XIV Convegno dell'Associazione Italiana Tecnologie Manifatturiere

AITEM 2019

Padova, 09-11 Settembre 2019

Laser machining of glass microreactors: a first experimental study

Michela Dalle Mura[a], Andrea Rossi[a], Michele Lanzetta[a*], Gino Dini[a]

[a] *Department of Civil and Industrial Engineering, University of Pisa, Via Diotisalvi, 2 , Pisa 56122, Italy*

Abstract

The use of microreactors is one of the latest innovations in the chemical and pharmaceutical industry. One of the main issues in the fabrication of microreactors is the use of a proper technique to obtain the micro channels, in order to give them the desired shape and section so that reactants flowing inside are correctly fed through inlet branches and mixed. This paper proposes an experimental study on glass machining for the fabrication of microreactor channels through the use of a CO_2 laser source. The aim of the experiments is to analyse the effects of a CO_2 laser beam on glass and to study the influence of process parameters, such as laser power, focal distance and scanning speed, on the shape of the channel section and on the surface finish.

Keywords: Microreactors; Laser Machining; Glass

1. Introduction

A microreactor is a microfluidic device constituted by micro-channels of width less than 1 mm, in which reactants are fed and mixed so that chemical reactions take place.

The use of microstructured reactors is one of the latest innovations in the chemical and pharmaceutical industry. These micro-devices are well suited for all chemical and biochemical transformations that benefit of enhanced mixing and heat transfer in a well controlled time and confined environment. Microreactors are currently studied and applied in the field of microprocess engineering, to guide chemical-physical reactions.

One of the main issues in the fabrication of microreactors is the use of a proper technique to obtain the micro-channels, in order to give them the desired shape and section so that reactants flowing inside are correctly fed through inlet branches and mixed.

* Corresponding author. Tel.: +0-000-000-0000 ; fax: +0-000-000-0000 .
E-mail address: m.lanzetta@ing.unipi.it

The material to be used for microreactors manufacturing is one of the major factors driving the choice on the fabrication technique. The material is selected depending on the desired application, and in particular on aspects such as temperatures reached, pressure range, corrosivity of the fluids, specific heat capacity and electrical properties. Another fundamental aspect to be considered is the design of micro-channels, as certain shapes can only be obtained on certain types of materials. Also, the material must be selected according to desired surface quality, which depends on the production technique too, the choice of which takes into account, among others, the number of devices to be realized, time and costs required for the manufacturing process. The most used materials for the fabrication of microreactors are: metals, in particular precious metals; ceramics, suitable for high temperatures; polymers, economic and easy machinable; glass, specifically borosilicate and soda-lime glasses. Among others, glass is particularly appreciated for its compatibility with organic solvents, chemical resistance and transparency, that allows an external observation and analysis of reactions taking place inside the microreactor.

2. State of the art

Microfluidic devices have had a considerable impact on the fields of biomedical diagnostics, waste water monitoring and are widely used in the food and chemical industries. Liquids and gases conveyed in channels with cross-sectional dimensions up to 0.5 mm can undergo chemical and physical changes or mix when covering predetermined paths [1]. The microchannel devices material can provide good optical properties, well-understood surface characteristics (wall wetting) as well as high resistance to mechanical and chemical stress. As already stated, glass is very interesting because despite the low cost has a high transparency in ultraviolet to infrared regions, shows good thermal and electrical characteristics, and does not react easily with most of chemicals.

In developing microfluidic devices, chemical-based and machining processes can be used. Laser eliminate the requirement for corrosive and hazardous chemical etchants and the need for high resolution photomasks. Therefore, the overall microchip development time is significantly reduced respect to chemical processes, electrophoresis, photomask generation, photolithography, and etching process [2,3].

Functional microfluidic devices have regular section along the mixing stretch and different paths or junctions before the outlet channel where the mix occurs [4]. Versatility in developing paths for microfluidic devices can be obtained by subtractive processes, as laser ablation and micro-milling [5]. Additive and rapid prototyping methods lead to higher geometric deviations due to the melting in a powder bed layer-by-layer which imposes a polishing process after deposition to observe their functional characteristics [6].

Laser machining is associated with little focused laser spot and high energy density that reduce the processing time and provides very small details or radii. Laser production is faster than micro-milling, where the feed rate of the focusing point is expressed in mm/s. The resolution of laser micromachining can be as small as the wavelength of the laser. It is capable of fabricating accurate structures in microscale which are difficult to achieve if conventional milling process is used. In addition, low-cost, commercially available CO_2 laser systems can also be used for this type of application [3].

CO_2 laser ablation has been used for fast prototyping on polymeric materials (polymethyl methacrylate, [7,8]), polycrystalline ceramic (zirconia, [9]) and glass [10]. A variety of glasses are commonly used in microchannel applications, from the cheapest soda lime glass to co-doped glass, which provides more performing technological and optical characteristics. Hodgson et al use a co-doped boroaluminosilicate glass to impact on surface roughness, gloss and wettability performance [11]. There features are well suited to technologies requiring increased infra-red transparency and for use in industries like photovoltaics where the glass may be subjected to high temperatures during semiconductor deposition and require as much light as possible to pass through to the absorber layer. However, the need to have such strong characteristics does not justify its higher cost in the creation of microfluidic chips, but rather the transparency in the visible and the regularity of the section along the stretch of mixing of the channel. CO_2 laser ablation leads to crack-free cutting on soda-lime and borosilicate glass [3,22] a prerequisite that has a positive impact on transparency.

A good compromise for widespread applications where good optical quality is required (transparency and wettability) can be achieved with borosilicate glass. Laser-ablated pattern on borofloat and soda–lime glass where the fabrication parameters are the same for both substrates shows distinct cracks when they are observed at SEM images.

The light scattering generates by cracks affects the fluorescence background. On soda–lime, it was measured to be 2.5 to 3 times higher than that on borofloat [3].

However, a few papers have shown functional glass microfluidic devices by CO_2 laser of channels or thin holes glass while some applications with more complex and expensive ultrafast femtosecond laser have been addressed [12,13,14]. Glass has a high absorption of the CO_2 laser output energy (λ = 10.6 μm). Hence, the CO2 laser micromachining of glass is essentially a photothermal process which results in channels featured a narrow Gaussian shape, typically obtained by CO_2 ablation of PDMS and PMMA under high power [8,15]. Due to the low thermal conductivity and significant coefficient of thermal expansion of common soda lime glass, the local heating caused during the ablation of microfluidic chips generates thermal stress and often results in continuous micro-cracking and/or a poor surface quality [16,17]. Yet, each method requires extra procedures or additional equipment than a laser source alone as the scribing with a diamond wheel (peeling method, [18]), the cover by a sacrificial layer [19,21] or proceeded upon using additional equipment [20,3].

Chung and Lin use a layer of water on the surface of the glass, small holes (100–200 μm of diameter) can be produced in Pyrex [20]. Unfortunately, due to the thermal stress on the surface, larger features (>300 μm holes) rendered surfaces with extensive cracking. Da Costa et al improve the process by using a sacrificial layer of paraffin wax as heat sink and avoiding the drawbacks of liquid water (non‐uniform thickness, electrical incompatibility, etc.) [21]. They engraved glass-based capillary electrophoresis devices with semi-elliptical shape channels with aspect ratio of about 0.2 (400 μm width vs 70 μm depth) on standard glass microscopes slides (1mm-thick). This process led to some small cracks around the channels and other superficial defects at the borders. The distortion of the channel has been reported in deviation from width and depth where the respective standard deviations on n=10 measurements were of 20 μm and 2.5 μm. They sealed the engraved glass layer to PDMS cover to make irrelevant the superficial defects.

The peeling method of soda-lime and borosilicate glass has been proposed by Zheng and Lee [18]. It prescribes a straight line on the glass surface with a diamond tip which served as a point of initiation for fracture to occur. The CO_2 laser beam of power density 17 kW cm^{-2} and the scan rate 20 cm s^{-1} was then scanned over the scribed line. The molten materials are subsequently blown away by an assist gas. On the average, they obtained borosilicate glass channel depth of 55 μm and width of 300 μm. The formed groove has been found crack free but cyclic deviation along the channel and striation marks on the side of the wavy edge of the groove have been also observed.

Chung et al presented a liquid assisted CO_2 laser processing with galvanometer mirrors for for microchannel fabrication where the test sample is immersed into water [20]. They found that the high cooling rate of workpiece in water could reduce the defects of bugle, debris, cracks and scorch that often take place in laser machining in air, so achieving crack-free cutting on Pyrex 7740 glass with an average thickness of 500 μm. However, the heat-affected zone and the recast layer formation on finished surfaces may lead to defects like chipping on the top edge and cause the weakening of the material strengths cannot be definitively eliminated in underwater machining [22].

CO_2 laser ablation at 800 mJ mm^{-1} linear energy density has been used by Yen et al. to speed etchings up to 30 mm s^{-1} (25 W laser power) on 0.5 mm-thick polished pyrex and 0.7 mm-thick soda-lime glass [3]. They use multiple passes to obtain well-bonded grooves. For 0.1 mm-deep with maximum aspect ratios of 1.5 they repeat 4 times the ablated process. During laser ablation, they prevented cracking of the glass substrate by heating the glass to 300 °C. The results have shown that despite the presence of channel distortion and some debris, the CO_2 laser ablation system can provide a high-quality surface finishing with no evidence of cracks in the groove.

In general, in the complex of the bibliography analyzed in the realization of microchannels on glass samples with CO_2 laser, surface defects are observed due to the re-solidification of a small percentage of material removed. In addition, how to obtain a channel with negligible distortion it is not addressed yet.

2.1 Aim of the present work

Based on the previous considerations, this contribution proposes a first experimental study on glass machining for the fabrication of microreactor channels through the use of a CO_2 laser source. The motivation is to investigate a novel fabrication process to obtain the micro channels and to evaluate a possible competitive advantage over conventional methods by means of an expected increased efficiency.

3. Methodology

The aim of the proposed experimental apparatus is to preliminary analyze the effect of a CO_2 laser beam on glass and to study the influence of process parameters on the shape of the channel section and on the surface finish. To avoid possible surface defects due to the re-solidification and localization on the channel of machined glass, an air flow system has been realized and used in the experiments longitudinally to the channel, as described in Fig. 1.

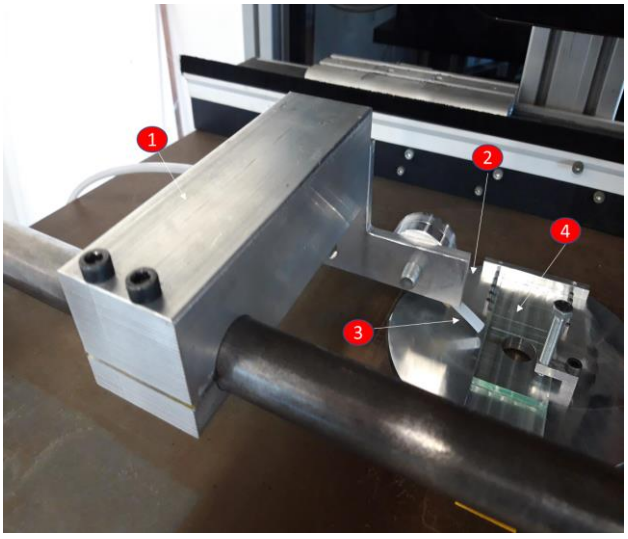

Fig. 1. Equipment realized for the experiments: 1) equipment support; 2) reference system for sample materials; 3) air nozzle placed longitudinally to the machined channels; 4) glass sample.

The methodology of investigation adopted for the present experimental study consists of three steps, described below:

1. Laser machining, executed through a continuous wave 28 W CO_2 laser source
2. Profile detection, performed through a roughness tester;
3. Channel surface, conducted with an optical microscope.

3.1 Material selection

The experiments have been performed on glass samples having the properties reported in Table 1.

Table 1. Characteristics of the material used in the experiments.

	Melting temperature [°C]	Thermal expansion coefficient [K^{-1}]	Thermal conductivity [W/m K]	Specific heat [J/kg K]	Density [kg/dm^3]
Float glass Planibel	1500	$9 \cdot 10^{-6}$	1.16	720	2.5

3.2 Experimental set-up

The process parameters investigated in the experiments are: focal distance *f*, laser power *W*, scanning speed *v* and number of passes *n*. A preliminary parameter analysis has been conducted to determine the range of variation of each parameter. Within these ranges, the values reported in Table 2 have been chosen to perform the experiments.

Table 2. Process parameters.

Focal distance (*f*) [mm]	Laser power (*W*) [W]	Scanning speed (*v*) [mm/s]	Number of passes (*n*)
190	28	5	1
195	21	50	2
199	14	75	3
200	7	100	-

4. Preliminary results

A first example of result is reported in Fig. 3 and Fig.4, where channels in terms of section shape and surface appearance is shown.

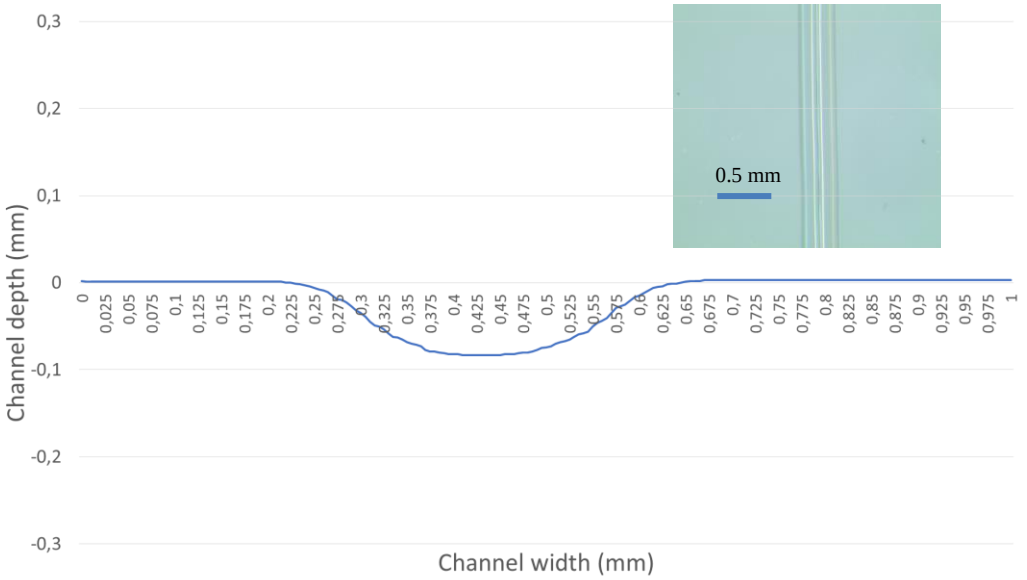

Fig. 3. Channel profile obtained with parameters set to: f=190 mm; W= 21 W; v=100 mm/s; n=1.

As can be noted by Figures 3 and 4, the channels show a regular shape with a width slightly lower than 0.5 mm and a depth of approximately 0.1 mm. No surface defects due to re-solidified glass on the channels can be detected, thus demonstrating a correct operating mode of the compressed air system. This first part of the experimental study proves that, as regards the process parameters, better results are obtained for 1 pass and high scanning speeds, as can also be noticed by the value of *n* and *v* for the best channels reported in Figure 3 and 4. In addition, better results are given when a lower value of the maximum power is employed, as for 28 W glass has been noted to fracture, with a consequently not acceptable quality of the machined surface.

The plot in Figure 3 has been obtained by CMM measurement with a stylus ball diameter of 0.3 mm. To obtain the exact shape of the channel cross section by using a profile scanner, a soft laser machining achieved by lowering the energy density has to be used because of the vertical range of the used scanner is 0.05 mm. In this experiment, it has been used a laser power *W*=7 W, a scanning speed *v*=100 mm/s and *n*=1.

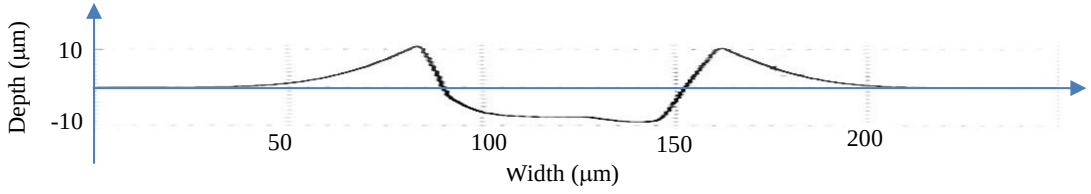

Figure 4. Channel profile obtained with parameters set to: f=200 mm; W= 7 W; v=100 mm/s; n=1.

Figure 4 shows a bottom of the channel it is almost flatter for a section of about 40 μm where the difference of elevation is about 3 μm (<1° of slope). The presence of symmetrical promontories, lateral to the channel, is highlighted, whose peaks are about 80 μm away with a profile height of P_t=19.5 μm. Compared to the previous case in Figure 3, the width of the channel is about one fifth and the depth about one quarter. Therefore, the channel aspect ratio (width/depth) is lower, i.e. 4.7 vs 4.1. This shows that the convex envelope of the profile obtained with a 0.3 mm-diameter stylus ball on a channel of similar dimensions to those of Figure 3 does not differ significantly from the real one.

Also, in this experiment, no surface defects due to re-solidified glass on the channels can be detected. This supports the hypothesis that this type of process does not produce such defects within a wide range of values of its parameters.

Once two channels have been produced on two separate glass slides, they are specularly joined with a thermal bonding process to obtain a closed channel. A very important aspect is therefore the transparency at the bottom of the channel to be able to observe properly the species mixing along the enclosed channel.

To analyses the transparency on the bottom of the microchannels, an optical device focalizes images where the glass specimen is contrasted by background to increase sharpness [5]. The aim has been to compare the high transparency of the blank glass slide with the machined surface at the bottom of the slot by a sharpness of black/white transition algorithm, which we will briefly report.

Considering a pixel's image *M*. Assuming that *L* is the value o pixel on a grayscale 8 bits image, L_b is the value of the pixel on a blank slide image and L_m is the value of the pixel on an image of the machined surface.
For each cof the image, are calculated the means M_b and M_m of, respectively, L_b and L_m obtaining two arrays: C_b=[M_{1b}, M_{2b}, …,M_{nb}] and C_v=[M_{1m},M_{2m}, …,M_{nm}], with *n* number of rows of images; μ_b is the mean of C_b values and μ_m is the mean of C_m values.

Then is evaluated the gap between each value M_i and the value mean μ_i of its row *i* (*i*=1,..,*n*), $\Delta_i=|M_i-\mu_i|$, for both the images, obtaining two arrays of differences: D_b=[Δ_{1b}, Δ_{2b},…, Δ_{nb}] and D_m=[Δ_{1m}, Δ_{2m},…, Δ_{nm}].
Defined MD_b and MD_m as the means of D_b and D_m arrays, the final transparency index T is obtained by:

$$T = 1 - \frac{|MD_m - MD_b|}{MD_b} \qquad (1)$$

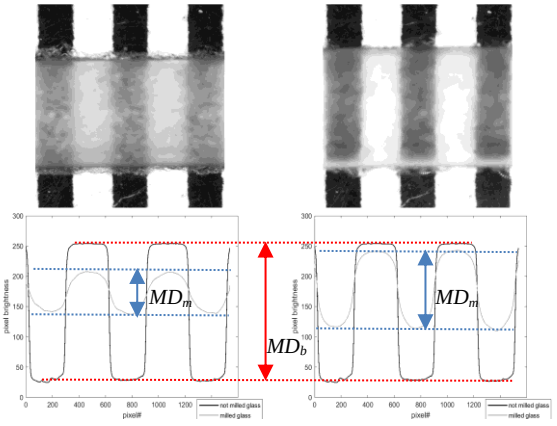

Figure 5. Transparency index (*T*) evaluation on the bottom of a micro end-milled channel, 3 mm-thin slide, reported by in reference [5].

Figure 5 shows MD_b and MD_m, where those difference impacts on the transparency index. The less difference in contrast there is between the blank and the machined slide, the more transparent the bottom of the channel. At this

stage of the process development, we have replaced the optical measurement of transparency just described with a faster measurement obtained with a Perthometer S3P, as the ratio of arithmetic mean deviation of the roughness profile R_a (to which an intensification factor of 2 is applied) and the mean peak-to-valley height, R_z. The rationale for this formula and a performance comparison between the two indices, *T* and *BT*, can be found in the reference [5]. Let *BT* be this index. The limitation in the application of *BT* is that the raw material must be transparent, so it is possible to apply it to float glass.

The roughness along the bottom of the canal has been R_a= 9 nm and R_z=110 nm, thus the BT index is 0.7 10^{-3}. This value is better the one reported in [5], which was 23 10^{-3}, although this value was obtained by a different process of processing. Therefore, the optical transparency index *T* should have a very higher value than micro end-milling.

5. First conclusions and future developments

This paper proposes a preliminary experimental analysis to examine the application of the laser machining process for the fabrication of glass microreactors. Sample materials of glass have been processed, resulting in a good quality in terms of section shape and surface finish for certain combinations of process parameters. The first results obtained for the research activity currently in progress have demonstrated that this technique could be successfully implemented for this purpose.

In order to pursue the proposed aim, further experiments could be conducted, in particular by setting the number of passes equal to 1 and exploring more combinations of high values of scanning speed and low values of laser power, as suggested by the first evidence.

Finally, as the research activity is aimed at creating microreactor channels, a further plan of experiments should be designed to investigate the quantity and level of overlap of multiple passes for obtaining a channel with a desired shape and section so that reactants flowing inside are correctly fed through inlet branches.

References

1. Lee, C. Y., Wang, W. T., Liu, C. C., & Fu, L. M. (2016). Passive mixers in microfluidic systems: A review. *Chemical Engineering Journal*, *288*, 146-160.
2. Baker, C. A., Bulloch, R., & Roper, M. G. (2011). Comparison of separation performance of laser-ablated and wet-etched microfluidic devices. Analytical and bioanalytical chemistry, 399(4), 1473-1479.
3. Yen M H, Cheng J Y, Wei C W, Chuang Y C, Young T H (2006). Rapid cell-patterning and microfluidic chip fabrication by crack-free CO2 laser ablation on glass. Journal of Micromechanics and Microengineering, 16(7), 1143
4. Galletti C, Roudgar M, Brunazzi E, Mauri R. (2012). Effect of inlet conditions on the engulfment pattern in a T-shaped micro-mixer. Chem Eng J. 185: 300-313.
5. Lanzetta M, Rossi A, Barsotti L. Micro slot milling of glass microfluidic mixers. Submitted to Precision Engineering
6. Luo, J., Pan, H., & Kinzel, E. C. (2014). Additive manufacturing of glass. Journal of Manufacturing Science and Engineering, 136(6), 061024.
7. Nayak, N. C., Lam, Y. C., Yue, C. Y., & Sinha, A. T. (2008). CO2-laser micromachining of PMMA: the effect of polymer molecular weight. Journal of micromechanics and microengineering, 18(9), 1-7.
8. Romoli, L., Tantussi, G., & Dini, G. (2011). Experimental approach to the laser machining of PMMA substrates for the fabrication of microfluidic devices. Optics and Lasers in Engineering, 49(3), 419-427
9. Dalle Mura, M, Dini, G, Lanzetta, M, & Rossi, A (2018). An experimental analysis of laser machining for dental implants. Procedia CIRP, 67, 356-361
10. An, R, Uram, J D, Yusko, E C, Ke, K, Mayer, M, Hunt, A J (2008). Ultrafast laser fabrication of submicrometer pores in borosilicate glass. Optics letters, 33(10), 1153-1155
11. Hodgson SD, Waugh DG, Gillett A, Lawrence J. High speed CO2 laser surface modification of iron/cobalt co-doped boroaluminosilicate glass and the impact on surface roughness, gloss and wettability. Laser Physics Letters, 2016, 13.7: 076102
12. Darvishi, S, Cubaud, T, Longtin, J P (2012). Ultrafast laser machining of tapered microchannels in glass and PDMS. Optics and Lasers in Engineering, 50(2), 210-214.
13. Ham, S S, Byeon, C C, Lee, H (2019). Surface characteristics of alkaline earth boro-aluminosilicate glass following single picosecond laser pulse exposure at different focal positions. Optics & Laser Technology, 113, 437-446.
14. Sugioka K, Hanada Y, Midorikawa K (2010). Three-dimensional femtosecond laser micromachining of photosensitive glass for biomicrochips. Laser & Photonics Reviews 4:386-400
15. Fogarty B A, Heppert K E, Cory T J, Hulbutta K R, Martin R S, Lunte S M (2005). Rapid fabrication of poly (dimethylsiloxane)-based microchip capillary electrophoresis devices using CO 2 laser ablation. Analyst, 130(6), 924-930.
16. Buerhop C, Blumenthal B, Weissmann R, Lutz N and Biermann S (1990) Glass surface treatment with excimer and CO2 lasers Appl. Surf. Sci. 46 430–4

17. Allcock G, Dyer P E, Elliiner G and Snelling H V (1995) Experimental observations and analysis of CO2 laser-induced microcracking of glass J. Appl. Phys. 78 7295–303
18. Zheng H Y, Lee T (2005). Studies of CO2 laser peeling of glass substrates. Journal of micromechanics and microengineering, 15(11), 2093.
19. Chung C K, Lin S L (2010). CO2 laser micromachined crackless through holes of Pyrex 7740 glass. International Journal of Machine Tools and Manufacture, 50(11), 961-968.
20. Chung, C. K., Sung, Y. C., Huang, G. R., Hsiao, E. J., Lin, W. H., & Lin, S. L. (2009). Crackless linear through-wafer etching of Pyrex glass using liquid-assisted CO 2 laser processing. Applied Physics A, 94(4), 927.
21. Da Costa E T, Santos M F, Jiao H, do Lago C L, Gutz I G, Garcia C D (2016). Fast production of microfluidic devices by CO2 laser engraving of wax-coated glass slides. Electrophoresis, 37(12), 1691-1695
22. Yan Y, Li L, See T L, Ji L, Jiang Y (2013). CO2 laser peeling of Al2O3 ceramic and an application for the polishing of laser cut surfaces. Journal of the European Ceramic Society, 33(10), 1893-1905.