Laser-Induced Plasma-Assisted Ablation (LIPAA) of Transparent Materials

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1 Introduction

Microchannels are simple, recognisable patterns created to permit a regulated flow of fluids through them. The passages usually with a diameter below 1 mm are referred to as microchannels. Microchannels have widespread applications in the development of biomedical devices. The microchannel-based lab-on-a-chip [1–3] and microreactors [4] are some of the growing applications that can be used as customised diagnostic devices. Figure 1 shows some microchannel-based applications in real life.

Microchannels are fabricated on different materials like glass [5], metals [6] and polymers [7–9]. But then again, for all intents and purposes, microchannels demand its fabrication on materials with high transparency and high optical clarity. As such, machining of transparent materials with high precision is of great significance.

2 Transparent Materials in Scientific and Industrial Applications

Transparent materials like glass, polycarbonate (PC), polyimide (PI), polydimethyl-siloxane (PDMS), polymethylmethacrylate (PMMA), etc. are the most trending transparent material. It is due to their eco-friendly nature and high transparency in the visible and near-IR spectral range [6]. Most transparent materials have exceptional resistance to chemical reactions and high thermal stability.

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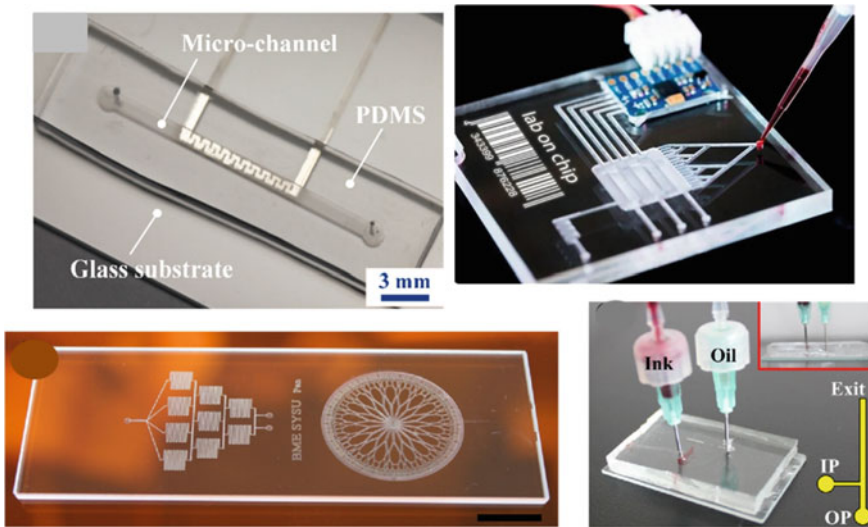e-mail: snj@iitg.ac.in

Fig. 1 Microchannel-based lab-on-a-chip set-ups [1, 2] (reproduced with permission from Elsevier)

Glass microfluidic devices provide exceptional chemical resistance, biocompatibility and optical properties, in addition to mechanical stability, which prevents swelling and deformation. After the initial focus on silicon, which is comparatively expensive and visually opaque to certain electromagnetic wavelengths, glass was chosen to build microfluidic chips, limiting its applications in optical detection [10]. Hnatovsky et al. [11] fabricated high-quality microchannels on fused silica and BK7 glass using femtosecond laser dielectric modification combined with selective chemical etching. Also, Rodriguez et al. [12] described two rapid and economic methods for fabricating microfluidic systems in glass. These glass microchannels were then applied in capillary electrophoresis where the robust surface characteristics of glass proves to be a convenient device. However, the expensive and time-consuming process for fabricating microchannels on glass and also the brittleness of glass restrict the development of glass-based microfluidic devices.

Because of the inherent impact strength, dimensional stability and optical clarity of PC, it is considered an ideal material for the medical device industry. Many researchers have reported microchannel fabrication in PC [13, 14]. Its ability to transmit light in a large range of wavelength makes it effective in visual monitoring of blood or other biological fluids. It is also used in developing Polycarbonate Urethane, (PCU) that acts as the bearing material in orthopaedic prosthesis, knee prosthesis [15], etc.

The unique properties of PDMS make it an important material for microchannels too. It is transparent and electrically and thermally insulating [8]. One can easily and affordably create microchips for biomedical purposes using PDMS-based microfluidic devices. Fujii [16] worked on PDMS-based microfluidic devices for applications,

where microreactors, microchips and hydrophobic vent valves are successfully integrated into the microchannels. Additionally, PDMS has qualities that make it a good substrate for miniature biological devices by fabricating PDMS microstructures [17].

PMMA, also known as acrylic or acrylic glass, is a transparent and rigid thermoplastic material widely used as a shatterproof replacement for glass. It is used in biomaterial applications such as bone cement, lenses, bone substitutes and drug delivery systems. Smooth walled cylindrical microchannels with diameters in the range of 8–20 μm were fabricated on PMMA substrate by Day and Gu [18]. Dudala et al., [19] and Prakash and Kumar [20] also fabricated microchannels on PMMA substrate using the CO_2 laser for microfluidic applications. Further, PMMA microfluidic device with filtration features was used to separate red blood cells from blood [21]. Microchannels in PMMA substrates bonded to porous PETE track-etched membranes are also utilised for the cytotoxicity testing of anticancer drugs in a microfluidic device [22].

3 Microchannel Fabrication Technologies

Microchannels can be generated on substrates by using conventional as well as unconventional manufacturing processes, viz. microwire moulding, imprinting, lithography, chemical etching, plasma etching and laser-based machining. These techniques are capable of machining microchannels on a variety of materials; however, some of these have certain limitations. Due to the degassed polymer spilling out of the mould, more waste is generated during microwire moulding. Additionally, the technique is expensive and time-consuming because to the complexity of the mould and its operation. Whereas, in lithography, the substrate often absorbs the developing solution during the production of microchannels. Its need for a chamber that blocks UV light also makes it an expensive operation. In the imprinting approach, the delayed mass movement and ongoing material entrapment in the metal blocks result in a non-uniform distribution of material. However, if laser parameters like wavelength, laser intensity, pulse duration, etc. are properly tuned, laser direct machining has been proven to be a promising tool. On opaque materials, laser processing has demonstrated its capacity to create neat and uniform channels [23].

4 Laser-Based Micromachining

In laser-based micromachining, the material is removed from the substrate using thermal energy that is derived from the light energy of a highly coherent stream of photons. The substrate is exposed to a laser beam, which is mostly absorbed and some of which is reflected. The energy that is absorbed is instantly transformed into heat energy, raising the temperature in the area that has been exposed to radiation. The substance melts and vaporises when the laser energy is high enough. The vapour that

follows from the vaporisation creates a recoil pressure at the melt pool's surface and causes the melt to be ejected. As such, this process works effectively with materials that are capable of absorbing laser energy.

4.1   Effect of Workpiece Material Properties

During laser-based machining, the material ablation is a thermal process. The temperature distribution is mainly responsible for the desired process outcome. The thermal and optical properties of the workpiece materials have a major effect on the laser ablation process. The important materials properties are discussed below.by lip

Optical property

An optical property of a substance called absorptivity specifies how much light may be absorbed in a material, proportion to the amount of light that is incident on it. The wavelength and direction of the incident light, the kind of material, its chemical content and physical structure, as well as the condition of the material and its surface, all affect the absorptivity value. Absorptivity (A) can be calculated as:

$$A = 1 - R - T \tag{1}$$

where R is the reflectivity and T is the transmissivity of the material.

A workpiece surface does not totally absorb the laser beam. A portion of the beam is absorbed and the remaining portion is reflected back into the environment. Increase in absorptivity increases the laser energy input into the workpiece surface. In a time period of around 10^{-13} s, the absorbed energy stimulates the free electrons, which instantly transforms into heat [24]. The heat is subsequently disintegrated through a variety of heat transmission mechanisms, including conduction, convection and radiation, but conduction has the most significant impact [25]. The heat conducted into the metal surface raises the surface temperature, assisting the laser ablation process. Lawrence [26] discovered that a high-power diode laser is more reliable than a CO_2 laser because the diode laser's wavelength is small, which increases absorption because most materials are greatly absorbing at low wavelength. Similarly, Li et al. [21] examined the effect of the absorptivity of metal on femtosecond pulsed laser ablation. It was observed that the absorptivity of the material increases with the temperature evolution with time and as such, an increase in the ablation is achieved.

Transparent materials, on the other hand, are highly transmissible to laser beams over a wide wavelength range. The laser beam passes through the transparent material without disruptions, resulting in no thermal effect on the material. Researchers from all over the world have used CO_2, excimer and Nd: YAG lasers to fabricate microchannels in transparent materials like glass [27] and polymers [18]. It was also discovered that CO_2 and excimer lasers could effectively machine the transparent polymer material because most polymers have significant absorptivity in the far IR spectrum and low UV wavelength [20].

Thermal property

The temperature distribution in a workpiece is controlled by its thermal properties. Thermal conductivity (k) and heat capacity (c) are the important thermal properties. The thermal conductivity of metals is such a thermal property that signifies its ability to conduct heat into the material. In metals, the value of thermal conductivity varies in a wide range, from a value of approximately 8 W/mK to a value of about 400 W/mK. Thermal conductivity affects the thermal gradient and peak temperature because it determines heat transfer into the surrounding material [28]. Peak temperature and temperature gradient both decrease as thermal conductivity increases. It is because of the rapid heat dissipation in high conductivity materials [29]. Benton et al. [30] studied the effect of thermal conductivity on laser micromachining of microchannels and observed that the melted and vaporised volume in the metal target increases with the increase in the thermal conductivity value of the material.

Specific heat capacity on the other hand signifies the amount of heat required to be supplied per unit mass to raise the temperature by unit degree. In metals, its value range from a lowest value of about 120 J/kgK to a highest value of 3500 J/kgK. Similar to thermal conductivity, specific heat also governs the peak temperature obtained during the laser irradiation. In reality, the specific heat of a material governs the development of the peak temperature when various materials absorb the same amount of heat. The smaller the specific heat is, the higher the peak temperature is obtained [31]. Benton et al. [30] also investigated the effect of specific heat capacity on laser micromachining of microchannels and reported that, the higher the specific heat of a metal, the lower the depth of cut for a given laser power is obtained.

From the aforementioned studies, it can be observed that depending on the various factors such as wavelength of the incident laser beam, surface roughness of the material and the temperature evolution on the surface, the metals get highly absorbing thereby causing thermal ablation on its surface. Transparent materials exhibit significant absorptivity at the far IR spectrum and low UV wavelength. No laser beam can be absorbed in the visible and near-IR spectral range making the laser machining of transparent materials in such spectral range a challenging task. It may be worthy studying the laser machining process of transparent materials in the visible and near-IR spectral range.

4.2 Motivation for LIPAA Process

The laser must be strongly absorbed by the sample when fabricating microchannels with lasers. But nevertheless, most microchannels necessitate the use of transparent materials. Transparent materials with high transparency do not absorb laser energy, making laser machining difficult. Nonetheless, ultrashort lasers can process transparent materials because they generate a highly concentrated light field that is absorbed into the transparent material via nonlinear absorption and is powerful enough to ionise any atom. Short wavelength lasers, like ultrashort lasers, can

also process transparent materials. Thus, it is rather challenging to perform laser processing on transparent materials using long-pulsed, long-wavelength lasers. However, it should be mentioned that at such condition, the LIPAA technique is capable of processing transparent materials.

5 Theoretical Background of LIPAA Process

LIPAA involves placing an extra absorbent layer below the transparent material. There are three categories for the LIPAA process depending on the absorbing layer's material (i) Laser-Induced Backside Wet Etching (LIBWE), (ii) Laser-Induced Backside Dry Etching (LIBDE) and (iii) Laser Etching at a Surfaced-Adsorbed Layer (LESAL). Under the transparent material in LIBWE, a highly absorbing solvent is being employed. It is distinguished by a low rate of etching, a smooth surface and an incubation effect [32]. Whereas, by continually adsorbing hydrocarbon by-products from a gaseous organic medium, LESAL creates a thin absorbent layer on the backside of the transparent material [33]. Likewise, a thin metal is positioned below the transparent material in LIBDE. It is distinguished by a fast etching rate and the absence of incubation effects [34]. Figure 2 shows the principal experimental set-up for the three categories of LIPAA.

LIBDE on the other hand is often denoted by the general term LIPAA. In the LIPAA process, plasma is generated on the rear side of the transparent material, assisting the ablation of the material on its rear side. In this process, the transparent material is placed above a metal target sheet with no pressure being exerted on the transparent material. The schematic representation of the LIPAA experimental set-up and its mechanism is shown in Fig. 3. A detailed flow chart describing the mechanism of LIPAA is also being shown in Fig. 4.

The transparent material is translucent to a wide range of laser wavelength. Thus, the incoming laser beam passes through the transparent material and is focused on the upper surface of the metal target sheet. A fraction of the laser energy is absorbed by the absorbing metal target sheet. The absorbed energy results in the excitation of the free electrons, which instantaneously gets converted into heat energy [24]. This heat energy then gets dissipated through various modes of heat transfer, viz. conduction, convection and radiation. Conduction plays a vital role in conducting the energy into the metal surface, thereby increasing the temperature generation on the metal target. Once the intensity of laser is high enough ($> 10^5$–10^8 W/cm^2), the temperature generated on the metal target sheet surpasses its melting and boiling point temperature. The vapour thus formed from the metal surface contains a cluster of molecules. Subsequently, the interactions of the laser beam with the vapour lead to the ionisation of the vapour molecules resulting in the formation of opaque and dense plasma. The plasma generated again interacts with the laser beam, resulting in Inverse Bremsstrahlung absorption and leads to an expansion of the plasma [1]. The plasma now has a significant thermal effect on both the transparent and the metal target sheet, thereby ablating both the materials.

Fig. 2 Principal
experimental set-up for **a**
LIBWE, **b** LIBDE and **c**
LESAL [1, 35, 36]
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from Elsevier)
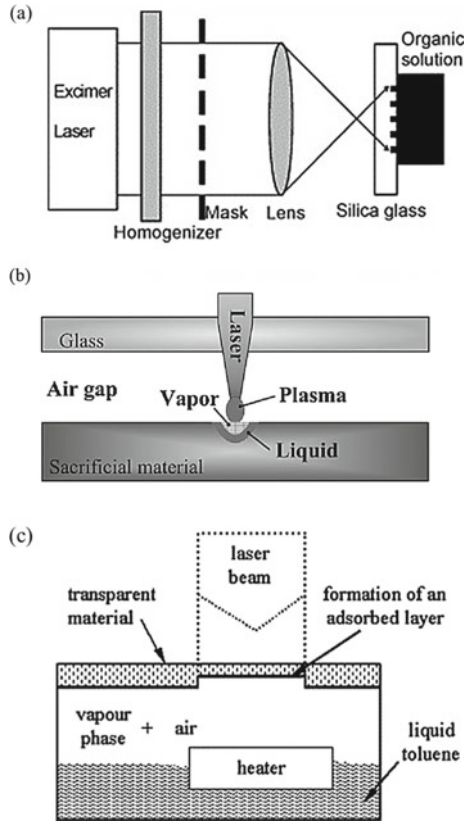
6 Fabrication of Microchannels on PC By LIPAA

Using the LIPAA process, microchannels were successfully fabricated in our laboratory on transparent polycarbonate (PC) sheet. A conventional solid-state Nd: YAG pulsed laser of 1064 nm wavelength and pulse width in the millisecond range has been utilised for microchannel fabrication. The experimental set-up of the LIPAA process is presented in Fig. 5. The transparent material is a PC sheet having a thickness of 1 mm, while the metal target taken is a sheet of copper of 1 mm thickness.

The microchannel fabrication on PC using LIPAA is carried out by varying three laser parameters, viz. pulse repetition rate (PRR), pulse width (PW) and pulse power density (PPD). The microchannel dimensions are measured and analysed form FESEM images. The FESEM images of a microchannel created by LIPAA are shown in Fig. 6 under the process conditions of 60 Hz PRR, 4 ms PW and a 3.055 MW/cm^2 PPD.

The investigation reveals that when the laser parameters increases, the channel dimensions also rise. It is because more stimulated emission occurs with a higher pulse power density. As a result, increased photon exposure on the metal sheet causes
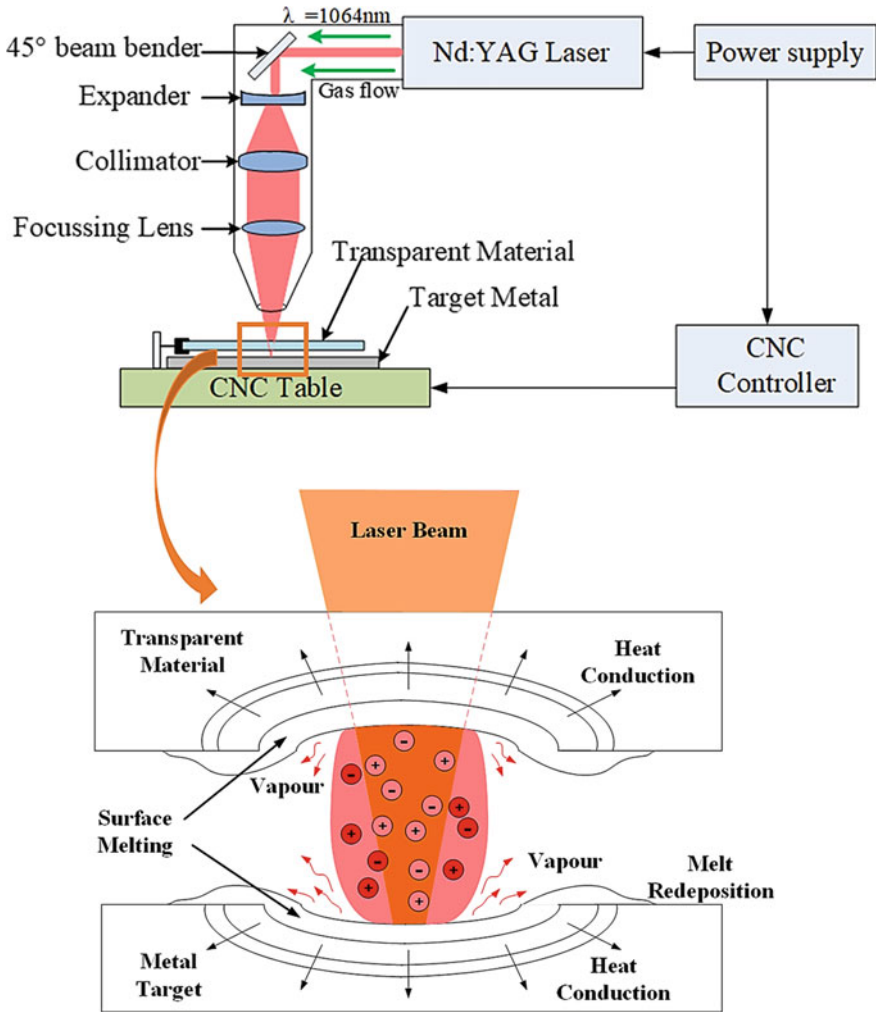
Fig. 3 Schematic representation of the experimental set-up and mechanism of LIPAA

a rise in the electron and ion number density. It is known that, generation of plasma is governed by the electron and ion density, increasing which will result in an enriched plasma generation [37]. Similar to this, the quantity of laser pulses engaging with the metal sheet grows as the pulse repetition rate does. In turn, the molecules in the vapour become more vaporised and ionised. Additionally, an increase in plasma synthesis is correlated with an increase in pulse duration. As a result, plasma formation increases along with the laser parameters. The polycarbonate sheet is thermally affected by this enhanced plasma, increasing the channel dimension.

A layer of carbon particles with some minute traces of copper and oxygen particles also gets deposited on the edge and bed of the microchannel. However, the deposited
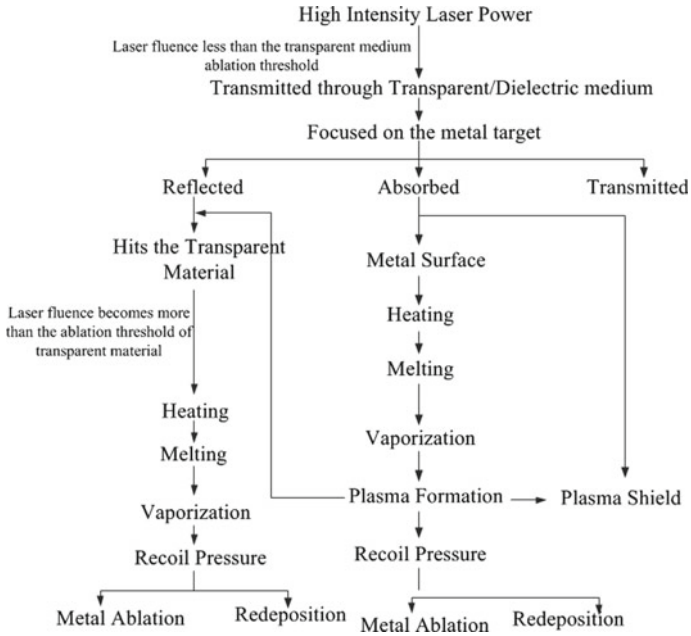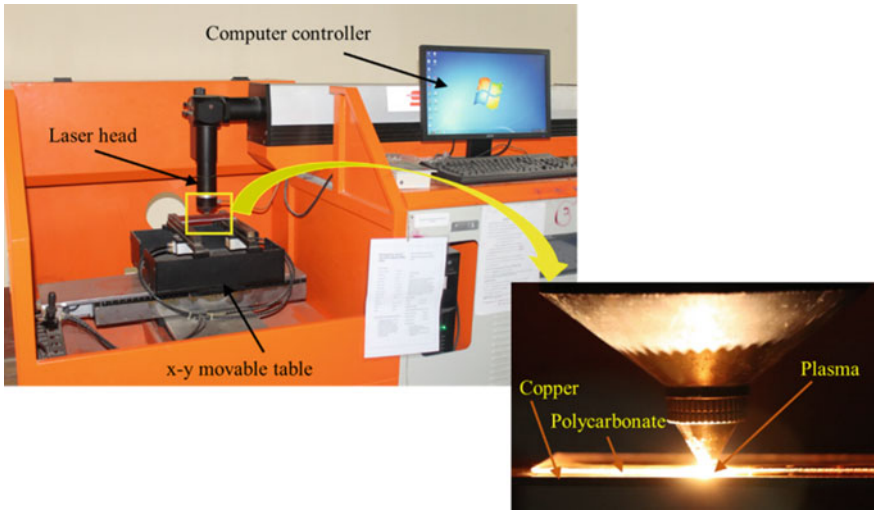
Fig. 4 Mechanism of LIPAA

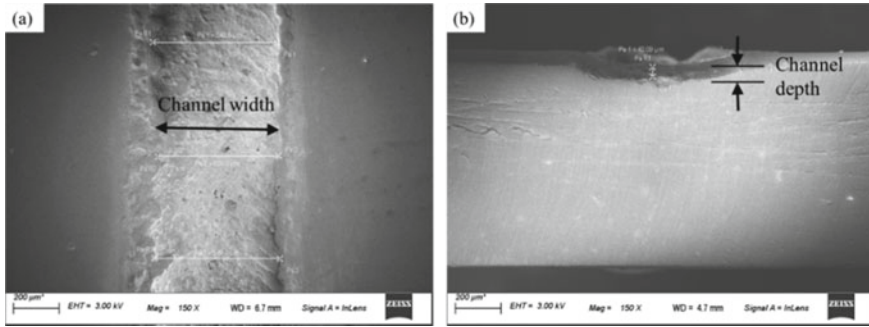**Fig. 5** Nd: YAG laser machine set-up for LIPAA process

Fig. 6 FESEM image of **a** C_{width} and **b** C_{depth}

carbon, aluminium and oxygen particles are not permanent in nature and can be cleaned ultrasonically. The FESEM images and the EDX analysis shown in Fig. 7. Prove the presence of carbon, oxygen and copper particles on and around the channel bed. It can be noticed from the figure that, the deposition of copper particles from metal target on the channel bed is not as much as that on the microchannel edge. It is because of the shock wave at the irradiated zone of the PC and copper sheet that leads to an explosive melt expansion resulting in deposition of the melted material on the channel edge.

7 Summary

Microchannels have become an indispensible part of micro technology in today's world. They allow easy transportability of devices and incorporate several processes into one device called lab-on-a-chip. Microchannels can be fabricated on a variety of materials but for all intents and purposes, microchannels demand its fabrication on materials with high transparency and high optical clarity. Most transparent materials have a very good resistance to chemical reactions, high thermal stability and high hardness and as such, find wide scientific and industrial applications. Materials like glass, PC, PI, PDMS, PMMA, etc. are the most trending transparent material. Microchannels can be generated using conventional as well as unconventional manufacturing processes, viz. microwire moulding, imprinting, lithography, chemical etching, plasma etching and laser-based machining. Laser direct machining has however been found as a promising tool if it is applied with proper setting of laser parameters, viz. short wavelength and ultrashort pulse. The laser must be highly absorbed by the material. But high transparency of the transparent material does not allow laser energy to be absorbed at longer wavelength lasers and longer pulses. Hence, it is difficult to machine transparent material by a laser. LIPAA however has the potential to process transparent materials. As such, a brief discussion on microchannel fabrication on PC using LIPAA has been presented in the current
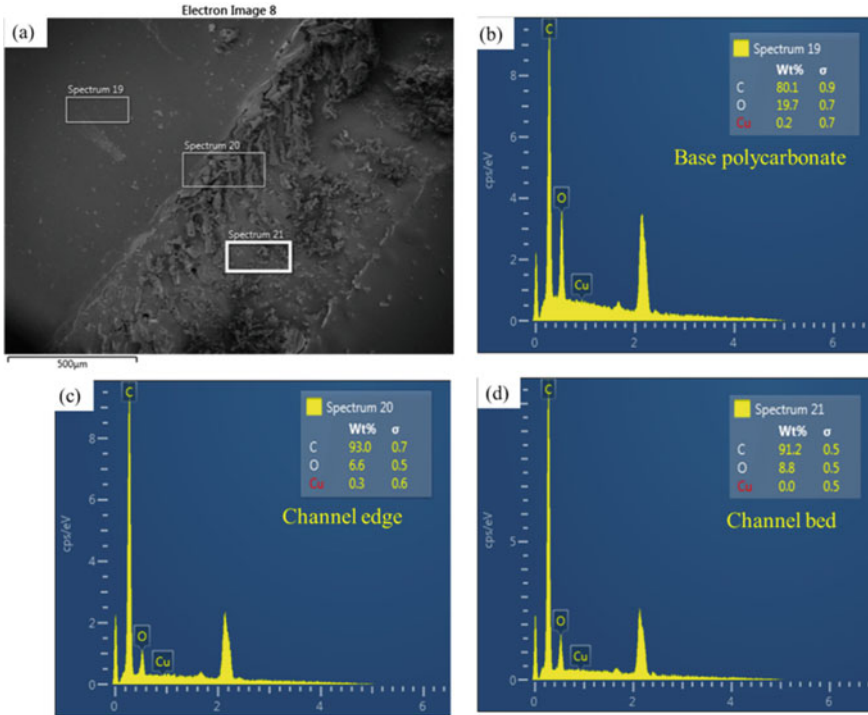
Fig. 7 EDX analysis showing the elemental composition at **a** base polycarbonate, **b** channel edge and **c** channel bed

chapter. Further, minute traces of copper and oxygen particles deposited on the edge and bed of the microchannel have also been analysed. The deposits are however not permanent in nature and can be cleaned ultrasonically.

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