Laser Assisted Fabrication of Polymer Based Microfluidic Devices

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Submitted for the degree of Doctor of Philosophy

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June 2015

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Abstract

This thesis describes the development of a laser based microwelding method for the assembly of polymeric microfluidic devices. Packaging of microfluidic devices is still a challenge for low cost applications. Some of the major challenges are: rapid and low cost bonding processes, bond reliability, ability to withstand a dynamic environment of usage and issues of biocompatibility. In this thesis, a laser microwelding technique for assembly of transparent microfluidic devices was studied. The laser welding method was developed using a thin metal film as the absorbing material at the interface of the polymer substrates. The thin metal film absorbs the incident laser radiation and enables localized melting and joining of the substrates. Laser based microwelding methods offer major advantages in encapsulation of microfluidic structures by utilizing the localized heating effect as well as the ability to reach the processing temperature rapidly resulting in a fast process. The laser based bonding method was studied for the fabrication of PMMA, PC and SU-8 microfluidic devices using a fibre coupled diode laser system operating at 970 nm. The experimental results have shown that a strong bond can be produced between the polymer substrates. Successful encapsulation of the PMMA, PC and SU-8 microfluidic channels was carried out. Fluidic tests conducted on the bonded samples showed leak-free operation of the laser assembled microfluidic devices. The results of tensile test show strong bonding between the PMMA substrates with a tensile strength greater than 5 MPa. The results of the shear strength indicate a shear strength of 8 MPa. It has been found that control of the temperature at the interface during the bonding process was a critical parameter affecting the bond quality. This was achieved by controlling the laser power and bonding time. The work demonstrates a new microwelding method for potential application in manufacturing of lab-on-chip devices and systems.
Dedication

To my family
Acknowledgements

At the outset, I would like to thank my supervisor Dr. Changhai Wang for giving me the opportunity to carry out this research work. I would like to express my gratitude to him for his patience, guidance and help throughout this study. I would also like to thank my second supervisor, Dr. Paul Record, for his help and guidance.

I would like to thank all my colleagues and friends within the Microsystems Engineering Centre and from elsewhere in the University. Special thanks to Dr Maiwenn Kersaudy, Dr Deirdre Kavanagh, Dr Yves Lacrotte, Dr Suzanne Costello, Dr David Watson, Komson Kanjanasit, Xin Jiang, Elizabeth McKeever, Stefan Wilhem, Pinar England and Dr Sumanth Pavuluri for all the useful conversations and help in fabrication and measurement work. I would also like to express my special thanks to Mark Leonard for his help and guidance in fabrication.

I would like to thank my family for their continuous support, encouragement and guidance. My deepest gratitude to my mum for being my constant source of strength and inspiration.
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<tbody>
<tr>
<td>µ TAS</td>
<td>Micro Total Analysis Systems</td>
</tr>
<tr>
<td>LOC</td>
<td>Lab-On-Chip</td>
</tr>
<tr>
<td>POC</td>
<td>Point of Care</td>
</tr>
<tr>
<td>MEMS</td>
<td>Micro Electro Mechanical Systems</td>
</tr>
<tr>
<td>RF MEMS</td>
<td>Radio Frequency Micro Electro Mechanical Systems</td>
</tr>
<tr>
<td>PMMA</td>
<td>Poly (methyl methacrylate)</td>
</tr>
<tr>
<td>PDMS</td>
<td>Polydimethylsiloxane</td>
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<tr>
<td>PC</td>
<td>Polycarbonate</td>
</tr>
<tr>
<td>PS</td>
<td>Polystyrene</td>
</tr>
<tr>
<td>$T_g$</td>
<td>Glass transition temperature</td>
</tr>
<tr>
<td>HAZ</td>
<td>Heat Affected Zone</td>
</tr>
<tr>
<td>COC</td>
<td>Cyclic Olefin Copolymer</td>
</tr>
<tr>
<td>STD</td>
<td>Sexually Transmitted Disease</td>
</tr>
<tr>
<td>PCR</td>
<td>Polymerase Chain Reaction</td>
</tr>
<tr>
<td>STCM</td>
<td>Surface Tension Confined Microfluidics devices</td>
</tr>
<tr>
<td>SERS</td>
<td>Surface Enhanced Raman Spectroscopy</td>
</tr>
<tr>
<td>FTIR</td>
<td>Fourier Transform Infrared Spectroscopy</td>
</tr>
<tr>
<td>EOF</td>
<td>Electro Osmotic Force</td>
</tr>
<tr>
<td>BCB</td>
<td>Benzocyclobutene</td>
</tr>
<tr>
<td>PA</td>
<td>Polyaniline</td>
</tr>
<tr>
<td>PVC</td>
<td>Polyvinyl Chloride</td>
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Chapter 1 Introduction

1.1 Background

Microfluidics and the development of microfluidic devices emerged due to the interaction of the bio-analytical and microelectronics disciplines with applications encompassing virtually every field of science and technology. The field of Micro Total Analysis systems (µ TAS), also called Lab-On-Chip (LOC), is a rapidly developing field and its development has had to keep in pace with the expanding application demand from the bio-analytical industry. The field of microfluidics has grown considerably and there is an unquenchable demand for rapid fabrication and assembly of microfluidic devices for low cost and disposable applications such as point of care testing and diagnostics.

Microfluidics offers several advantages that make it one of the most promising technologies for bio-analytical industry. Some of the advantages that microfluidic devices offer are less sample requirement, less reagent usage, better sensitivity, portability, low power consumption and parallelisation. These advantages make it possible to achieve ‘Point of Care’ (POC) diagnosis adding a new dimension to delivering health care. With escalating health care costs, health care providers are now focussing on preventive medicine, with an emphasis on point of care screening and early diagnosis. The increasing demand in sensor technologies will drive the microfluidics industry which is poised for a growth of $4.5 billion by the year 2022 [1]. Figure 1.1 shows a graph of the estimated growth in the sensing and microfluidics industry over the next decade. It is estimated that market growth for microfluidic sensors would outpace the growth rate of the overall medical device industry over the next decade.
The key factors for growth of microfluidics based sensors and sensing technologies will be:

1. To improve and meet challenges in fabrication of microfluidic devices in order to provide stable, sealable, low cost and high performance devices.

2. To realise new POC applications for existing clinical tests.

3. To facilitate development of novel sensors to support new applications.

The fabrication techniques for microfluidic devices have been defined predominantly by the technologies used in microelectronics and MEMS (Micro Electro Mechanical Systems). Photolithography, additive techniques for fabrication like chemical vapour deposition, physical vapour deposition, deposition involving evaporation and sputtering, Sol-Gel deposition, spin coating and wet/dry chemical etching, are some of the widely used fabrication methods [2].

Several materials have been used successfully for fabrication of microfluidic devices such as glass and silicon but in recent years polymers have emerged as low cost materials for microfluidic device fabrication due to the advantages associated with it like low cost, ease of fabrication, mechanical strength, optical transparency, surface properties and biocompatibility, although auto-fluorescence and poor chemical resistance of polymers present challenges for use in some microfluidic applications.
Polymeric materials such as PMMA (Poly(methyl methacrylate)), PDMS (polydimethylsiloxane), and PC (polycarbonate) have been widely used to fabricate microfluidic devices [3-5]. Typically microfluidic systems are composed of platforms containing sealed microfluidic channel networks. These channels are fabricated using several microfabrication techniques and then sealed with a lid. The lid and channel substrates are typically about 1mm thick while the channels in the platform can have a width and depth smaller than 100 µm.

1.2 Motivation

The requirements of packaging are growing with the miniaturization of the microsystems and also due to dynamic and varying environment of its usage. The bonded lid must provide suitable protection of the functional microfluidic structures and depending on the application it has to allow optical, electrical or fluidic interconnects. Several methods for bonding of polymeric microfluidic devices have been investigated like thermal bonding, surface treatment, solvent based approaches, ultrasonic welding, microwave welding, lamination and induction heating based welding etc. All of the bonding methods work towards establishing a good balance between the bonding strength and structure integrity. In most cases excessive bonding leads to destruction of the microstructures.

Packaging of microfluidic devices has significance in the context of determining the cost of the device. It has been established that the cost of packaging contributes significantly towards the total cost of the device thereby influencing its market and applicability [6]. A good packaging method allows for integration of several functions of a system, reducing the utilization of large and expensive set-ups. The various bonding processes and techniques used have differing drawbacks, for example in thermal bonding the substrates must be heated at or above the glass transition temperature (T_g) to achieve a strong interfacial bond. The microstructure channels could be easily deformed under this condition [7]. The solvent based bonding method relies on softening a thin layer of the material on the substrate surface and can realise appropriate bonding at a lower temperature. However, polymer flow at the interface is difficult to control and can cause issues such as channel filling [8]. The surface treatment method alters the surface properties of the microfluidic substrate by making it
more hydrophilic which is not desirable in some applications [9]. Ultrasonic bonding requires the substrates to be immersed in a solvent based ultrasonic bath which may cause contamination of the resultant devices [10]. In the induction based heating approach the heat generated in a susceptor layer is used to melt the surrounding polymer. It involves the use of a ferromagnetic material and hence could be an issue when the microfluidic devices are intended to be used in an environment involving a magnetic field [11]. Most of the bonding processes are cost-intensive and slow compared to the other manufacturing steps, thereby forming the bottleneck in mass production. Hence a rapid and low cost technique to seal and interconnect microfluidic devices is needed. A single technique that is low cost, rapid and has the ability to do both sealing and interconnecting sequentially or even at the same time, would be the ideal solution.

The focus of this project has been to investigate laser assisted bonding techniques for bonding of polymeric microfluidic devices. The polymeric materials used in the study are SU-8, PMMA and PC. Laser transmission welding has been identified as a technique for sealing and packaging of polymer microfluidic devices. Laser processing is of particular interest due to non-contact processing, localized heating, the possibility of sealing and interconnecting simultaneously, fast manufacturing and good control over the time and temperature window for processing. Laser welding is a well-established technique and has been used in steel, aircraft and automobile industry for hardening, melting and welding of extremely small components to very large components [12]. Laser transmission welding is of particular interest for sealing of microfluidic devices due to some of its unique advantages including localized welding, minimal heat affected zone (HAZ), single side access to areas that are difficult to reach, precise control of the processing temperature thereby minimising the damage to the surrounding structures and heat sensitive elements. It is also a rapid and flexible technique suitable for manufacturing of low cost disposable devices. In the laser joining approach a laser beam is absorbed usually by an opaque substrate to produce a temperature change to cause the polymer to melt at the interface and then to produce a fused bond. In the earlier studies an opaque (absorbing) substrate was used in fabrication of microfluidic devices. The strength of polymer to metal bond was poor when a bulk metal substrate was used and this type of bonding procedure is not suitable for devices requiring optical transmission through a microfluidic device. Laser transmission welding of injection moulded PMMA and COC (Cyclic Olefin Copolymer) biochip with selective removal of a carbon based absorbing layer has been
studied by Singh et al. [13]. The absorbing carbon layer was deposited over the entire surface of the microfluidic substrate and removed selectively to avoid deformation of the channel structures during the assembly process. The problems in the existing methods provide motivation for further research.

1.3 Thesis objectives

The aim of the thesis was to develop a laser assisted bonding technique for sealing of polymeric devices. The device design chosen has been for micro capillary electrophoresis application as it is the most widely used technique for bio-analytical applications. The polymeric materials used for the study are SU-8 epoxy polymer, PMMA and PC. The possibilities and limitations of the laser based bonding method for the sealing of polymer microfluidic systems are investigated. A novel method of heating and joining of substrates using patterned metal absorber lines has been investigated.

The main objectives of the thesis work were:
1. In depth literature review of the existing techniques for fabrication and bonding of polymeric microfluidic devices in general, but especially the SU-8 and PMMA polymer based microfluidic channels.
2. Fabrication of SU-8 polymer micro channels and development of a low temperature bonding, exposing and transferring technique for fabrication of micro-capillary electrophoresis devices.
3. Design and development of laser assisted methods for bonding of the polymeric devices for thermoplastic polymer (PMMA) based microfluidic channels.
4. Laser based fabrication of PMMA microchannels for micro-capillary electrophoresis applications.
6. Analysis and evaluation of bond characteristics.
7. Study of the fabrication and laser bonding process to bond PC based microfluidic devices.
8. Laser bonding of SU-8 polymer microchannels using PMMA cover and reliability studies of the bonded devices.
The contributions of this thesis are related to the design, fabrication and characterisation of a novel laser assisted bonding method for sealing of polymeric microfluidic devices. This method may provide a basis for the development of a cost-effective and rapid method for manufacturing of polymer based microfluidic devices.

1.4 Thesis outline

Chapter 2 contains the literature review on fabrication and assembly of polymeric microfluidic devices. A detailed background of various substrates, fabrication and assembly methodology used in microfluidic technologies with particular emphasis on polymeric materials is presented.

Chapter 3 details the design and fabrication of SU-8 polymer based microcapillary electrophoresis devices. Fabrication of SU-8 microchannels for electrophoresis applications is detailed with inclusion of design, processes, fabrication facilities and processing parameters. A low temperature bonding, exposure and transferring technique for fabrication of stand-alone multilayer SU-8 micro capillary electrophoresis devices is presented.

Chapter 4 presents the design and fabrication of PMMA polymer micro-capillary electrophoresis devices using laser micromachining and bonding methods. The physics of laser welding with modelling studies of laser transmission welding of PMMA thermoplastics is presented. Laser bonding of the micromachined channels using laser heating of the patterned metal absorber layer is discussed. The parameters influencing the bonding and characterization of the bond formed are presented.

Chapter 5 presents the design and fabrication of PC polymer micro-capillary electrophoresis devices using laser micromachining and bonding methods. The modelling studies of laser transmission welding of PC thermoplastics are studied. Laser bonding of the micromachined channels using laser heating of the patterned metal absorber layer is discussed. The parameters influencing the bonding and characterization of the bond formed are presented.
Chapter 6 discusses the results of bonding dissimilar polymers (thermoplastic to thermoset) using the laser assisted method. In this chapter laser bonding of SU-8 microchannels using a PMMA capping substrate is detailed. A study of laser bonding of surface modified PMMA to SU-8 channels is also discussed. The results of leak tests and the comparison of this method of bonding to the established techniques are presented.

Chapter 7 presents the main conclusions from the previous chapters. The contributions of the study are summarised. A final section on future work describes the potential areas of improvement.
CHAPTER 2 Literature Review

In this chapter the background literature of the microfluidic systems and the manufacturing methods especially for the assembly is reviewed. The advantages and the challenges associated with some of the common techniques used for the sealing of polymeric microfluidic systems are described. The principles of laser based joining method, their current impact and its suitability as the alternative technique for the joining of polymeric microfluidic systems are also discussed.

2.1 Overview of microfluidic systems

Microfluidics deals with the behaviour, precise control and manipulation of fluids that are geometrically constrained to a small dimension, typically to a sub-millimetre scale. Microfluidics lies at the interface of engineering, biology and chemistry. The significant growth in the field of study of microfluidics over the last two decades can be attributed to the rapid progress in the miniaturisation of devices due to the advances in microfabrication techniques. At the same time there was a need for miniaturisation of the analytical techniques in the chemical and biology industry. Merging of the bio-analytical and the microelectronics disciplines can be considered as the birth of microfluidics. The initial research in this area was carried out at Stanford University in 1979 [14], which involved the development of a gas chromatograph on a silicon wafer. In 1977, IBM developed the ink jet printer nozzles [15]. These two devices, which are now legendary, provided huge impetus to the field of microfluidic device fabrication and application. Though the initial development in microfluidics was primarily focused on the miniaturisation of the analytical techniques, over the years that followed the field of microfluidics has grown enormously with applications extended to several areas of science and technology. In analytical chemistry, the microfluidic devices have been used for chemical monitoring [16]. They have also found applications in biotechnology industry such as chips for environmental monitoring [17], for analysing DNA, proteins, and cells [18]. Microfluidic systems are also used for drug delivery and diagnostic applications (e.g. blood sugar or alcohol tests) in the medical field. They are also used in applications in the automobile and space technologies wherein high pressure systems are used in micro-engine and micro-rocket devices [19] and for high precision spacecraft thrusters. Application of microfluidics has also been developed in the areas
of RF-MEMS, optics and physics [20]. It is now possible to integrate electrical
components, optical components, pumps, mixers, filters, reaction chambers and
detectors onto a single platform to provide micro total analysis systems (μTAS) and lab-
on-a-chip (LOC) device to do complete analysis and processing [21]. The application of
microfluidics is ever expanding and this is due to the various advantages associated with
it. Some of them are:

1. **Portability**: This offers the usability of microfluidics based devices outside the
   laboratory. In many health care applications like diagnosis of Sexually Transmitted
   Diseases (STD), testing can be performed at the point of care [22].

2. **Decrease in sample size**: The sample size used in the microfluidics devices are in
   the order of nl (nano litre). For example, in the case of blood samples less invasive
   methods of collection can be used thereby reducing patient discomfort.

3. **Decrease in reagent consumption and waste**: It has been seen that with
   microfluidic devices there is a decrease in the reagent consumption as the sample
   size is small. This is of importance when expensive reagents are used.

4. **Faster separation and analysis**: In comparison with the conventional techniques
   the microfluidics techniques offer faster analysis. For example, DNA amplification
   using PCR (Polymerase Chain Reaction) has been reduced from hours to minutes
   due to the reduced volumes leading to faster heating and cooling cycles [23].

5. **Low power consumption**: The device size is typically in the range of µm and also
   the use of novel inexpensive materials has reduced the power consumption. The use
   of paper based microfluidics has been reported for low cost disposable applications
   [24-25].

6. **Parallelisation**: This feature enables several assays to be multiplexed or run in
   parallel on a single chip [26].

7. **Improved efficiency**: The efficiency of the analytical techniques is greatly
   improved in the microfluidic devices because of the increase in the surface/volume
   ratio.

In addition to the advantages of what microscale devices can offer, the fluid physics
also changes at the microscale and several of these phenomena are very useful. Laminar
flow of fluids, surface tension and diffusion are some of the fluid physics useful for the
microfluidic applications. Figure 2.1 shows one of the applications of laminar flow in a
microchannel. In this example, an interface between two liquids is created using laminar flow, exposing the cell to two different environmental conditions.

Figure 2.1 Application of laminar flow in a microchannel. Schematic of a chip layout with three inlets and one outlet (a, b). Fluorescent image of an epithelial cell exposed to membrane permeable Mitotracker Green FM and Mitotracker Red FM fluorophores using laminar flow (c). Migration of the fluorophores after 2.5 hours showing the intermixing of mitochondria (d) [27].

Diffusion and surface tension are some of the phenomenon that have found application in the microscale. Figure 2.2 shows the H-Filter developed by Paul Yager et al. [28], which uses diffusivities to separate species in a stream.

Figure 2.2 Application of diffusion in a microchannel. Schematic of a H filter chip designed to enable convenient extraction of small molecules from complex fluids into simpler buffer streams [28].
Surface tension is now a commonly used phenomenon in microfluidics for the development of 2-D platform that demonstrates several advantages in comparison to 3-D microfluidic devices such as, reduction in power consumption, ease of introduction of fluids into the microchannels without the need for micropumps and the control of flow rates and the like. 3-D microfluidic devices typically includes multiple layers of channels having three-dimensional paths and networks. Some of the interesting applications of surface-tension-confined microfluidic devices (STCM) are paper based bio-assays, urine analysis, chemical analysis and chemical imaging by combining with Surface Enhanced Raman Spectroscopy (SERS) and Fourier Transform Infrared Spectroscopy (FTIR) [29].

Microfluidic devices have enabled novel applications in many fields. These applications have been possible due to advantages of miniaturisation, as mentioned earlier. In addition to the possibilities of what miniaturisation offers, microfluidics enables to study phenomena that are difficult to replicate in large-area devices. For example, microfluidic channels can approximate the flow conditions found in capillaries thereby leading to accurate modelling of fluid flow and greater understanding of biology [30]. Table 2.1 lists some of the areas of application of microfluidics.

**Table 2.1** Potential applications of microfluidic devices.

<table>
<thead>
<tr>
<th>Area</th>
<th>Application</th>
</tr>
</thead>
<tbody>
<tr>
<td>Genomics and proteomics</td>
<td>Gene expression assays, cellomics, Immunology, DNA fingerprinting, forensics, integration of fluidics with DNA arrays [31,32,33,34,35]</td>
</tr>
<tr>
<td>Environmental monitoring</td>
<td>Analysis of environmental contamination [36]</td>
</tr>
<tr>
<td>Biological defense</td>
<td>Early detection and identification of pathogens [37]</td>
</tr>
<tr>
<td>Clinical analysis</td>
<td>Rapid analysis of blood and bodily fluids, enzymatic assays, electro-chemical detection, and cell counting [38,39,40,41]</td>
</tr>
<tr>
<td>High throughput screening</td>
<td>Toxicological assays [42]</td>
</tr>
<tr>
<td>Biomedical devices</td>
<td><em>In vivo</em> monitoring for disease diagnosis and devices for drug delivery [43,44]</td>
</tr>
<tr>
<td>Implantable devices</td>
<td>Studies on EOF and laminar flow in small channels [45,46]</td>
</tr>
<tr>
<td>Systems for the study of fundamentals of fluid flow</td>
<td>Detection of single molecules [47,48]</td>
</tr>
<tr>
<td>Systems to study small amounts of sample</td>
<td></td>
</tr>
</tbody>
</table>
However, in the past few years there has been a rising demand for LOC devices that can provide Point of Care (POC) diagnostics for quick testing and analysis of biological samples. The advantages of the POC testing namely, result at the site of testing, quick and immediate diagnosis enabling early treatment of patients, make it an exciting proposition. The added advantage of the POC devices include the possibility of taking healthcare to people, especially to people in vulnerable areas who have limited access to healthcare facilities. One of the challenges of the POC systems has been to provide results with sensitivity and specificity levels better than that of the conventional laboratory techniques. Another challenge of the POC devices is to keep the cost to the consumer low so as to enable wider use and applicability. The manufacturing techniques along with materials used play an important role to determine the cost to consumer. The LOC devices that are low cost, simple to use, portable with high sensitivity and specificity, are the need in the microfluidics industry in general and to the field of Bio-MEMS in particular. Most of the research today is orientated in this direction. Some examples of the current POC systems include glucose, cholesterol, drug, HIV, pathogen, ovulation, pregnancy and fertility tests [9]. With the cost of the microfluidic devices largely depending on the material and fabrication process, low cost fabrication techniques like reel-to-reel fabrication are desirable to bring the cost down. The following section details some of the widely used materials for the microfluidic device fabrication with particular emphasis on the polymeric materials and the associated fabrication methods used for device fabrication.

2.2 Manufacturing of microfluidic systems

Microfluidic systems are typically made up of two parts. One part consists of the microfluidic platform containing the channel and other elements. The second part is the lid that is used for the sealing of the device. The manufacturing principles of the microfluidic systems are similar, with the channels fabricated on one of the platform and the device sealed using a capping substrate. The method of fabrication depends largely on the material used, which is further dependent on the function of the microfluidic device. The method of sealing also varies with the material used with most sealing methods being directed towards achieving fast, low cost, reliable and stable bond/seal. In the following sections a brief review of the materials used for the
fabrication of the microfluidic devices is described. In-depth review of the methods used for the sealing/bonding is also described in the subsequent sections.

2.2.1 Substrate materials

The early techniques used for the microfluidic device fabrication are identical with those used in the Integrated Circuit (IC) fabrication [49]. Silicon has been the choice of material in most of the early microfluidic device fabrications as it is a standard substrate material used in IC fabrication. Silicon microfabrication processes are well established and its surface chemistry can be modified to be similar to glass by oxidising silicon. Several microfluidic devices have been fabricated using silicon. The use of silicon substrate material enables the integration of electronics and circuitry. Along with its favourable electrical properties, single crystal silicon also has an excellent mechanical property, which enables the design of micromechanical structures. A large number of micromachining techniques have been developed to structure silicon substrates [49]. Silicon is one of the most common substrate materials for the microfabricated sensors. However, the application of silicon in microfluidics has some disadvantages; optical detection from the device is difficult due to opaque substrate material and the application of high electric fields requires thick insulation layers. Thermal growth of silicon dioxide on top of channels can be time intensive for high voltage applications [50]. The silicon microfabrication is also time consuming and expensive.

Glass exhibits attractive dielectric and optical properties. Glass and its types have been widely used for the microfabrication of microfluidic devices as it is a well-established fabrication technique. The earlier microfluidic devices were made of glass. Glass is an ideal material for microfluidic chip fabrication as its material properties are well known. A number of micromachining techniques, such as isotropic wet etching or anisotropic dry etching, have been developed to structure glass. Glass also comes in different forms like quartz, fused silica and borosilicate glass. Since glass is transparent to visible light, it is particularly suited for devices using optical detection principles. Glass is also chemically inert and suitable for high-temperature applications. However, the micropatterning of glass is difficult in comparison to silicon microfabrication. Wet etching produces round structures and smaller features are difficult to fabricate. Inlet drilling with glass is fragile and is prone to breakage. Wet etched structures on glass are
not the most suited for fluidic applications, but it is possible to have almost circular channels by bonding two chips together [51]. Reactive Ion Etching (RIE) of glass is expensive and has its own limitations such as appearance of surface defects and roughening [52].

Over the recent years, polymers have taken a significant role as substrate materials for microfluidic devices. Polymers are organic materials consisting of macromolecules. Depending on its cross-linking and the glass transition temperature ($T_g$), polymers are categorised into elastomeric materials, duroplastic materials and thermoplastic materials. The parameter $T_g$, which is one of the most important parameters, has its origin in the molecular behaviour of the polymer material. When a polymer is heated up to a certain temperature, the energy of motion of parts of the polymer chain becomes large enough to overcome the intramolecular friction leading to significant softening of the material. This temperature is called the glass transition temperature or $T_g$ and can be measured as a more or less distinct bend in the curve of the specific heat capacity versus temperature. Below $T_g$ the polymer behaves like a rigid and solid material; beyond $T_g$, the material becomes soft and flexible. Heat distortion temperature (HDT), another important parameter, is described as the maximum temperature for structural use of the material. The polymer cannot be exposed to any mechanical stress beyond the HDT as it would lose structural integrity. A third parameter relevant for polymers is the decomposition temperature (TD), which is defined as the temperature at which the polymer chains are broken leading to irreversible damage and deformation. Elastomeric materials have weakly cross-linked polymer chains and often regain their shape after stretching once the stress is removed. Elastomers such as PDMS are typically used for low volume manufacturing of the microfluidic devices due to their low cost and ease of handling. However, the PDMS polymer does swell in the presence of some organic solvents, which is a challenge and novel materials are being developed to overcome some of the limitations of PDMS [53]. Duroplastic polymers also known as thermosets cross-link and undergo irreversible chemical reaction upon curing or exposure to radiation. These polymers are rigid and do not soften before their decomposition temperature. The most widely used thermostet polymers for microfluidic applications is SU-8 negative photoresist. Polyimide, a thermostet material, is also used frequently for the fabrication of flexible microelectrodes and as a substrate material due to its durability and high temperature stability characteristics. Thermoplastics have weakly linked polymer chains and can be softened and molded at temperatures between their glass transition and
decomposition point. There is no curing of the polymer between these temperatures and
the polymer can be molded to take any shape. However, these polymers undergo some
extent of thermal degradation depending on how many times the polymer is remoulded.
PMMA and Polycarbonate (PC) are examples of thermoplastics that are used for
microfluidic device fabrication.

The material properties of polymers are very much suited for microfluidic application.
For example, properties like high strength, good insulation, chemical inertness, optical
transparency and surface properties can be used to advantage in several microfluidic
applications. However, certain properties like autofluorescence, solvent instability and
thermal properties set some limitations. Some polymeric materials are self-fluorescent
at low temperatures, which may affect the sensitivity of microfluidic applications with
fluorescent detection system. Polymers also have poor chemical resistance to solvents,
which may set some limitation on its applications. Despite some disadvantages,
polymers have recently emerged as the material of choice for microfluidic device
fabrication. The surface properties of polymeric materials can be changed to suit certain
needs, for example, in micro-capillary electrophoresis the surface charge density plays a
key role in the electro-osmotic flow. The surface charge can be selectively increased by
treating the polymeric substrate. One of the notable advantages of using polymers is that
most of them are biocompatible, which makes them suitable for use as microfluidic
devices for biomedical applications. Some of the polymers that have been used for
device fabrication are polycarbonate (PC), polymethylmethacrylate (PMMA),
polyamide (PI), PDMS, SU-8 photo resist etc. Each of these materials has different
properties and hence different advantages and disadvantages. Table 2.2 provides an
overview of some of the properties of silicon, glass and the different types of polymers
[53]. The choice of material used depends on the application and environment of usage.
Table 2.2 Characteristics of common materials for microfabrication [53]

<table>
<thead>
<tr>
<th>Properties</th>
<th>Silicon</th>
<th>Glass</th>
<th>Technical thermoplastics (e.g. PMMA, PC, PEEK)</th>
<th>Thermoset polymers</th>
<th>Elastomers</th>
</tr>
</thead>
<tbody>
<tr>
<td>Microfabrication</td>
<td>Easy-medium</td>
<td>Easy-medium</td>
<td>Easy</td>
<td>Medium</td>
<td>Easy</td>
</tr>
<tr>
<td>Structuring processes</td>
<td>Wet and dry etching</td>
<td>Wet etching, photostructuring</td>
<td>Injection molding, hot embossing, thermoforming, laser ablation</td>
<td>Casting, lithography, etching</td>
<td>Casting</td>
</tr>
<tr>
<td>Possible geometries</td>
<td>Limited, 2D</td>
<td>Limited, 2D</td>
<td>Many, 2D, 3D</td>
<td>Mostly 2D, 3D possible</td>
<td>Mostly 2D, 3D possible</td>
</tr>
<tr>
<td>Assembly</td>
<td>Easy</td>
<td>Medium</td>
<td>Easy</td>
<td>Medium</td>
<td>Easy</td>
</tr>
<tr>
<td>Interconnections</td>
<td>Difficult</td>
<td>Difficult</td>
<td>Easy</td>
<td>Easy</td>
<td>Easy-medium</td>
</tr>
<tr>
<td>Mechanical stability</td>
<td>High</td>
<td>High</td>
<td>Low-medium</td>
<td>High</td>
<td>Very low</td>
</tr>
<tr>
<td>Temperature stability</td>
<td>High</td>
<td>High</td>
<td>Low-medium</td>
<td>Medium</td>
<td>Low</td>
</tr>
<tr>
<td>Acid stability</td>
<td>High</td>
<td>High</td>
<td>High</td>
<td>High</td>
<td>High</td>
</tr>
<tr>
<td>Alkaline stability</td>
<td>Limited</td>
<td>High</td>
<td>High</td>
<td>High</td>
<td>High</td>
</tr>
<tr>
<td>Organic solvent stability</td>
<td>High</td>
<td>Medium-high</td>
<td>Low-medium</td>
<td>Medium-high</td>
<td>Low</td>
</tr>
<tr>
<td>Optical transparency</td>
<td>No</td>
<td>High</td>
<td>Mostly high</td>
<td>Partly</td>
<td>High</td>
</tr>
<tr>
<td>Material price</td>
<td>Medium</td>
<td>Medium-high</td>
<td>Low-medium</td>
<td>Medium</td>
<td>Low</td>
</tr>
</tbody>
</table>

Special fabrication processes such as hot embossing, injection moulding, laser machining or stereo lithography have been developed to structure polymer materials even in the micrometer range. Polymeric materials have the potential for rapid manufacturing and are used to meet the cost of fabrication. The manufacturing turnaround time is 2 hours compared to up to 80 hours for the glass based devices [54]. The use of polymeric materials enables to have high throughput, cheap and disposable devices, which is suitable for the microfluidic applications.
2.2.2 Polymer microfabrication for microfluidics

Polymer microfabrication is a relatively new field in microfabrication. Several fabrication techniques have been developed to meet the requirements of polymeric microfluidic devices. There are various fabrication methods used for the polymer materials and the choice of fabrication methodology primarily depends on the properties of the materials. Depending on the application, there are several polymers that can be used. The fabrication method used commonly takes advantage of one or several properties of the polymers. Polymer fabrication processes are broadly classified into direct and replication fabrication techniques. Direct fabrication techniques create structures directly onto polymers by using the same techniques as in silicon and glass microfabrication. Replication techniques are methods that apply master or stamp to transfer the structure onto the polymers. These methods take advantage of the low forming temperature of most polymers and are in essence an extension of the manufacturing methods for macroscopic structures with the processes adapted for micropatterning.

2.2.2.1 Direct microfabrication techniques

Direct microfabrication techniques are often used to transfer pattern structures directly onto the polymers. Some of the direct polymer microfabrication techniques are lithography, laser ablation, polymer surface microfabrication, polymer etching and 3D printing.

Lithography
In lithography a radiation sensitive polymeric layer is deposited on top of a substrate and exposed with light through a mask. Silicon and glass can be used as the substrates and different structures can be patterned on the polymer film. The image is developed and the pattern obtained is either the positive or negative of the mask depending on the photo-properties of the polymer. The light that is used can be UV, X-ray or ion radiation. Mostly UV light is used for exposure. The masks that are used to transfer the pattern are normally made of glass, nevertheless polymeric films are also used. Polymer masks have the advantage of being low cost in comparison to glass. The disadvantage of using polymer masks is that it is not possible to get very sharp features in comparison to glass masks.
Good mechanical strength and uniform polymer layer deposition are some of the properties required for successful polymeric patterning using lithography. Cross linked polymers are found to have greater strength in comparison to unlinked polymers. Therefore, negative photoresist materials are preferred instead of positive ones as they lack the mechanical, thermal and chemical durability required. X-ray and Ion lithography are more expensive techniques but can be used to define very fine structures. Ion beam lithography is done by computer controlled pixel by pixel exposure which eliminates the use of a mask altogether.

Lithography technique for patterning of polymer photoresist produces near vertical side walls and features can be well defined on the polymer material. Negative epoxy photo resist SU-8 is the most widely used polymer that is patterned lithographically for microsystem applications. The SU-8 polymer is mechanically strong, chemically inert, biocompatible and optically transparent, which makes it a suitable material of choice for microfluidic device fabrication. It is often used to produce multilayer and high aspect ratio structures. The aspect ratios that have been obtained using UV exposure are up to 190:1 [55]. It is also possible to fabricate thick SU-8 layer and a thickness of over 2 mm has been achieved [56]. Despite several advantages SU-8 can be difficult to process due to the generation of high internal stresses in the film leading to structural deformation upon its release from the carrier substrate. The very high strength and rigidity of cured SU-8 make it impossible to remove after curing, which can also prove to be a disadvantage in some applications. The SU-8 polymer has emerged as one of the most widely lithographically patterned polymeric material for microfluidic / BioMEMS applications. In this thesis work, the SU-8 polymer has been used to fabricate microfluidic structures for fabrication of free standing microelectrophoresis devices and also for the development of a novel laser bonding technique for fabrication of polymeric microelectrophoresis devices. Typically, the photoresist is coated on a substrate (e.g., silicon/glass) and a high energy UV light is irradiated through a patterned mask directly to the top of the coated photo resist, a so-called front side exposure. The photo-cured polymer is then developed to yield simple 2D structures. There have been several variations to the conventional UV lithography like deep X-ray lithography [57], proton beam writing [58] and electron-beam lithography [59] that have been utilised to create high-aspect ratio microstructures as well as sub-micron scale structures in SU-8.
Various novel fabrication methodologies have been investigated for the fabrication of 3D microstructures using SU-8. The use of reversal UV print method has been demonstrated by Hu et.al [60] for the fabrication of 3D SU-8 micro and nanostructures. In this method the SU-8 polymer is coated on a surface treated and patterned glass mold and then transferred onto various substrates using reverse UV imprint method at low temperature and pressure. Figure 2.3 shows the procedure of this method. The UV curable polymer is first spin coated onto a glass mold (Figure 2.3 (a)), which is then brought in contact with a substrate at low temperature and moderate pressure (Figure 2.3(b)). After initial adhesion of the SU-8 polymer to the substrate, UV exposure is done through the glass mold to enable cross-linking and hardening of the polymer (Figure 2.3(c)). The glass mold is removed and the molded SU-8 structures are left on the substrate (Figure 2.3(d)).

Fabrication of multi-level channels using SU-8 having spacing between 400 nm-10 μm has been demonstrated. The control of the surface energies of glass and substrate surface which is different from glass is reported to be the key factor in the successful transfer and adhesion of the SU-8 pattern.
Inclined UV exposure

It is a method for the fabrication of microstructures by varying the inclination of the UV beam. In inclined UV lithography the incident UV light angle is not perpendicular to the wafer but at an angle. This inclined exposure is achieved by tilting the substrate or the UV source. Fabrication of 3D microstructures such as embedded channels, angled cylinders, bridges, cones using SU-8 has been demonstrated by Han et al. [61] using this method. Figure 2.4 shows the schematic of the inclined UV exposure based fabrication method. Figure 2.5 shows the images of the developed 3D structure.

![Figure 2.4 Schematic diagram of 3D oblique microstructure fabrication [61].](image)

(a) Exposure process                                    (b) PR structure

The refractive index (n) of SU-8 at UV exposure wavelengths is approximately 1.67 [62]. The maximum inclined angle in SU-8 microstructures using inclined UV exposure is limited to 36.78°, which is (\(\sin^{-1} (1/1.67)\)), as given by the Snell’s law. Immersion lithography technique was suggested by Hung et al. [63] in order to overcome this limitation. In their work, they used a photomask directly in contact with coated SU-8 substrate and the SU-8/mask was immersed in glycerol solution to achieve larger angle inclined microstructures. Microstructures with inclined angles up to 70.8° have been demonstrated.

![Figure 2.5 Images of the 3D oblique microstructures (Scale bar 100 µm) [61].](image)
**Back-side UV exposure**

In thick photoresist layers the UV exposure dose difference between the top and bottom parts of the photoresist layer is very large. This results in a non-uniform UV exposure of the photoresist layer. The top surface is over exposed while the bottom part is underexposed leading to wider top and narrower bottom microstructures in photoresists like SU-8. Back-side UV exposure through a transparent substrate such as glass has been used as a method to fabricate microstructures with relatively wider bottom and narrower top structure. The use of this method has been demonstrated by Kim et al. [64] so as to create a hollow micro needle array. Inclined UV exposure was also reported with back side exposure to fabricate inclined microstructures. Figure 2.6 shows the schematic of the various UV exposure schemes for the fabrication of microstructures.

![Figure 2.6 Schematic of the various UV exposure schemes for the fabrication of microstructures.](image)

(a) Normal front side exposure (b) Normal reverse side exposure through transparent substrate (c) Inclined front-side exposure (d) Inclined reverse side exposure through transparent mask [66]

**Other lithography techniques**

Sato et al. [65] developed a fabrication process to demonstrate a completely enclosed SU-8 T shaped microfluidic channel with built-in mesh using bonding and lift-off of a sacrificial layer. The shape of the mesh was determined by the number of exposures and
the angle of UV exposure. Tall, high aspect ratio micro-column structures of SU-8 have been fabricated by Yoon et al. [66] using the multiple inclined back-side UV exposure technique. Drawing lithography is another variation of the conventional lithography technique developed for the fabrication of tall (high aspect ratio > 100:1) micro needles using SU-8 [67]. In this work the soft baked SU-8 polymer was mechanically pulled/drawn to create tall pillars. The structures were then cured and it was drawn the second time to break the tips. Nickel electroplating was then carried out on the thermally cured SU-8 to create high aspect ratio micro needles. This particular technique can be applied to most thermosetting polymers as well. Mask-less lithography techniques wherein UV exposure is realised using Light Emitting Diode (LED) has been demonstrated by Guijt et al. for manufacture of a simple SU-8 pattern, which was used as a template for the fabrication of PDMS microfluidic channel [68]. In this work a commercially available UV LED was used and the light was collimated with the use of a pinhole, a plastic tube and a microscopic objective. The collimated UV light was then exposed onto the surface of the SU-8 to pattern it. Holographic interference lithography is another maskless lithography technique that uses interference fringes of multiple collimated interfering laser beams as the exposure source for the photoresist layers. 3D photonic crystal made of SU-8 for the visible spectrum was patterned using this method [69]. Liquid photo-polymerisation is a special case of lithographic patterning. Here a mould is placed on top of the substrate and is filled with polymer solution. The solution of the polymer is photo-polymerised through a mask and the pattern is transferred. This method eliminates the need to use spinable materials and is useful for thick structure fabrication. The choice of materials is large but this technique is not widely used in fabrication of microfluidic devices since the structures obtained are large. It is also difficult to define the cavity thickness and fabrication of thin structures are a challenge [70]. Gray scale electron beam lithography has been used as a one-step process for the fabrication of SU-8 components for use in microphonics [71]. In gray scale lithography the incident beam energy is controlled by passing it through gratings. Varying this energy across the resist gives rise to structures of varying depth.

Stereolithography is another technique that can be used for obtaining 3D structures. In this method the structure is created by exposing a liquid resin locally to two high intensity light beams. The beam used is a single split beam or two laser sources. The individual intensity of the beam does not cause any change in the polymer. However, at the point of meeting of the two beams the intensity is high enough to cross polymerise
the photoresist. Embedded 3D structures can be fabricated using this technique [72]. One of the advantages of this technique is that structures can be built directly around other materials. The long cycle time for each device is considered to be one of the drawbacks of this method. Some other lithographically patterned polymers are polyimide (PI), AZ9260, AZ4562 and photo definable BCB and Teflon type polymers.

**Laser ablation**

Laser ablation is a method that uses high energy laser light to remove material from the bulk material [73]. This method eliminates the need for development as it is required in standard lithography procedure. The pattern creation is done by using a high power laser to ablate away small portions of the polymer. Laser energy and pulse width can vary widely depending on the properties of the materials. The spot size of the laser defines the amount of material removed and the spot size can vary from sub micrometer to millimetre. The laser source is generally fixed with the wafer being moved to enable the pattern generation. The design can be transferred directly onto the polymer without the need for a mask. This method can be used to make a quick prototype model. The typical lasers used for this method are pulsed lasers. Each laser shot ablates some material depending on the material type, laser wavelength and intensity. The ablated material (debris) is removed by suitable means such as vacuum suction. Nevertheless, the accumulation of debris increases the surface roughness. The surface properties of the polymer also change and the roughness of the surface of the microchannel is found to be more in comparison to that of the other techniques. This is advantageous in some fluidic applications that need more charged walls, which support electro-osmotic flow better than normal polymer surfaces but is a disadvantage when it comes to channel enclosure as the surface becomes uneven during ablation [73]. Poly(methylmeth acrylate) (PMMA), polycarbonate (PC), polyimide (PI) are some of the polymeric materials patterned using this method. PMMA is a widely used material for microfluidic device fabrication and continuous wave CO₂ laser has been used to pattern it extensively [74]. Femtosecond lasers have been reportedly used for micromachining of transparent materials. Zhang et al. reported high aspect ratio micromachining of PMMA using ultrafast lasers [75]. Figure 2.7 shows the schematic of the ultrafast laser micromachining setup.
Figure 2.7 Schematic of ultrafast micromachining setup [76].

The mechanism of laser ablation depends to a large extent on the type of laser used. Continuous wave laser removes material primarily by melting. This creates a large heat affected zone around the removed material. The melted material has to be removed as fast as possible in order to avoid redeposit on the material. In nanosecond pulsed lasers the material is removed by melt expulsion driven by vapour pressure. For picosecond/femtosecond lasers the pulse duration is very small and the energy is concentrated over a small region. The material absorbs the energy completely taking it past the melting temperature into vapour phase. The material is removed by direct vaporisation. The heat affected zone is very small and very fine sharp features of the resolution of 1 µm are formed with the use of a pulsed laser beam. Figure 2.8 illustrates the interaction of the continuous wave, nanosecond and pico/femtosecond laser pulses with the material during the ablation process [76]. The black region indicates the heat
affected zone while the blue line shows the shock waves created by the laser pulses.

Figure 2.8 Laser material interactions for different types of lasers [76].

**Plasma etching**

Plasma etching is another direct method used to etch channel structure on the polymer. In this method the plasma of a diluted gas containing highly reactive gas radicals is used to preferentially react with the organic material creating channels or holes. Various microstructures can be realised using a suitable mask. The etch rate depends on the polymeric material as well as on the etching tool used. The etching profile is usually isotropic and the masking material used is sputtered or evaporated. Plasma etching as a method for mass-producing microfluidic devices in polymer substrates has been described by Rossier et al. [77].

**3D printing**

3D printing also known as additive manufacturing is a method of making 3D solid objects from a digital file. In this type of additive manufacturing an object is created by laying down successive layers of material until the entire object is created. Each of these layers can be seen as a thinly sliced horizontal cross-section of the final object. The printing technology used in 3D printers differs although most of them are additive differing mainly in the way layers are built to create the final object. Selective Laser Sintering (SLS) and Fused Deposition Modelling (FDM) use softening of material to
produce the layers. Curing of photo active resin one layer at a time using UV laser or another source is another method of printing. Several microfluidic devices have been realised using this technique. Erkal et al. [78] used this method to fabricate 3D printed device for electrochemical detection enabling a module-like approach to the experimental design. Paydar et al. [79] developed an interconnecting method using 3D printing for microfluidic devices eliminating the need for adhesive.

2.2.2.2 Replication techniques

Replication techniques transfer a master design onto the polymer of interest. This method of fabrication is collectively referred to as soft lithography. Some of the methods for replicating microfluidic chips are casting, hot embossing and injection moulding. The techniques differ from one another based on the processing conditions, polymer behaviour, master material requirements, replication tools and fabrication time. The chip replication time from the master and the throughput time are some of the important parameters of the fabrication techniques. The advantage of replication techniques for microfabrication is the short throughput time, which is good from the commercial aspect. PDMS, PMMA, PC and PS are some of the polymers that have been widely used for microfabrication using this method.

Casting

Casting, which is also known as moulding is a widely used replication method. In this method a polymer solution of low molecular weight is poured on top of a previously made master. The polymer is then cross-linked by curing. Curing of polymer is normally done by heating or at room temperature. Then the polymeric material is separated from the mould. The process is relatively easy and hence there is no need for any special tools. PDMS is the most used polymer for this method. The master is usually made of material that has poor adhesion to the polymer. For PDMS microfabrication using casting, SU-8 material has been widely used to make the master. The SU-8 master is coated for easy separation and to extend its lifetime. Several materials can be used as the master and it can be reused several times, which is an advantage for low cost mass production. One of the advantages of casting method in comparison to other replication methods is that it allows the integration of functional components such as ports, spacers etc. This process is not only suitable for micro patterns but can also be used for nano patterns [80]. One of the drawbacks of this process is the possible change in structure of the material during curing and release.
Figure 2.9 shows the casting process for the fabrication of PDMS channel using an SU-8 master [81].

![Casting process for the fabrication of PDMS channel using SU-8 master](image)

Figure 2.9 Casting process for the fabrication of PDMS channel using SU-8 master [81].

**Hot embossing**

Hot embossing also called as imprinting is a method that can be used for patterning of large variety of polymers. It is a very versatile replication method, which uses high pressure and elevated temperature to create microstructures like channels in the substrate. All thermoplastic materials are suitable for embossing due to their low forming temperature. In this method the polymer substrate is heated above the glass transition temperature and is patterned by pressing the master to the polymer sheet. The pressure is applied until the sheet is cooled to below its glass transition temperature ($T_g$) and the master is released. This method is most suitable for mass production. Thermoplastic polymers like PMMA and PC are fabricated using this process [82, 83]. In this method the replication time is reduced and is suitable for commercial purpose but the manufacturing of the master is time consuming, which increases the throughput time. The drawback of this technique is the possibility of filling of narrow gaps and that only simple structures can be realised using this technique. Multilayer structures are difficult to fabricate and integration with other structures is also difficult on embossed substrates. Figure 2.10 shows the process steps for replicating a metallic micromold by the hot embossing method using PMMA [84].
In injection moulding a molten polymer is injected into an enclosed cavity containing the master. Once the polymer has cooled down it can be separated from the master. This method requires higher temperature than casting or embossing as the polymer has to be completely melted. Pressure is also used to ensure complete moulding. Polymers that have been micro-injection moulded are mostly PMMA, PS and PC. The fabrication process yields better structures but the polymer needs to be melted and deformations can occur in the moulded structure. Polymer shrinkage has to be small to be able to reproduce structures accurately. The master and the polymer should be made of material that tolerates high temperature and pressure. Good heat transfer of the material is also required for fast cooling. This technique is used to replicate low aspect ratio structures and also when the cycle times are very short [85]. Table 2.3 gives a comparison of the three replication methods for fabrication of microstructures [86].
Table 2.3 Comparison of the replication methods for fabrication of microstructures [86]

<table>
<thead>
<tr>
<th>Process</th>
<th>Hot Embossing</th>
<th>Injection Moulding</th>
<th>Casting</th>
</tr>
</thead>
<tbody>
<tr>
<td>Materials</td>
<td>Thermoplastic Durable thin films</td>
<td>Thermoplastic Duroplastics</td>
<td>Elastomers (PDMS)</td>
</tr>
<tr>
<td>Tool costs</td>
<td>Low-medium</td>
<td>High</td>
<td>Low</td>
</tr>
<tr>
<td>Cycle time</td>
<td>Medium-long (3-10 min)</td>
<td>Short-medium (0.3-3 min)</td>
<td>Long (min-h)</td>
</tr>
<tr>
<td>Forces</td>
<td>High (kN)</td>
<td>High</td>
<td>No forces</td>
</tr>
<tr>
<td>Temperature</td>
<td>Around T (100-200°C)</td>
<td>Above melting (150-400°C)</td>
<td>Room temperature</td>
</tr>
<tr>
<td>Automation</td>
<td>Little</td>
<td>Yes</td>
<td>Little</td>
</tr>
<tr>
<td>Geometry</td>
<td>Planar, eg., wafers, plates</td>
<td>Bulk variety, spherical</td>
<td>Planar</td>
</tr>
<tr>
<td>Min. dimensions</td>
<td>nm (nanoimprint)</td>
<td>some 10µm</td>
<td>nm</td>
</tr>
<tr>
<td>Aspect ratio</td>
<td>50 for small areas, 5 for wafer scale</td>
<td>50 for small areas, 5 for large areas</td>
<td>About 1</td>
</tr>
</tbody>
</table>

Direct fabrication techniques can provide structures similar to those of silicon or glass. The range of structures and geometries possible with this technique is enormous. Most of the direct fabrication techniques are suited for research applications. The replication techniques are mostly suited for volume manufacturing and where the throughput time is important. Although the polymer processing techniques are enormous the best fabrication methodology depends on the material chosen for fabrication and the feature resolution required. The possibilities for development of fabrication processes for polymeric materials are enormous with prime focus on development of low cost microfluidic platforms.

2.3 Bonding methods for microfluidic systems

Bonding or sealing of microfluidic devices is considered as a first step in the assembly process. Bonding is a very important and challenging aspect of fabrication of polymeric microfluidic devices. The bonded cover must provide suitable protection of the functional microfluidic structures making them leak proof and depending on the application it has to allow optical, electrical or fluidic interconnects. There are several methods that can be used to achieve bonding. The method used must not cause blockage of the microfluidic channels or change their wall properties. Several applications such as micro-capillary electrophoresis rely on uniform channel wall charge for uniform Electro-Osmotic Force (EOF). Hence, bonding methods ensuring uniform sidewalls of single material are preferred in microfluidic devices. If there is use of additional material, it must be benign to the fluids and materials used in order to cause minimum
interference in the performance of the device. Bonding of polymeric materials does not necessarily produce hermetic sealing because polymers are usually permeable to gases. Tsao has reviewed the various bonding methods for thermoplastic polymers [87]. A review of bonding methods for sealing of polymeric microfluidic devices elucidating the advantages and challenges is described in the following sections.

2.3.1 Adhesive bonding

Adhesive bonding is a type of wafer level bonding technique that uses adhesives as the bonding material. This method for channel enclosure is done by pressing the channel chip against a flat substrate that has fluidic inlets drilled through it. This requires completely flat surfaces of the structural and sealing substrates. Pressure, heat and UV light may be used to establish the bond. One of the primary challenges of using adhesive bonding technique is in preventing channel blockage due to flow of the adhesive during bonding. In most commonly used adhesive wafer bonding processes, a polymer adhesive is applied to one or both of the wafer surfaces to be bonded. After joining the wafer surfaces, pressure is applied to force the wafer surfaces into close contact. The polymer adhesive is then converted from a liquid or viscoelastic state into a solid state. This is typically done by exposing the polymer adhesive to heat or ultraviolet light. Figure 2.11 shows the typical steps involved in the SU-8 based adhesive bonding process [88]. This method of bonding is widely used to bond SU-8 and Benzocyclobutene (BCB) based devices.

![Diagram of adhesive bonding process](image)

Figure 2.11 a) Spinning of SU8-5 photoresist on a dummy wafer, b) contact imprinting of SU8-5 photoresist by attachment of cover wafer on the dummy wafer, c) detachment of cover wafer d) alignment and contact, e) wafer-to-wafer bonding [88].
One of the main advantages of adhesive wafer bonding is the relatively low bonding temperature. Adhesive bonding is a comparatively flexible, robust and low-cost process. But concerns such as limited temperature stability and limited data about the long-term stability of many polymer adhesives in demanding environments need to be considered. Also, adhesive wafer bonding does not provide hermetically sealed bonds. Wetting of the surfaces by the liquid or semi-liquid polymer adhesive is critical in adhesive bonding. The cleanliness of the surfaces is important for establishing a strong bond [89]. The drawbacks of this technique are channel filling and non-uniformity in the application of heat or pressure resulting in unbonded areas. The alignment of the wafers is also crucial in ensuring good bond. To improve bonding with adhesive technique additional structures have been used to hinder adhesive flow into the microchannels [90]. In their work Liming Yu et al [88] have used SU-8 as adhesive for wafer level bonding of microfluidic devices. The bonding was carried out between 100°C and 200°C at a pressure of 1000 N using a wafer bonding system. Santeri and Sami [91] have in their work demonstrated the possibility of achieving bonding at low temperature (75°C). Multilevel structures using SU-8 have been bonded successfully. Their work also incorporated the use of moat channels to reduce unbonded areas in the bonded samples and to increase the yield. Figure 2.12 shows the free standing adhesive bonded SU-8 microfluidic device after release from the carrier substrate.

Blanco et al. [92] in their work have reported bond strength of 8 MPa for an adhesive wafer bonded 3D microfluidic device. It has been demonstrated that this technique can be used to bond several combinations of materials like silicon and Pyrex. Adhesive bonding of SU-8 to
PMMA using spinnable PMMA as the adhesive layer has been demonstrated by Bilengburgh et al. [93].

2.3.2 Solvent bonding
This is a method which uses solvent to dissolve the top layer of the polymer. The structural polymer substrate and cover are pressed together and bonded during evaporation of the solvent. Solvent selection and time for successful bonding has to be optimised for each polymer separately. This is a low temperature method and is inexpensive if alignment is not required. However, the drawback of this method is that it can result in channel filling. To avoid this, sacrificial channel filling with paraffin wax that is removed after bonding via the inlets has been demonstrated [94]. The time of exposure is also crucial to avoid deformation of the polymer structure and channel filling problem. C.H. Lin et al. developed a method for sealing PMMA based microfluidic systems at room temperature using the solvent based bonding approach [95]. They reported a bond strength of 3.8 MPa using this technique. Figure 2.13 shows a capillary electrophoresis device bonded using this method. This technique is most suitable for PMMA based devices.

![Figure 2.13 PMMA based micro capillary electrophoresis device bonded using solvent bonding [95].](image)

2.3.3 Bonding using sacrificial channel filling material
In this method channel enclosure is made based on a technique wherein the channel sealing is made before opening the channels. The sacrificial material is then removed to open the channels.
This method is usually performed with direct microfabrication technique. The method has the disadvantage of longer removal time. The material selection plays a very important role in this method. The advantage of this method is that channel blocking by the sealing layer can be avoided. Wet chemical release of the sacrificial material is commonly done using a developer solution or solvent. Microfluidic devices made of parylene are mostly manufactured using this technique. SU-8 polymer based microchannels bonded using sacrificial removal methods have been demonstrated. This is done by selectively exposing the different layers of the channel to different dosage. This method has been realised using E-beam, UV and laser exposures [96-98]. However, the selectivity between the exposed and unexposed SU-8 is not very good.

### 2.3.4 Thermal bonding

Thermal bonding of PMMA based microfluidic system has been reported by Chen et al. [99]. In this method the PMMA substrates are sandwiched between glass plates and the entire assembly is put into an oven under vacuum pressure. As the temperature of the oven is held above glass transition temperature it leads to fusion of the two surfaces creating a tight seal. The higher the temperature, the greater is the strength of the bond due to the increased molecular connections on cooling. However, thermal degradation occurs at higher temperature causing channel distortion and loss of feature acuity. The bond strength was determined to be 153 kPa using this method. This is a widely used method to seal PMMA devices due to the ease of procedure and short bonding times. Figure 2.14 shows a thermal bonded PMMA device [100].

![Thermal bonded PMMA microfluidic device leak tested using red food dye diluted with water](image)

In order to reduce the effect of temperature during the thermal bonding process several methods have been proposed. Kelly and Woolley [101] clamped a blank PMMA layer and one with microchannels together and put the setup into boiling water. The bonded system had a failure pressure of 130 kPa. The entire system could stay hydrated...
throughout the assembly process, which could be useful for incorporation of membranes into microfluidic systems. Another method of using in situ polymerisation to join PMMA layers has been demonstrated by Chen et al. [102]. The bonding temperature using this method was 95°C, which is lower than the glass transition temperature of PMMA (105°C). Further research to reduce the impact of thermal heating and the need to use localised heating and bonding led to the use of ultrasound, microwave, induction heating and lasers to bond polymeric substrates.

### 2.3.5 Ultrasound bonding

The use of ultrasonic vibrations to enable low temperature bonding of MEMS devices was studied by Kim et al. [103]. The principle of ultrasonic welding is the transmission of high frequency sound vibrations to the bond area. This melts the plastic just enough to create a bond. The processing temperature and pressure are much lower than other conventional techniques making it a rapid and low temperature bonding technique. This method does require a precise control of the processing parameters like co-planarity to produce a sealed device. In 2010 Zhang et al. [104] developed a thermally assisted ultrasonic bonding method for PMMA microfluidic devices. In this method a hot plate was used to preheat the polymer substrates to room temperature (20°C-30°C). A low amplitude ultrasonic frequency was applied to generate heat at the interface. The interface was heated to $T_g$ but the bulk temperature of the substrates was well below $T_g$. This caused minimum deformation to the microstructures. Yi Luo et al. [105] studied heat assisted and solvent assisted ultrasonic bonding of thermoplastic polymers without the need of an energy director. The bonding times for the heat assisted and solvent assisted process were reported to be 30 s and 20 s respectively. The tensile strengths for the heat assisted ultrasonic bonding and solvent assisted ultrasonic bonding processes were 0.95 MPa and 2.25 MPa. Figure 2.15 shows the schematic of the heat assisted ultrasonic bonding system.
The ultrasound bonding system typically consists of a power supply, an actuator and a converter booster stack horn. The actuator generates the stroke and welding pressure. The converter consists of piezoelectric elements that convert electrical energy to mechanical energy. The converter is normally attached to booster that amplifies the ultrasonic vibration. The booster is connected to a horn that directs the ultrasonic wave to the work piece holding the sample. Ultrasonic bonding causes localised joining at the contact interface. Ng et al. [106] have shown the use of ultrasound bonding to join connectors using PMMA. Their work showed a reduction of dead volume in the connectors and also the ability of the connectors to withstand fluid flow tests. However, it was shown that a sleeve structure has to be incorporated to restrict the weld zone and to prevent blockage.

2.3.6 Microwave bonding
Microwave technology offers a method for packaging microfluidic systems. The microwave based sealing method has a preferential heating capability coupled with non-contact delivery of energy which makes this method highly desirable. This technology relies on the interaction of microwave energy with a microwave absorbing material like a conductive polymer. Conductive polymers such as polyaniline, polypyrrole and polythiophene have been used as a new class of microwave absorbing susceptor [107]. An extensive review of microwave welding of thermoplastics with details on microwave susceptible implant materials such as metals, carbon black and polyaniline
Microwaves can create plasma for cleaning and activating the surfaces of polymer substrates, or heat up the conductive parts of the system making the surrounding material melt thereby creating a bond. A microwave based polymeric microfluidic sealing approach using thin metal layers has also been reported [109]. A solvent based polyaniline was widely used as the absorbing layer due to its good patternability. Yussuf et al. [110] have demonstrated microwave welding of a PMMA polymer microfluidic device using the solvent form of polyaniline. The bonding time for this method was reported as 15 s at 300 W of microwave power with bond strength of 1.18 MPa. This method of bonding requires fabrication of channels for holding the conductive polymer polyaniline. Figure 2.16 shows the fabricated microfluidic and polyaniline channels fabricated using a CNC controlled micro-milling machine for microwave bonding.

This method was further improvised by using a screen printing technique to deposit the polyaniline [111]. This eliminated the need to prepare the channels for polyaniline as it could be directly printed along the microfluidic channels. Figure 2.17 shows the SEM images of cross section of a sealed PMMA microfluidic device.
Holmes et al. [112] have further extended this technique and used a thin layer of polyaniline delivered through capillary action between two surfaces to create a microlayer that would absorb the microwave radiation thereby increasing the interfacial temperature to induce bonding. It has been reported that defect free seals were obtained with breakage tests requiring in excess of 1kN of force.

Microwave bonding by surface activation of the polymers has been demonstrated by Hui et al. [113] using PDMS slabs. The PDMS slabs were surface activated in a microwave plasma chamber at a power of 30 W for 30-60 seconds and sealed irreversibly to form microfluidic devices that could sustain fluid flow of 42 psi without leakage. The plasma chamber is a commonly available product and this method of plasma treatment is shown to be a low cost alternative to the more expensive plasma treatment techniques. However, the plasma treatment time is shown to affect the bond quality with longer treatment duration leading to failure of the formed bond. The schematic of the microwave plasma chamber bonding system is shown in Figure 2.18.
Microwave heating for bonding was also achieved using metal as the susceptor layer. This was shown by the work of Lei et al. [114] where PMMA to PMMA and PMMA to silicon bonding was achieved by covering the material with gold. The gold layers (0.1 µm) were melted on both surfaces causing further melting of PMMA. These surfaces were brought together during the bonding process to form a bond at the interface. Due to the problems with the surface non-uniformity of the PMMA substrates a tin-lead pre-form of 50 µm thickness was used for the PMMA-silicon bond. The bonding was done at 30 W of applied power for 180 seconds. For bonding of PMMA-PMMA a power of 10 W for 120 seconds was used. The bond formed was shown to hold the substrates together under an applied tension greater than 7 kg/cm².

2.3.7 Induction bonding

A joining technique based on induction heating principle has been used to weld and bond polymeric materials. Induction based joining process is a non-contact electromagnetic process allowing precise heating through the use of the specially designed coils offering a localised method of heating. Induction heating of a material occurs when an induction coil, which generates a magnetic field, is placed near the
material and heats a susceptor. The efficiency of various susceptors such as iron, iron oxide and stainless steel has been investigated by Schwatrz [115] and Benatar et al. [116]. Due to the highly directional method of heating, induction heating based bonding technique can be applied to very small areas of work-piece without affecting the surrounding areas and the heat is delivered only to the area where it is needed. It is also possible to make continuous joints by moving the coil along the joint. Early work using this method of heating has been for packaging of MEMS. Yang et al. used Ni/Co spacers and a Sn/Pb solder to bond silicon to silicon and silicon to glass [117]. A spacer height of more than 40 µm was manufactured with use of 10 µm thick solder. A coil was used to generate an alternating magnetic field at 100 kHz, which caused the spacer to heat up and melt the solder thereby creating a bond between spacer and lid. The bond strength achieved between the silicon wafers has been reported to be higher than 18 MPa. It has been seen that thick and round shaped susceptor designs are better suited for heating as it allowed the current to flow more efficiently. The requirement of thick susceptor layers can be a limiting factor for this technique. Suwanwatana et al. [118] in their work have used induction heating to bond thermoplastic composites. In their work a 250 µm thick matrix of polymer and nickel granules was used as the susceptor and was heated by an alternating magnetic field at the frequency of 2.25 MHz. The generated bonds had strengths of more than 20 MPa. The influence of particle size [119] and oxidation effects [120] on the hysteresis heating has also been studied. It has been shown that a matrix with nanoscale nickel particles exhibited a better heating rate than a matrix composed of the same volume of nickel but with microscale particles.

Knauf et al. [11] in their work have shown the use of low frequency induction heating for sealing of polymeric microfluidic devices. In their work PMMA microfluidic channels are sealed with the use of induction heating. The bond strength reported is 590kPa. The susceptor was a 5 µm thick layer of evaporated Ni covering the whole surface on one plate. In the second design a 7.5 µm thick Ni foil was placed in selected area and was clamped between the plates. One of the challenges of this bonding technique is to manage the heat dissipation to prevent distortion of the microfluidic structures. This technique involves the use of a ferromagnetic material and hence could be an issue when the microfluidic devices are intended to be used in an environment involving magnetic field. Figure 2.19 shows a bonded microfluidic device tested with a coloured ink.
2.3.8 Laser bonding

Laser transmission welding has been identified as a technique for sealing and packaging of polymer microfluidic devices. Laser processing is of particular interest due to the fact that it offers a cost-effective alternative in comparison to traditional methods involving adhesives [121]. Decreased mechanical stress, non-contact processing, localised heating, the possibility of sealing and interconnecting simultaneously, fast manufacturing and good control over the time and temperature window for processing make laser welding an exciting possibility.

Laser welding is a well-established technique and has been used in steel, aircraft and automobile industry for hardening, melting and welding of extremely small components to very large components [12]. The initial work on laser welding of thermoplastic polymers was carried out in the early 1970’s, wherein a CO2 laser was used to join 100µm thick polyethylene film using an overlap joint [122]. Renaissance came in 1990’s with the development of stable, high power diode lasers in the wavelength range of 800-1100 nm with power levels up to 200 W. The diode lasers with their small size, high reliability and efficiency make them simple to handle and easy to integrate into an equipment system. Their high electrical-to-optical output efficiency of about 50% and low service needs reduce the running costs in comparison to the conventional high power lasers [123]. Several other types of lasers such as Nd-YAG, disc lasers and fiber lasers are being used for polymer processing. Laser transmission welding is of particular interest for sealing of microfluidic devices due to some of its unique advantages. These include localised welding, minimal heat affected zone (HAZ), single side access to areas that are difficult to reach, precise control of the processing temperature thereby minimising the damage to the surrounding structures and heat sensitive elements. The
mechanical stress to the surrounding is also small with practically no formation of residues or particle generation. It is also a rapid and flexible technique suitable for manufacturing of low cost disposable devices. Laser polymer welding does offer certain advantages in comparison to welding by traditional methods like hot tool welding, vibration welding or ultrasonic welding. This is due to fact that the traditional methods are less sensitive to polymer material processing. However, laser polymer welding requires special characteristics like suitable optical properties, thermal and mechanical properties. These properties significantly affect the outcome of the welding process.

**Basic polymer welding process**

In the laser joining approach, a laser beam is absorbed, usually by an opaque substrate, to produce a temperature change to cause the polymer to melt at the interface and then to produce a fused bond. Figure 2.20 shows a schematic description of the transmission welding process [121]. The technique of laser welding involves bringing two layers in contact. A laser beam goes through the first layer, which is mostly transparent and gets absorbed by the second layer, which is opaque. The second layer absorbs the laser light due to chemical dyes or pigments called as ‘absorbers’ in the material. These absorbers can be integrated into the polymer or deposited over it. The most commonly used absorber is carbon black. Recently, liquid transparent IR absorber called ‘clear weld’ has been used to join polymers by adding it to the surface before welding [124]. Due to the energy absorption at the interface during the welding process the material is therefore heated up at the interface. This causes local fusion of the materials due to the increase in temperature thereby creating a bond.
In most of the earlier studies an opaque (absorbing) substrate was used in fabrication of microfluidic devices. The strength of polymer to metal bond was poor when a bulk metal substrate was used and this type of bonding procedure is not suitable for devices requiring optical transmission through a microfluidic device. Laser transmission welding of injection moulded PMMA and COC biochips with selective removal of a carbon based absorbing layer has been studied by Singh et al. [13]. The absorbing carbon layer was deposited over the entire surface of the microfluidic substrate and removed selectively to avoid deformation of the channel structures during the assembly process. A laser welding method has been used to construct a micropump for lab-on-chip applications using two polycarbonate substrates and a weldable thermoplastic elastomer based intermediate layer [125]. Mask based welding of patterned PC microfluidics devices has been also been demonstrated [126]. Figure 2.21 shows the laser bonded device.

Figure 2.21 Laser welded microfluidic device 20mm x 30mm with 400 μm wide channels [126].
The use of a clear absorbing layer like ‘clearweld’® has been demonstrated for laser welding of PC layers [127]. This technique necessitates the spraying of the absorbing material as a thin layer. The thickness and uniformity of the material affects the laser absorption and sample movement can affect the uniformity of the deposited layer.

The previous sections have described several techniques used to seal microfluidic systems. Most of the methods have their own shortcomings like need for complex assembly, poor yield of bonding, need of expensive setup, issues of channel filling, low bond strength, disintegration of bond line, non-compatibility with polymers, to mention a few. As these processes form bottleneck for mass production, improved bonding methods are required. As described laser welding of polymers offers an excellent alternative due to its fast output, low cost, high selectivity and possibilities of bonding dissimilar polymers. The design of the absorption layer is a critical aspect of this technique. The key process parameters for laser transmission welding are: laser power, welding speed, beam spot area and clamping pressure, which control the temperature field inside the weld seam, and hence the weld quality. Good control and optimisation of these process parameters is key to the success of this technique. Modelling studies of laser transmission welding have been studied for various thermoplastics [128-130]. The work is useful for understanding the heat distribution and weld characteristics.

2.4 Summary

In this chapter, the literature related to the research work of the thesis has been discussed. The various microfabrication methods for fabrication of polymeric microfluidic devices have been reviewed. The bonding techniques for assembly of polymeric microfluidic devices have been discussed. The design considerations and how the laser based joining technique could address some of the challenges of other techniques are discussed. The laser based polymer joining technique is a promising solution for bonding of polymeric devices and its possibility to offer a one step solution for assembly and interconnection of microfluidic devices has been discussed.
Chapter 3 Design, Fabrication and Bonding Free Standing SU-8 Based Microfluidic Devices

In this chapter, the design, fabrication and assembly of a free standing SU-8 polymer electrophoresis device is presented. A study of fabrication of a SU-8 polymeric electrophoresis device on substrates like glass and polyimide (Kapton) is described. The Kapton film has been found to be a better substrate in comparison to the glass for the SU-8 based microfluidic structures. An adhesive based bonding technique using SU-8 for the development of a free standing structure is investigated. The bonding has been carried out under low temperature (52°C) without the need for high vacuum, temperature or pressure. Bonding, exposure and a transfer technique using Kapton film as the release layer for the fabrication of free standing SU-8 devices has also been developed. The optimisation of the fabrication and bonding procedures has been done for the successful fabrication of the electrophoresis device. The characterisation of the bond has been done using leak test, which showed successful bonding of the device.

3.1 Microcapillary electrophoresis

Microchip capillary electrophoresis is a widely used analytical technique for the analysis of analytes in samples. The early work in this method was initiated by Manz et al. in 1993 [131]. It is a separation technique based on the differential migration of the molecules when subjected to an electric field. The capillary electrophoresis technique has several advantages in comparison to the conventional electrophoresis method such as small sample volume, faster separation, high resolution separation and parallel processing. The capability to introduce fluids passively also played a huge role in the growth of this technique for the development of disposable applications. The field of microcapillary electrophoresis has grown exponentially with applications developed in DNA analysis, biological, industrial and environmental applications [132-136]. The current development in this field is in the integration of various functions onto a miniaturised platform for the development of Lab-on-a-Chip total analysis systems wherein pre-processing and post-processing of the sample can be integrated onto a single platform to enable a one step read out device.
The theory of separation for microchip capillary electrophoresis is based on that of the conventional capillary electrophoresis. The Electro-Osmotic force (EOF) plays an important role in the separation of the analytes. The velocity of a given analyte species is determined by the mobility of the analyte plus the EOF as shown in equation (3.1) [137].

\[ V = (\mu_e + \mu_{eof}) E \]  

(3.1)

\( V \) is the velocity of the analyte, \( \mu_e \) is the electrophoretic mobility of the analyte, \( \mu_{eof} \) is the EOF and \( E \) is the electric field strength. The surface charge density and the EOF are determined to a large extent by the channel material, surface treatment or modification and also to some extent by the fabrication methodology including the environment of fabrication. It is seen that PMMA channels prepared by laser ablation have higher EOF than from hot embossing due to the integration of reactive carboxylate species into the surface of the polymer during the ablation process [138]. It has also been found that microfluidic devices fabricated under different atmospheres show different surface properties. Polyvinyl chloride (PVC) and Polycarbonate (PC) microchannels have been found to have greater EOF when the ablation atmosphere is oxygen rather than nitrogen or argon. The surface characteristic of PMMA has been found unaffected by the ablation atmosphere [139]. The SU-8 epoxy photoresist is a widely used material for the fabrication of microfluidic electrophoresis devices due to its physical, chemical stability, inertness to analytes after development, optical transparency and biocompatibility. The surface properties of the SU-8 can also be altered to make it more hydrophilic than its native hydrophobic form by means of surface modification thereby altering the EOF [140].

The design of the microchannel for capillary electrophoresis consists of cross shaped design with one of the limbs elongated (separation channel), wherein the separation process takes place (Figure 3.1). There are four reservoirs positioned at the end of the channel, two of them for the introduction of the sample and buffer solution and the other two are waste reservoirs. The electrodes that are present in all reservoirs provide connection to a high voltage power supply. The sample is injected electrokinetically by the application of an external electric field across the separation channel. The sample present at the intersection is subjected to separation when electric field is applied across the separation channel. The injection and separation steps are controlled by independent
high voltage power supplies. The separation voltage (1-5 kV) is applied for separation of analytes before they reach the detection window for detection using suitable techniques. The typical dimensions of the channel are 15-50 µm in depth, 50-200 µm in width and around 1-10 cm in length. The sample volume injected varies between 100-500 pL.

![Figure 3.1](image.png)

Figure 3.1 Schematic drawing of the microchip for electrophoresis [141].

There are several detection methods used for the quantitative detection of the analytes. The most commonly used detection technique is laser induced fluorescence (LIF) as it is a highly specific and sensitive technique. Another technique commonly used is electrochemical detection. Three modes of electrochemical detection commonly used are namely amperometry, conductrometry and potentiometry, with amperometry being the highly preferred mode due to its high sensitivity and ease with which it can be integrated in the electrophoresis device. Mass spectrometry detectors have also been used successfully for the detection in the electrophoresis devices.

### 3.2 Design of the microchannel

The capillary electrophoresis microchannel has been designed for the generation of photomasks. Photomasks are used for the purpose of transferring the pattern onto the photoresist during UV lithography. Two designs of capillary electrophoresis channels have been used. The schematic drawings of the designs are shown in Figure 3.2 (a) and 3.2 (b). The schematic drawing of the inlets is shown in Figure 3.2 (b). The dimensions of the channel and inlets are given in Table 3.1
In design 3.2 (a), the separation channel was kept at 3.5 cm. The diameter of the inlets was 1500 µm. In design 3.2 (b) the design for the inlets was done keeping the inlet diameter at 2000 µm. Another design with the separation channel at 3 cm and injection channel at 1 cm was also designed. The total length of the device was 4 cm. Designs of channel with varying width of 80µm, 100µm, 120µm, 150µm and 200 µm were done. For the fabrication of SU-8 structures, photomasks for a negative photoresist were designed. All the designs were transferred onto an A4 size format for the purpose of printing of the mask. The designs were drawn using Tanner L-Edit, which is a software package for the specific purpose of designing the photomask. The designs can be drawn with great precision to the resolution of a few nanometres. All designs were drawn in the units of microns. The designed photomask patterns were printed on a flexible acetate films (JD Photo Tools UK). A high resolution plotter (64,000 dpi) was used for the printing of the photomasks. Figure 3.3 shows the photograph of the masks used for the fabrication of the microchannels. The transparent areas in the film mask allows the UV light to pass through, while the black areas in the film served as the UV absorption layer, blocking the UV light.
Figure 3.3 Photographs of the mask used in the fabrication of the microchannels using SU-8, (a) channels and reservoirs and (b) inlets and outlet.

3.3 Materials

3.3.1 SU-8 photoresist material
The SU-8 is a negative epoxy photoresist that was developed and patented by IBM in 1989 (US patent No. 4882245) [142]. The chemical structure of the Bisphenol A epoxy oligomer in the SU-8 photoresist is shown in Figure 3.4. The presence of the epoxy groups enables high level of cross-linking after exposure to UV light. The SU-8 has many excellent properties that are well documented such as mechanical strength, chemical resistance, optical properties and biocompatibility. All these properties make the SU-8 a good material of choice for various BioMEMS applications. The SU-8 has been used in the fabrication of capillary electrophoresis devices [143]. However, the high coefficient of thermal expansion (CTE) can be considered to be one drawback as it can cause high thermal stress and fracture at elevated temperatures.

Figure 3.4 Chemical structure of the Bisphenol A epoxy oligomer in the SU-8 photoresist [144].

The fabrication procedure of the SU-8 photoresist is less sophisticated and low cost. SU-8 has the unique capability of producing high aspect ratio structures. Structures as
thick as 2 mm with an aspect ratio more than 20 can be fabricated using the standard lithography process. The SU-8 photoresist used in this work has been prepared in a class 1000 cleanroom. The SU-8 resin (EPON (R)) has been mixed with the solvent Gamma Butyrolactone (GBL) [Alfa Aesar] and Cyracure photoinitiator (UVI-6974) [Union Carbide] in proportion to yield the SU-8 photoresist of different formulations. For the fabrication of the microchannels the formulation used in this work is SU-8 65. 100 ml of the prepared SU-8 65 formulation contains 65 mg of SU-8 resin, 29 ml of GBL and 6 ml of the photoinitiator. For the use of adhesion of the flexible substrate Kapton onto the glass substrate SU-8 2 formulation has also been prepared. 100 ml of the prepared SU-8 2 formulation contains 50 mg of SU-8 resin, 46 ml of GBL and 4 ml of the photoinitiator. SU-8 10 from MicroChem has been used in the bonding studies. The developer used for the development of microstructures is propylene-glycol-monoether-acetate developer (PGMEA) from MicroChem. The physical and thermal properties of the SU-8 photoresist are given in Table 3.2.

**Table 3.2** Physical and thermal properties of the SU-8 2000 photoresist [145].

<table>
<thead>
<tr>
<th>Characteristics</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Maximum modulus of elasticity (E)</td>
<td>4.95 +/- 0.42 GPa</td>
</tr>
<tr>
<td>Bi-axial modulus of elasticity (E/(1 - ν))</td>
<td>5.18 +/- 0.89 GPa</td>
</tr>
<tr>
<td>Film stress</td>
<td>19 - 16 Mpa</td>
</tr>
<tr>
<td>Maximum stress</td>
<td>34 Mpa</td>
</tr>
<tr>
<td>Plastic domain limit</td>
<td>‘no’ plastic domain observed</td>
</tr>
<tr>
<td>Maximum bond strength</td>
<td>20.7 +/- 4.6 MPa</td>
</tr>
<tr>
<td>Glass temperature (T_g)</td>
<td>~50 °C</td>
</tr>
<tr>
<td>Thermal expansion coefficient</td>
<td>52 ± 5.1 ppm K–1 at 95 °C</td>
</tr>
</tbody>
</table>
3.3.2 Substrate materials

The substrates used for the fabrication of SU-8 microchannels are glass and Kapton film. The glass wafers (Chance glass UK) of 2.5 inch and 3 inch diameter with a thickness of 1 mm were used. The polyimide film (Kapton) from DuPont with a thickness of 125 µm was used. It is a flexible substrate with excellent thermal and mechanical properties [146]. It has a very poor adhesion to cured SU-8, which enables its use as a release layer for the easy release of SU-8 structures. The physical and thermal properties of polyimide film are given in Table 3.3.

Table 3.3 Physical and thermal properties of DuPont Kapton polyimide film from Kapton® [146].

<table>
<thead>
<tr>
<th>Characteristics</th>
<th>Value at 23°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tensile Strength</td>
<td>231 MPa</td>
</tr>
<tr>
<td>Elongation</td>
<td>72%</td>
</tr>
<tr>
<td>Poisson ratio</td>
<td>0.34</td>
</tr>
<tr>
<td>Tensile Modulus</td>
<td>2.5 GPa</td>
</tr>
<tr>
<td>Density</td>
<td>1.42 gm/cc</td>
</tr>
<tr>
<td>Coefficient of Friction, static</td>
<td>0.63</td>
</tr>
<tr>
<td>Heat Sealability</td>
<td>not heat sealable</td>
</tr>
<tr>
<td>Thermal Coefficient of Linear</td>
<td>20 ppm/°C</td>
</tr>
</tbody>
</table>

3.4 UV photolithography

UV photolithography is the most widely used patterning method for the fabrication of the SU-8 photoresist. The photolithographic process involves substrate preparation followed by spin coating, soft baking, exposure, hard baking and development. Figure 3.5 shows the process flow of the steps involved in a standard photolithography process for the patterning of the SU-8 photoresist [145].
The process starts with the substrate pre-treatment. A clean substrate has been found to be critical for good and uniform deposition of the photoresist. This is followed by the coating of the photoresist on the substrate. The most commonly used technique is spin coating but blade coating can also be used for the coating of thicker photoresist layers. The photoresist is then soft baked for the removal of the solvent before exposure to UV light. In negative photoresists like SU-8, the UV exposed areas are cross-linked (hardened) while the unexposed areas are dissolved on development thereby transferring the pattern from the photomask to the SU-8 film. The exposure step is followed by post-baking for further cross-linking and hardening of the photoresist. The final steps of development and rinsing are carried out to complete the process of fabrication.

3.5 Fabrication of SU-8 polymer microchannels

The design of the microchannel structures has been described in section 3.3. Several designs of the microchannel of varying width and depth have been fabricated. The microchannels were produced on glass wafers and Kapton film based flexible substrates.
3.5.1 Fabrication of SU-8 microchannels on glass substrate

The glass wafers were cleaned in an ultrasonic bath (Grant MXB14) with diluted detergent (Decon 90) for 30 minutes to ensure that they were free of contaminants. The detergent was diluted with de-ionised (DI) water in the ratio of 1:500. The wafers were then rinsed with DI water and placed in the ultrasonic bath for further 30 minutes. This was repeated to remove every trace of the detergent. The wafers were then blow dried using compressed air and baked on a hot plate at 150°C for 1 hour. Dehydration of the glass wafer has been found to be important for the good adhesion of SU-8. Figure 3.6 shows the photograph of the ultrasonic cleaning system used in substrate cleaning.

![Figure 3.6 Photograph of the ultrasonic bath used in cleaning of the substrates.](image)

The prepared SU-8 65 was placed in a warm water bath of temperature not more than 40°C for 30 minutes. This was done to eliminate air bubbles. A small amount of SU-8 65 was then pipetted out and dispensed onto the centre of the clean glass wafer. The spin coating parameters were chosen to produce the desired thickness. Spin coating at higher speeds will yield a thinner film. The thickness of the coated SU-8 film determines to a large extent the various fabrication steps like soft baking, exposure, post baking and development. Hence, the fabrication has to be optimised for the spin coating conditions determining the film thickness. Figure 3.7 shows the graph of the estimated thickness of SU-8 2000 MicroChem formulation with changing spin speed.
The process of spin coating not only determines the thickness of the SU-8 polymer but also the uniformity of the coated SU-8 layer. A two step, ramped coating method has been found to enhance the uniformity of the coated SU-8 layer. The edge bead effect has been noticed in all the samples. This effect was not very profound when a three step coating program with graded spin speeds and longer coating time was employed. Therefore, a three step coating program has been used to coat all the samples. At first a low spin velocity of 100 rpm with an acceleration rate of 30 rpm/s was carried out for 10 seconds followed by a second spin velocity of 500 rpm with an acceleration rate of 300 rpm/s for 10 seconds, followed by the final spread cycle of 2000 rpm spin velocity with acceleration of 500 rpm/s for 20 seconds. On completion of spin coating the surface of the photoresist was inspected for the presence of any bubbles. Large bubbles if present were removed using the tip of a tweezer. Figure 3.8 shows a photograph of the spin coater used for deposition of the photoresist.
The SU-8 coated glass substrate was then soft baked at 65°C and 95°C on a hot plate. The time for soft baking varies with the thickness of the SU-8 layer. The MicroChem datasheet for the fabrication of SU-8 2000 series has been used as a guide to determine the baking time and exposure dosage.

The soft baked SU-8 layer was then exposed to UV light using the Tamarack mask aligner (mask alignment and collimated UV exposure system, Model 152, Tamarack Scientific Co. Inc). Figure 3.9 shows the photograph of the Tamarack mask aligner. An i-line filter was used to filter out excessive UV light below 365 nm. The polyester photomask with the pattern of the microchannels was placed on the mask holder and secured with vacuum. The photomask was placed with the pattern facing down. The exposure energy is determined by the thickness of the SU-8 layer. Excessive dosage as well as low dosage can cause the fabrication to fail to produce the desired structures. Excessive dosage makes the SU-8 difficult to remove during development and low dosage causes insufficient cross-linking deep into the SU-8 layer. The exposure dosage was thus optimised for good quality of fabrication.
The exposure was followed by post bake, which hardens the cross linked SU-8 structures. It has been observed that a relaxation time of around 1 minute before post exposure bake reduces the stresses on the surface of the SU-8 layer. It is also important to provide ramped heating and cooling during the baking process. This has been effective in reducing the thermal stress on the surface. The width of the microchannel depends on the design in the photomask. Several designs of varying width have been fabricated. For glass wafers the optimised fabrication parameters are given in Table 3.4.

<table>
<thead>
<tr>
<th>Spin speed (rpm)</th>
<th>Soft Baking</th>
<th>Exposure dosage with i-line filter mJ/cm²</th>
<th>Post exposure baking</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>65°C minutes</td>
<td>95°C minutes</td>
<td></td>
</tr>
<tr>
<td>2000</td>
<td>3</td>
<td>6</td>
<td>400</td>
</tr>
</tbody>
</table>

The development was done following post baking using propylene glycol methyl ether acetate (PGMEA) in a wet bench. Mild mechanical agitation was provided during development. The development time was also found to be an important factor for fabrication. Over development and under development both cause poor definition of the structures. The development time was optimised over several trials for a set of
fabrication parameters. For the sample prepared using the above fabrication conditions, the development time was 3.40 minutes. The development was completed with a rinse of isopropyl alcohol (IPA) and the wafer was dried using compressed air.

The fabricated glass wafer was observed under the optical microscope for clear channels and assessment of the development. The measurements of the channel width and depth were done using a Zygo white light interferometer. The fabrication has been consistent and the quality of the fabricated microchannels has been found to be good. Figure 3.10 shows the Zygo image of a microchannel with good side walls fabricated on glass. The surface profile of the microchannel is shown in Figure 3.10 (b). The depth of the channel was around 65 microns. The surface has been found to be fairly uniform. One of the important criteria for good fabrication of the SU-8 microchannels onto glass substrate is the pre-treatment of the substrate and dehydration, which promotes good adhesion of the SU-8 onto glass. Glass substrate has been found to be a good material for fabrication of the SU-8 microchannels. But interconnections through glass require etching or drilling through the glass substrate.
Figure 3.10 (a) Cross junction of the SU-8 channel fabricated on glass, (b) Surface profile of the SU-8 channel, and (c) 3D view of the cross junction of the microchannels.
3.5.2 Fabrication of SU-8 microchannels on polyimide (Kapton) substrate

Free standing SU-8 structures are difficult to realise using a glass substrate as it is not possible to release the cured SU-8 structures from the glass surface. Free standing SU-8 structures are particularly useful in microchannels for electrophoretic separation applications where uniform surface charge density is desired. In applications where microchannels have been used for mixing and as reaction chambers, it is important to have the same material surrounding the channel in order to have uniform surface properties. The Kapton film or polyimide film has been used as the substrate for fabrication of the SU-8 microfluidic channels. The Kapton film has a good balance of properties over a wide range of temperatures (-269°C to 400°C). The Kapton film has very poor adhesion to the cured SU-8 thereby SU-8 microchannels can be easily released from the Kapton substrate. The Polyimide film was cut to the shape and size as required. Pre-treatment of the Kapton film was similar to that of glass. The Kapton film was cleaned with diluted detergent in ultrasonic bath followed with rinsing using DI water. The film was then dried using compressed air. The substrate was then dried on a hot plate at 150°C for 1 hour. Due to the flexible nature of the Kapton film it cannot be used directly to spin coat the SU-8 photoresist. The cleaned Kapton film was fixed onto a glass substrate using an adhesive coat of SU-8 2. The glass substrate was coated with a very thin layer of SU-8 2 by spin coating it at 1000 rpm/s for 10 seconds. The thickness of the layer is around 3-5 µm. The Kapton film was then placed onto the coated glass wafer. This was placed onto the hot plate at 95°C for 2-3 minutes for temporary bonding. The substrate was then used for the fabrication of the SU-8 microchannels. The fabrication procedure differs from that used for glass. A two layer fabrication methodology is adopted to get a free standing SU-8 microfluidic device after bonding. The fabrication steps are illustrated in Figure 3.11.
Figure 3.11 Process steps for the fabrication of two layer SU-8 microchannel.

The fabrication begins with coating the first layer of SU-8 65. This first layer was called the inlet layer as only the inlets are exposed. On soft baking and exposure of inlets the first layer is rested for 45 minutes before a second layer of SU-8 65 (channel layer) is coated on the inlet layer. Post exposure bake was not done with the inlet layer. The channel layer was soft baked, exposed and post baked prior to development. The fabrication parameters have been optimised after several trials. The optimised
fabrication parameters are given in Table 3.5. Two layer fabrication of the SU-8 microchannels is challenging in that the fabrication parameters of the first and the second layer influence the quality of structures. Alignment of the second layer and the first layer over the dark background of the Kapton film was found to be challenging.

**Table 3.5** Process parameters for fabrication of SU-8 structures on Kapton film

<table>
<thead>
<tr>
<th>Layer</th>
<th>Spin speed (rpm)</th>
<th>Soft Baking</th>
<th>Exposure dosage with i-line filter mJ/cm²</th>
<th>Post exposure baking</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>65°C minutes</td>
<td>95°C minutes</td>
<td>65°C minutes</td>
</tr>
<tr>
<td>1</td>
<td>1000</td>
<td>5</td>
<td>20</td>
<td>400</td>
</tr>
<tr>
<td>2</td>
<td>2000</td>
<td>4</td>
<td>10</td>
<td>550</td>
</tr>
</tbody>
</table>

The development times have been optimised over several trials. The development is done for 8.30 minutes using PGMEA as the solvent in a glass Petri dish with a mechanical stirrer for constant agitation. The fabricated microchannels are observed and measurements of the channel dimensions were taken using the Zygo white light interferometer. Figure 3.12 shows the microscope picture of the inlet of a single layer SU-8 microchannel. Figure 3.13 shows the Zygo measurement of the cross junction of the microchannel.
Figure 3.13 (a) The cross junction of the SU-8 microchannel fabricated on a Kapton film, (b) the depth profile of the microchannel, and (c) 3D view of the microchannel.
The channel walls fabricated on a Kapton film are found to be straight with sharp corners. The depth of the channel was measured to be around 48 µm and the width of the channel was also found to be consistent with the design dimension (100 µm). The reproducibility of the SU-8 microchannels using the above fabrication condition was found to be good. Microchannels of several depths have been fabricated by altering the spin speed of the photoresist coating process. The depth measurements are the average of five measurements. Table 3.6 shows the microchannel fabrication conditions for varying spin speed of the coating process. The fabricated channels can then be bonded using an adhesive based bonding method to yield a standalone SU-8 device. The bonding procedures are discussed in subsequent sections.

**Table 3.6** Process parameters for fabrication of SU-8 structures on Kapton film

<table>
<thead>
<tr>
<th>Spin speed (rpm)</th>
<th>Soft Baking</th>
<th>Exposure dosage with i-line filter mJ/cm²</th>
<th>Post exposure baking</th>
<th>Channel depth (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>65°C minutes</td>
<td>95°C minutes</td>
<td>65°C minutes</td>
<td>95°C minutes</td>
</tr>
<tr>
<td>750</td>
<td>5</td>
<td>30</td>
<td>650</td>
<td>1</td>
</tr>
<tr>
<td>1000</td>
<td>5</td>
<td>20</td>
<td>600</td>
<td>0</td>
</tr>
<tr>
<td>1500</td>
<td>4</td>
<td>15</td>
<td>550</td>
<td>1</td>
</tr>
<tr>
<td>2000</td>
<td>4</td>
<td>10</td>
<td>550</td>
<td>1</td>
</tr>
</tbody>
</table>

Glass and Kapton film as substrates yielded good results in fabrication of the microchannels with optimised fabrication procedures. However, the refractive indexes of the materials are different. The refractive index of the Kapton film, n, is 1.7 (DuPont Data sheet) and that of the glass is 1.47. The refractive index of SU-8 is 1.67 (UV light). This causes the bottom of the substrate to be exposed to the reflections at the interface between the photoresist and wafer when using glass as substrate. This causes the side walls to form a trapezoidal channel cross-section. This effect was found to be more profound in thick structures. On using the Kapton film, the side walls are straight. For multilayer fabrication and for standalone SU-8 devices it is seen that Kapton film is more suitable. However, it is important to completely cross link the SU-8 on Kapton film. The SU-8 micro channels are very brittle and handling the device on the flexible substrate was found to be a challenge.

**3.6 Bonding**

Bonding of open channel structures for the fabrication of devices has been done using several methods. The various bonding techniques have been reviewed extensively in
Chapter 2. In this work, two methods of bonding the SU-8 channels have been developed. Both of the techniques developed are based on the adhesive based bonding method. Adhesive bonding has been studied widely for the fabrication of SU-8 devices. In the first method, a low temperature bonding protocol has been developed using SU-8 10 as the intermediate adhesive layer. In 2005 Santeri Tuomikoski et al. [91] demonstrated the use of adhesive wafer bonding technique for the fabrication of free standing SU-8 microfluidic devices. However, in their work they incorporated moat channels in their design for improving the bonding efficiency. Additionally, the bonding process was carried out at 68°C. In this work, a low temperature bonding technique has been developed for the fabrication of free standing SU-8 devices. The bonding is attempted at a lower temperature of 52°C without the need for external pressure or vacuum. A second bonding approach for the simultaneous bonding and transferring of microstructures has been attempted using an acetate film. The Kapton film has been used for the release of the SU-8 microstructures.

3.6.1 Low temperature adhesive wafer bonding of SU-8 microstructures
A low temperature bonding method without the need for external pressure and vacuum has been studied using SU-8 to create SU-8 based free standing microfluidic structures. The substrate material used was Kapton film. The SU-8 photoresist was used as the structural material for the channel as well as for bonding. A two layer channel fabrication method was used as described in section 3.5.2. The fabrication begins with the preparation of the glass substrates using the standard cleaning procedure. A thin layer of SU-8 2 formulation was coated on the glass substrate and a cleaned Kapton film was placed on it. The fabrication of the channel and bonding layer was done simultaneously in order to carry out the bonding process after the development and drying of the microchannels. The process steps for the fabrication of the bonding layer are shown in Figure 3.14.
Figure 3.14 Process steps for the fabrication of the bonding layer.

For the fabrication of the bonding layer SU-8 65 was used for the first layer and the adhesive bonding layer was a thin layer of SU-8 10. The first layer was fabricated using the parameters shown in Table 3.7.

<table>
<thead>
<tr>
<th>Spin Coating (rpm)</th>
<th>Soft Baking</th>
<th>Exposure dosage</th>
<th>Post exposure baking</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>65°C minutes</td>
<td>95°C minutes</td>
<td>65°C minutes</td>
</tr>
<tr>
<td>1000</td>
<td>10</td>
<td>30</td>
<td>400</td>
</tr>
</tbody>
</table>

Table 3.7 Process parameters for the fabrication of the bonding layer

The spin coating parameters similar to the one used for the fabrication of the microchannel was used. The first layer was designed to be a thick film. Spin coating at 1000 rpm produces a thickness of 150 to 175 µm. The critical aspect was the uniform coating of the SU-8 layer. It has been seen that non-uniform coating resulted in poor bonding. The baking step was followed with exposure to cross link the SU-8 65. It is important that the layer is completely cross linked for its release from the Kapton film after bonding. The chip was allowed to rest for about an hour before coating with the
The bonding step was initiated by placing the Kapton film with fabricated SU-8 microchannels onto a heated circular weight. The circular weight was heated to have a surface temperature of 55°C. The adhesive layer was coated at a spin speed of 3000 rpm to yield a very thin layer of SU-8 of around 8-12 µm. The coated bonding layer was soft baked for 60 seconds at 65°C and 90 seconds at 95°C. The two layers were brought into contact and pressed firmly. Pressure was applied using a rubber roller along the length of the channel to bond the channel and to allow trapped air to escape. It is important to bring the two layers together gently to minimise trapped air. After bonding, the Kapton film substrate was peeled away from the glass substrate at first and the microchannels were released by peeling off the Kapton layer. The bonded device was UV cured with an exposure dosage of 350 mJ/cm². Figure 3.15 shows the schematic of the process steps for the bonding of the SU-8 microfluidic device.
Figure 3.15 Schematic of the bonding process.

The Figure 3.16 shows a photograph of the bonded and released SU-8 device. Bonding of the SU-8 microchannels has been achieved at a lower temperature without the use of vacuum or pressure bonder device. The bonded structures were visually inspected for bonding and it was found that certain areas of the device remained unbonded. These unbonded areas were outside of the channels. The channels were bonded to yield a tight seal. The baking temperature and baking time of the adhesive layer has been found to be
one of the determining factors for a successful bond. The uniformity of the channel layer as well as the bonding layer was found to be an important factor in order to determine the success of the bonding. The bonded device was placed in an ultrasonic bath for 2 hours and was found to be stable. The bonded layers remained bonded without peel-off. The structure was however very brittle and many devices failed the fabrication due to break off during the release from the Kapton film.

![Figure 3.16 Photograph of the bonded and released SU-8 device.](image)

3.6.2 Bonding, exposure and transferring technique for the fabrication of free standing SU-8 devices

A fabrication process using acetate film as the mask as well as the bonding substrate has been developed for the development of a one-step bonding and exposure protocol. The acetate film used in this study was a standard transparency sheet on which the mask for the inlet layer was printed using a laser printer. The mask was designed using the software PCB 123. The acetate film was cleaned prior to printing. Once the acetate mask was printed it was kept as clean as possible and cut to the required size. It has been seen that the SU-8 has a very poor adhesion to the acetate film and it is possible to reuse the mask by cleaning with IPA or Acetone. This method can be extended for the fabrication of multilayer 3D structures. The channel fabrication was similar to what was done in the previous method. A two layer fabrication method for the fabrication of open channels using SU-8 65 photoresist was used. The substrate used for the fabrication of microchannels was Kapton film. However, the first layer was kept as a blank layer without the inlets. The significant contribution in this method has been the use of acetate layer as the mask to pattern the inlets as well as to perform the steps of bonding.
at the same time. Similar work has been reported by Aracil et al. [147] wherein an additional layer of cured PDMS was used for the release of the SU-8 as well as to increase the surface uniformity. In their work, the SU-8 microchannels were fabricated on a rigid FR4 substrate. The bonding method developed in this thesis eliminates the need of an additional PDMS layer for the fabrication of free standing SU-8 devices. By fabricating the channels on a flexible substrate it is possible to release the bonded device for the fabrication of free standing device. Free standing devices can be used for a wide range of applications and it is possible to use with ‘Plug and Play’ systems for quick interfacing of the device.

The process steps for the fabrication of the bonding and inlet layer are shown in Figure 3.17.

![Substrate (Acetate film with inlets printed) on a glass plate](a)

![SU-8 coated on the substrate](b)

Figure 3.17 Process steps for the fabrication of the bonding layer on an acetate film.

For the fabrication of the bonding layer SU-8 65 was used. A thin layer of SU-8 2 was spin coated on the glass substrate and the acetate film with the inlets designed on it were fixed on to the glass substrate. A layer of SU-8 65 was then spin coated on it. The layer was fabricated using the parameters shown in Table 3.8.

<table>
<thead>
<tr>
<th>Spin Speed (rpm)</th>
<th>Soft Baking</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>65°C</td>
</tr>
<tr>
<td></td>
<td>95°C</td>
</tr>
<tr>
<td></td>
<td>minutes</td>
</tr>
<tr>
<td>3000</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>5</td>
</tr>
</tbody>
</table>

Table 3.8 Process parameters for the fabrication of the bonding layer

The spin coating process is similar to the one used for the fabrication of the microchannel as described in section 3.5.1. Soft baking was carried out to evaporate
some of the solvent. The bonding step was initiated by placing the coated acetate film on to the surface of the prepared microchannel. No excessive weight or pressure was used. The two layers were brought into contact manually and pressed lightly. This was then exposed to UV light to enable bonding and transferring of the inlet pattern. Exposure was done at 400 mJ/cm² of UV dose. Post exposure bake was carried out for 1 minute at 65°C and 5 minutes at 95°C. The glass and acetate layers were released and the bonded device was developed for 2 minutes in order to develop the inlet pattern. Figure 3.18 shows the schematic of the process steps for the bonding and pattern transferring using acetate film.

Figure 3.18 Schematic of the bonding and transferring technique.

A photograph of the bonded device is shown in Figure 3.19. Coloured liquid leak tests have been done by immersing the bonded device in coloured water. The immersed device was left in the coloured water for an hour. Figure 3.20 shows the photograph of the immersed device. The coloured water would leak into the device through the bonded interface. All successfully bonded devices passed the liquid test. Figure 3.21 shows the photograph of the bonded device after the leak test. It can be seen that the coloured water leaked only near the edges of the device. In samples wherein there were unbonded
areas the coloured water did not leak in due to the presence of bonding around it. Therefore, a combination of leak test and visual inspection of the bonded sample under the microscope was done to qualify the bond. The unbonded areas were reduced by further control of the fabrication condition. The outcome of the fabrication varies with small changes in the processing conditions. The SU-8 has a hydrophobic surface and hence, active pumping is required for injecting liquid into the channels. The surface can be made more hydrophilic by surface treatment but such techniques increase the roughness of the surface, which may make adhesive bonding more challenging.

Figure 3.19 Photograph of the bonded and released SU-8 device.

Figure 3.20 Photograph of the bonded device in coloured water.
3.7 Summary

The design, microfabrication and bonding methods have been developed for the fabrication of the SU-8 polymeric capillary electrophoresis device. A low cost photoresist material, SU-8, was prepared in different formulations. The microchannel structures designed were fabricated on glass and Kapton substrates for a comparative study of the influence of the substrate materials on the fabricated channel characteristics. It has been seen that Kapton film yielded better quality of channel side wall characteristic than glass. The fabrication process has been optimised and multiple samples of varying depth and width have been fabricated. Bonding techniques based on the adhesive bonding technique were developed. A low temperature bonding technique for the fabrication of free standing SU-8 devices has been reported. The temperature of bonding was 52°C, which is close to the glass transition temperature of uncured SU-8. Issues of channel blockage and reduction of unbonded areas were addressed by close control of the bonding process. The influence of uniformity of the surface layers in contact on bonding outcome has been observed. The reduction of edge bead effect for a more uniform SU-8 coating by adopting a three step spin coating has also been studied. The influence of bonding time, baking time and temperature has also been studied. It has been observed that baking for too long causes solvent to evaporate leaving very less adhesion on contact. Non-uniform application of pressure is also a factor causing unsuccessful bonding. Further a new technique of using acetate film as the mask as well as the substrate for establishing bonding and transferring at the same time has been developed. Free standing SU-8 devices have been demonstrated. The bonding layer was seen to have strong adhesion. Failure often occurred during the handling of the sample due to the brittleness of the cured SU-8.
Chapter 4 Assembly of PMMA Based Microfluidic Device
Using a Laser Microwelding Method

In this chapter, the development of a laser based microwelding method for assembly of PMMA polymer based microfluidic device is presented. A thin film intermediate metal layer was used as the absorber between two PMMA substrates. A laser beam was used to produce localised heating and joining at the interface thereby creating a bond. Numerical simulation of the bonding process has been carried out to study the effect of laser power and heating time on the temperature distribution at the interface. Further, experimental studies of the bonding process have been investigated extensively. The effect of laser power, processing time and bonding pressure on the bond characteristics namely the heat affected zone and melted zone, were investigated. Experiments to optimize the bonding conditions were carried out and a PMMA based microfluidic device for capillary electrophoresis was successfully bonded. Characterisation studies of the bonded device were done using shear tests and fluidic tests to establish leak-free function of the bonded device. The fabrication of channels on PMMA using the laser ablation based approach has also been studied. Channels of varying depth have been fabricated and the influences of laser power and speed of sample movement on the channel characteristics have been investigated.

4.1 Numerical simulation

Simulation of laser transmission welding requires an understanding of the theory of heat transfer, physics of the laser and the optical and thermal behaviour of the materials involved. The metal layer used as the absorber is titanium. Titanium is used as the absorber layer as it is a biocompatible material in addition to being a good absorber of the incident laser radiation. The polymer used for fabrication of channels and bonding is PMMA.

4.1.1 Theory of heat transfer

The theory of heat transfer can be used to study the energy transfer that takes place between materials due to the temperature difference. The three modes by which energy can be transferred from one place to another are conduction, convection and radiation.
Thermal conduction is one of the most important type of heat transfer. In conduction, heat is carried by means of collisions between rapidly moving molecules closer to the hot end of the material and the slower molecules closer to the cold end. Some of the kinetic energy of the fast molecules passes to the slow molecules and as a result of successive collisions, heat flows through the body of the matter from the hot end to the cold end. Solids, liquids and gases all conduct heat. Metals are the best heat conductors because some of their electrons are able to move freely and interact frequently by collisions. Gases are the poorest conductors of heat because their molecules are relatively far apart and interact less frequently than solids or liquids. In one dimensional heat conduction the rate at which heat is conducted through a slab of a particular material is proportional to the area $A$ of the slab and to the temperature difference, $\Delta T$, between its sides and inversely proportional to the slab’s thickness, $d$. The rate of conduction of thermal energy $Q$ that flows through the material in the given time $t$ is

$$\frac{Q}{t} = \frac{(kA\Delta T)}{d}$$

(4.1)

and thus,

$$k = \frac{Qd}{tA\Delta T}$$

(4.2)

Where $\Delta T = T_1 - T_2$, $T_1$ and $T_2$ are temperature of the sides, and $k$ is the thermal conductivity of the material which is a measure of its ability to conduct heat. The SI unit of thermal conductivity is $\text{Wm}^{-1}\text{K}^{-1}$. The thermal conductivity is usually considered to be constant. The thermal conductivity of a material varies with temperature but the variation can be small over a range of temperature. The thermal conductivity also varies depending on the orientation of the material [148]. For many applications Fourier’s law is used in one-dimensional form. In the x-direction this is given by

$$q_x = -k \frac{dT}{dx}$$

(4.3)

The heat conduction equation in the three dimensional cartesian space is given by

$$\frac{\partial}{\partial x} \left( k_x \frac{\partial T}{\partial x} \right) + \frac{\partial}{\partial y} \left( k_y \frac{\partial T}{\partial y} \right) + \frac{\partial}{\partial z} \left( k_z \frac{\partial T}{\partial z} \right) + q = \rho c_p \frac{\partial T}{\partial t}$$

(4.4)
Where \( q \) is the heat generated, \( \rho \) is the density of the material, \( C_p \) is the specific heat capacity and \( k_x, k_y, k_z \) are the thermal conductivities in the x,y and z direction.

Another mode of heat transfer is convection. Convection cooling is sometimes called ‘Newton’s law of cooling’. Newton’s law states that the rate of heat loss of a body is proportional to the difference in temperature between the body and its surroundings. This law assumes a constant heat transfer coefficient. The rate of heat transfer is given by

\[
\frac{dQ}{dt} = h \cdot A \cdot (T(t) - T_{env}) = h \cdot A \Delta T(t)
\] (4.5)

where \( Q \) is the thermal energy in joules, \( h \) is the heat transfer coefficient (assumed independent of \( T \)) (W/m\(^2\) K), \( A \) is the heat transfer surface area (m\(^2\)), \( T \) is the temperature of the object's surface, \( T_{env} \) is the temperature of the environment. \( \Delta T(t) = T(t) - T_{env} \) is the time-dependent thermal gradient between the environment and object. Convection can be of two types, free or forced, depending on the flow property. If the convection is caused by external influence, a forced convection occurs. Free convection occurs when fluid motion is caused by buoyancy forces that result from the density variations due to variations of thermal temperature in the fluid [149].

In radiation heat transfer, the transfer of energy from the movement of charged particles within atoms is converted to electromagnetic radiation. Thermal radiation is the result of the random movements of atoms and molecules in matter. Since the atoms and molecules are composed of charged particles (protons and electrons), their movement results in the emission of electromagnetic radiation, which carries energy away from the surface. The Stefan-Bolzmann equation describes the rate of transfer of radiant energy in a vacuum and is given by

\[
Q = \varepsilon \sigma T^4
\] (4.6)

For radiative transfer between two objects, the equation is

\[
Q = \varepsilon \sigma (T_a^4 - T_b^4)
\] (4.7)

Where, \( Q \) is the heat flux, \( \varepsilon \) is the emissivity (unity for a black body), \( \sigma \) is the Stefan-Bolzmann constant, and \( T \) is the absolute temperature in Kelvin. In a black body, 100% of the surface energy is emitted. Radiation is typically only important for very hot objects, or for objects with a large temperature difference [150].
In this work, the intermediate metal film (absorber) absorbs the energy from the laser beam to generate heat and raise the temperature locally to cause bonding. The heat transfer module in the simulation model has been used to define heat transfer across the bonding setup. The top surface of the bonding setup is exposed to atmosphere and the heat transfer is by convection. The heat transfer module incorporates the differential equations for the heat transfer. The co-ordinates and the boundary conditions have been defined. At the top surface of the bonding setup the heat transfer is by convection. The heat flux $h$ is user defined. The parameters for determining the conductive heat transfer, namely, density, specific heat capacity and thermal conductivities are user defined for the materials included in the model. A part of the incident laser beam is reflected by the cap material and the absorbed energy heats up the metal layer.

4.1.2 Laser welding physics

Laser welding of polymers is defined as the joining of polymers by local heating above the softening temperature by laser radiation. Several lasers like CO2 and Nd:YAG lasers have been used in laser welding. Laser welding offers specific advantages over conventional processes such as short processing time, contactless processing and minimal thermal stress and particle generation. The widely preferred geometry for laser polymer welding is overlap weld. Figure 4.1 shows the overlap geometry configuration with the intensity and temperature distribution at the interface.

There are a number of techniques available for laser welding. Contour welding is a welding process in which the beam is moved along the contour of the material.
Simultaneous welding is a technique wherein laser light covering the complete contour performs the welding. Mask welding is carried out through the exposure of laser light through a mask in order to create a certain pattern. Quasi-simultaneous welding is a combination of contour welding and simultaneous welding. Galvanometric mirrors are used to guide the laser beam along the weld profile. Figure 4.2 shows the various polymer welding methods.

![Polymer Welding Methods](image)

Figure 4.2 Polymer welding methods.

The effect of thermal, mechanical and optical parameters of the polymers is very significant in the laser welding of polymers and influences the outcome of the laser welding process.

### 4.1.2.1 Thermal behaviour of polymers

In comparison to metals, polymers undergo phase transitions when they are heated up. The phase change is not well defined unlike in metals. The phase change occurs over a range of temperatures which is due to the molecular structure of the polymer, the side chains, the crystallite size and molecular force. The different classes of polymers show totally different characteristics. Thermoplastic polymers are well suited for welding from the thermo-mechanical point. These types of polymers can be made to flow at the interface and hardened upon cooling producing a joint. As the temperature increases the materials normally expand. The thermal expansion coefficient of polymers is
considerably higher than for metals. Furthermore, the effect is much stronger for the partially crystalline material than it is for the amorphous. The strong heat expansion coefficient may cause mechanical stress after the seam has cooled down. The heat conductivity of polymers is 3 to 4 orders less than that of metals. The temperature of welding must be kept much lower than the decomposition temperature of the polymer.

4.1.2.2 Optical properties of polymers
The optical properties of the polymer influence the laser welding process considerably. The top polymer layer is usually transparent to allow the transmission of light. Reflection and absorption properties of the bottom layer are an important parameter for welding. The laser energy has to be absorbed completely at the interface to cause rise in temperature and thereby welding. The absorption and transmission spectrum of the polymer depends on the material characteristics. Amorphous and crystalline polymers have variable absorption spectrum with crystalline material showing greater scattering of the incoming laser energy thereby causing widening of weld seam. Scattering effect can also be caused due to filler material. The amount of scattering depends on the grain or particle size. Laser beam expansion by a factor of 3 has been observed on a 2mm thick PBT (Poly-Butylene-Terephthalate) sample [151].

4.1.2.3 Mechanical properties for polymer welding
Good welding between polymeric layers necessitates the presence of gap between the joining parts. The heat generated at the interface must be transferred to the non-conducting part by heat conduction. If the gap is too large no heat transfer would take place. The gap required depends on the weld geometry material properties and the flow characteristics upon heating. Clamping is used to provide optimum contact between the joining polymers.

4.1.2.4 Diode laser
High power diode lasers that are compact and reliable are gaining popularity for use in laser welding. In this work, a high power diode laser system with fibre-coupled output at 970 nm has been used as the heat source. The laser beam has a top hat shaped distribution. The dimensions for the top-hat beam were 6x6 mm. The top hat shaped profile applies heat to a well-defined spot on the material. The intensity of heating the material is assumed to be constant over the heating cycle. The beam profile of a top hat shaped laser beam is shown in Figure 4.3.
The beam is delivered to the work surface by means of a fibre optic cable. The focal length is 20 cm. The top substrate is transparent. The part of the laser energy absorbed is given by Beer’s law

$$I(z) = I_0 e^{-\alpha z} \quad (4.8)$$

Where $I(z)$ is the optical intensity as function of material depth, $I_0$ is the optical intensity at $z=0$, $\alpha$ is the absorption coefficient and $z$ is the material thickness. If the intensity of the laser beam is $I_0$ W/m$^2$ then the transmitted intensity through a surface is given by

$$I_{in} = I_0 (1-R) \quad (4.9)$$

where $R$ is the reflectivity of the material. The working plane is defined in the model. The material is heated statically over a range of time. The optical intensity decays exponentially inside the material and is given by

$$I_z = I_{in} \exp(-\alpha z) \quad (4.10)$$

where $\alpha$ is the optical absorption coefficient. The source is given by

$$Q = \alpha I_z = \alpha I_0 (1-R) \exp(-\alpha z) \quad (4.11)$$

The value of $Q$ is defined in the model. The heat source physics is set during the model generation. The square beam profile of laser is defined in the model using a two step function.
4.1.3 Materials

4.1.3.1 PMMA

Poly(methyl methacrylate) (PMMA) is one of the most widely used polymer materials for the fabrication of microfluidic devices. PMMA materials are polymers of the esters of methacrylic acids. The PMMA polymer is produced by the free-radical polymerisation of methyl-methacrylate. The chemical structure of PMMA is shown in Figure 4.4.

![Chemical structure of PMMA polymer](image)

PMMA polymer materials were used for the fabrication of the microchannels as well as for the bonding process. The material properties of PMMA differ from manufacturer to manufacturer due to the variation in composition as well as the manufacturing method. The widely used method for the manufacturing of PMMA is by either cast or extrusion process. The composition of the commercial PMMA material consists of pure polymer with added fillers and additives. Hence, the commercial polymeric material cannot be considered to be pure PMMA polymer but PMMA ‘plastic’. The PMMA plastic is commercially known as ‘acrylic glass’. In this study, the PMMA material was obtained from RS components (UK). The thickness of the material used was 2 mm for the fabrication of the devices and 1 mm for the fabrication of mask, respectively. The acrylic sheet was manufactured by casting process. The PMMA sheet has very good light transmission (92%) and excellent weather resistance with no degradation or discolouration of the polymer [153]. The properties of the PMMA material are shown in Table 4.1.
Table 4.1 Properties of PMMA material [153].

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density</td>
<td>1.19 g/cm³</td>
</tr>
<tr>
<td>Modulus of Elasticity (Et at 23°C)</td>
<td>3300 MPa</td>
</tr>
<tr>
<td>Tensile stress at break (23°C)</td>
<td>76 MPa</td>
</tr>
<tr>
<td>Elongation at break (23°C)</td>
<td>6%</td>
</tr>
<tr>
<td>Tensile strength at yield</td>
<td>65 MPa</td>
</tr>
<tr>
<td>Max operating temperature</td>
<td>70°C</td>
</tr>
<tr>
<td>Water absorption</td>
<td>0.005%</td>
</tr>
<tr>
<td>Thermal Conductivity</td>
<td>0.19 W/m.K</td>
</tr>
<tr>
<td>Specific heat</td>
<td>1466 J/Kg.K</td>
</tr>
<tr>
<td>Melting Temperature</td>
<td>160°C</td>
</tr>
</tbody>
</table>

The PMMA polymer is a widely used material for the manufacture of microfluidic devices due to its optical transparency, low cost and good biocompatibility. Various methods have been used for the fabrication of channels but laser ablation process has emerged as an exciting new technique. The laser ablation method has been used for fabrication of microchannels using PMMA and a wide range of applications in biology have been demonstrated [154-155]. The interest in laser based fabrication of polymers is also due to the excellent absorbance of the polymer at the wavelength of operation of the laser. In tunable lasers the wavelength can be changed to match the absorbance wavelength of the polymer. The transmission spectrum of a PMMA polymer is shown in Figure 4.5.

Figure 4.5 Ultraviolet, visible and near infrared transmission spectrum of PMMA [156].
It can be seen that there is low transmission at 2200 nm which implies maximum absorbance at that wavelength. A laser with operating wavelength at low transmittance is suitable for ablation of the material as most of the laser energy is absorbed at the surface of the polymer thereby melting the polymer.

4.1.3.2 Titanium

Titanium film was used as the absorber of laser radiation. The titanium material absorbs the laser radiation completely (assuming negligible scattering) thereby increasing the temperature locally. By placing the titanium material at the interface of two PMMA plates the polymer can be heated locally to cause melting and joining at the interface. The titanium film is expected to absorb the entire laser energy as the laser light is transmitted through the PMMA material. Table 4.2 lists the properties of the titanium material.

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density</td>
<td>4.50 g/cm³</td>
</tr>
<tr>
<td>Thermal Conductivity</td>
<td>21.9 W/m.K</td>
</tr>
<tr>
<td>Specific heat</td>
<td>530 J/Kg.K</td>
</tr>
<tr>
<td>Melting Temperature</td>
<td>1668 °C</td>
</tr>
</tbody>
</table>

4.1.4 Simulation study

COMSOL Multiphysics version 5.0 was used to carry out the simulation study. COMSOL Multiphysics is a software that provides an interactive environment for modelling and simulating physical and engineering problems. There are 30 different modules that can be applied to solve a wide range of engineering and physical problems. The Physics Builder, allows to create custom made physics interfaces that are accessible from the COMSOL desktop with the same feel as the built-in physics interfaces. The COMSOL tool also provides for entering coupled systems of partially differential equations (PDE’s) in addition to its conventional physics based interfaces. The Applications Builder is also available with COMSOL which allows to save models
as specialized applications for use without going into the details of the simulation model. The Model builder can be used to build models of all design and dimensions. It also has the additional feature of importing model designs from CAD software. Built in library of standard models can also be used. The powerful graphical user interface (GUI) of COMSOL enables to work on several physical interfaces and carry out various studies. Live link with software like Matlab enables COMSOL to work in conjunction with Matlab thereby making it a powerful tool for simulation and analysis studies [158].

The ‘heat transfer model in solids’ module was used in this study. The heat transfer function is based on conduction with the associated equations implemented in the module. All of the modules can be applied as 1D, 2D or 3D for both stationary and time dependent studies. The 3D time dependent model for heat transfer in solids was used in this study. The model wizard was used to make this selection. The Figure 4.6 shows the model wizard interface at the launch of COMSOL. On completion of this a blank model is created wherein the geometry, materials and study are to be defined.

![Figure 4.6 The model wizard interface.](image-url)
4.1.4.1 Model Geometry

The model geometry was drawn to replicate the assembly setup during laser bonding. The assembly schematic is shown in Figure 4.7.

![Schematic of laser bonding of PMMA.](image)

The length of the titanium absorber layer is 5mm. The width of the line is 1mm and the thickness is 500 nm. The dimension of the glass cover and steel plate are modelled as 30 x 20 x 0.5 mm³. The dimensions of the PMMA substrates are 20 x 10 x 1 mm³. The laser power is assumed to be transmitted through the glass plate and top PMMA plate to be absorbed completely by the titanium film. The titanium film absorbs the laser energy to heat the PMMA substrates. The 3D model geometry of the PMMA laser bonding is shown in Figure 4.8.

![3D model geometry of PMMA bonding.](image)

The mesh configuration is set for convergence of the model to yield results. The mesh number of the titanium layer is kept ‘fine’ for greater accuracy. Fine mesh yields more
accurate results but increases the computation. Figure 4.9 shows the mesh configuration of the simulation work.

Figure 4.9 The mesh model of PMMA bonding.

The heat loss at the top surface of the glass plate and the edges of the assembly is by convection as it is exposed to the surrounding air. The initial temperature is assumed as 293.15 K. The heat transfer coefficient $h = 2 \text{ W/m}^2\cdot\text{K}$, was used for free convection correlations. The rest of the surfaces other than the top surface and the edges of the assembly are assumed to be adiabatic. The material properties have to be defined for the materials used in the geometry. The COMSOL library can be used to access the material parameters. User defined input of material properties is also possible and has been done with this model. The material properties used are density, thermal conductivity and heat capacity at constant pressure. Table 4.3 shows the material properties used in this simulation study.

<table>
<thead>
<tr>
<th>Material</th>
<th>Density $\rho$ (kg/m$^3$)</th>
<th>Heat capacity at constant pressure $C_p$ (J/kg·K)</th>
<th>Thermal conductivity $k$ (W/m·K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Glass</td>
<td>2200</td>
<td>480</td>
<td>1.1</td>
</tr>
<tr>
<td>PMMA</td>
<td>1180</td>
<td>1420</td>
<td>0.19</td>
</tr>
<tr>
<td>Titanium</td>
<td>4506</td>
<td>522</td>
<td>21.9</td>
</tr>
<tr>
<td>Steel</td>
<td>7850</td>
<td>475</td>
<td>228</td>
</tr>
</tbody>
</table>
The time dependent studies were defined for the model. The domains were defined in the heat transfer model. It is possible to include or exclude selective domains for the study. The generated model is then computed for convergence.

4.1.4.2 Simulation results
The numerical simulation results were used to understand the temperature change with time. Figure 4.10 (a) shows the surface temperature distribution on the device. Figure 4.10 (b) shows the cross-sectional temperature distribution. The heating time is 20 s.

![Surface Temperature Distribution](image)

(a)

![Cross-Sectional Temperature Distribution](image)

(b)

Figure 4.10 (a) surface temperature distribution on the device and (b) cross-sectional temperature distribution for heating time of 20 s.
It can be seen from the temperature distribution that the titanium film is heated to a temperature of 400 K. The surface of the PMMA substrate is at room temperature and most of the heat is around the titanium film. It can also be seen that the temperature at the centre of the titanium film is higher than the edges which implies heat transfer to the surrounding PMMA material. Figure 4.11 shows the temperature distribution at the interface of the PMMA substrates for time intervals between 0 – 30 s at a step of 5 s. It can be seen from the graph that the heating effect is almost instantaneous with the titanium film reaching a temperature of 330 K in 5 s.

![Line Graph: Temperature (K)](image)

Figure 4.11 Temperature distribution at the interface between PMMA substrates.

The film thickness for experimental studies was fixed at 500 nm. The value of Q in the expression was kept as 25. The simulation studies give a preliminary understanding of the heating during bonding. Further understanding of the laser welding process has been attempted with experimental studies.
4.2 Experimental

The experimental studies include the fabrication of microchannels on PMMA substrates and the subsequent laser based welding of the PMMA substrates for the fabrication of microfluidic devices.

4.2.1 Laser micromachining of PMMA substrate for microchannel fabrication

Laser based microfabrication methods are advantageous in comparison to the conventional approaches due to the flexibility, speed, non-contact processing, ease of control and scope of automation. The microfluidic structures were fabricated using a CO2 laser system (Epilog, UK). The laser system operates with the substrate placed on the fixed working stage. The stage can be translated in the z-direction to allow the laser to be focussed on the surface of the substrate. This enables the laser to be used with substrates of varying thickness. The beam of the laser can then be translated in the x and y directions, by mirrors and focussing lenses, which are controlled by two DC servomotors. The maximum resolution for rastering is 1200 dpi. The laser system can operate at a maximum power of 40W and a maximum scan speed of 96 mm/s. The fabrication parameters were set as percentage of the maximum power and speed. The wavelength of operation of the laser is 10.6 µm. The spot size of the laser beam can be varied from 76 µm – 127 µm. The substrate material PMMA has good absorbance at the wavelength of operation of the laser. The PMMA material surface roughness was determined using a Dektak 3 surface profilometer. The average value of roughness, Rₐ, was 104.1 nm. The surface of the polymer is very smooth and uniform. Figure 4.12 shows the photograph of the Epilog laser system used in the microfabrication of the microchannels.
The design of the microfluidic channels has been described under section 3.2. The designs were produced using CorelDraw X4 (Corel Software, UK), which was interfaced directly with the CO2 laser system enabling the design to be transferred directly onto a PMMA substrate. The power and scan speed of the laser beam can be adjusted to obtain varying channel depths and profiles. The polymer absorbs the laser power and vaporises the material at the spot area of the laser beam forming a pattern. The scanning speed of the laser beam influences the degree of laser ablation. A study of laser power and speed was done to determine its influence on the channel depth and profile. Fabrication of varying the width of the microchannels was also studied to determine the influence of the spot size on the channel profile. The number of laser passes was also varied to study its influence on channel fabrication. All measurements were made using a Dinolite microscope.

### 4.2.1.1 Study of the influence of scan speed on the channel profile

The influence of the scanning speed was studied by varying the laser power from 10% to 100% of 40 W for scan speeds fixed at 100%, 50% and 25% of the maximum speed (96 mm/s). Figure 4.13 shows the graph of channel depth obtained by varying the laser power with the scan speed fixed at 100%. Figure 4.14 shows the graph of channel depth obtained by varying the laser power with the scan speed fixed at 50%. Figure 4.15 shows the graph of channel depth obtained by varying the laser power with the scan speed fixed at 25%.
Figure 4.13 Graph of channel depth obtained by varying the laser power with the scan speed fixed at 100%.

Figure 4.14 Graph of channel depth obtained by varying the laser power with the scan speed fixed at 50%.
The influences of the scan speed has been determined. It can be observed that low scan speed results in deeper channels. For 100% power it can be seen that the channel depth is almost doubled by decreasing the scan speed by half. Decreasing the speed gives a greater time for the polymer to interact with the laser beam and thus removing more material. Figure 4.16 (a) shows the microscope picture of the PMMA channel for scan speed of 50% and power 100%. Figure 4.16 (b) shows the microscope picture of the PMMA channel for scan speed of 100% and power 100%.
4.2.1.2 Study of the influence of laser power on the channel profile

The influence of laser power has been studied by varying the scan speed from 10% to 100% of 96 mm/s with the laser power fixed at 100%, 50% and 25% of the maximum. Figure 4.17 shows the graph of the channel depths obtained for varying laser scan speed with the power fixed at 100%. Figure 4.18 shows the graph of the channel depths obtained for varying laser scan sped with the power fixed at 50%. Figure 4.19 shows the graph of the channel depths obtained for varying laser scan speed with the power fixed at 25%.

Figure 4.17 Graph of channel depths obtained for varying laser scan speed with the power fixed at 100%.

Figure 4.18 Graph of channel depths obtained for varying laser scan speed with the power fixed at 50%.
The effect of laser power on channel dimensions has been studied. For higher laser power deeper channels are obtained for low scan speed. It can also be observed that for value of low laser power, the ablation effect is insignificant. The missing data points on the graph could not be determined for high scan speed values. For low scan speed values the laser cut through the polymer.

4.2.1.3 Study of the influence of varying channel width design on the channel profile
The design channel width was varied from 100 µm to 500 µm with a step of 100 µm. The power and scan speed were fixed at 60% and 50% of the maximum power and speed respectively. The beam profile is Gaussian and the channels are formed as the inverted Gaussian profile. Figure 4.20 (a) shows a microscope picture of the channel at design depth of 300 µm and (b) at design width of 500 µm. It can be observed that the channel cross-section moves from an inverted Gaussian to a more rectangular shape. In rectangular channels the fluid flow characteristics are different from the ‘v’ shaped channel. The flow of fluid has been found to be more even in the rectangular shaped channels [159].

Figure 4.19 Graph of channel depths obtained for varying laser scan speed with the power fixed at 25%. 

![Graph of channel depths](image-url)
Figure 4.20 (a) Microscope picture of the channel with design width of 300 µm and (b) 500 µm.

4.2.1.4 Study of the influence of the number of laser passes on the channel profile

The effect of varying the number of laser passes on the channel profile has been studied. Figure 4.21 (a) and (b) show the channel profile for single pass and double pass. The laser power was kept at 50 % of the maximum and scan speed at 60 % of the maximum. The doubling of the laser pass increases the fabrication time. However, deeper channel profiles can be obtained. Doubling of the laser passes created deeper channel of 680 µm.
Figure 4.21 (a) Microscope picture of the channel with single laser pass and (b) double laser pass.

The influence of various parameters on the channel fabrication has been determined. It can be seen that channels of varying depths and profile can be fabricated. The fabrication is also sensitive to the substrate materials. Most of the channel profiles are inverted Gaussian. The method of channel fabrication is by ablation of the material at the focal point of the laser. It has been seen that not all material is ejected and rough edges are formed as residual polymer condenses. The roughness of the channel wall could create resistance for the movement of the liquid in the channel. Micro-bubbles are formed along the edge of the channel when vapours are trapped by the molten material
during re-solidification. Figure 4.22 shows a photograph of the fabricated microchannel for electrophoresis.

![Figure 4.22 A photograph of the fabricated PMMA microchannel.](image)

**4.2.2 Design and fabrication of shadow mask for the deposition of titanium film**

The shadow mask for electron beam deposition of the titanium thin film pattern onto the PMMA substrate was produced using the EPILOG laser. The shadow mask was designed using Coral Draw. Photographs of the mask in two sections are shown in Figure 4.23 (a) and (b). A PMMA sheet of 1 mm thickness was used to fabricate the mask for selective electron beam deposition of the titanium film. The titanium lines were designed to run along the channel edge for producing sealed channels after laser bonding of a cover plate. Two masks are designed so as to produce a complete line around the channels. A small overlap was provided for alignment and to ensure continuity of the metal line. The width of the titanium line was kept at 1 mm throughout the study. The spacing between the channel wall and the titanium line was varied from 0.75 mm to 1.5 mm at a step size of 0.25 mm in order to investigate the effect of channel deformation in the laser assembly process. The fabricated masks were cleaned in an ultrasonic bath using Decon 90 for 30 minutes. The cleaning procedure was the same as that described in Chapter 3.

![Figure 4.23 (a) and (b) Photographs of the shadow masks used for fabrication.](image)
4.2.3 Deposition of titanium film on PMMA substrate

An electron beam based evaporation system was used for the deposition of titanium films. The 2 mm thick PMMA sheet was cut to the size of 60 mm x 25 mm and the inlets were fabricated using the Epilog laser. The substrates were cleaned using the standard cleaning procedure. The cleaned and dried substrates were placed in the oven for dehydration of the surface. The oven temperature was kept at 70°C to prevent any deformation. The samples were dehydrated for 5-6 hours. It has been observed that good dehydration of the surface enables good adhesion of the deposited titanium film. Figure 4.24 shows a photograph of the oven used.

![Figure 4.24 A photograph of the oven used for dehydration of the substrates.](image)

One of the shadow mask was placed over the cleaned substrate and fixed in place using a Kapton adhesive tape. This was then mounted on a glass wafer and placed on the wafer holders of the electron beam evaporation chamber. In the deposition process a titanium target source was hit by the electron beam. The electron beam direction can be controlled by an emission box in the X and Y directions. This enables to focus the electron beam on the target source. The evaporated material is deposited on the surface of the exposed substrate. The electron current can be adjusted to control the rate of deposition. A rate meter was used to monitor the thickness deposited. The chamber pressure was lowered to 2 x 10^{-5} mbar before the start of the evaporation. It takes around 2 hours to reach the required chamber pressure by vacuum pumping. The procedure was repeated with the second shadow mask to complete the deposition process of the complete titanium film. A cooling time of 1 hour was necessary between the depositions. Figure 4.25 shows a photograph of the electron beam deposition system used. The deposition conditions to produce 500 nm thick titanium film are 60 mA of
electron current. The deposition time at this current was around 5 minutes per wafer. For deposition of 1 µm film the deposition time was around 10 minutes per wafer. Figure 4.26 shows a photograph of the titanium film deposited on a PMMA substrate. The thickness of the deposited film was determined using the Zygo white light interferometer.

Figure 4.25 A photograph of electron beam evaporator.

Figure 4.26 A photograph of the PMMA substrate with the deposited titanium film.

4.2.4 Laser bonding

The laser used for bonding studies is a diode laser that operates in the near infrared wavelength region at 970 nm. The laser consists of a laser control unit, electrical power supply and cooling unit. The laser beam was transmitted to the work surface (stainless steel) by a fibre optic cable. The laser beam profile was discussed in section 4.1.2. The schematic of the laser bonding system is shown in Figure 4.27. The substrates are
placed on the stainless steel platform which is fixed at the focal point of the laser beam (20 cm). The beam transmission module consists of collimation optics followed by a focusing lens. The platform can be moved in the X and Y directions using two translation stages.

Figure 4.27 Schematic of the laser bonding setup.

During the laser bonding process, the capping substrate with the deposited titanium film was placed over the substrate with the fabricated microchannel. Manual alignment was done. The PMMA substrates were held together by placing a 4 inch circular glass wafer on top of the aligned substrates. Figure 4.28 shows a photograph of the substrates aligned prior to laser bonding.
The diameter of the optical fibre was 200 µm. The laser beam profile chosen for this study was a top-hat beam. The beam size was 6x6 mm$^2$ and its intensity distribution has been studied by Liu et al. [160]. A broad beam was used for easy alignment. The top hat beam profile is also desirable for generating a small heat affected zone beyond the melted zone. The substrate assembly was positioned using a computer controlled translation stage for accurate positioning. After one section of the bonding line was exposed to the laser beam for laser welding, the substrate assembly was moved by 5 mm for laser processing of the next section. The laser microwelding step was repeated for the closed loop welding line to complete the encapsulation of a microfluidic device. Figure 4.29 shows a photograph of the laser bonding system.
4.3 Results and analysis

4.3.1 Study of bonding parameters

The parameters that significantly influence the outcome of the laser bonding experiments were laser power, exposure time and the thickness of the absorber film. Initial study to determine the titanium film thickness was done by fabricating film thickness of 250 nm, 500 nm and 1 µm. The results of the bonding trials conducted showed that all of the three films resulted in successful bonding of PMMA substrates. However, the absorber film of 250 nm thickness was found to disintegrate during bonding. The film thickness of 1 µm required long deposition times and hence a film thickness of 500 nm was used for all further studies.

A set of experiments were conducted to study the influence of the laser power and exposure times on bonding of the microfluidic devices. An optical microscope was used to measure the melted zone and the heat affected zone. In the initial experiments to determine the minimum power required to establish a bond, the power was varied from 10 W to 15 W with exposure time of 10 s and it was determined that the laser power of 15 W power and 10 seconds of exposure time produced successful bonding. It can also be concluded that this is the laser power required to reach the glass transition temperature ($T_g$) of the PMMA material. The $T_g$ of the PMMA substrate was determined using a differential scanning calorimetry instrument (DSC). The value was determined
to be 132°C. The influence of power and bonding time was studied by varying the laser power from 15 W to 20 W. For each laser power, bonding times of 10 s, 12 s, 15 s, 18 s, and 20 s were studied. The melt zone and the heat affected zone of the bonded sample were investigated. The melt zone (MZ) is the area at the interface beyond the absorber film wherein there is melting or softening of the polymer to form the bond. In amorphous polymers the weld strength developed is a function of the amount of chain entanglement and bridging across the joint interface plus any joint strength due to wetting and formation of chemical bonds at the interface [161]. The heat affected zone (HAZ) is defined as the area beyond the melt zone which is not melted but has the microstructure altered due to the heating process. The HAZ depends on the material property and composition. The thermal diffusivity plays a huge role in determining the HAZ. In materials where the diffusivity is high, the material cooling rate is high and hence the HAZ is small. Materials with low diffusivity leads to slower cooling rate and hence the HAZ is large. Figure 4.30 shows the laser welded sample. Figure 4.31 shows a microscope picture of the bonded area showing the melt zone and heat affected zone.

Figure 4.30 A photograph of the laser welded sample.

Figure 4.31 A microscope picture of the bonded area showing the melt zone and heat affected zone of a sample bonded using 15 W laser power and 12 s bonding time.
It can be seen from the microscope picture that the heat affected zone is small in comparison to the melt zone. Figure 4.32 shows the graph of the value of melt zone obtained by varying the power and heating time. The value is the average of five values obtained from the same side of the weld line. Figure 4.33 shows the graph of the value of the heat affected zone obtained by varying the power and heating time. The value is the average of five values obtained from the same side of the weld line for the corresponding measure of melt zone.

Figure 4.32 Graph of the melt zone obtained by varying the power and bonding time.
The increase in power and bonding time shows a corresponding increase in the melted zone and heat affected zone. The width of the melted zone is calculated at a particular point on the bonded substrate on one side of the device. The increase in the area of the melted zone increases the bond strength. The heat affected zone is much smaller than the melt zone and is highly desirable in microfluidic devices wherein thermal effects on neighbouring functional structures is minimised. At higher power and longer bonding times the titanium absorber line disintegrated and diffused into the melted zone. Formation of bubbles was seen at higher power levels due to trapping of air on re-solidification. Figure 4.34 shows the disintegrated titanium film when a laser power of 20 W was used with a heating time of 18 s. A laser power of 15 W was fixed with a bonding time of 12 s for the bonding process.
The effect of weights on the bonding process was studied by varying the weights on the aligned PMMA substrates. Initial experiments were carried out without weight and successful bonding was achieved by placing a glass wafer on the aligned samples. The effect of weights during bonding was studied by placing various weights over the glass wafer during the bonding process. The value of melt zone has been determined. Table 4.4 shows the value of the melt zone for the different weights. The power of the laser was 15 W and the bonding time 12 s for all the samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Weights (kg)</th>
<th>Melt Zone (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0</td>
<td>0.297</td>
</tr>
<tr>
<td>2</td>
<td>0.240</td>
<td>0.310</td>
</tr>
<tr>
<td>3</td>
<td>0.500</td>
<td>0.420</td>
</tr>
<tr>
<td>4</td>
<td>0.740</td>
<td>0.469</td>
</tr>
<tr>
<td>5</td>
<td>1.000</td>
<td>0.522</td>
</tr>
</tbody>
</table>

It can be seen that the melt zone increases with the increase in weight during bonding. This is due to the melt area diffusion on application of weight causing greater intermolecular diffusion between the two substrates. The strength of the bonded device depends on the bonded area and with increase in the melt area on application of weights could increase the strength of the bonded device.
4.3.2 Reliability tests

Successful laser bonded samples were fabricated at laser power of 15 w and 12 s bonding time. Reliability studies on the samples were done to determine the strength of the bond. The samples were considered to be successfully bonded if they passed the leak test. Coloured water was injected into the sample to show leak-free performance if the water was contained within the bonded line. Leak tested samples were then dehydrated in the oven to evaporate the liquid. The same sample was further tested after 1 week to determine the stability of the bonded sample. This was repeated every week for 6 weeks and it was found that the bonded PMMA sample passed the leak test in all 6 weeks. Figure 4.35 shows the bonded PMMA sample filled with coloured water.

Figure 4.35 A photograph of the bonded PMMA sample filled with coloured water.

4.3.3 Re-work on bonded sample

The possibility of re-work on faulty bonded samples using this bonding technique was studied. In this test a sample was bonded by leaving an area unexposed to laser beam thereby creating a gap in the seal. As expected, the sample failed the leak test. The faulty sample was then dehydrated in the oven to evaporate the liquid. The dehydrated sample was then re-bonded in the area that was left un-bonded. The re-bonded sample was again tested with the leak test. The re-bonded sample passed the leak test thereby establishing the possibility of re-work with this bonding technique. This is an interesting aspect of this technique as in many bonding methods a failed sample cannot be re-worked on to make it functional. Laser bonded samples were fabricated at the laser power of 15 w and 12 seconds of bonding time. Figure 4.36 shows a photograph of the re-worked sample with the coloured liquid.
4.3.4 Thermal compression bonding

The most widely used method of bonding of PMMA polymeric devices is thermal compression bonding. In order to obtain a comparative analysis of the laser bonding process to the thermal compression method of bonding, PMMA substrates were bonded using the thermal compression method. A PMMA substrate with the inlets cut using EPILOG laser and laser patterned PMMA were put together and heated to the bonding temperature. Pressure was applied by keeping the aligned substrates sandwiched between two stainless steel plates. Glass wafer was placed on the aligned PMMA substrates. The alignment was done manually. The entire assembly was then placed in a hot oven. The PMMA material was kept at the bonding temperature of 140°C for 35 minutes before cooling. Ramped heating and cooling cycle was employed. Figure 4.37 shows the photograph of the thermal bonded device.

In this method of bonding the heat is applied over the entire device and the surface of the material can be altered due to application of heat. The side walls of the channels are often found altered due to the application of heat and pressure [162]. Non-uniformity in the application of pressure could cause some areas being un-bonded. In comparison to this technique in the laser based welding method the heat is localised and is kept away from the channels thereby keeping the channel profile and surface properties un-altered.
4.3.5 Fluidic testing

Fluidic testing of the bonded microfluidic devices was carried out to verify the response of the bonded device to fluid flow. For investigation of flow rate based testing, a flexible tube was connected to the inlet of the separation channel using an intermediate connector which was glued onto the PMMA cover substrate. A syringe pump was connected to the inlet port of a microfluidic device using a connector. The connector was secured to the inlet of the separation channel using epoxy glue. A syringe pump was used to inject coloured water through the channel at different flow rates. The flow rate was varied from 2 ml/h to 20 ml/hr. The flow rate was held for 2 minutes before it was changed. The two inlets of the injection channel were sealed in order to investigate the operation of the device under high flow rates. The fabricated microfluidic devices are found to withstand a wide range of fluid flow rates making them suitable for different applications. Figure 4.38 shows a picture of the setup for fluidic testing. The fluidic test was repeated for the sample after one week of the initial test. It was dehydrated prior to retest, the device maintained leak-free performance.

![A photograph of the syringe pump used for fluidic tests.](image)

A prolonged test of the microfluidic device at a constant flow rate of 3 ml/hr for three hours did not show any leak or structural degradation. However, when the device was tested continuously for more than 3 hours the liquid started to leak at the interface of the connector and the cover plate due to partial failure of the epoxy bond. The laser welded joint was reliable in all of the experiments. It has been shown that a device after fluidic testing can be operated again after drying in an oven for 24 hours. The microfluidic device showed no change in performance indicating that the laser microwelding method can produce stable and reliable devices. In contrast, in most of the previous work using
adhesive and solvent based methods, the bonded device fail after prolonged usage due to swelling at the interface [163].

**4.3.6 Bond strength testing**

Shear test and tensile test for the bonded samples was performed using a commercial tester (INSTRON 2715-015). The testing equipment can apply a load up to 30 kN. Tensile test and shear test of the bonded samples was also performed using the same tester. Figure 4.39 shows a photograph of the INSTRON tester used.

![INSTRON tensile tester](image)

**Figure 4.39** A photograph of the INSTRON tensile tester.

For the tensile test the sample ends were glued to PMMA rods with Araldrite epoxy glue. A tensile load was applied to determine the break point. It has been seen that epoxy bond failed before the laser bond. For the shear test the sample was mounted vertically and was designed to have one substrate with a projection of 2 mm at side and another having the same projection for the other side after laser bonding to facilitate shear strength measurements. A compression force was applied for the shear test and the load to cause the bond to break was obtained. Compression rate was set at 1mm/min. The load at the break point was recorded. Based on the applied tensile force at the break point and the total area of the laser welded loop, the tensile strength of the interfacial bond was determined to be greater than 5 MPa. Similarly the results of shear test show that the shear strength of the laser produced bond is 8 MPa. The results show that a strong bond between the PMMA substrate has been produced using the new laser microwelding method.
4.3.7 Cross-sectional study

The bonded microfluidic devices were cut transversely and polished to study the cross-section of the welded area. The cross-sections of the channel regions of the samples were studied using a microscope to examine the welded interface. Figure 4.40 shows a microscopic picture of the cross-sectional view of the laser bonded interface between a PMMA cover and a PMMA based microfluidic substrate. The traces of the titanium lines and the cross-sectional profile of the channel can be seen clearly in the picture. The channel profile shows no channel deformation in laser microwelding process. The titanium line was distorted in the laser welding process and the titanium material partially diffused into the surrounding PMMA material. Excessive power would cause further melting of the polymer and disintegration of the titanium line. The channel and its surface are unaltered during the bonding process. By close control of the laser power and selective exposure it is possible to keep the heat away from the channel.

![Microscope Image](image)

Figure 4.40 A microscope image of the cross-sectional view of a laser bonded PMMA-PMMA interface.

4.4 Summary

A new laser microwelding method for assembly of PMMA microfluidic devices has been studied. This method can provide a basis for the development of a cost-effective, rapid method for manufacturing of polymer based microfluidic devices. Transparent microfluidic devices have been fabricated using this method. Compared to the other bonding techniques the laser assisted bonding offers several advantages such as rapid bonding, low thermal impact and the possibility of achieving bonding and interconnection at the same time. The bonding contour is defined by the absorber
titanium line. The influence of laser power and bonding time on the melted zone has been studied. It has been found that the laser power of 15 W and bonding time of 12 s were the best parameters for high quality and reliable bonding. Laser based fabrication of PMMA channels has also been studied extensively and electrophoresis channels were fabricated on PMMA substrate. The influence of laser power and scan speed on the channel profile has been studied. Channels of varying width and profile were fabricated. Fluidic tests on bonded devices showed the potential for this technique for low cost manufacture for lab-on-chip applications. Alignment of the two substrates is also critical to ensure a leak free device. Laser welding based joining method melts the polymer on both surfaces causing joining and hardening on cooling. This ensures homogeneity of the surface properties over the entire channel. Tensile tests and shear test on the bond determined the bond strength of the sample to be > 8MPa. The high bond strength coupled with capability of the bonded device to handle high fluid flow indicates the success of the bonding process for the assembly of microfluidic devices.
Chapter 5 Laser Assembly of a Polycarbonate Based Microfluidic Device

In this chapter, the development of a laser based microwelding method for assembly of Polycarbonate (PC) based microfluidic device is presented. The methodology used in the development of the laser microwelding method for the assembly of PMMA microfluidic devices has been extended for the PC material. A thin film titanium metal layer was used as the absorber between two PC substrates. A laser beam was used to produce localised heating and joining at the interface thereby creating a bond. Numerical simulation of the bonding process has been carried out to study the effect of laser power and heating time on the temperature distribution at the interface. Experimental studies of the bonding process have been investigated extensively. The effect of laser power, processing time and bonding pressure on the bond characteristics namely the heat affected zone and melted zone, were investigated. The fabrication of channels on PC using the laser ablation based method has also been studied. Channels of varying depth have been fabricated and the influences of laser power and speed of sample movement on the channel characteristics have been investigated. Successful bonding of PC based microfluidic device for capillary electrophoresis was carried out. Fluidic tests were done to establish leak-free operation of the device.

5.1 Materials

5.1.1 Polycarbonate

Polycarbonate is a widely used thermoplastic polymer for the fabrication of microfluidic devices. It is a polymer that contains the carbonate group (-O-(C=O)-O-). It is fabricated by the reaction of bisphenol A and phosgene COCl₂. The chemical structure of polycarbonate is shown in Figure 5.1.

![Figure 5.1 Chemical structure of PC polymer [164].](image-url)
The transparency, stability, toughness and high $T_g$ (147°C) of the polycarbonate material make it suitable for various μ-TAS devices. In devices that require high operating temperature, such as PCR devices, PC material is highly suitable [165]. The PC polymer material is commonly known by its commercial names ‘Lexan’ or ‘Makron’. The PC polymer materials were used for the fabrication of the microchannels by laser ablation method as well as for the bonding process. The material properties of PC differ from manufacturer to manufacturer due to the variation in composition. The composition of the commercial PC material consists of pure polymer with added fillers and additives. In this study, the PC material was obtained from RS components (UK). The thickness of the material used was 2 mm for the fabrication of the devices. The PMMA masks used for the fabrication of titanium film in the earlier study was used as the shadow mask for the fabrication of the absorber film on PC substrates. The PC substrate has good light transmission (86%). The PC material does undergo some degradation on exposure to UV light. The properties of the PC material are shown in Table 5.1

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density</td>
<td>1.20 g/cm³</td>
</tr>
<tr>
<td>Poisson’s ratio</td>
<td>0.37</td>
</tr>
<tr>
<td>Tensile modulus (GPa)</td>
<td>2.3-2.4</td>
</tr>
<tr>
<td>Coefficient of friction</td>
<td>0.31</td>
</tr>
<tr>
<td>Tensile strength</td>
<td>55-75 MPa</td>
</tr>
<tr>
<td>Specific heat</td>
<td>1200 J/K/kg</td>
</tr>
<tr>
<td>Coefficient of thermal</td>
<td>66-70 (x 10⁻⁶/K)</td>
</tr>
<tr>
<td>expansion</td>
<td></td>
</tr>
<tr>
<td>Thermal Conductivity</td>
<td>0.19-0.22 W/m.K</td>
</tr>
</tbody>
</table>

There are several methods for the fabrication of channels on PC substrate such as hot embossing and milling but laser ablation process has emerged as a promising technique. In comparison to other fabrication techniques, laser ablation method is a direct and fast fabrication method. In addition to the speed of the fabrication process the flexibility of changing the design makes this technique highly useful for research studies. In this work, the CO₂ laser ablation method was used for the direct fabrication of channels on
PC substrate. The PC material absorbs the laser energy and vaporises to form the microchannels. The transmission spectrum of a PC polymer is shown in Figure 5.2.

![Transmission Spectrum](image)

Figure 5.2 The transmission spectrum of PC [167].

The polycarbonate material has good transmission at visible wavelength region which is suitable for microfluidic application. The wavelength of CO₂ laser used for ablation is 10.6 µm.

### 5.1.2 Titanium

A titanium film was used as the absorber of laser radiation. The titanium film was deposited on one of the two PC plates to absorb the laser radiation completely during bonding, thereby increasing the temperature locally. The temperature increase causes melting of the surrounding PC material to form a joint. The properties of titanium have been discussed in section 4.1.3.2.

### 5.2 Simulation study

COMSOL Multiphysics version 5.0 was used to carry out the simulation study. Details of COMSOL Multiphysics and the physics of heat transfer has been discussed in Chapter 4. The ‘heat transfer model in solids’ module used in the study of PMMA bonding has been used for the study of PC bonding. The model geometry is similar to the one used in PMMA bonding simulation. The schematic of the laser bonding model is shown in Figure 5.3.
The dimensions are similar to the model used for PMMA simulation work. The laser power is assumed to be absorbed by the titanium film. The initial values and the heat transfer model inputs are similar to the PMMA simulation work. The properties of PC material are defined in the model. The material properties of PC used in this study are given in Table 5.2. The material properties of glass, stainless steel and titanium used are as given in Table 4.3.

**Table 5.2** Material properties of PC used in simulation study.

<table>
<thead>
<tr>
<th>Material</th>
<th>Density $\rho$ (kg/m$^3$)</th>
<th>Heat capacity at constant pressure $C_p$ (J/kg·K)</th>
<th>Thermal conductivity $k$ (W/m·K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PC</td>
<td>1200</td>
<td>1200</td>
<td>0.20</td>
</tr>
</tbody>
</table>

**5.2.1 Simulation results**

The numerical simulation results were used to understand the temperature change with time. Figure 5.4 (a) shows the surface temperature distribution on the device. Figure 5.4 (b) shows the cross-sectional temperature distribution. The heating time is 20 s. The value of $Q$ in the heat transfer module expression is defined as 25. It can be seen from the temperature distribution that the titanium film is heated to a temperature of 580 K. The surface of the PC substrate is at room temperature and most of the heat is around the titanium film.
Figure 5.4 (a) surface temperature distribution on the device and (b) cross-sectional temperature distribution for heating time of 20 s.

Figure 5.5 shows the temperature distribution at the interface of the PC substrates in the z direction for time intervals between 0 – 30 s at a step of 5 s. It can be seen from the graph that the heating effect is almost instantaneous with the highest interface temperature of nearly 440 K in 20 s. It can also be seen that the temperature distribution towards the top part of the PC substrate from the interface (0-1.25 mm in the z direction) is different from that of the bottom substrate. This is due to the presence of stainless steel at the bottom of the substrate. The heat distribution is also different from that of PMMA material due to the difference in material properties (specific heat...
capacity). In comparison to PMMA material the heat loss to the stainless steel plate is quite gradual for PC material and hence more heat is retained by the bottom PC substrate.

![Figure 5.5 Temperature distribution at the interface between PC substrates.](image)

Experimental studies has been done to further understand the laser bonding process. The simulation studies give a preliminary understanding of the heating effect during bonding and the temperature distribution at the interface.

### 5.3 Experimental

The experimental studies include the fabrication of microchannels on PC substrates using the laser based ablation method and the subsequent laser based welding of the PC substrates for the fabrication of microfluidic devices.

#### 5.3.1 Laser micromachining of PC substrate for microchannel fabrication

In this work the CO$_2$ laser direct-writing ablation method described in Chapter 4 was used to fabricate the microchannels on the polycarbonate substrate. The laser used for this is the EPILOG CO$_2$ laser system. The principle of operation of the laser has been
discussed under section 4.2.1. The design and fabrication process is similar to that of PMMA material. The PC material is ablated as the laser moves over the surface thereby creating a microchannel. The ablation process creates rough channels and the surface profile is also not smooth. This is due to the presence of resolidified molten PC material. Figure 5.6 shows a microscope picture of the cross-section of an ablated channel. It has been observed that the channels are formed much wider than the design.

![Figure 5.6 Microscope picture of the laser ablated PC channel.](image)

Thermal decomposition of polycarbonate occurs due to the laser ablation process. The focussed laser beam increases the temperature on the surface of PC. The polycarbonate material at first melts and then decomposes due to chain scission reaction. This breaks the benzene rings in the molecule of PC to generate carbon dioxide gas, phenol and other components [168]. Initial experiments conducted showed significant fumes and burning occurring when the laser power was at 40% of the maximum or more. Due to this, the range of laser power over which the channels can be fabricated is limited. The influence of laser power and scanning speed on the channel depth and profile has been studied. The number of laser passes has also been varied to study its influence on channel fabrication. All measurements were made using a Dinolite microscope.
5.3.1.1 Study of the influence of laser power and scan speed on the channel profile

The laser power was varied from 10% to 30% of the maximum and the scan speed was varied from 10% to 100% of the maximum for each value of the laser power. For higher power, significant burning and fume generation was observed. A similar effect was observed at lower power and slower scan speed of the laser. Table 5.3 shows the results of channel depth obtained for the various values of power and scan speed.

Table 5.3 Channel depth of microchannel obtained by varying the laser power and scan speed.

<table>
<thead>
<tr>
<th>Power (W)</th>
<th>Scan Speed (mm/s)</th>
<th>Channel depth (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>12</td>
<td>48</td>
<td>ND</td>
</tr>
<tr>
<td>12</td>
<td>38.4</td>
<td>0.123</td>
</tr>
<tr>
<td>12</td>
<td>28.8</td>
<td>0.191</td>
</tr>
<tr>
<td>12</td>
<td>19.2</td>
<td>0.316</td>
</tr>
<tr>
<td>12</td>
<td>9.6</td>
<td>Burning</td>
</tr>
<tr>
<td>8</td>
<td>28.8</td>
<td>ND</td>
</tr>
<tr>
<td>8</td>
<td>19.2</td>
<td>0.143</td>
</tr>
<tr>
<td>8</td>
<td>9.6</td>
<td>0.295</td>
</tr>
<tr>
<td>4</td>
<td>9.6</td>
<td>ND</td>
</tr>
</tbody>
</table>

Note: ND – Not Determined

For the laser power of 12 W there was no significant rastering of channels when the scan speed of the laser was 50% or more of the maximum. The same effect was observed when the scan speed was 30% or more for laser power of 8 W. For 4 W laser power no significant rastering was observed. It can be determined from the results in Table 5.3 that decreasing the scan speed results in greater channel depth. However, greater power and slower scan speed can result in thermal degradation of the polymer. The power and scan speed was fixed at 30% of 40 W and 40% of 96 mm/s of the maximum for the rest of the study.

5.3.1.2 Study of the influence of the number of laser passes on the channel profile

The effect of varying the number of laser passes on the channel profile has been studied. Figure 5.7 (a), (b) and (c) show the channel profiles for single pass, double and triple pass. The laser power was kept at 30% and scan speed at 40% of the maximum. The fabrication time increases with increase in the number of passes, however deeper
channel profiles can be obtained. Doubling of the laser passes created a deeper channel of 276 µm. Table 5.4 shows the value of channel depth obtained for the corresponding number of laser passes.

![Figure 5.7 Microscope pictures of the channel profile for (a) single pass, (b) double pass and (c) triple pass.](image)

Figure 5.7 Microscope pictures of the channel profile for (a) single pass, (b) double pass and (c) triple pass.
Table 5.4 The values of channel depth obtained for different numbers of laser pass.

<table>
<thead>
<tr>
<th>Number of laser pass</th>
<th>Channel depth (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>123</td>
</tr>
<tr>
<td>2</td>
<td>276</td>
</tr>
<tr>
<td>3</td>
<td>475</td>
</tr>
</tbody>
</table>

The influence of various parameters on the channel fabrication has been determined. It can be seen that channels of varying depths can be fabricated. The laser beam profile is Gaussian and therefore the channel profiles are inverted Gaussian. The profile of the channel is not exactly symmetrical due to possible misalignment in the optics of the laser. Figure 5.8 shows a photograph of the fabricated microchannels for electrophoresis.

![Figure 5.8 A photograph of the fabricated PC microchannel.](image)

5.3.2 Fabrication of titanium film on polycarbonate substrate

The design and fabrication of shadow mask for the deposition of titanium film was done as described in 4.2.2. The mask used for the deposition of titanium film on PMMA substrate was used for the metal film deposition on PC substrate. The substrate preparation and deposition procedure were as described in section 4.2.3. Figure 5.9 shows a photograph of the PC substrate with the deposited titanium film.

![Figure 5.9 A photograph of the PC substrate with the deposited titanium film.](image)
5.3.3 Laser bonding

The diode laser used in the bonding studies of PMMA substrates has been used for the bonding experiments. The diode laser operates in the near infrared wavelength region at 970 nm. The laser system and the physics of laser operation has been discussed in Chapter 4. The schematic of the laser bonding set up was shown in Figure 4.21. The substrates were placed on the stainless steel platform which is fixed at the focal point of the laser beam. The platform can be moved in the X and Y directions using two translation stages.

The laser bonding process was initiated by placing the capping substrate with the deposited titanium film over the substrate with the fabricated microchannel. Manual alignment of the substrates was done. The PC substrates were held together by placing a 4 inch circular glass wafer on top of the aligned substrates. The substrate assembly was positioned using a computer controlled translation stage for accurate positioning. After one section of the bonding line was exposed to the laser beam for laser welding, the substrate assembly was moved by 5 mm for laser processing of the next section. The laser microwelding step was repeated for the closed loop welding line to complete the encapsulation of a microfluidic device.

5.4 Results and analysis

5.4.1 Study of bonding parameters

A study of the parameters that significantly influence the outcome of the laser bonding experiments was carried out. The laser power and exposure time was varied to determine its influence on the bonding process. Based on the earlier bonding study using PMMA substrate the thickness of the titanium line was fixed at 500 nm. An optical microscope was used to measure the melted zone and the heat affected zone. Initial experiments were done to determine the minimum power required to establish a bond by varying the laser power from 10 W to 15 W with exposure time of 10 s. It was determined that the laser power of 15 W power and 10 seconds of exposure time produced successful bonding. This is similar to the value of the laser power and exposure time required for successful bonding of PMMA devices. The glass transition temperature ($T_g$) of the PC material is 147°C. The influence of power and bonding time was studied by varying the laser power from 15 W to 20 W. For each laser power,
bonding times of 10 s, 12 s, 15 s, 18 s and 20 s were studied. The melt zone and the heat affected zone of the bonded sample were investigated. The melt zone (MZ) is the area at the interface beyond the absorber film wherein there is melting or softening of the polymer to form bond. The heat affected zone (HAZ) is defined as the area beyond the melt zone which is not melted but has the microstructure altered due to the heating effect. Figure 5.10 shows a microscope picture of the bonded area showing the melt zone and heat affected zone for the bonding conditions 17 W of laser power and 20 s for bonding time.

Figure 5.10 A microscope picture of the PC bonded device showing the melt zone and heat affected zone for bonding condition of 17 W laser power and 20 s bonding time.

Figure 5.11 shows a graph of the value of melt zone obtained by varying the power and heating time.
Figure 5.11 Graph of the thickness of the melt zone obtained by varying the power and bonding time.

Figure 5.12 shows a graph of the value of heat affected zone obtained by varying the power and heating time.

The increase in power and bonding time shows a corresponding increase in the melted zone and heat affected zone. The width of the melted zone is calculated at a particular point on the bonded substrate on one side of the device. In comparison to the results obtained with PMMA material the melt zone is smaller for PC material. The HAZ is similar for both materials. The heat affected zone is much smaller than the melt zone thus the thermal effects on any neighbouring functional structures is minimised. The disintegration of the titanium film at higher laser power was observed. A laser power of 15 W was fixed with a bonding time of 12 s for the bonding process.

The effect of the weight on the bonding process was studied by varying the weight on the aligned PC substrates. Initial experiments were carried out without weight and successful bonding was achieved by placing a glass wafer on the aligned samples. The effect of weight during bonding was studied by placing various weights over the glass wafer during the bonding process. The value of melt zone has been determined. Table
5.5 shows the value of the melt zone for the different weights. The power of the laser was 15 W and the bonding time 12 s for all the samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Weights (kg)</th>
<th>Melt Zone (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0</td>
<td>0.095</td>
</tr>
<tr>
<td>2</td>
<td>0.240</td>
<td>0.175</td>
</tr>
<tr>
<td>3</td>
<td>0.500</td>
<td>0.254</td>
</tr>
<tr>
<td>4</td>
<td>0.740</td>
<td>0.383</td>
</tr>
<tr>
<td>5</td>
<td>1.000</td>
<td>0.440</td>
</tr>
</tbody>
</table>

Table 5.5 Effect of weights during bonding on the melt zone.

It can be seen that the melt zone increases with the increase in weight during bonding. The strength of the bonded device depends on the bonded area and with increase in the melt area on application of weight could increase the strength of the bonded device. The increase in the melt zone is due to greater intermolecular diffusion and contact between the two substrates.

5.4.2 Reliability tests

Successful laser bonded samples were fabricated at laser power of 15 w and 12 seconds of bonding time. Reliability studies on the samples were done to determine the quality of the bond. Coloured water was injected into the sample to show leak-free performance if the water was contained within the bonded line. The samples were considered to be successfully bonded if they passed the leak test. The sample was then dehydrated in the oven and the leak test was repeated after one week. This was repeated every week for four weeks and the bonded device passed the leak test in all tests. The reliability of the bonded device was found to be stable over four weeks. Figure 5.13 shows the bonded PC device filled with coloured water.

Figure 5.13 A photograph of the bonded PC device filled with coloured water.
5.4.3 Thermal compression bonding

One of the widely used methods of bonding of PC polymeric devices is thermal compression bonding. In order to obtain a comparative analysis of the laser bonding process to the thermal compression method of bonding, PC substrates were bonded using the thermal compression method. A PC substrate with the inlets drilled and laser patterned PC were put together and heated to the bonding temperature. Pressure was applied by keeping the aligned substrates sandwiched between two stainless steel plates. Glass wafer was placed on the aligned PC substrates. The entire assembly was then placed in a hot oven. The PC material was kept at the bonding temperature of 170°C for 40 minutes before cooling. Ramped heating and cooling cycle was employed. Figure 5.14 shows a photograph of a thermal bonded device.

![Figure 5.14 A photograph of the thermal bonded PC device.](image)

In this method of bonding the heat is applied over the entire device and the surface of the material can be altered due to application of heat. The thermally bonded sample did not show any heat related deformation as in the case of PMMA material. However, there is possibility of channel wall deformation as the heat is applied throughout the device. The bonding times are more than 1 hour due to the ramped heating and cooling times. In comparison, laser welding method of joining of polycarbonate devices is a rapid technique with bonding time for the entire device being 2-3 minutes and the heating is localised causing minimal thermal stress to the channel structures. The surface properties of the channel are also unaltered.

5.4.4 Cross-sectional study

The bonded microfluidic devices were cut transversely and polished to study the cross-section of the welded area. The cross-sections of the channel regions of the samples were studied using a microscope to examine the welded interface. Figure 5.15 shows a microscopic picture of the cross-sectional view of the laser bonded interface between
the PC substrates. The channel profile shows no channel deformation in laser microwelding process. The channel depth of the fabricated microchannel is 123 µm.

Figure 5.15 A microscope image of the cross-sectional view of a laser bonded PC-PC interface.

**5.5 Summary**

A laser microwelding method for assembly of PC microfluidic devices has been studied. The rapid method of fabrication of microchannels on PC substrates using CO₂ laser has been studied and channels of varying depths have been fabricated. The effect of laser processing parameters on the channel profile has also been established. A new bonding method based on laser welding of polycarbonate substrates to yield transparent microfluidic devices has been developed. The influence of laser power and bonding time on the melted zone has been studied. It has been found that laser power of 15 W with bonding time of 12 s produces successful bonded devices. The influence of increase in the laser power and bonding time on the melt zone and the heat affected zone has been studied. Leak test on the bonded samples established the suitability of the bonding technique for microfluidic applications. A laser based fabrication and assembly method for the polycarbonate based microfluidic devices has been developed.
Chapter 6 Bonding of Dissimilar Polymers Using a Laser Based Welding Method

In this chapter, the development of a laser based microwelding method for assembly of dissimilar polymers, PMMA and SU-8 is presented. The work on bonding of thermoplastic polymers PMMA and PC was extended to bond SU-8 microfluidic devices to PMMA. In the laser based welding method it is essential for the heated material to melt and produce a joint at the interface. The work in Chapter 4 and 5 involved the same polymer material on either side of the interface that enabled the formation of a strong bond due to the interaction of the material and the homogenous properties of the material across the interface. In this study, a thin film of titanium metal layer was used as the absorber between the PMMA cover substrate and the SU-8 microfluidic structure. A laser beam was used to cause localised heating and joining at the interface thereby creating a bond. Experimental studies of the bonding process have been investigated. The effects of laser power, processing time and bonding pressure on the bonding process were investigated. The fabrication of SU-8 polymeric microchannel was done using the standard lithography technique. Successful bonding of PMMA-SU-8 based microfluidic device was carried out. Fluidic tests were done to demonstrate leak-free operation of the device. Furthermore, surface modification of the polymer has been studied to determine its influence on the bonding process.

6.1 Materials

The materials used for this study are PMMA and SU-8 epoxy polymer. The PMMA material was used as the cover substrate and the inlets were fabricated using the EPILOG laser. The titanium absorber film was deposited on the PMMA substrate using the E-beam evaporator. SU-8 epoxy polymer was used for the fabrication of the microchannel using photo lithography technique described in Chapter 3. The SU-8 65 formulation was used for the fabrication of microfluidic channels. The material properties of the polymer material PMMA has been described in section 4.1.3.1. The material property of SU-8 epoxy polymer was discussed in section 3.3.1. The material property of titanium has been discussed in section 4.1.3.2.
6.2 Fabrication

6.2.1 Fabrication of SU-8 microfluidic channel
The SU-8 epoxy negative photoresist was mixed in the cleanroom to yield the formulation SU-8 65. This was used for the fabrication of microchannels. The preparation of the SU-8 photoresist and the fabrication process has been detailed in Chapter 3. The channels were fabricated on polyimide substrates. The fabrication steps were described in section 3.5.2.

6.2.2 Fabrication of titanium absorber film on PMMA
The PMMA material was cut to size and inlets were made using the EPILOG laser. The cleaning of the PMMA substrate has been discussed in Chapter 4. A titanium absorber film was deposited on the cleaned PMMA substrates. The shadow masks used in the previous work was used for the electron beam deposition process. The thickness of the deposited film was 500 nm. The design of the shadow mask and the deposition process were described in section 4.2.2 and 4.2.3 respectively.

6.3 Laser Bonding

The diode laser used in the bonding studies of PMMA and PC substrates has been used for the bonding experiments. The laser system and the physics of laser operation has been discussed in Chapter 4. The schematic of the laser bonding set up used in this study was shown in Figure 4.21. The substrates are placed on the stainless steel work platform which can be moved in the X and Y directions using two translation stages. The laser bonding process is initiated by placing the capping substrate with the deposited titanium film over the substrate with the fabricated microchannel. Manual alignment of the substrates was done.

In the bonding experiments the substrates were held together by placing a 4 inch circular glass wafer on top of them. The substrate assembly was positioned using computer controlled translation stage for accurate positioning. After one section of the bonding line was exposed to the laser beam for laser welding, the substrate assembly was moved by 5 mm for laser processing of the next section. The laser microwelding
step was repeated for the closed loop welding line to complete the encapsulation of a microfluidic device.

6.4 Results and analysis

The results from the study of bonding PMMA substrates in Chapter 4 were used in this work. In the initial experiments, a glass wafer was placed on the aligned substrates before bonding. The laser power was varied from 15 W to 20 W for bonding time of 10s. It was observed that none of the samples could be bonded under these conditions. In order to improve the contact between the aligned substrates the bonding experiments were carried out by placing a weight (load) on the aligned substrates. The power was varied from 15 W to 16 W to find the influence of laser heating time and weight. For each laser power, bonding times of 12, 15, 18 and 20 s were studied. This was repeated for weights of 0.5 kg, 0.750 kg and 1 kg.

For the laser power of 15 W it was seen that none of the samples was bonded successfully. Some samples did bond initially when the weights of 0.750 kg and 1 kg were used but these samples delaminated after a short period or on the removal of weights. The period of delamination varied from sample to sample. In some samples the delamination occurred as soon as the weights were removed and in some samples the delamination was after few minutes of bonding. For the laser power of 16 W it was observed that bonding using the weight of 0.500 kg was unsuccessful. However, successful bonding was achieved when weights of 0.750 kg and 1 kg was used. Most of the samples that were bonded under the bonding conditions of 16 W for laser power and 0.750 kg of weight were successful. It was found that bonding under more weight did not improve the success of the bond. The samples bonded using the weight of 1 kg showed higher failure rate due to delamination. The delamination of the bonded sample occurred after bonding. In some of the cases the delamination occurred as soon as the weight was removed and it was observed that some samples delaminated after several minutes or hours after bonding. The bonded sample was tested by injecting coloured water to determine if the bond was successful. The successful bonding parameters for the bonding of PMMA to SU-8 are shown in Table 6.1
Table 6.1 Bonding parameters for successful laser bonding of PMMA-SU-8 devices.

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Power (W)</th>
<th>Bonding time (s)</th>
<th>Weight (kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>16</td>
<td>12</td>
<td>0.750</td>
</tr>
<tr>
<td>2</td>
<td>16</td>
<td>15</td>
<td>0.750</td>
</tr>
<tr>
<td>3</td>
<td>16</td>
<td>18</td>
<td>0.750</td>
</tr>
<tr>
<td>4</td>
<td>16</td>
<td>20</td>
<td>0.750</td>
</tr>
</tbody>
</table>

The bonding parameters of 16 W of laser power and 12 s of bonding time with a weight of 0.750 kg were repeated to establish reproducibility of the bonding process. It was observed that bonding was successful in most samples. A few samples failed after a few hours. On average, it was found that the success rate of the bonding process was around 70%.

Figure 6.1 shows a photograph of a laser bonded sample. Figure 6.2 shows a microscope picture of the bonded interface. It has been difficult to measure the melt zone and heat affected zone against the dark background of the polyimide film.

![Figure 6.1 A photograph of the laser bonded sample.](image1)

![Figure 6.2 A microscope picture of the laser weld seam.](image2)
Leak test of the bonded sample has been carried out to verify the success of the bonded device. Figure 6.3 shows the microscope picture of the bonded sample with coloured water.

The channel dimensions of the SU-8 microchannel are very small in comparison to that of the PMMA or PC microchannel. The width and depth of the channels were 150 µm and 68 µm. The coloured water filled in the gap between the channel wall and the bonded line. However, it can be seen that the coloured water did not flow beyond the bonded line which implies successful bonding.

Successful bonding of SU-8 microfluidic devices using laser microwelding was established. The bonding parameters were 16 W for laser power with 12 s for bonding time and the weight of 0.750 kg. It has also been established that the bonded samples passed the leak test. The process was reproducible and a novel method to bond SU-8 microfluidic channels using PMMA has been developed.

In the experiments leading to the development of the bonding technique it has been observed that several parameters influence the outcome of the bonding process. As the bonding is between two dissimilar materials the surface roughness plays a very important role in determining the contact between the two surfaces. Optimum contact between the two surfaces is critical and initial experiments without weight showed this. None of the samples could be bonded when no weight was used during the bonding process. The contact conduction is inversely proportional to the surface roughness.
hence the variation in roughness is an important factor in heat transfer [169]. The thermal behaviour of the material is another parameter that influences the outcome of the bonding process. In dissimilar material joining the coefficient of thermal expansion (CTE) varies for the materials and this could contribute to the thermal stress at the interface which could cause the bond to fail. In order to reduce the thermal stress at the interface and also to improve the yield of the bonding process surface modification of the polymer was studied.

6.5 Surface modification of polymer

Surface modification of polymers has been studied using various techniques. Surface modifications are techniques wherein the surface properties of the polymer are modified by radiation or chemical means in order to increase the surface energy. Improved surface energy improves the wettability between the joining surface enabling better contact and enhanced inter-diffusion of the polymer chains between the surfaces. Surface modification also produces surface possessing high specific energy in the form of polar functional groups. These functional groups can produce hydrogen or covalent bonds across the interface thereby improving the bond strength [170]. Surface modification by plasma treatment of polymeric materials like PDMS is commonly used for bonding by creating silanol groups resulting in covalent bonding with the bonding surface [171]. The plasma modification technique of surface treatment has been reported as a method for improving the bond strength for a wide range of thermoplastic polymers like PMMA [172], PS [173] and PC [174].

6.5.1 UV surface treatment

Surface treatment of polymers by application of ultraviolet light has been found to be a simple alternative to plasma treatment. Exposure of thermoplastic polymers to UV light results in photo-degradation of the polymer. The surface of the polymer undergoes photo-oxidation along with chain scission of the polymer chains on the surface. The UV light breaks the chemical bonds and results in the formation of lower molecular weight radicals due to chain scission [175]. Studies on surface modification of thermoplastic polymers have established that the UV surface treated polymer has a lower $T_g$ in comparison to the untreated polymer [173]. The thickness of the affected polymer is determined by the optical absorption length therefore the change in property is observed at the surface of the polymer with the thermomechanical properties of the bulk polymer remaining unchanged by UV exposure. It has been established that exposure of polymer
to light in the range of 300-400 nm is sufficient to break the chemical bonds with most thermoplastic material. The UV surface treated polymer also has a lower density in comparison to the untreated polymer. The weight loss of the polymer was used as a method to determine the extent of surface modification. The contact angle measurements on UV surface modified PC have shown that the contact angle of water on an untreated surface was 70·3° and for the treated surface (3 minutes) was 61·2° [176]. The surface of the modified polymer is more hydrophilic in comparison to the untreated polymer. The $T_g$ of PMMA was lowered by 60 K using this method enabling the UV-exposed microfluidic chips to be bonded at temperatures well below the bulk $T_g$ [177]. Successful low temperature bonding of the surface treated PMMA has been attempted and it has been seen that there has been no surface deformation or reduced bond strength. This method of surface treatment has also been found to be successful with PC microfluidic devices [178].

6.5.2 UV surface treatment of PMMA

In this study the PMMA surface was modified using UV exposure. The PMMA material was cut to size and cleaned using diluted detergent in ultrasonic bath. The cleaned substrate was dried using compressed air. The initial studies were done by exposing the cleaned PMMA substrate to UV light for 15 minutes and 30 minutes. The UV mask aligner (Karl Suss) was used for exposure. The wavelength of the UV light used was 345 nm. Figure 6.4 shows the photograph of the mask aligner used for UV exposure of PMMA samples.

Figure 6.4 A photograph of the mask aligner used for surface treatment of PMMA.
6.5.3 Analysis of surface modified PMMA

In order to understand the change in surface property of PMMA on UV treatment, analysis of the treated surface was done using the Zygo white light interferometer. The Zygo measurements of the surface roughness and profile were analysed to understand possible changes in the surface roughness values due to the surface treatment. The FTIR (Fourier Transform Infrared Spectroscopy) spectra were also obtained for the treated and untreated PMMA samples to analyse the change in the functional bonds on the surface of the polymer. Figure 6.5 shows the photograph of the Zygo instrument used for measurement of surface roughness.

Figure 6.5 A photograph of the Zygo interferometer.

6.5.4 Results of the surface modification of PMMA

Roughness Average Analysis: The surface roughness is an important criteria for ensuring good contact between the substrates during the bonding process. The surface roughness of blank PMMA substrate was measured to be 2.4 nm and that of UV surface treated surface was 5 nm. The variation in the surface roughness can be observed although it is small. Figure 6.6 shows the surface scans of PMMA material obtained on Zygo for both treated and untreated samples. The material was treated for 30 minutes. The sample treated for 15 minutes did not show any significant change in surface roughness.
Figure 6.6 Zygo pictures of (a) untreated PMMA surface and (b) UV treated PMMA surface after 30 minutes.

**FTIR Analysis:** The FTIR (Fourier Transform Infrared Spectroscopy) analysis is one of the standard measurement technique used in the determination of the effect of surface modification. In FTIR, infrared radiation is passed through a sample. A part of the radiation is absorbed by the sample and some of it is transmitted. The resulting spectrum represents the molecular absorption and transmission. This is unique for a molecular structure. Therefore, FTIR is useful in detection of change in molecular structure or new molecular structures on the sample surface.

The FTIR spectra were taken for the blank PMMA substrate and the UV surface treated substrate. Figure 6.7 shows the transmission spectrum for the blank PMMA substrate.
The FTIR spectrum scan of PMMA reflects the presence of C-O bonds within the polymer. The C-O bonds dominate the majority of the vibrational peaks shown in Figure 6.7. Figure 6.8 shows the FTIR spectrum obtained of UV surface treated PMMA substrate (15 min). In comparison with Figure 6.7 it can be seen that there is only very slight variation in the percentage transmittance of the peaks. Figure 6.9 shows the FTIR transmission spectra of a UV surface treated PMMA substrate (30 min).
Figure 6.8 FTIR transmission spectrum for the surface treated PMMA substrate (15 min).

Figure 6.9 FTIR transmission spectrum for the surface treated PMMA substrate (30 min).

The FTIR spectra of the surface treated polymer (30 min) shows significant change in the absorption peaks. The change in the absorption peaks is attributed to the stretching vibration of the C-O bonds. The change is significant for peaks corresponding to wavenumber 1140 and 1721 cm$^{-1}$. It has also been seen that this technique of surface
modification does not create new bonds on the surface as there is no appearance of new peaks in the modified spectra. This is an advantage in comparison to modification techniques that create functional groups on surface as it can produce undesirable electrostatic interactions with the analyte molecules. UV surface treatment method is also less expensive in comparison to plasma treatment.

6.6 Laser bonding of surface modified PMMA

The diode laser was used to bond the surface modified PMMA cover substrate to the SU-8 substrate with microfluidic structures. The UV surface modified PMMA substrate was bonded immediately after treatment. The bonding setup and procedure were similar to that used in the work described in section 6.3. The bonding process was carried out by placing weight of 0.750 kg on the aligned substrate. The laser power was varied from 15 W for bonding times of 10, 12, 15, 18 and 20 s.

The UV surface modified substrate was bonded successfully for all bonding conditions. In the previous experiments on bonding of untreated PMMA substrate to SU-8 using bonding condition of 15 W laser power and 0.750 kg weight for various bonding time did not result in bonding. Successful bonding on untreated PMMA to SU-8 bonding was obtained for the bonding condition of 16 W laser power with 12 s bonding time and weight of 0.750 kg. The surface modification of PMMA could have altered the $T_g$ of the PMMA surface to a lower value than that of the untreated PMMA. This enables to melt the polymer at lower laser power thereby enabling bonding. This significantly reduces the thermal stress at the interface. The samples were bonded successfully for bonding conditions of 15 W for laser power and 10 s for bonding time. Figure 6.10 shows the photograph of the bonded device. Figure 6.11 shows the microscope picture of the weld line.

Figure 6.10 Photograph of a laser bonded SU-8 device using a UV modified PMMA substrate.
The bonding experiments were repeated to check for the reproducibility of the bonding technique. All samples were bonded successfully without delamination. The surface modification assisted laser bonding improved the efficiency of the bonding by reducing the laser power needed to establish a bond.

6.7 Summary

A novel method for assembly of SU-8 microfluidic devices by laser microwelding has been studied. The bonding method provides an alternative approach for bonding SU-8 microfluidic devices. The influence of laser power and bonding time on the bonding process has been studied. The influence of weight on the bonding process has also been determined. The use of weight during the bonding process improved the contact between the substrates however; it generated thermal stress at the interface due to the mismatch of the CTE between the joining materials. Successful bonding of the samples was achieved for bonding condition of 16 W laser power with 12 s bonding time and using weight of 0.750 kg during the bonding process. Leak test of the bonded sample has shown defect free bonding. Surface modification of PMMA using UV exposure has been studied as a method to alter the $T_g$ of the PMMA substrate. Characterisation of the modified surface has been done and the effect of surface modification on the laser bonding method has been studied. Bonding of SU-8 microfluidic devices using the UV treated PMMA was achieved at bonding condition of 15 W laser power with 10 s
bonding time with weight of 0.750 kg. It has been observed that decrease of thermal stress due to surface modification increases the reliability of the bonded devices.
Chapter 7 Conclusions and Future Work

7.1 Conclusions

This thesis investigated and developed a novel laser welding method for assembly of polymeric microfluidic devices. The laser welding method incorporates a metal absorber based line at the interface of the joining substrates for absorption of the laser energy. The thin film metal line was fabricated by e-beam based vacuum deposition of titanium. The absorbed laser energy causes localised heating thereby creating a joint at the interface. The weld contour was designed to be around the channel but away from the channel wall so as to keep the heat away from the microfluidic channel. The polymeric microfluidic channels were fabricated using PMMA, PC and SU-8 based materials. Laser based fabrication of PMMA and PC microfluidic devices was studied for enabling low cost and rapid laser based fabrication of polymer based microfluidic devices. The laser welding method of assembly was developed for PMMA, PC and SU-8 based devices.

A laser microwelding technique for the assembly of PMMA based microfluidic devices has been developed. Fabrication of microchannels using a laser based ablation method has been studied for the fabrication of channels of varying profiles. A detailed investigation of the various parameters that influence the fabrication has been undertaken. The influence of laser power and laser scan speed on the channel profile has been established. Channel dimensions ranging from 82 µm – 946 µm in depth have been fabricated. The increase in the depth of the channel with the number of laser passes has been established which enabled fabrication of very deep channels. The alteration of channel profile to suit a microfluidic application could be achieved by the variation of the process parameters. Design and fabrication of microfluidic channels for capillary electrophoresis has been done. A laser welding based bonding process for the fabrication of PMMA electrophoresis device has been studied. Experiments to study the various parameters influencing the bonding process have been carried out. The influence of the laser power and bonding time has been studied. The variation in the melt zone and heat affected zone to the changing process parameters has been determined. The optimum laser process conditions for obtaining a good seal were determined to be 15 W for laser power and 12 s for bonding time. Bonding could be achieved without application of external weight. The melt zone and heat affected zone increase with both laser power and bonding time. An increase in the weld zone was also
observed with the applied weight. Better contact between the substrates resulted in larger weld zones. With increase in the weld zone the bond strength of the device would increase due to the increase of the total weld area. The process parameters can be varied to alter the width of the weld zone. The heat affected zone was observed to be small in comparison to the weld zone which is key advantage of the laser welding process. This enables to keep the heat away from the microchannel and is useful in bonding of devices containing heat sensitive elements. Mechanical and fluidic tests have been performed on the bonded device to establish its suitability for microfluidic applications. The results of the reliability tests prove the laser welded device to be stable over a period of at least 6 weeks. The usability of the laser bonded microfluidic device over a wide range of fluid flow from 2ml/hr to 20 ml/hr has been established in the fluidic test. The bond strength test on the laser welded device has established that the interfacial bond has a tensile strength greater than 5 MPa and shear strength of 8 MPa. A comparative analysis with the thermal compression bonded PMMA device has further established laser welding bonding method as a rapid, localised method of bonding transparent microfluidic device without any alteration to the surface or channel properties. Numerical simulation of the laser welding process has been carried out for initial understanding of the heating process and temperature distribution at the interface.

A laser based microwelding method for assembly of polycarbonate based microfluidic devices has been developed. The methodology used in the development of the laser welding process for PMMA polymeric material has been extended for PC. Rapid fabrication of microchannels on PC substrate has been studied using the laser ablation method. The variation of the laser power and scan speed has been studied to analyse its impact on the channel profile. Channels of dimensions varying from 123 µm – 475 µm in depth have been fabricated. The fabrication of deeper channels has been achieved by increasing the number of laser pass. The effects of the various process parameters such as laser power, bonding time and weight on the weld characteristics have been studied. The optimum laser bonding conditions for a good weld seam has been found to be 15 W for laser power and 10 s for bonding time. This is similar to that determined for PMMA material. However, the width of the melt zone is smaller in comparison to that of PMMA. This is due to less amount of polymer softening in the case of PC as the $T_g$ of PC material is 147°C in comparison to 132°C for PMMA. The variation of the melt zone and heat affected zone to the changing process parameters has been determined.
The heat affected zone of the PC material is similar to that of PMMA. Liquid test to demonstrate leak-free bond has been carried out. A comparative analysis with a thermally bonded sample in an oven has established the suitability of laser microwelding technique for rapid, localised assembly of PC based transparent microfluidic device. Numerical simulation of the laser welding process has also been carried out for preliminary understanding of the heating process and temperature distribution.

A laser microwelding method for the assembly of dissimilar polymers has been studied. Bonding of SU-8 microfluidic substrate to PMMA has been carried out using the laser microwelding method. Fabrication of SU-8 microfluidic devices for electrophoresis applications has been carried out on glass and polyimide substrates. Polyimide has been found to be a better substrate for the fabrication of SU-8 microfluidic channels. A laser microwelding method to bond SU-8 microfluidic channel to PMMA cover substrate has been studied. The laser process parameters have been varied to study their influence on the bonding process. It has been observed that the bonding is established only with the use of weight during the bonding process. The bonding parameters for laser power, bonding time and weight have been studied and successful bonding of SU-8 microfluidic devices has been demonstrated. The bonding conditions for the bonding process were 16 W of laser power and 12 s of bonding time with 0.75 kg of weight. Leak test using coloured water was carried out on the bonded device to establish leak-free performance of the device. The reproducibility of the bonding technique has been studied and the success rate of the bonding process has been observed as high as 70%. To improve the yield of the bonding technique and to minimise the failure of the technique due to thermal stress, surface modification studies of PMMA material were carried out. The surface modification of the PMMA substrate was made using UV light exposure. The characterisation of the modified surface was carried out using Zygo and FTIR based methods. Bonding studies using surface modified PMMA to SU-8 were carried out and it has been observed that bonding can take place for less laser power than for the untreated PMMA cover. The yield of the bonding process was improved significantly with surface modification of the PMMA cover substrates. Successful bonding was established for bonding condition of 15 W of laser power for 10 s of bonding time using 0.75 kg of weight. This was due to the lowering of surface $T_g$ of the polymer due to surface treatment.
A low temperature (52°C) adhesive bonding technique for the fabrication of free standing SU-8 microfluidic devices has been studied. A bonding, exposure and transferring technique for the fabrication of SU-8 electrophoresis devices has been studied. A polyimide film was used as the carrier substrate for the fabrication of SU-8 microchannels. The use of acetate film as mask as well as the substrate for a one step process of exposure and bonding has been demonstrated.

In summary, a laser welding method for bonding of polymeric microfluidic devices has been studied. The technique of laser welding is a rapid, low cost and a localised heating method which is suitable for fabrication of transparent microfluidic devices. The bond strength and fluidic tests of the laser welded device has established the suitability of this technique for lab-on-chip devices.

7.2 Future work

In this thesis, a new laser based microwelding method for the assembly of polymeric microfluidic devices has been studied. Future work in this technique of bonding could be in the direction of bonding new thermoplastic material like cyclic olefin copolymer (COC) and bonding of dissimilar polymers like COC and polystyrene (PS). This process could also be extended to study assembly of 3D microfluidic devices. Surface modification studies of the joining polymers could be carried out to determine its impact on the joining process and the surface chemistry of the modified polymer. Deposition of the absorber film by inkjet printing methods could also be investigated to enable ‘out of cleanroom’ manufacturing of functional microfluidic devices.
References


122. http://www.twi.co.uk/content/ksab002.html (10/06/2015)


158. Introduction to COMSOL Multiphysics, Version 5.0, COMSOL.
166. http://uk.rs-online.com/web/p/solid-plastic-sheets/2586613/ (Date: 10/06/2015)


178. Park DSW, Hupert ML, Witek MA, You BH, Datta P, Guy J, Lee JB, Soper SA, Nikitopoulos DE, Murphy MC. *A titer plate based polymer microfluidic platform*