absorption (TPA) polymerization

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Abstract: In this paper, we demonstrate a simple, fast and single-step method for fabricating self-enclosed fluidic channels via TPA. Pairs of parallel, polymerized ribs are linked by the subsequent polymerization with correctly predetermined offset between the ribs. The region, where the radicals are initiated but its concentration is below the threshold, we called it a sub-activated region. The subsequent polymerization is triggered by the overlap of the sub-activated regions of the two adjacent ribs. The dimensions of the self-enclosed channels depends on the offset between ribs, the scan speed as well as the laser parameters such as pulse energy, pulselength and repetition rate.

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References and links

1. Introduction

While the IC industry had been witnessed phenomenal growth in the last few decades, a comparable revolution is quietly gaining attention is microsystem technology. Since the emergence of the lab-on-a-chip (LOC) and micro-total-analysis-systems (µTAS), micro- and nano-fluidics has rapidly gained interest from researchers around the world because of its unique properties. Such microsystems represent the potential to shrink conventional bench chemical systems to the size of a few square centimeters with major advantages in terms of speed, performance, integration, portability, sample/solvent quantity, automation, hazard control and cost. These advantages are important for a variety of applications in analytical chemistry, biochemistry, clinical diagnosis, medical chemistry and industrial chemistry [1]. Underlying these applications is the integration of a number of analytical processes in microfluidic flowing streams that requires fluidic channels for separation, mixing, synthesis and analysis. However, advances in micro- and nano-patternning techniques are essential for fabricating fluidic channel arrays.

It is very critical to have enclosed channels to avoid evaporation of sample and chemical regent. So far, many versions of lithography techniques have been developed to fabricate enclosed fluidic channels. Nonetheless, to a great extent these lithography techniques rely on a mask or mold fabrication, which is very expensive, time consuming and not feasible for rapid prototyping. In addition, they have complicated fabrication steps, and require multiple sacrificial layers. A laser direct write method is a good alternative to lithography, but it still requires substrate bonding to enclose the channels. Many channel enclosing methods have been studied, including sealing with soft elastomers [2], fusion bonding [3], and depositing materials over sacrificial layers followed by wet etching or thermal decomposition [4] etc. All the aforementioned methods have their own advantages and disadvantages. The soft elastomers (e.g. polydimethylsiloxane, PDMS) provide a uniform sealing over a large area but the channels might be clogged as soft materials can be easily pressed into the channels [5]. The most commonly used thermal bonding requires stringent cleaning and high temperatures, often resulting in channel morphing and weak bonds [6]. The residuals stuck to the channel walls after removal of sacrificial layer may hinder the flow inside the channels [7]. Finally, these enclosing methods require multiple steps: hence, it significantly increases the complexity. To overcome these shortcomings, we developed a novel approach of creating self-enclosed channels in a single step by two photon absorption (TPA) polymerization.

2. Experimental setup and fabrication process

The resin used for this experiment was Ormocomp Low Viscosity, with 1%(w/w) concentration of Darocur 4265. Darocur 4265 has three absorption peaks: 240 nm, 272 nm and 380 nm. A diode-pumped Yb-doped fiber oscillator/amplifier system with repetition rate of 13 MHz and 26 MHz, and pulse duration of 214 fs and 3.14 ps was used. The laser was generated with 1030 nm central wavelength. The details of experimental setup have been presented in [8]. However, second harmonic (515 nm) central wavelength was used to expose the resist. Several factors motivated us to use the second harmonic. Firstly, with 1030 nm multi-photon absorption is more likely to occur. In comparison, 515 nm will result in two photon absorption. With reduction in the order of multi-photon absorption, it is easier to achieve better polymerization efficiency and smaller special resolution [9]. Secondly, absorbance of the photoinitiator, Darocur 4265, at 240 nm and 274 nm is much higher than that at 380 nm. Therefore, photoinitiation threshold at 515 nm will be much lower than that at 1030 nm, which in turn further improves spatial resolution [10]. Finally, shorter wavelength proportionally reduces the diffraction limit focal spot size and results in smaller feature size.

A glass substrate was spin-coated with Ormocomp (Microchem Technology GmbH) to achieve desired thin film thickness. A controlled laser beam with various scan speed was steered across the substrate in predefined geometric patterns created in AutoCAD. The theoretical laser spot radius \( r_0 \) was calculated using \( D_0 = 1.27 \lambda d/f \) [11]. Here, \( f \) is the effective focal length of the telesentric lens, \( \lambda \) is the wavelength of the laser and \( D \) is the laser
beam diameter. Values for these parameters were 12.478 mm, 515 nm and 8 mm respectively. Hence, the theoretical spot size diameter was calculated to be 1.02 µm.

In order to investigate the formation of the enclosed channels, a systematic series of experiments were carried out. The focus of experiments was the formation of adjacent pairs of ribs and cross-linked on the top surface creating hollow channel between them. A typical exposure steps used are shown in Fig. 1(a). First the laser was scanned in a forward path (FP), and then with a defined offset it was scanned in a parallel return path (RP). When the return path was placed close enough to the forward path, the two parallel polymerized ribs linked at the top. Figure 1(b) illustrates a channel formed by linking two adjacent ribs at the top. Experimental trails showed that the linking is greatly affected by pulse energy, scanning speed, line offset, pulselength and repetition rate. With correct combination of the laser parameters, we were able to create arrays of self-enclosed channels by scanning laser beam in parallel lines. For further investigation, the sample was exposed for average laser powers ranging from 80 mW to 700 mW, repetition rates of 13 MHz and 26 MHz, various scans speeds and offsets.

3. Discussion and results

3.1 Channel formation by subsequent polymerization

Figure 2 is a SEM image of a micro-fluidic channel created by the proposed method with a repetition rate of 26 MHz, an average power of 828 mW, a pulsewidth of 428 fs, and a scanning speed of 300 mm/s. The wall thickness of the two ribs is 2.62 µm, the width of the enclosed channel is about 2.44 µm. The total height of the enclosed channel is around 10 µm. The offset between the two parallel adjacent walls is measured (center to center) as 6 µm. TPA is a nonlinear process; thereby, it has well-defined threshold type behavior. The minimum fluence required to convert photoinitiators into radicals, whether it is by single pulse or multiple pulses in a short timeframe, is called photoinitiation threshold fluence. The volumetric region, that has the fluence greater than photoinitiation threshold, generates highly...
active radicals, which triggers the solidification of the resin. According to the scaling laws of
TPA polymerization [12], polymerized region forms in an ellipsoid shape with the center
plane at the focal plane. It is named voxel (volumetric pixel) and depicted as solid voxel in
Fig. 3. However, its surrounding is not a clear-cut division of solid and liquid phases. This
intermediate region resulting from the concentration gradient of the active radicals is a sub-
activated region, where radicals are initiated but its concentration is below the threshold.
According to Nitin Uppal [13], with a 1-µm laser spot, this region is about 10 µm in radial
direction and about 150 µm from the focal plane in the axial direction. The voxel was
calculated to be 2-4 µm in radial direction [13], which agrees well with the wall thickness.

Figure 4 illustrates the polymerization mechanism resulting of subsequent polymerization
phenomena. In the first step, the laser is scanned in FP with specific pulse energy, repetition
rate, and scan speed. In a following step, the laser is scanned in a parallel RP with same
parameters. The exposure dosage determines the actual size of the solidified ribs. If FP and
RP are close enough, there will be an overlap of the sub-activated region. In our case, the
offset between the two adjacent walls (6 µm as measured) is comparable to the radius of the
sub-activated region, which is calculated to be 5 µm in radius [13]. Therefore, we could
conclude that this overlap did occur. The overlap would increase the concentration of the
active radicals in the sub-activated region, thus increases the probability of the completion of
the polymerization process by combining with oligomer molecules. The remainder of the sub-
activated region with low concentration radical will diffuse, finally dissolved and removed by
post-exposure development step. Only those, at the vicinity of the solid walls, are attached
with the oligomer molecules and form a roof on top of the walls.

Figure 5(a) shows a linking is created along two adjacent walls. However, since the two
walls are far away, about 15 µm offset, the linking is scarce and random. When parallel walls
are placed close enough, as shown in Fig. 5(b) where the offset is 6 µm, the substantial
linking occurred and the enclosed channels formed. However, since the array of walls are
evenly spaced, interweaved linking took place. This can be avoided by placing pairs of walls
with wider spacing. For a Gaussian beam, the highest absorption rate occurs at the focal point.
Because of the greater availability of high density of photons at the focal plane, the
concentration of active radicals would be highest here. Therefore, when the focal plane is
above the substrate, as depicted in Fig. 4(a), the linking most likely to initiate at the focal
plane and continues along the axial direction because of the radical concentration gradient.
Also, at the focal plane the two voxels are the closest, thereby, they provide physical support
for the adhesion. Another scenario is depicted in Fig. 4(b). Here, the focal plane is below the substrate, thereby, the linking initiates at the substrate/resist interface and forms ripple structures at the bottom of the channels (see Fig. 6). The growth in the axial direction is again determined by the radical concentration, reducing as moving away from the focal plane. In the actual experiments, it was challenging to control the location of the focal plane due to the lack of automated focusing mechanisms. Therefore, in some samples, we observed co-existence of roof and ripples, as shown in Fig. 7. This ripple structures at the bottom of a channel may be useful for some applications. For example, it may be desirable for a fluidic mixer. With proper control over laser parameters and accurate positioning of focal plane, enclosed channels with various parameters can be created. A couple of such example is presented in Fig. 8.

![Fig. 6. Ripple at the bottom of the channel, 2.48 ps, 26 MHz, 274mW, 150 mm/s](image)

![Fig. 7. Co-existing roofing and ripples 2.48 ps, 26 MHz, 230mW, 150 mm/s](image)

![Fig. 8. Enclosed fluidic channel arrays 2.48 ps, 26 MHz, 300 mm/s (a)932 mW (b) 587 mW](image)

![Fig. 9. Enclosed fluidic channels (a) 428 fs, 26MHz, 455mW, 100 mm/s (b) 1.42 ps, 26MHz, 587mW, 100 mm/s (c) 2.48 ps, 26MHz, 320mW, 100 mm/s](image)

3.2 Effect of pulsewidth

Laser pulsewidth is the most significant laser parameter in TPA polymerization. One way to look at pulsewidth is the irradiation time for the resist. We employed 214 fs, 1.45 ps and 3.57 ps laser to investigate pulsewidth effect on the linking mechanism. With the longer pulsewidth, the irradiation time was increased, and as a result, the radical generation was sufficiently larger at the focal area. The peak intensity in picosecond is less in comparison to
the femtosecond. Hence, the TPA polymerization region in picosecond laser was not as confined to the close vicinity of the focal spot as in the case of femtosecond laser. However, providing high enough energy by increasing laser power for picosecond laser, TPA polymerization was successfully achieved. In picosecond, the pulse energy is less localized and the concentration of active radicals has wider distribution for a given laser spot. Therefore, the sub-activated region is significantly evident in picosecond laser exposure, and therefore, the probability of linking via subsequent polymerization is high. As the pulsewidth increases, the active radical concentration as well as its diffusion increases in radial direction due to the energy distribution. Figure 9(a)-(c) shows channels fabricated with pulsewidth of 428 fs, 1.42 ps, and 2.48 ps, respectively. As the pulsewidth increases, the sub-activated region expands, thereby, the channel transforms from a tall-narrow (with an apex on top) to a uniform circular profile. It is noteworthy that there are not ripples at the bottoms of these channels which indicate the growth of ripple structure is controllable.

3.3 Effect of scan speed

Other than controlled spacing between the ribs and an optimal spot size, the width of the ribs and the height of the micro-channels can also be controlled dynamically by manipulating the laser average power and the scan speed, as a measure of the laser fluence and the exposure time, respectively. Previous work has shown that the effective number of pulses, $N_{eff}$, is a convenient measure of accumulated fluence for a moving target. $N_{eff}$ can be calculated from

$$N_{eff} = \frac{\pi}{2} \frac{\omega_0^2}{f \nu}$$

Here, $\omega_0$ is the machining spot radius of 0.51 µm, $f$ is the laser repetition rate and $\nu$ is the scanning speed. The expression relates accumulated fluence of multiple pulses with a Gaussian intensity profile for subsequent laser spots separated by $R = \frac{\nu}{f}$. With constant repetition rate, the value of $R$ is smaller for low scan speed. If the value of $R$ is less than the spot size, there will be an overlap between two consecutive spots. The spot-overlap as a percentage of focal spot diameter can be given as $\text{spot-overlap} = \left(1 - \frac{R}{2\omega_0}\right)\times100$. The spot-overlap is necessary to obtain uniform, continuous ribs with well-defined edges. Figure 10 illustrates the three spot-overlap conditions and their determining effects on the final polymerized ribs. The slower scan speed with tighter resolution and greater spot-overlap results in higher degree of polymerization. The linearity of the ribs significantly improves with high percent spot-overlap, which is necessary to have good sidewalls of fluidic channel.

![Fig. 10. Polymerized ribs with spot-overlap (a) no spot-overlap (b) 55% spot-overlap (c) 90% spot-overlap](image)

3.4 Effect of laser repetition rate

The time period from the end of the first pulse until the second pulse arrives is called a dark period [13]. The free radical chain polymerization reaction takes place during this period because of longer time duration available to complete polymerization, in comparison to time duration of the pulse irradiation [15]. Therefore, dark period is essential for the degree of polymerization and can be controlled by manipulating the pulse repetition rate. The $N_{eff}$ for 26 MHz and 13 MHz was calculated to be 56 pulses and 28 pulses, respectively, for the scan speed of 300 mm/s. The conversion ratio of the chain of monomers from active radicals increases as the number of pulses increases. Hence, for 26 MHz the active radical concentration is greater than for 13 MHz. However, the laser fluence decreases as the repetition rate increases. It can be said that the resist is likely to polymerize even with low laser fluence, if the $N_{eff}$ is high enough to provide sufficient concentration of active radicals required to start photoinitiation. This phenomenon can be further explained by the Gaussian
energy distribution of laser pulse [8]. The laser effect of multiple laser pulses focused into the same point will accumulate, if the dark period is shorter than the cooling time. Thus, if the single pulse energy is too low to induce photoinitiation, it can be induced by multiple pulses with high pulse repetition rate (i.e. shorter dark period), because of the accumulation.

4. Conclusion
A novel fabrication process of a single step self-enclosed fluidic channels employing TPA polymerization has been proposed and successfully demonstrated. In this process, we used ultrafast laser to polymerized parallel pairs of ribs and crosslinked two adjacent ribs via subsequent polymerization to form hollow channel in between. The laser parameters such as the pulse energy, repetition rate and pulsewidth, along with process parameters, the scan speed and line offset were investigated for greater controllability of the process. Finally, proposed method is a simple, fast and inexpensive process for creating enclosed fluidic channels in a single step makes, which makes it a very attractive method for rapid prototyping for LOC and μTAS.

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