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POLYMER EMBOSSING TOOLS FOR RAPID PROTOTYPING OF PLASTIC MICROFLUIDIC DEVICES

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ABSTRACT

In this work, a new MEMS technology for hot embossing using polydimethylsiloxane (PDMS) tools is developed and characterized. The developed technology will permit low cost, simple, and rapid fabrication of disposable microfluidic biochips and plastic microstructures for numerous BioMEMS applications.

For traditional planar systems, a negative photoepoxy (SU-8) or thick positive photoresist (AZ4620) on silicon were used to form micromolds, upon which PDMS was cast. Fabrication time of these PDMS tools was considerably less than that of conventional ones made from nickel or silicon, and remained the same regardless of the feature aspect ratios. The developed PDMS tools were used to rapidly prototype microchannels and microfluidic biochips in polymethyl-methacrylate (PMMA) of aspect ratios up to two, with depths ranging from 5 to 250 μm, and features as small as 40 μm in width. The use of a soft PDMS tool material increased cycle time and embossing force, and limited the tool lifetime to approximately 20 cycles.

The technique was also extended to fabrication of orthogonal 3-D microfluidic systems using multiple lithography steps. In addition to microchannels of the traditional planar systems, these 3-D systems contained features on the microchannel bottom surface, providing obstructions in the flow field. The orthogonal 3-D PDMS tools were fabricated by casting in a micromold formed on silicon substrates using a combination of SU-8 and AZ4620 photoresists. This approach proved to be a much simpler and faster process that the conventional multi-step nickel electrodeposition method.

Overall, the developed technique enables simple and low cost fabrication of planar and orthogonal 3-D microfluidic systems, and is particularly well suited for rapid prototyping applications, where fast processing and low cost are important and the number of samples is relatively low. Combined with a high-resolution mask printing on transparencies, a complete microfluidic device could be fabricated in less than 24 hours.

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CHAPTER 1

INTRODUCTION

Micromachining and microelectromechanical system (MEMS) technologies can be used to produce complex structures, devices, and systems on the scale of micrometers [1]. The application of MEMS technologies in various fields such as mechanics, fluidics, optics, and electromagnetics has resulted in the evolution of microdevices that are the miniaturized versions of their macroscale counterparts. Medicine and biology are among the most promising and at the same time most challenging fields of application for MEMS technologies [2]. Medical applications not only motivate miniaturization of mechatronic systems, but also encourage the development of novel concepts and technologies for the integration of artificial and biological components into hybrid microelectromechanical systems [3]. Lab-on-a-chip or integrated fluidic analytical systems are the most prominent biomedical MEMS (BioMEMS) applications as they offer advantages in terms of reduced sample consumption, faster analysis, higher sensitivity, disposability, and cost compared to the existing macroscale systems.

Microfluidic devices or micromachined fluidic systems [4-17] have assisted the growth of MEMS applications in the biological sciences, medicine, and biotechnology, which are often referred to as biomedical MEMS (BioMEMS). In analytical chemistry and biotechnology, MEMS technologies have enabled the fabrication of biochips with microchannels for applications such as, electrophoresis [4-6], polymerase chain reaction (PCR) [7,8], electrical

field flow fractionation [9,10], gas chromatography [11,12], liquid chromatography [13,14], DNA separation techniques [15,16], and drug delivery devices [17]. In addition, the concept of microscale total analysis system (μTAS) [18] to perform the functions of large analytical devices in small, often disposable units relies primarily on microscale fluid flow as these systems must contain elements for the acquisition, pretreatment, separation, post treatment, and detection of samples.

Earlier biochips were fabricated in either silicon [8,11-14] or glass [4-6,17] using technologies developed extensively in the microelectronics industry. A number of microfluidic devices for various applications, especially in biotechnology, were fabricated by defining the features using standard photolithography followed by etching the substrates using chemicals or plasma and then sealed with a cover plate. Glass and oxidized silicon have desirable surface characteristics: they possess a negative charge and support electroosmotic flow and glass systems have proved successful especially when applied to separating and sequencing DNA [19]. The use of silicon and glass as the substrate material was primarily because of the existing and established microfabrication methods to fabricate microelectronic devices.

However, silicon as a material for biotechnology exhibits limitations in the form of protein adsorption, conductivity in electrophoresis applications, microchannel cross-section geometry due to crystallographic plains when using wet etching, lack of simple surface modification techniques, opaqueness in visible and UV spectra, and necessity of specialized equipments to fabricate high aspect ratio vertical trenches. Glass offers considerable advantages compared to silicon in terms of lower cost (10-40 cents/cm^2) [20], reduction in fabrication complexity, and transparency in visual and UV spectra for easier inspection and sample detection. Glass surface, being hydrophilic, is valuable for fabricating drug delivery devices

dealing with liquids. However, wet etching of amorphous glass resulted in the fabrication of microfluidic channels that are isotropic and dry etching of glass to fabricate vertical trenches required specialized equipments. In both the fabrication technique, sealing or bonding of the channels imposed considerable problems as it involved either high temperatures or high voltages and long processing. Biocompatible, UV-cured adhesives were also used to perform room temperature bonding of glass biochips [17,21]. Although, clogging of the microchannels was avoided by cleaning the channels with solvent, it adds an additional step in the overall fabrication.

Clearly, there is a need for materials and fabrication methods that allow rapid evaluation of biomedical microfluidic systems, especially at the exploratory stages of μTAS development, while maintaining low cost and using mechanically robust materials [18]. In a recent work, Becker et al. [22] outlined requirements of an ideal microfluidic device, including parameters such as ease of manufacturing, suitable microfabrication technologies for a large varieties of geometries, low cost for high volume production, surfaces compatible to the media used, low conductivity for electrokinetic pumping and electroosmotic separation, optimized surface modification techniques, and disposable on a biocompatible substrate.

Polymers as substrate material offer a possible solution to address these challenges and lend themselves to the mass fabrication of microfluidic devices. Polymers offer a wide range of advantages compared to silicon or glass in microfluidic applications and are most promising due to the ability to fabricate microfluidic devices using mass replication technologies as well as for rapid prototyping [20]. Replication technologies (hot embossing, injection molding, and casting) are well suited for these applications because the principles behind these processes are already well established in the macroscale world. A number of microfluidic systems have been recently

demonstrated in polymers for biomedical applications, including miniaturized electrophoresis chips [19,23,24], microfluidic mixers [25-27], pumps and valves [28], devices for cell or protein patterning [29,30], and microfluidic switches [31]. A number of polymers have been used for micromachining including polyamide (PA), polybutyleneterephthalate (PBT), PMMA, polycarbonate (PC), cycloolefin coplymer (COC), polyoxymethylene (POM), polypropylene (POM), polyphenylene ether (PPE), polystyrene (PS), and polysulfone (PS) [20]. Becker et al. [32] list the advantages of using polymers as the substrate material for microfluidic applications including: (a) a wide range of available material properties and surface chemistries that permit application-specific substrate optimization; (b) suitable microfabrication technologies for a large variety of geometries (rectangular, rounded, high aspect ratio, etc.); (c) low conductivity for electrokinetic pumping or electrophoretic applications; (d) low material cost, which us key for disposable devices or high volume production; and (e) ease of manufacturing due to replication-based fabrication.

Further, the need for high aspect ratio features for various life science applications posed a serious problem with the existing microfabrication technologies using silicon and glass. The solution to the fabrication and material problems for the production of these structures lies in the use of polymers as substrate materials and replication method for component fabrication. Apart from the inherent material properties, the rapid growth of polymers in applications involving chemistry and biology is also due to the established replication technologies such as hot embossing, injection molding and methods of rapid prototyping like casting and laser micromachining. Injection molding [20,33,34], hot embossing [20,22-24,32,33], casting [18-20,25,26,31], and laser ablation [20,30,35-37] are the techniques typically used to micromachine polymers.

Microinjection molding represents an advantageous replication technology for microcomponents with a special qualification for large-scale series production. A schematic representation of the machine is shown in Figure 1.

Casting is an inexpensive but slower replication technique to fabricate microfluidic devices in elastomers, where the elastomer precursor and the curing agent are mixed at a fixed ratio and poured over the template. Laser ablation is a direct technique in which the energy of a laser pulse is used to break bonds in a polymer molecule and to remove the decomposed polymer fragments from the ablation region. Hot embossing is a reasonably fast and moderately expensive technique used to replicate microfluidic channels in thermoplastics. It is a simple process, where the polymer and the tool are heated above the glass transition temperature (T_g) of the thermoplastic and a controlled force is applied under vacuum. With the force still applied, the assembly is cooled below the T_g and they are de-embossed. Becker et al. [20] compared the prominent replication technologies with respect to different properties including cycle time, materials, process conditions, automation, and geometry.

The success of any replication technology is highly dependent on the tool (sometimes

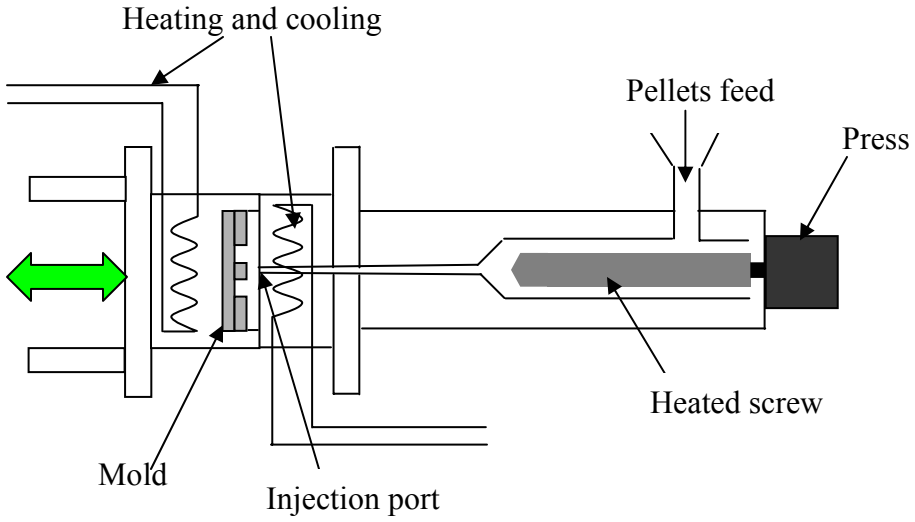


Figure 1. Schematic of an injection molding machine.

called the master or mold). There is no single ideal technique to fabricate the tool for hot embossing. The choice of technique is entirely dependent on the feature size, aspect ratio of the structures, and of course, and facilities available in the laboratory. An overview on the existing tool or master fabrication methods is given in [33], where hot embossing and injection molding are used as the replication technologies. One problem frequently encountered by researchers without specialist microfabrication facilities is how to fabricate prototype devices rapidly at a realistic cost. Though the replication technologies provides the scope for simpler fabrication in polymers, the existing tool fabrication procedures offers considerable limitation with respect to rapid prototyping, as each technique exhibits complexity in terms of facilities and time at one stage or the other.

Further, there is no simple process for fabricating orthogonal 3-D microfluidic devices in thermoplastics (e.g., polymethylmethacrylate, cycloolefin copolymers) [27], which are harder materials and are capable of supporting significantly higher fluidic pressures than PDMS. By inclined x-ray exposure or by using two-stepped resist structures as well as by the combination of several micromachining techniques, multi-stepped structures can be generated. Following inversion by electroplating, mold or tool inserts for 3-dimensional plastic structures are obtained [34]. But the current ways of fabricating orthogonal 3-D embossing tools are quite complex, time consuming, and involve creation of layered structures through repetitive steps, such as multiple lithography followed by etching silicon or electroplating nickel. The risk of fabrication error in such a multiple processing system is much higher and can lead to more number of iterations before achieving reasonable success in demonstrating the final device.

In this work, we present a simple technique that enables rapid and low-cost fabrication of embossed planar microfluidic channels in thermoplastics using tools made from PDMS. This

technique is also extended for fabricating orthogonal 3-D microfluidic systems incorporating features within microchannels by combining photolithography processes using AZ4620 and SU-8 resists. This technique has tremendously reduced the complexity involved in fabricating both planar and orthogonal 3-D embossing tools. Combined with a high-resolution mask printing on transparencies, a complete microfluidic device can be fabricated within 24 hours. Since PDMS retains it physical characteristics up to 200^0C, the tools may be extended to emboss other thermoplastics such as polycarbonate, polypropylene, or cycloolefin copolymer.

Following this introduction, chapter two will overview the hot embossing process and the conventional embossing tools, and will discuss their application to fabricating microfluidic channels. Chapter three will describe the process developed for fabricating planar and orthogonal 3-D tools polymer embossing tools and their application to rapid prototyping of microfluidic systems. Fabrication results and process characterization will be presented in chapter four. Finally, chapter five will provide a summary and will discuss possible future directions of this work.

CHAPTER 2

BACKGROUND

This chapter discusses the conventional techniques of fabricating microfluidic devices in various substrates such as silicon, glass, and polymers. Further, the basic principle, operation, and application of hot embossing technique, which is the method of fabrication in our work, to fabricate microfluidic systems will be discussed. This discussion includes the embossing parameters involved in the fabrication, properties of certain thermoplastics commonly used for biochips, critical issues involved in the technique, and materials used for the fabrication of the mold for hot embossing. This is followed by a detailed comparison of different tools (molds) fabricated for hot embossing. The comparison is based on the materials used and their properties, embossing parameters, complexity of the process to fabricate, lifetime of the molds, properties of the finished molds. A table compiled from relevant references and practical knowledge is included to compare these issues.

Current Methods of Microchannel Fabrication

Microchannels in biochips are typically fabricated in silicon, glass, polymer, or quartz substrates by means of standard microfabrication processing techniques. The fabrication in silicon or glass involves the conventional steps such as, photolithography followed by wet or dry etching, and substrate bonding [4-6,8,11-14,17]. The etching process depends on the morphology of the channel needed for the final application. Wet etching of silicon and glass

results in trapezoidal and semicircular channels respectively. Dry etching of silicon or glass using specialized RIE system is performed to fabricate microfluidic channels with high aspect ratio and vertical walls. The etched wafers are then bonded to silicon or glass by fusion [38-40], anodic [38], or adhesive bonding techniques [17]. The microchannel fabrication process in silicon and glass is schematically illustrated in Figure 2. As discussed in Chapter 1, polymers offer advantages compared to silicon and glass in life science applications. As shown in Figure 1, injection molding is a high temperature process where the polymers, which are initially in the form of pellets are fed into a cylinder, a heated screw and melted. The temperature though vary depending on the polymer used, is in the range of 200^0C to 350^0C for common thermoplastics such as PMMA and PC. The melt is injected at high pressure (600-1000 bar) into the evacuated cavity, against the tool to replicate features [20]. The process can be automated and used to fabricate biochips at a very fast rate, but is limited by the materials used for the tool and the availability of the appropriate polymers.

The common injection molding parameters like relatively low tool temperatures and injection pressures lead to an incomplete filling of the microstructured mold insert. As the feature size of the device gets smaller, the less material has to be injected into the cavity and the cavity has to be heated closer to the melting point of the polymer material to allow the polymer to flow into the small structures and then the cavity is cooled to allow the ejection of the microstructured part [33,34]. This process pushes the cycle time close to conventional hot embossing. However, for low aspect ratio structures, cycle time for injection molding is much shorter than for hot embossing.

Though casting can be done for various elastomers, the most prominent elastomer used is polydimethylsiloxane (PDMS) and the casting template can be fabricated by the conventional

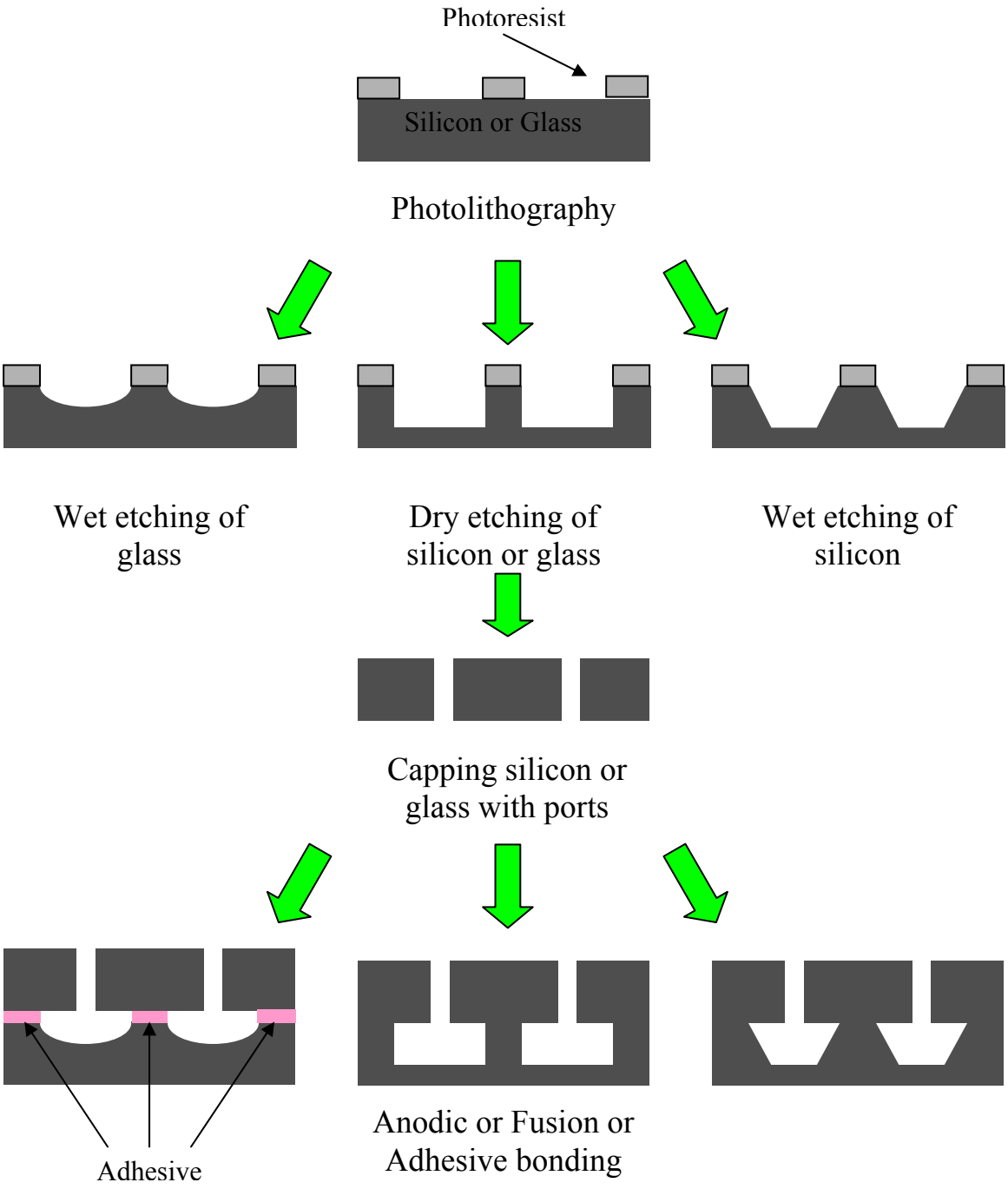


Figure 2. Schematic diagram illustrating fabrication of microfluidic channels in silicon and glass.

micromachining techniques [18-20,25,26,31,41]. One of the important advantages of PDMS processing is the ease and flexibility associated with the bonding process. Both reversible and irreversible bonding can be achieved in sealing PDMS to glass, silicon, or plastic. Whitesides et al. found that oxidation of PDMS using plasma renders the surface hydrophilic and introduces silanol groups to ensure irreversible bonding to glass, silicon, and silicon oxide. Further, with a high-resolution image setter used to print the design on a transparency, casting makes it possible to fabricate the complete microfluidic system within 24 hours in PDMS. Further, casting facilitates the fabrication of 3-D microfluidic systems with just an additional photolithography stage in fabricating the casting template. Recently, PDMS casting was used to fabricate passive microfluidic mixers. Beebe et al. [25] presented an orthogonal 3-D serpentine mixer fabricated in PDMS enhancing chaotic advection. Stroock et al. [26] presented a passive mixing device in PDMS with ridges fabricated in the bottom surface of microchannels using two-stage photolithography to define the casting template.

The mechanism involved in laser ablation is a complex combination of photochemical and photothermal processes. This means that some chemical bonds of the substrate are broken directly during the process of photon absorption while others are broken thermally by the released heat of those excited molecules that do not break up photochemically [35]. High aspect ratio holes (~10) have been machined in polymers using beam of 100fs laser pulses. When deeper structures are machined, tapering and sometimes bending of the holes can occur [36]. Laser micromachining techniques for fabricating biodegradable microdevices in polymers for applications in biomedical engineering were demonstrated. Microchannels and holes were fabricated in poly-D-lactic acid and poly-vinyl alcohol using ultraviolet lasers [37]. However,

the interaction of the laser light and the polymer material induces surface modifications compared to the untreated material.

The underlying principle of polymer microfabrication involves the replication of a master or tool or mold which is the negative replica of the desired, final microfluidic polymer structure [20]. It begins with the fabrication of the tool using microfabrication principles or by traditional machining such as sawing, cutting, and milling. The microchannel fabrication process in thermoplastic substrates is schematically illustrated in Figure 3. The choice of technique is entirely dependent on the feature size and aspect ratio necessary for the application. The tool fabricated can be replicated into the thermoplastic structure either by hot embossing or injection molding. The substrate with the microchannels is then bonded to a capping polymer by several methods such as lamination, adhesives, fusion (heat and pressure), and welding.

Microchannel Fabrication Using Hot Embossing

Currently, the most widely used replication process for fabricating channel structures for microfluidic applications is hot embossing. Figure 4 shows a schematic of an embossing machine. The machine has a force frame, which delivers the force required during embossing. The tool and the thermoplastic are mounted on the heating plates (hot plates), which also have the cooling channels.

The embossing tool and the polymer are heated in a vacuum chamber above the glass transition temperature T_g of the polymer to soften the surface of the thermoplastic. The temperature usually used is between 100^0C to 180^0C as the T_g of the standard thermoplastics such as PMMA and PC is 106^0C to 150^0C respectively. The vacuum is necessary to prevent the formation of any air bubbles in small cavities. Further, it also allows the water vapor to be

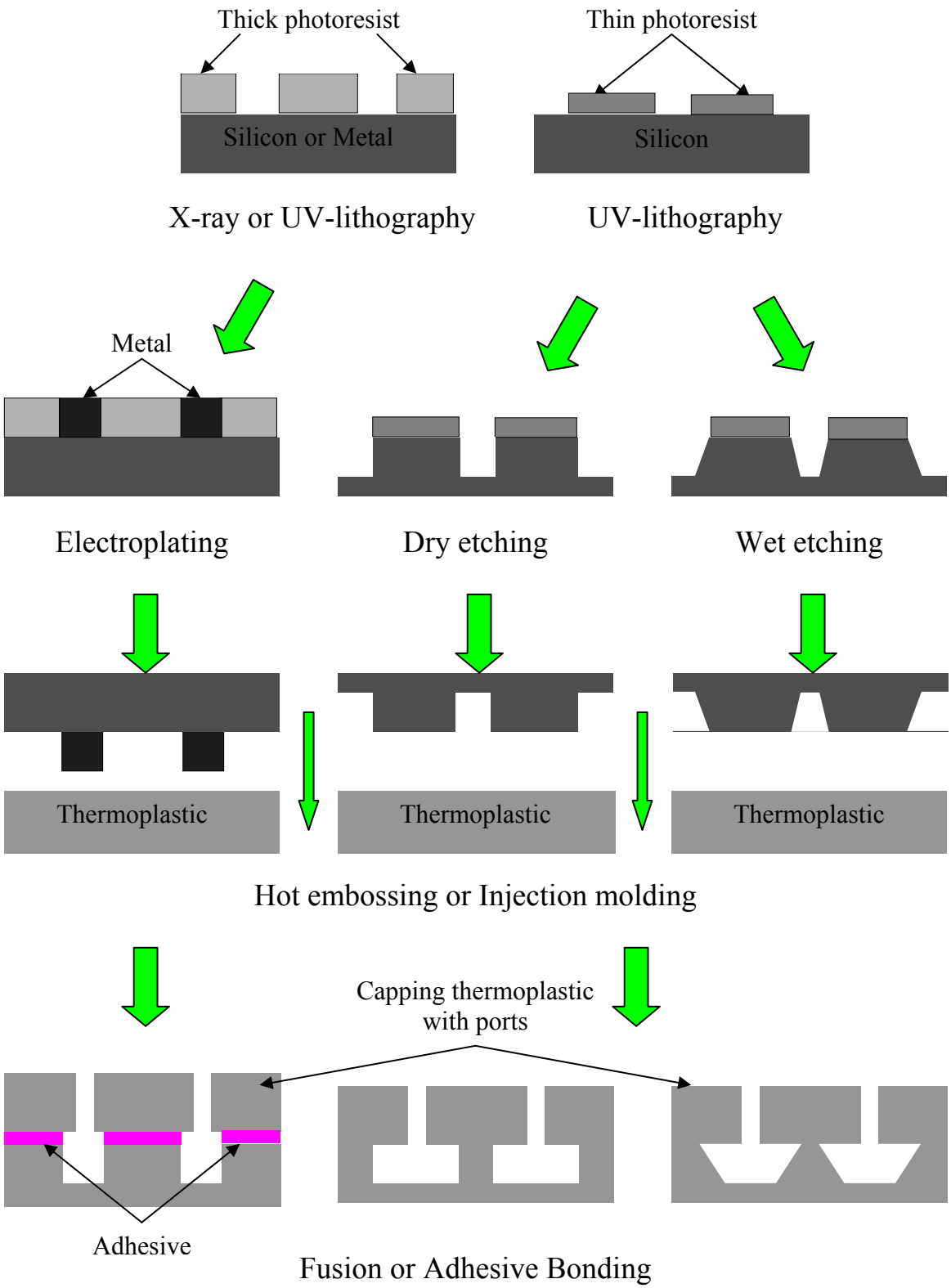


Figure 3. Schematic diagram illustrating common typical polymer microchannel fabrication processes.

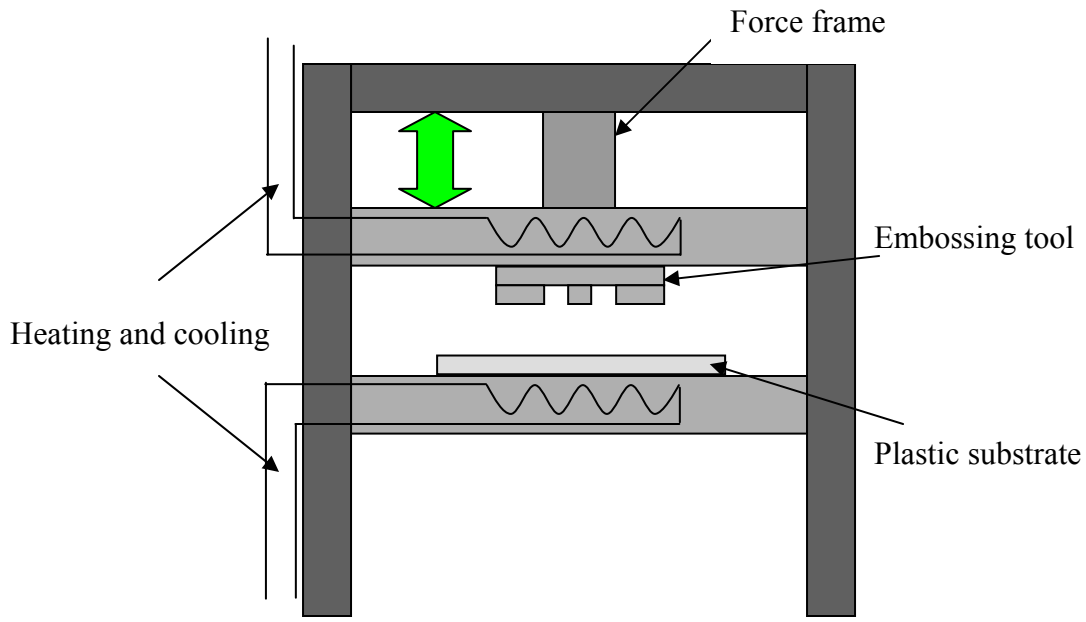


Figure 4. Schematic of a hot embossing machine.

removed. The force frame delivers the embossing force to replicate the tool features into the polymer. Typical embossing force densities are on the order of 0.5-2 kN/cm^2 [20]. The force is applied for a very small duration for about a minute, which is referred as the "hold time". Still applying the force, the tool-substrate sandwich is cooled down below T_g. The thermal expansion coefficients of the materials used should be considered to keep this thermal cycle as small as possible to prevent any thermal stresses and replication errors. For example, thermal expansion coefficient of polymers is around $7x10^{-5}$ /K while silicon has about $1.5x10^{-6}$ /K and nickel around $1x10^{-5}$ /K which determines this thermal cycle to be about 30^0C for PMMA and PC [32]. After reaching the lower cycle temperature, the embossing tool is driven apart (de-embossing) automatically from the polymer, which has the desired features. The overall "cycle time" of the process is between 3-10 min [20] and varies with the features and aspect ratio involved in the process.

The high fidelity of the replication process is governed by sidewall roughness of the embossing tool, adhesion between the tool and polymer, sidewall angles of the tool, and temperature coefficients of the materials used. The frictional forces during the de-embossing step is kept minimum to prevent any damage to the features embossed in the polymer. Therefore, care is to be taken in the microfabrication process to minimize the roughness, as rough sidewalls in the tool increase the friction between the tool and polymer.

The sidewall angle is a critical parameter in determining the release of the tool from the polymer in de-embossing and it is specific to the application. Angles greater than 90^0 results in the loss of adhesion between the features to the substrate of the tool and in turn reduce the life of the tool. If the application and tool fabrication allow angles less than 90^0, this is advantageous in the embossing process [32].

The other property that determines the life of the tool is the chemical interface between the tool and the polymer. Adhesion between embossing master and polymer creates an additional force during de-embossing and it is vital to have both the surfaces with minimum chemical surface bonding sites. Release agents often used on the macroscale to aid release of complex structures, are often not suited for microfluidic devices, as they tend to increase the polymer autoflourescence and may diffuse into the polymer matrix affecting surface properties [20].

As discussed earlier, the temperature coefficient of various materials involved is another important parameter that is to be considered in setting the “hold time” and in turn the “cycle time” to avoid any shrinkage of the polymer material.

Conventional Fabrication of Tools

In general, the success of any replication technology is completely dependent on the tool (also called the master or mold) since any surface defect will be replicated faithfully in the polymer. For example, a tool for injection molding must be a rigid material to withstand the high pressure and should have good thermal properties at high temperatures. There are number of methods used to fabricate tools for various replication technologies, including the traditional CNC machining, X-ray or UV LIGA followed by electroplating of nickel, and wet or dry etching of silicon. Surface morphology, adhesion properties to the thermoplastic, lifetime, feature sizes, and costs are the critical factors to be considered when a tool is fabricated.

CNC machining of materials such as stainless steel offers a very long lifetime but is used only for large features (>100 μm) with tolerances in the range of about 10 μm [20,22,23,33] and is limited by difficulties in machining complex designs. As the entire tool is made of a single material, any adhesion problem between the tool and substrate is avoided which results in longer lifetime. With established micromachining techniques and suitable thermal properties, silicon is considered to be a very good material for use as an embossing tool [20,22,23,42]. Wet etched silicon tools can be used directly to replicate low aspect ratio features. A major limitation is in the form of the trapezoidal shape, which results due to the crystallographic planes inherent to silicon. Alternatively, dry etching techniques such as deep reactive ion etching (DRIE) can be used to fabricate deep, high aspect ratio structures with vertical walls. However, scalloping or high surface roughness due to non-optimized or fast etches can limit the achievable depth of structures and can result in poor de-embossing characteristics. Additionally, specialized equipment is necessary to perform DRIE which may not be available in all research laboratories.

Conventional lithography, X-ray or UV LIGA followed by electroplating of nickel or nickel alloys on silicon or nickel substrates is a common technique of fabricating tools with very small and complex features [20,22,23,43]. The electroplated nickel surface can be very smooth and has good surface chemistry with many polymers [20]. However, electroplating of tall, high aspect ratio structures has to be done for a very long time [43-45] and increasing the current density to speed up the process typically increases stress levels. In addition to stress, poor adhesion to the substrate seed layers and non-uniform deposition are the other issues to be considered in electroplating. X-ray LIGA offers a potential solution in fabricating tools with very small, complex features, and high aspect ratio structures [20,34,46,47] but is highly limited by the restricted availability and high cost associated with the synchrotron radiation sources. Replication tools with aspect ratio from 10 to 600 can be fabricated using LIGA, and the lifetime of these molds were as high as 1000 cycles [34]. The surface roughness of these molds were reported to be 10nm [20].

Replication using polymer tools has been gaining popularity due to considerable reductions in cost, complexity, and fabrication time. Chiang et al. [48] characterized the process of double-casting using the standard lithography to define a silicon casting template and casting PDMS against the template. A second casting was done using this PDMS as the tool and the microstructures were fabricated on various polymers such as polyurethanes, epoxies, and Teflon. However, double-casting typically is done with slow-curing polymers to obtain faithful replication of the PDMS tool, resulting in the increase of process time. Also, the surface chemistry of various castable polymers offers a potential problem of adhesion, which in turn necessitates the use of release agents during the separation of the two polymers. Edwards et al. [49] used negative resist SU-8 as a tool for injection molding and replicated parts in

polycarbonate and polypropylene. Following, hard baking, the negative epoxy SU-8 was used directly as a tool for embossing or injection molding. The lifetime of these tools is very short due to poor adhesion of SU-8 to the base substrate during de-embossing. All of these techniques are time consuming and required specialized equipments that are not available in every clean room. Thus, there is a need for more rapid, simpler, and cost effective approach to fabricate the tools for the replication techniques.

Summary

Silicon, glass, and polymers are the three prominent materials used to fabricate microfluidic systems. Fabrication in silicon or glass involves conventional processing steps such as photolithography followed by wet or dry etching and substrate bonding. Since polymers offer a wide range of advantages compared to silicon and glass in life science applications, they are becoming increasingly important in microchannel fabrication. Hot embossing is a reasonably fast and moderately expensive technique used to replicate microfluidic channels in thermoplastics. Although there are many methods of fabricating tools for the replication techniques, all of them are time consuming and often require specialized equipment that is not readily available in every clean room. Thus, there is a clear need for a faster, simpler, and cost-effective approach to prototyping microfluidic systems in thermoplastics.

CHAPTER 3

FABRICATION OF POLYMER EMBOSSING TOOLS

As discussed in the previous chapter, the embossing tools fabricated by various micromachining technologies using silicon, metals, and recently polymers have their own advantages and limitations. Though the choice of technique mainly depends on the feature size and aspect ratio of the microfluidic system components, it also relies on the facilities available for tool fabrication and replication. We developed a rapid and simpler approach to fabricating embossing tools from PDMS elastomer and using them to emboss PMMA thermoplastic. The technique is aimed at rapid prototyping of microfluidic systems in 24 hours with mostly the basic clean room facilities. Further, the technique is also extended to fabricate orthogonal 3-D microfluidic passive mixers. In this chapter, we will discuss the developed fabrication process.

Fabrication Method Overview

Our fabrication process used a single layer of SU-8 (2075 series (MicroChem Corp.) or AZ 4620 (Clariant Corp.) photoresist to define a template for casting PDMS (Sylgard 184, Dow Corning Corp.) to form the embossing tool. The PDMS tool can then be used to emboss the microchannels in thermoplastics (PMMA, PC, COC, etc.) substrates. In this work, the PDMS tool was used to emboss PMMA substrates. We formed the orthogonal 3-D microfluidic devices using a second photolithography step to define features inside the main channel before casting PDMS. Overall, the fabrication steps involved in this process included photolithography, PDMS

casting, embossing PMMA, and bonding the microchannels with a capping PMMA wafer. The mask design to demonstrate the fabrication of planar channels had arrays of straight channels with widths ranging from 5 μm to 600 μm sand different center-to-center spacing. The design used for orthogonal 3-D passive mixers had 1 mm wide mixing channels with 500 μm wide features located along the centerline.

PMMA substrates and their preparation

The 3" diameter circular PMMA substrates (GE Polymershapes, Cincinnati, OH) used in this work were 1mm thick and had a glass transition temperature about 106^0C. It is important to note that material properties of PMMA can differ considerably depending on the grade and manufacturer. In general, the glass transition temperature (T_g) of PMMA varies between 45^0C to 140^0C [62] depending on it's grade.

The substrate was cleaned in isopropyl alcohol or methanol for 10 minutes in a Petri dish. The cleaning process was done mainly to remove any impact of the protective covers on the surface of the polymer. Once cleaned, the wafer was subsequently rinsed in deionized (DI) water before blow drying with N_2. The wafer was then placed in a convection oven at 60^0C for about 2 hours to remove any moisture present in the polymer. Care was taken not to expose the PMMA wafers to acetone as it is conventionally done with silicon and glass wafers to clean them. Acetone attacks PMMA and alters the surface properties of the polymer and is one of the solvents used to bond PMMA to another PMMA by fusing the two surfaces in contact.

Embossing Tools

Fabrication of planar and orthogonal 3-D polymer tools is schematically illustrated in Figure 5.

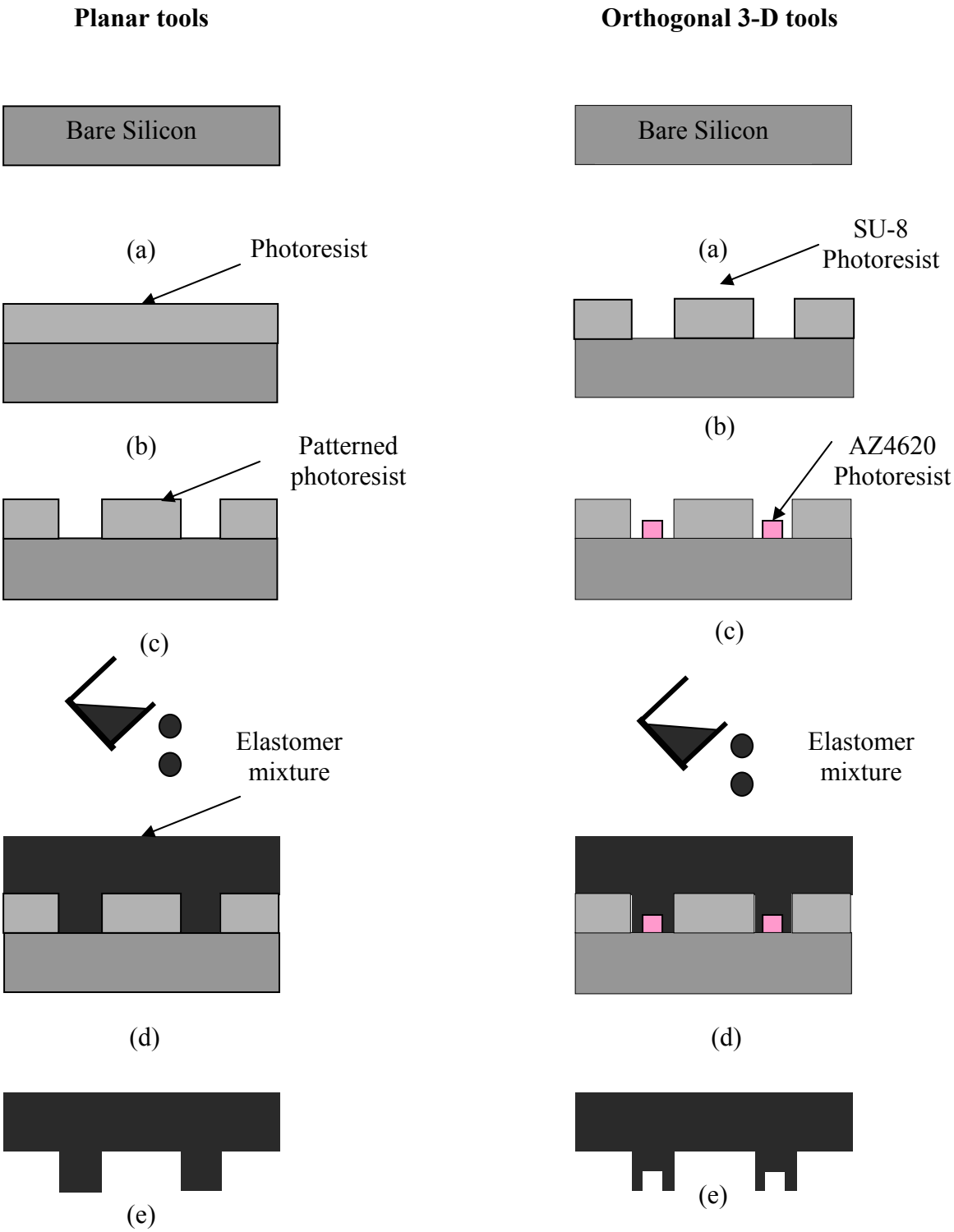


Figure 5. Schematic diagram of the PDMS tool fabrication process. Planar tool are shown on the left; orthogonal 3- D tools are shown on the right. Fabrication steps include substrate preparation (a), one or two-stage photolithography (b) and (c), PDMS casting (d), and a finished PDMS tool (e).

Planar Embossing Tools

Template for casting PDMS was fabricated by standard photolithography on a 3" diameter silicon wafer 300-400 μm in thickness (Wafer World Inc.). The substrates were cleaned with a 7:3 solution by volume solution of H_2SO_4: H_2O_2 (piranha solution) for 5 min at room temperature to remove any impurities on the surface. The substrates were then rinsed in de-ionized water for 5 min to completely remove H_2SO_4 from them. The native oxide and the oxide grown due to the piranha solution, on the wafers were etched in a 2% HF solution for about 30 seconds to a minute. After rinsing with DI, the wafers were dried and then placed in an oven at 120^0C for at least 15 minutes to remove any moisture on the surface. The oxide etching and baking was done to prevent any adhesion problems between the photoresists used and silicon. Two photoresists, AZ 4620 for thickness varying between 5 μm to 40 μm and SU-8 for thickness above 40 μm were used for fabricating the casting templates.

Taking the 20 μm case, AZ4620 was spun at a speed of 500 rpm for 10 s and then accelerated to 1,000 rpm and kept at that speed for 20 s. When spun, a swab or straw was gently placed on the edge of the wafer to remove any edge bead formed during the spin coat. The wafers were carefully set on a leveled plate for about 4 min at room temperature for the photoresist to settle down uniformly. The resist was then soft baked at 65^0C for 4 min in a convection oven followed by 100^0C on a leveled hot plate for 4 min. The wafers were once again placed at 65^0C in an oven for 4 min and then rested at room temperature for 30 min. After the soft bake, the photoresist was exposed to UV-radiation through the appropriate masks for 2 min. Hard contact between the photoresist and the mask was ensured to keep the angle of the feature walls to the substrate close to 90^0. Once exposed, the wafers were developed in AZ400K developer, diluted in DI water at a ratio of 1:3.5 for 2.5 min. The wafers were then rinsed in DI

water and finally blown dry in nitrogen. The exposure and development times had to be increased when they were performed at lower humid conditions.

PDMS elastomer precursor and the curing agent were well mixed in a plastic beaker at the ratio of 10:1. The mixed elastomer was poured against the silicon wafer to generate the negative replica of the features in the template. The mixture was allowed to settle down for about an hour to remove the bubbles formed during the mixing and pouring. It was then cured on a leveled, flat hot plate at 60^0 C for 3 hours. The flatness and proper leveling of the hot plate were critical to ensure that the PDMS tool is uniform in thickness throughout. In turn, the uniformity in the thickness of the tool was necessary to have a faithful replica of the tool during embossing. The cured PDMS was peeled off carefully from the silicon casting template to release the embossing tool.

For thickness of 100 μm and above, negative epoxy SU-8 2075 was used as the photoresist for the casting template. The high viscous resist was spun at 500 rpm for 10 s with a ramp rate of 100 rpm/s and then ramped at 300 rpm/s to a final speed of 1700 rpm for 30 s to achieve 100 μm. The spun resist was allowed to settle on the wafers for at least 10 min on a highly leveled and flat plate. The flatness and leveling of the plate was to prevent any non-uniformity in the thickness of the resist along the diameter of the wafer. The wafers were covered with Petri dishes to prevent any impurities that could fall on the resist. Many investigators [50-59] have optimized SU-8 processing for different applications involving various aspect ratios and feature sizes. After removing the Petri dishes, the photoresist was soft baked in a programmable, convection oven at 65^0 C for 10 min and then at 95^0 C for an hour and 45 min. The ramp rate in both the cases was 1^0 C/min. The resist was allowed to cool down naturally to room temperature before the exposure. The energy required to crosslink the negative

photoresist is entirely dependent on the thickness of the resist spun and the feature size. Exposure energy between 500 – 600 mJ/cm^2 was used for a thickness of 100 μm depending on the minimum features size involved in the experiment. The intensity of the exposure system used was around 7 mW/ cm^2 at 365 nm and thus the resist was exposed for 72 –86 s. For further cross-linking, the resist was baked in the same programmable, convection oven at 65^0 C for 10 min and then at 95^0 C for 20 min. The ramp rate in both the cases was 1^0 C/min. The resist was allowed to cool down naturally to room temperature. The photoresist was developed in the SU-8 developer for 45 min and then was blown dry with nitrogen. Isopropyl alcohol was used to confirm the complete development of SU-8 as any undeveloped resist will release a milky white solution. The wafers were then exposed to O_2 plasma for 10 min to remove the debris on the sidewalls of the developed resist. An optional hard bake at a temperature around 100^0 C to 150^0 C for 5 min was performed for a permanent adhesion of SU-8 to the base silicon. The casting was performed exactly the way discussed above for an AZ4620 template. It was interesting and important to note that the thickness of SU-8 2075 obtained for various spin speed was not a constant. Since the viscosity of SU-8 2075 was around 27000 cP, any minor variation in the temperature of the clean room reflected on the thickness obtained. It was found from the manufacturer that there could be a maximum of 15% variation with 1^{0}C change in the temperature. Care was also taken in storing the photoresist almost at constant temperature to negate any major variation in the thickness achieved.

Orthogonal 3-D Embossing Tools

The schematic representation of the procedure for fabricating the orthogonal 3-D tool was shown in Figure 5. As mentioned earlier, there is no simple process for fabricating orthogonal 3-D microfluidic devices in thermoplastics (e.g., polymethylmethacrylate, cycloolefin

copolymers), which are harder materials and are capable of supporting significantly higher fluidic pressures than PDMS, due to the lack of simpler methods of fabricating tools. The procedure established in this work to fabricate planar embossing tool was further extended to fabricate orthogonal 3-D microfluidic passive mixers in thermoplastics.

The fabrication of orthogonal 3-D embossing tools was similar to the fabrication procedure described earlier. The key difference was the second photolithography step done to define the features within the microchannels. Once the SU-8 layer was patterned to define the main channel, AZ4620 was spun for 20 μm and patterned to define the features inside the main channel. The photolithography was performed exactly the way explained earlier. This silicon wafer with both SU-8 and AZ4620 served as the casting template and the rest of the processes from casting PDMS to bonding PMMA was done exactly the same way as for the planar microfluidic devices.

Hot Embossing

Hot embossing and bonding of PMMA using PDMS tools is schematically shown in Figure 6. The embossing machine used in this work shown in Figure 7 had a stationary top hot plate and a movable bottom hot plate on which the tool and polymer were placed. A vacuum pump was connected to the machine to provide high vacuum during the entire embossing cycle. Unlike the embossing machine showed in Figure 2, this machine cannot hold the tool and the substrate separately. The PDMS tool and the PMMA substrate along with some Teflon support were placed on the bottom hot plate. The Teflon support was to deliver uniform force throughout the diameter of the substrate. The PDMS embossing tool and the thermoplastic (PMMA) were heated together to a temperature of 145^0 C, which is 45^0 C above the glass

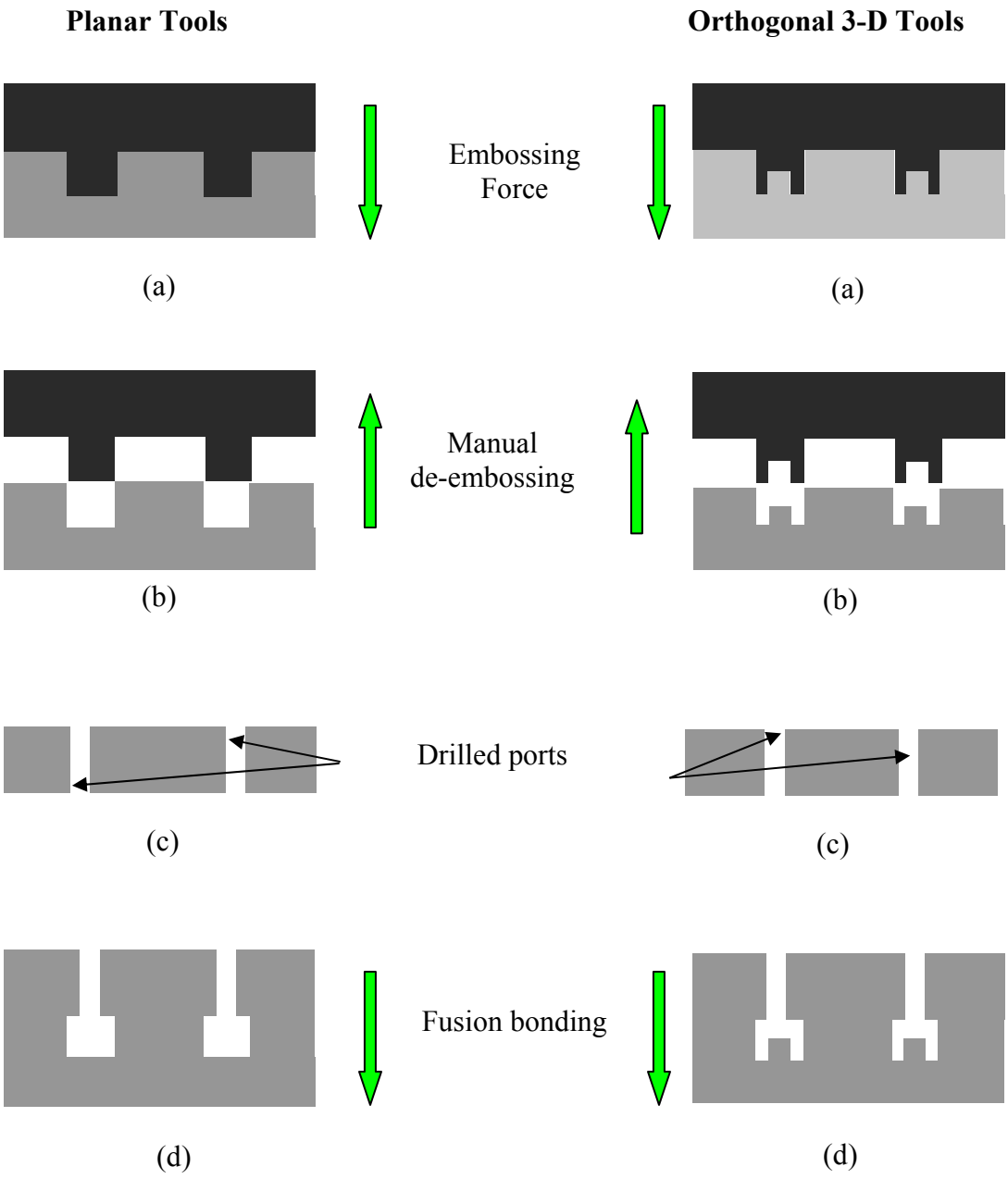


Figure 6. Schematic diagram of the hot embossing and fusion bonding procedures using planar (left) and orthogonal 3-D (right) PDMS tools. (a) embossing PMMA, (b) de-embossing PMMA, (c) capping PMMA with ports, (d) fusion bonding PMMA.

transition temperature of PMMA under high vacuum. The vacuum was used to prevent the formation of air bubbles during the embossing process. After the tool-polymer sandwich reached the temperature, the system was allowed to rest at that temperature for about 15 min to make sure that all the materials inside the chamber reached the desired temperature. Then a uniform, controlled force of 4.45 kN was applied by raising the bottom hot plate and held against the top stationary hot plate for 15 min. With the force still applied, the system was cooled down below the glass transition temperature and then finally cooled to the room temperature. Due to the active cooling of the assembly, an increase in the force applied was essential to prevent any replication errors due to thermal stresses. On reaching the room temperature, the force was released by moving down the bottom hot plate to its original position. The tool-polymer sandwich was taken out of the machine and de-embossing was done manually by peeling the PDMS tool from the PMMA. The entire embossing cycle, including heating and cooling of the hot plates, was approximately an hour and this was the procedure followed to emboss features of different depths.

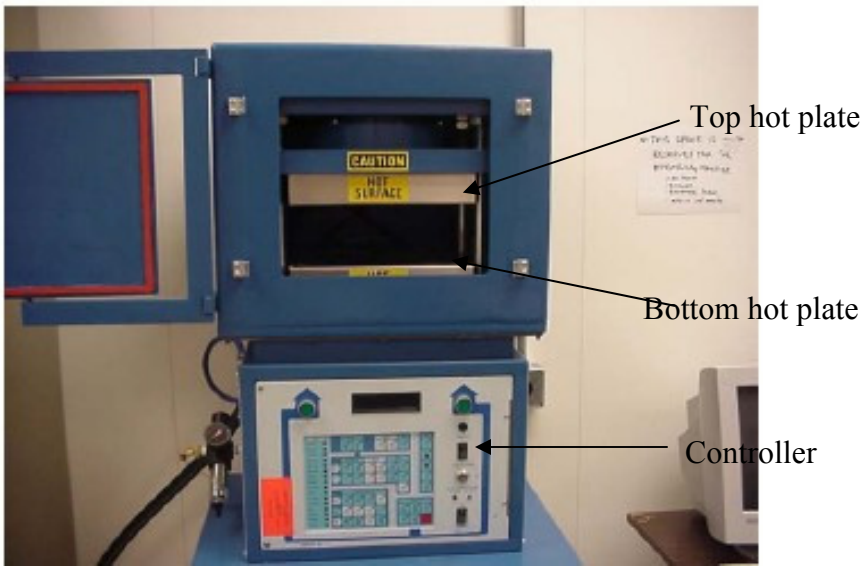


Figure 7. Hot embossing machine at University of Cincinnati.

Polymer Fusion Bonding

After drilling the holes for the input and output ports, the microchannels were sealed with a capping PMMA sheet by fusion bonding. The bonding was done in the same embossing machine, just below the glass transition temperature of the thermoplastic and a uniform, controlled force was applied to seal the plastic chips throughout. With 1 kN force applied, the thermoplastics were heated to 98^0 C to 100^0 C and were rested at that temperature for 15 min. The force was then increased to 2.225 kN and was applied for about 60 min after which the machine was cooled down to room temperature.

Microchannel Packaging

The plastic chips were packaged using standard fittings purchased from Upchruch Scientific. A flangeless ferrule, 1/16" was placed on top of the input port. A viscous 5,000 cP, UV-adhesive (3316, Loctite Corp) was coated on all sides of the ferrule with a syringe. The high viscosity of the adhesive prevented the flow of adhesive towards the port and thus avoided any clog. A commercially available UV-lamp (118 V, 0.35 A, 60 Hz) preheated to 15 W cured the adhesive for 5 min. Once the ferrule was fixed, the fluid delivery PEEK tubing 0.030" ID was inserted into the ferrule and was fixed using the same procedure. PEEK tubing material was chosen instead of Teflon since the UV-adhesive does not adhere well to Teflon. Further, connection between the pump and the PEEK tubing was provided using silicone tubing, which was directly connected to the needle of the syringe pump.

Summary

A rapid fabrication technique to develop prototypes of microfluidic systems in thermoplastics using hot embossing was discussed in this chapter. The tool or master or mold

used for the replication method was fabricated in a much simpler, rapid, and cost effective way in PDMS. This process is an alternative to the current techniques to fabricate embossing tools using silicon etching, CNC machining, X-ray or UV LIGA. Casting PDMS on various polymeric materials without adhesion problem is the key advantage for the success of this technique. The fabrication steps involved in this process were, conventional photolithography using SU-8 or AZ4620, PDMS casting, embossing PMMA, and bonding the microchannels with a capping PMMA wafer using heat and pressure. Further, this technique was also extended to fabricate orthogonal 3-D microfluidic mixers in thermoplastics. The only additional step was the second stage photolithography to define the features in AZ4620 inside the main channel defined by SU-8. Overall, the described method has tremendously reduced the time needed to fabricate embossing tools which in-turn has reduced the time to fabricate the final microfluidic system in thermoplastic.

CHAPTER 4

RESULTS AND DISCUSSION

This chapter will present fabrication results and will discuss the various issues that were encountered in optimizing the parameters for the different fabrication steps. The choice of PDMS as an embossing tool will also be discussed. Photolithography involved the optimization of different parameters such as baking time and temperature, exposure energy based on the features sizes, development conditions, and plasma processing of photoresist. The most important parameters to be optimized in hot embossing and fusion bonding were the force and temperature at which the respective processes occurred. Casting PDMS on SU-8 templates posed some critical issues with plasma processing of the templates. Issues on the second stage photolithography in fabricating orthogonal 3-D devices are also included. Appropriate pictures and scanning electron micrographs are used for the better understanding of these issues and the results obtained in both the fabrication.

The ultimate motivation being the optimization of a fabrication system to produce prototype microfluidic devices in thermoplastics, it was important to choose a material that had proved its worthiness in microfluidics. Though there are a number of elastomers, fabrication of prototype microfluidic systems in PDMS by casting against templates that are usually created by photolithography is a technique followed by many research groups [18-20,25,26,28,31,41].

PDMS is also an excellent material for the fabrication of microchannels for use with biological samples in aqueous solutions [41].

The multiple reasons for using PDMS in this work are, features on the micron scale can be reproduced faithfully, it is optically transparent, cures at low temperature which is compatible to the photoresist used, it is non toxic, a durable material, resistant to chemicals and irrespective of the feature sizes and the aspect ratio, the process time to fabricate the embossing tool was the same. It has a decomposition temperature of approximately 200^0 C. Since PDMS is inert, it does not stick to many materials, which was an important criterion for an embossing tool and it is inexpensive.

Further, the poor adhesion between PMMA and PDMS [19] was used as an advantage in our technique to ensure that there was no adhesion between the tool and thermoplastic during the de-embossing stage. The most important issue in an embossing system without automated de-embossing facility was the loss of adhesion between the metal electroplated and the base substrate during de-embossing. When manually de-embossed, even a very small angle in the sidewalls of the tool will result in the peel of the metal. An ideal embossing tool in this situation would be the use of same material for the base and features, which was offered by PDMS.

Planar Microfluidic Systems

The described fabrication process has been used to fabricate planar embossing tools for different thickness in PDMS. To demonstrate the PDMS tools, we fabricated photoresist molds of different thickness, ranging from 5 to 90 μm. While in this work we emboss PMMA, similar results can be obtained using polycarbonates, cycloolefin copolymers, and other thermoplastics. Profilometer measurements and scanning electron microscopy were used to assist the optimization of the various embossing parameters and lifetime of the PDMS tool. A sample

PDMS tool for a microfluidic system consisting of a reservoir and an array of seven microchannels is shown in Figure 8. The tool is 90 μm thick and was formed using an SU-8 casting template. Individual microchannels are 150 μm and over 10 mm long at 250 μm center-to-center spacing. The reservoir is 2 mm wide and 750 μm long. A sample embossed PMMA substrate is shown in Figure 9. The array contains channels of 300 μm wide and 90 μm deep at 500 μm center-to-center spacing. The close-up of the channels are shown in Figure 10.

As discussed earlier, deeper channels were fabricated using SU-8 epoxy resist as casting template. Though a number of research groups had already optimized the processing conditions for SU-8 version 50 and 100, the SU-8 2000 series was fairly new and required a lot of experimentation. Adhesion of the resist to the silicon substrate was one problem encountered and was resolved by changing different parameters including cleaning procedure, exposure energy and the spin speed. Initially, the photoresist was spun at 500 rpm for 10 s with a ramp

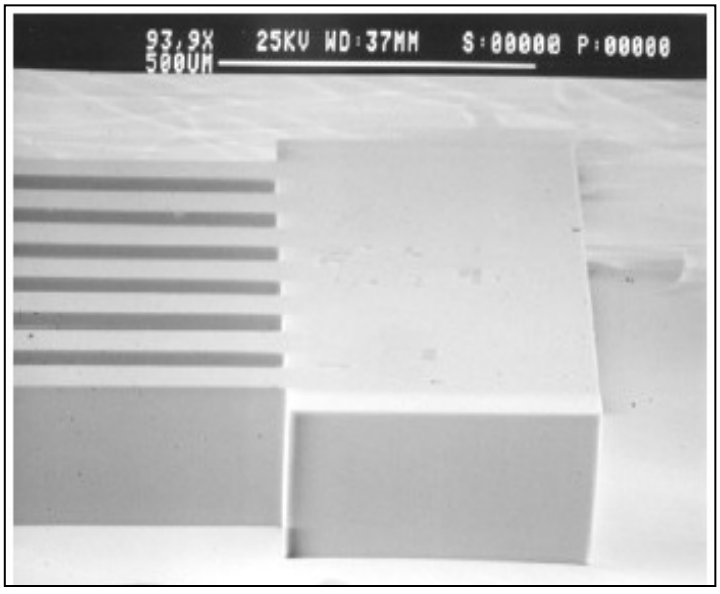


Figure 8. SEM of a 90 μm thick PDMS tool. An array of 150 μm wide features with 250 μm center-to-center spacing is shown.

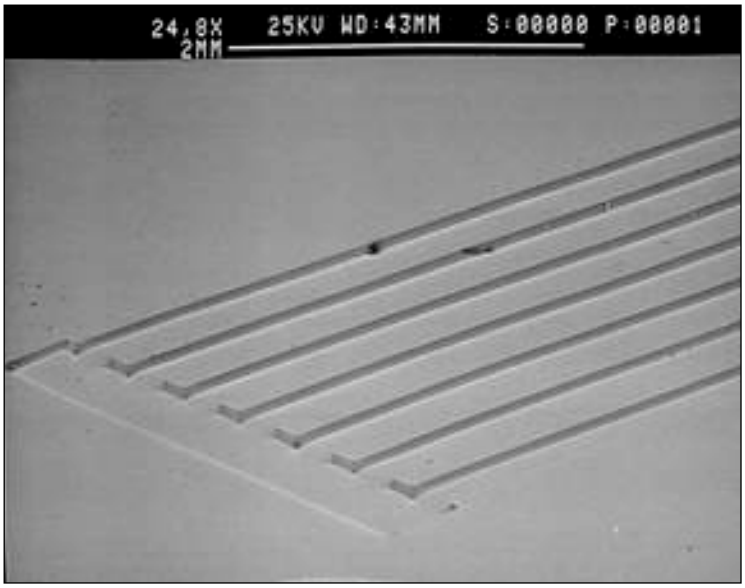


Figure 9. SEM of a 90 μm deep PMMA channel. An array of 300 μm wide features with 500 μm center-to-center spacing is shown.

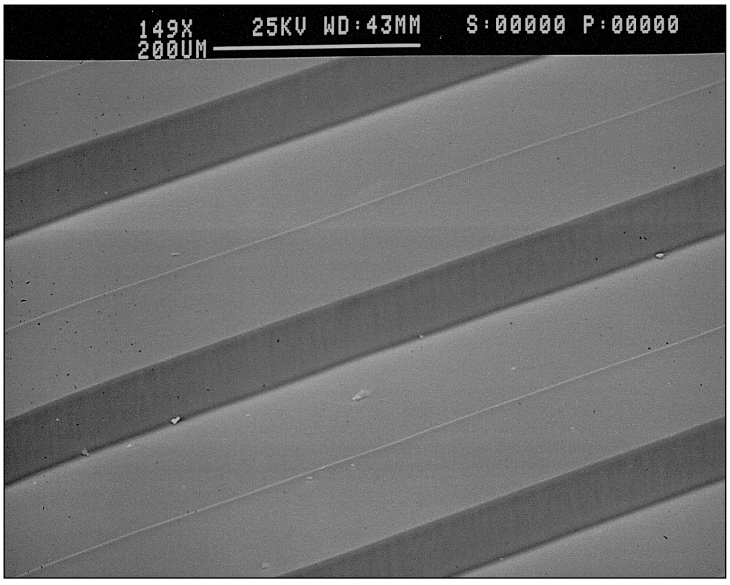


Figure 10. Close-up of the microchannels in Figure 9.

rate of 100 rpm/s and then ramped at 300 rpm/s to a final speed of 1000 rpm for 30 s to achieve 150-160 μm. The soft baking was done exactly as explained in the earlier chapter. The recommended exposure energy for this thickness was 650 mJ/cm^2. The wafers processed with these conditions resulted in adhesion losses of the resist to substrate. It was found out that the resist wasn't soft baked enough to evaporate the solvent present. After a number of iterations with variations in the spin speed and exposure energy, it was optimized to use a spin speed of 1,600-1,700 rpm and exposure energy between 500-600 mJ/cm^2 for the same baking conditions to prevent any adhesion losses

It was also found that any oxide grown thermally resulted in the loss of adhesion between the resist and substrate. Oxide etch was a mandatory step to be done after piranha cleaning to avoid this effect. SEM of a 250 μm deep PMMA channel is shown in Figure 11. It consists of an array of 600 μm wide features with 1 mm center-to-center spacing. Molding template used was SU-8. The process parameters were varied accordingly for this thickness. The final spin speed was 600 rpm and the photoresist was soft baked in a programmable, convection oven at 65^0 C for 10 min and then at 95^0 C for two hrs and 30 min. The ramp rate in both the cases was 1^0 C/min. The resist was then allowed to cool down naturally to room temperature before the exposure. The exposure energy used was 700 mJ/cm^2 and the post exposure bake was done in a programmable, convection oven at 65^0 C for 10 min and then at 95^0 C for 40 min.

On the contrary, fabrication of shallow channels was straightforward with well established processing conditions for AZ4620 resist used as the casting template. PDMS tool fabricated using AZ4620 casting template is shown in Figure 12. The tool has an array of 5 μm deep features that are 40 μm wide features with 90 μm center-to-center spacing. SEM of the resulting 5 μm deep array of PMMA microchannels, 40 μm wide with 90 μm center-to-center

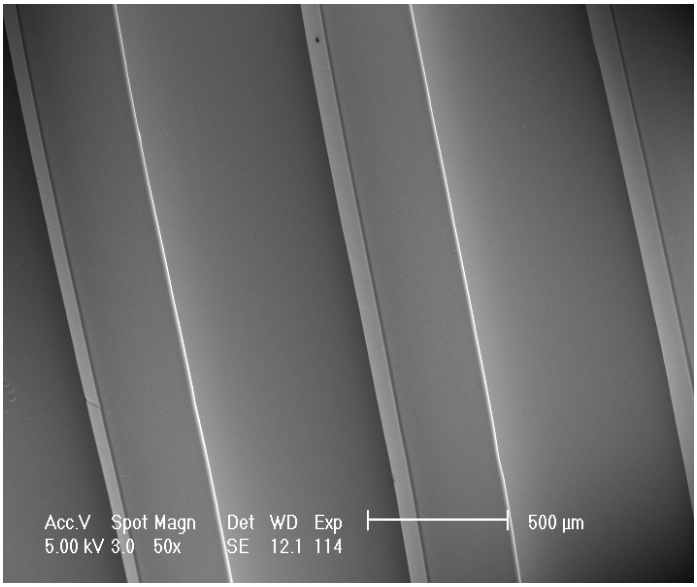


Figure 11. SEM of a 250 µm deep PMMA channel. An array of 600 µm wide features with 1 mm center-to-center spacing. Molding template was SU-8.

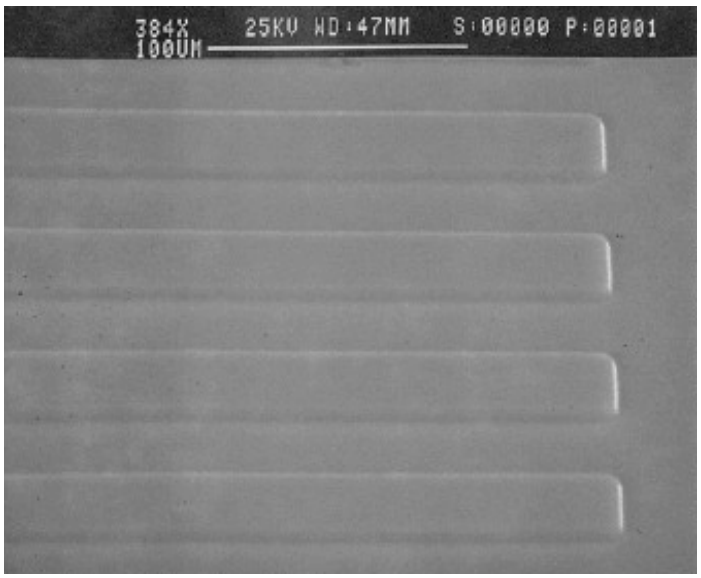


Figure 12. SEM of a 5 µm thick PDMS tool; an array of 40 µm wide features with 90 µm center to center spacing. Molding template was AZ4620.

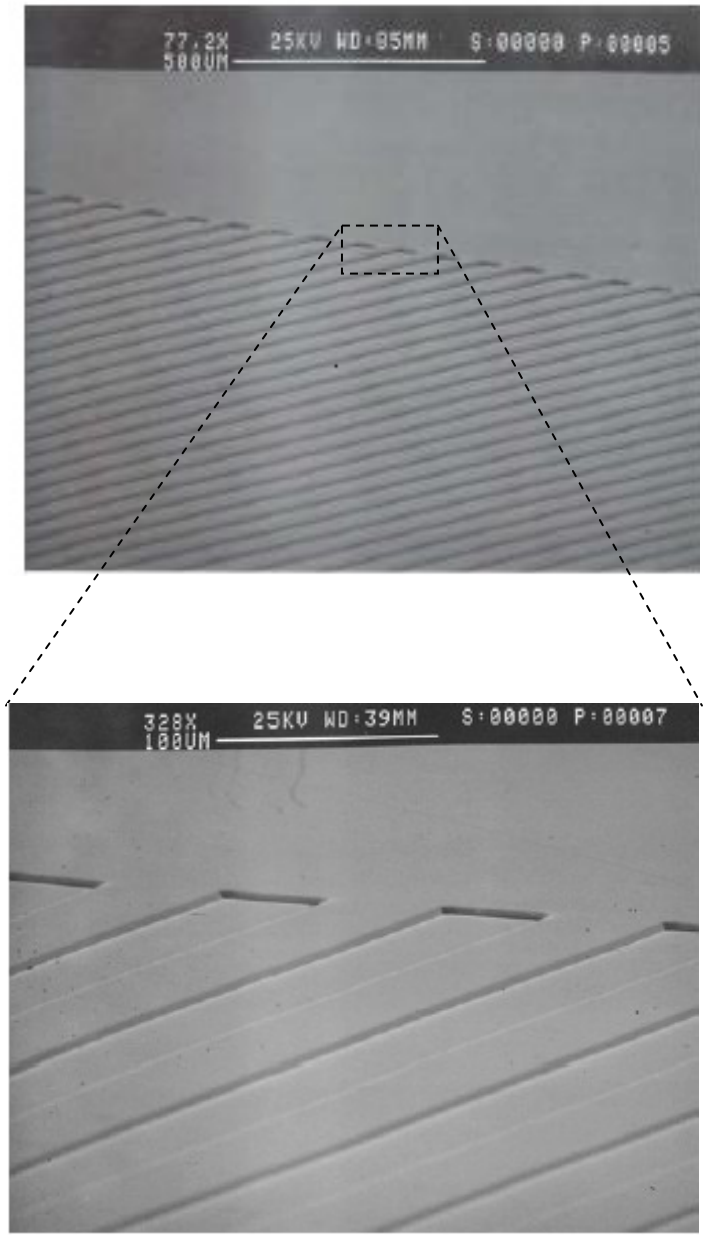


Figure 13. SEM of a 5 µm thick PDMS tool; an array of 40 µm wide features with 90 µm center to center spacing. Close-up of the microchannels is also shown.

spacing, fabricated using AZ4620 casting template is shown in Figure 13.

Orthogonal 3-D Microfluidic Systems

The fabrication procedure discussed in this work was extended to fabricate orthogonal 3-D microfluidic passive mixers. The idea being to enhance passive mixing of liquids by fabricating obstructions in the flow field inside a wide channel. The tools were fabricated by casting PDMS in a mold template formed on silicon substrates in two stages—first by patterning negative SU-8 photoepoxy followed by patterning positive AZ4620 components. This approach proved to be a much simpler procedure to fabricate orthogonal 3-D systems in thermoplastics using hot embossing.

The laminar flow of liquids presents great difficulty in mixing liquids in microchannels. The Reynolds number, $Re = \rho v D_h/\mu$, where ρ is the density, v is the velocity, D is the hydraulic diameter, and μ is the viscosity is always low due to the small dimensions involved. Due to the lack of turbulence, mixing of two flow streams in the microchannel is entirely diffusive. The time for a particle to diffuse a given distance depends on the square of that distance [38], $T_d = L^2/D$ where T_d is the time, L is the mixing length (width of the channel), and D is the diffusion coefficient. As seen from the above equation any increase in the width of the microchannel will increase the time taken for mixing. An application involving both mixing and wider channels is seriously limited by this phenomenon.

Although a number of active mixers have been described in the recent years, passive mixing in a single microchannel remain attractive due to the reduced complexity of implementation and a single channel that maintains a relatively constant cross section [25]. Passive mixing was accomplished by fabricating either serpentine-shaped channels [25] or

complex microchannels with successive separation and recombination of liquid streams to increase contact area between the liquids [62]. The serpentine shaped mixer enhanced mixing by producing eddies at the bends of a channel. Most recently, very effective chaotic stirring in 3-D serpentine mixers and mixers with ridges in microchannel bottoms have been demonstrated in PDMS [26]. The asymmetric grooves on the floor of the channels provide a transverse component to the flow when an axial pressure is applied.

However, currently there is no simple process for fabricating such 3-D microfluidic devices in thermoplastics (e.g., PMMA, PC) [27], which are typically stronger materials and are capable of supporting significantly higher fluidic pressures than PDMS. The current ways of fabricating the 3-D embossing tools are quite complex, time consuming, and involves creation of layered structures through repetitive steps, such as multiple lithography of SU-8 on silicon, multiple etching of silicon, or electroplating of nickel.

The initial design was to fabricate a simple Y-shaped channel with 500 μm wide inlets channels and 1 mm wide mixing channel with obstructions of different shapes in the mixing channel. Triangular, rectangular, and circular shaped features, 500 μm wide were fabricated exactly at the center of the mixing channel. The fabrication of the orthogonal 3-D microfluidic mixers was no different from the procedure employed for planar devices except for a second stage photolithography to define the obstructions within the mixing channel. The casting template was a silicon wafer with both SU-8 and AZ4620 photoresist, defining the flow channels and the obstructions. Fabrication of these devices was much simpler as photolithography, embossing using PDMS tools, and bonding PMMA were already optimized when fabricating planar devices.

A PDMS tool demonstrating the orthogonal 3-D features is shown in Figure 14. The embossing tool has rectangular features (500 μm x 250 μm) at 1 mm spacing inside a 110 μm thick mixer microchannel. A resulting embossed PMMA channel with internal rectangular, circular, or triangular features have been fabricated. Figure 15 shows the 1 mm wide and 110 μm deep PMMA channels. The triangular, rectangular, and circular features formed on the bottom of the microchannels are 500 μm wide and 20 μm tall with 1 mm spacing from each other. Figure 16 shows the close-up of the different obstructions fabricated. A careful observation shows that the sidewalls of these obstructions are not straight. This was due to the lack of hard contact between the mask plate and wafer during the second stage photolithography, which in-turn diffracts the UV-rays passing through the mask plate and exposes the photoresist. The developer etches the exposed resist resulting in an angled feature which also shows up in the final PMMA device.

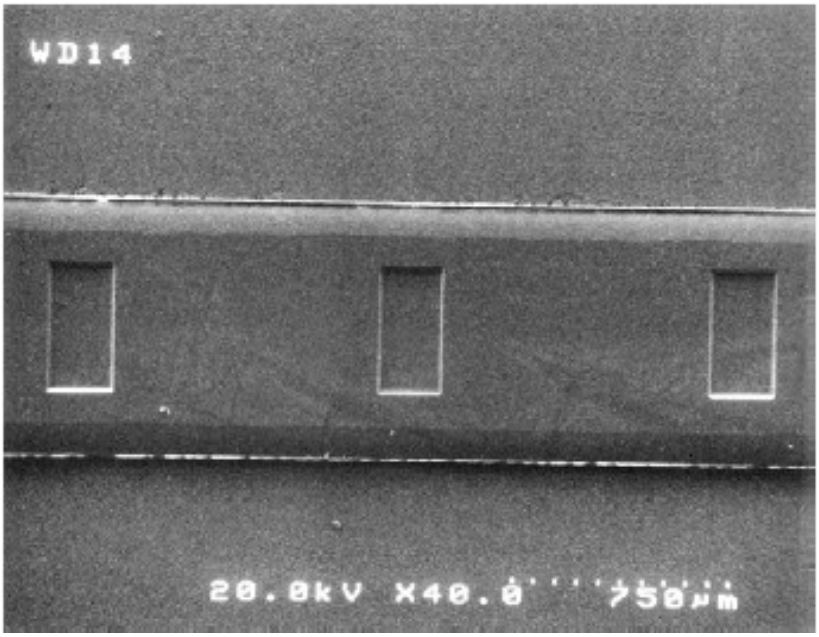
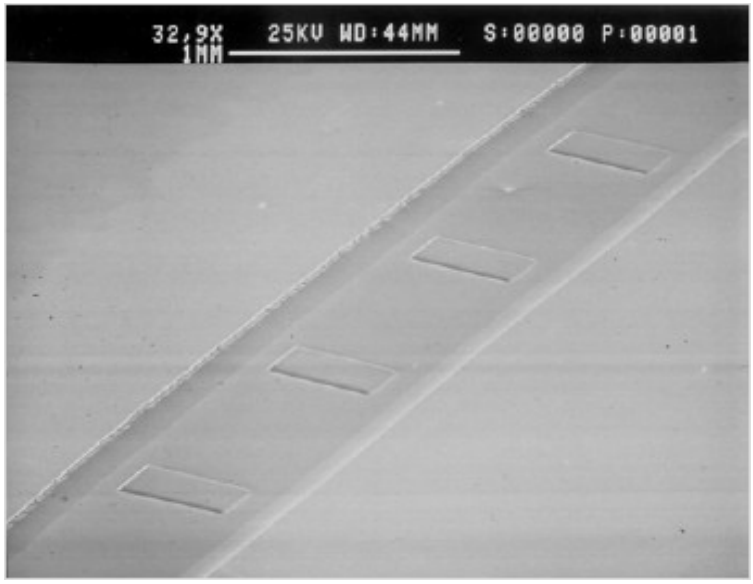
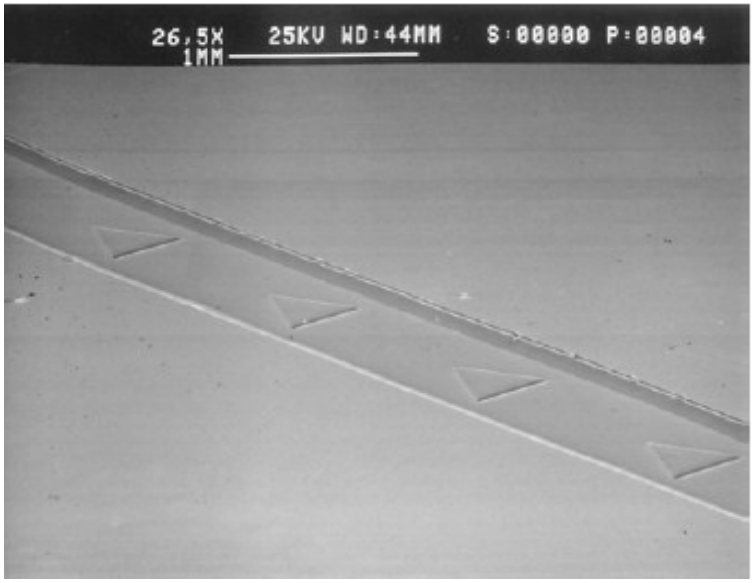


Figure 14. SEM of the PDMS embossing tool illustrating the 20 μm deep rectangular indents (250 μm x 500 μm) on the 110 μm thick structure.

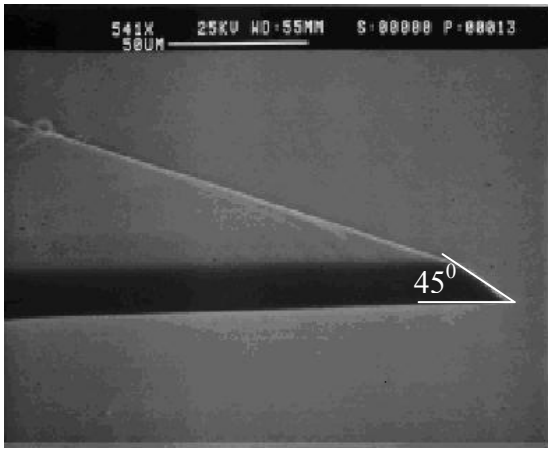


(a)

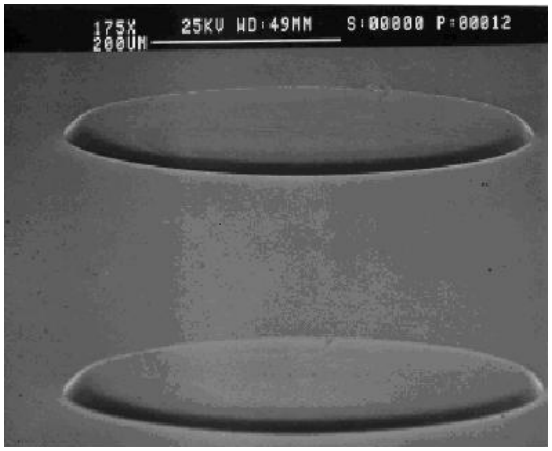


(b)

Figure 15. SEM of the embossed orthogonal 3-D PMMA channel. Top: 20 µm thick rectangular features (250 µm x 500 µm) spaced 1000 µm from each other inside the mixing channel. (Bottom) 20 µm thick triangular features 500 µm wide at the base spaced 1000 µm from each other and 250 µm from the channel wall on wither side.



(a)



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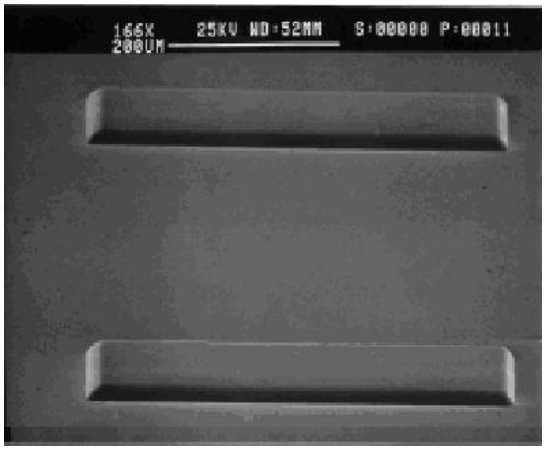


(c)

Figure 16. SEM of the embossed obstructions in PMMA. 20 μm thick triangular, circular, and rectangular triangular with angled sidewalls.

PDMS is a durable material and regardless of the aspect ratio and feature sizes, the overall time to fabricate the tool remains the same. PDMS is an inert material and does not adhere to many materials, which is an important criterion for an embossing tool. Further, like CNC machining, the entire tool is fabricated of the same material, which prevents any adhesion problem between the tool ad substrate during de-embossing. Though the molding template for casting can be fabricated by many techniques including etching of silicon, electroplating nickel, or conventional machining of hard materials, a lithographically defined template in SU-8 or AZ4620 on a silicon wafer is by far the simplest. After the development of SU-8, the photoresist was exposed to oxygen plasma for about 5-10 min to etch out the debris on the sidewalls and the floor of the channels. The sidewall of the PDMS tool (Figure 17) and the PMMA channel (Figure 18) demonstrate the high fidelity of the embossing process for deep channels.

The tool sidewall roughness is the direct result of photoresist processing during mold fabrication and not due to de-embossing, since PDMS casting has been shown to be accurate to the nanometer scale [48] and PDMS is known to have poor adhesion to PMMA [19]. Modifying the sidewall of SU-8 with O_2 plasma can reduce the roughness, although the experimental evidence showed increased adhesion between plasma processed SU-8 and cured PDMS. We believe that this might be due to the addition of hydrophilic groups to the photoresist layer, which enhances the adhesion between the resist and PDMS. Figure 19 shows the PDMS adhered to SU-8, which resulted in incomplete peel after the casting process. In this case, further processing of the SU-8 template with fluorine based plasma (e.g. CF_4 or CHF_3) was necessary to negate the effect of the O_2 plasma. Exposing the photoresist to silane-based chemicals to facilitate easier removal of the cured PDMS had been reported [31]. Figure 20 shows the removal of the casted PDMS from SU-8 after CF_4 or CHF_3 treatment.

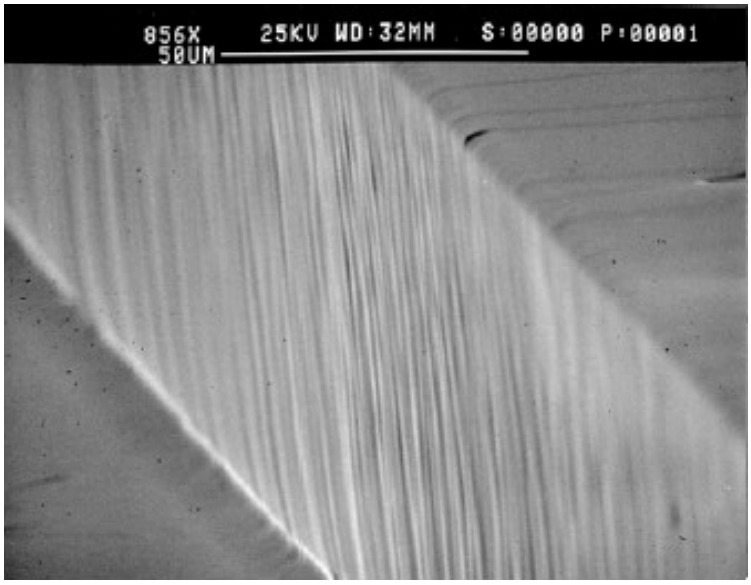


Figure 17. SEM of the sidewall of a 90 μm thick PDMS tool

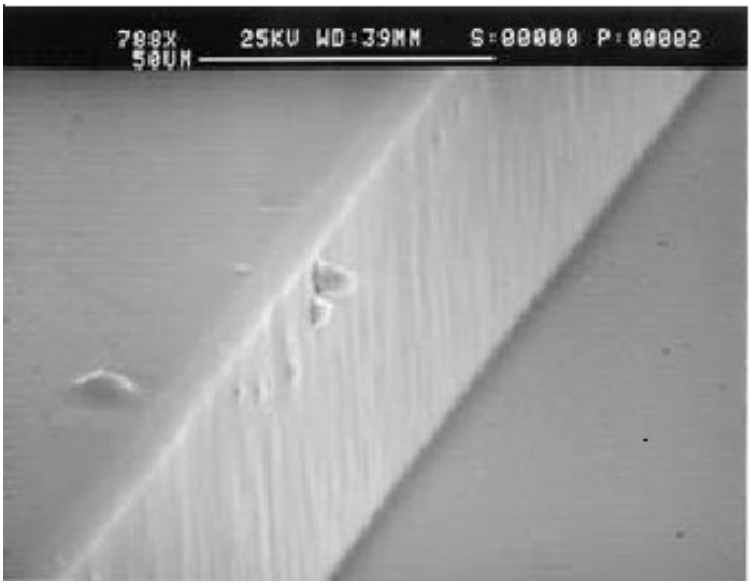


Figure 18. SEM of the sidewall of a 90 μm deep PMMA channel

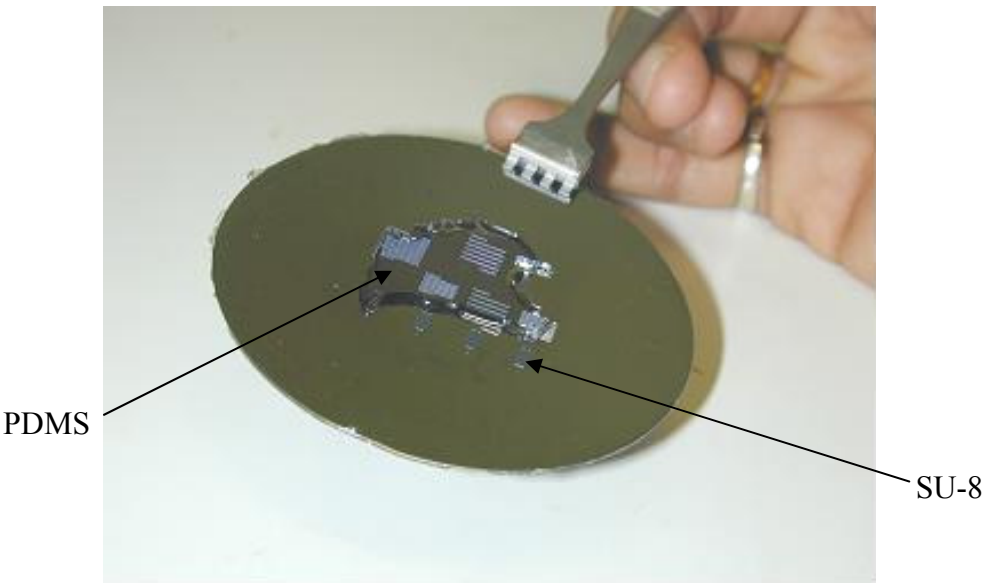


Figure 19. Photograph of PDMS adhered to SU-8 after O_2 plasma treatment.

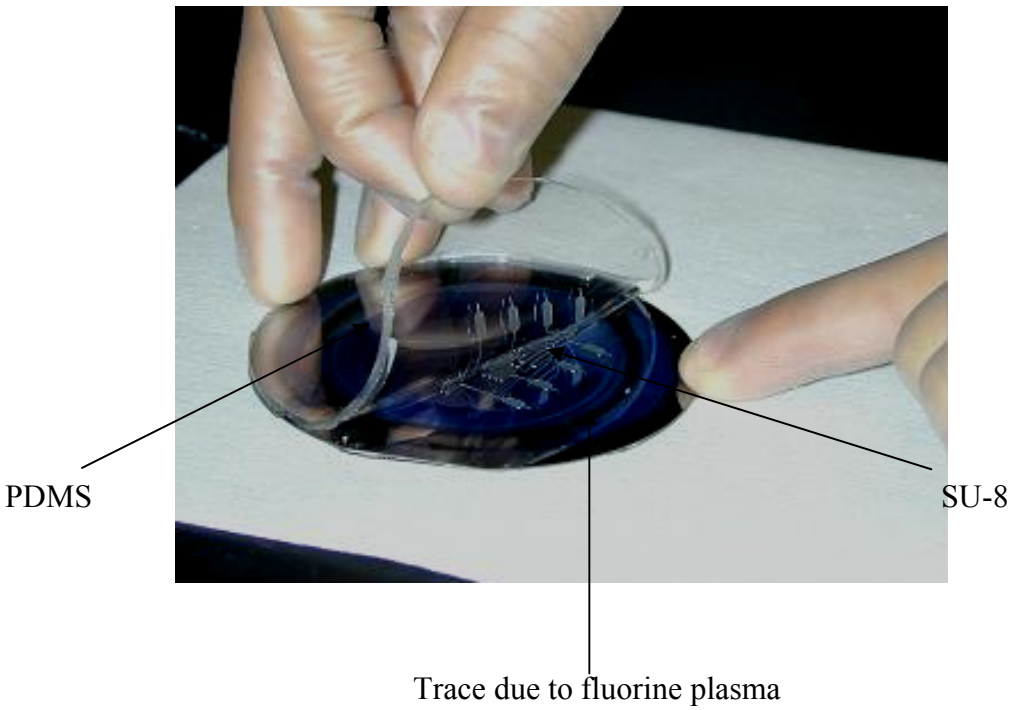


Figure 20. Photograph illustrating removal of PDMS from SU-8 after fluorine-based plasma treatment.

It was also observed that the treatment of SU-8 using O_2 plasma resulted in the removal of about 0.5 μm for every minute. Care should be taken to avoid excessive removal of SU-8 during plasma treatment as it might result in a much thinner resist layer than the proposed thickness for that application. Faithful replication during hot embossing with tools fabricated by any technique, demands uniform force to be applied throughout the thermoplastic. The uniform force was needed to prevent any non-uniformity in depths of the channels and to protect the tool during the de-embossing stage. This was especially critical in our process where de-embossing was done manually, by peeling off the tool from the plastic. Since the embossing tool used in this process was an elastomeric material, the overall thickness of the tool was another important factor that was considered. Casting a thick layer of PDMS minimized the effect of vertical compression on the flexible PDMS during embossing. Our experiments suggest that thickness of the PDMS tool was to be at least 5 mm, to uniformly transfer the force applied on it. Since PDMS tools were much softer than the conventional tools, the force applied (4.45 kN) in our process was much higher than the force used with other tools (0.5-2 kN) [20]. This was necessary to ensure faithful replication of features. Additionally, force uniformity was critical to avoid any inconsistency in channel depths and also to protect the tool during de-embossing.

Further, the embossing temperature was about 45^0C above the T_g of PMMA, which ensured a faithful replication of the tool. We believe that this larger increase in temperature, as compared to embossing with conventional tools, is needed to further raise mobility of PMMA chains to permit embossing with a soft tool. Profilometer measurements showed considerable compression effects when embossing was performed at a lower temperature.

The thermal properties of the materials used in embossing determine the process parameters such as residence time, embossing time, and the force applied was also considered.

The thermal conductivity of PDMS is approximately 0.2 W/mK [2], much lower than the thermal conductivity of the other materials such as Ni (~150-500 W/mK) or Si (~157 W/mK) [60] often used in embossing. Increasing the residence time (i.e., time taken for the materials to reach the final temperature) will compensate for the lower thermal conductivity but increased the overall processing time.

The other contributor to the increased cycle duration was the extended embossing time when the PDMS tool was driven into the softened PMMA thermoplastic. PDMS is a soft material and has a relatively low modulus of elasticity, approximately 750 kPa for the standard 10:1 formulation of the elastomer precursor and curing agent mixture [61]. By contrast, traditional embossing tools are significantly harder, 200 GPa for nickel and 47 GPa for silicon [60]. Thus, PDMS tools must be driven into thermoplastics at a lower rate than nickel or silicon tools. Further, we hypothesize that during the initial moments of the embossing process, PDMS partially compressed and additional time was needed to permit PDMS chains to relax and force PMMA chains apart. Table 1 shows the properties of materials predominantly involved in hot embossing. However, the embossing time (currently 15 min) should be kept as short as possible to minimize the effects due to thermal stresses. After a series of experiments by altering residence and embossing times, the microchannels fabricated with a residence time of 15 min and an embossing time of 5 min showed the optimized replication. The results (Figure 21 & Figure 22) obtained by increasing the embossing time to 15 min and residence time to 25 min did not show any significant improvement from the earlier results.

To investigate the fidelity of the replication procedure, two test PDMS tools 20 μm and 70 μm thick were used to emboss PMMA for 25 cycles. Profilometer measurements were taken

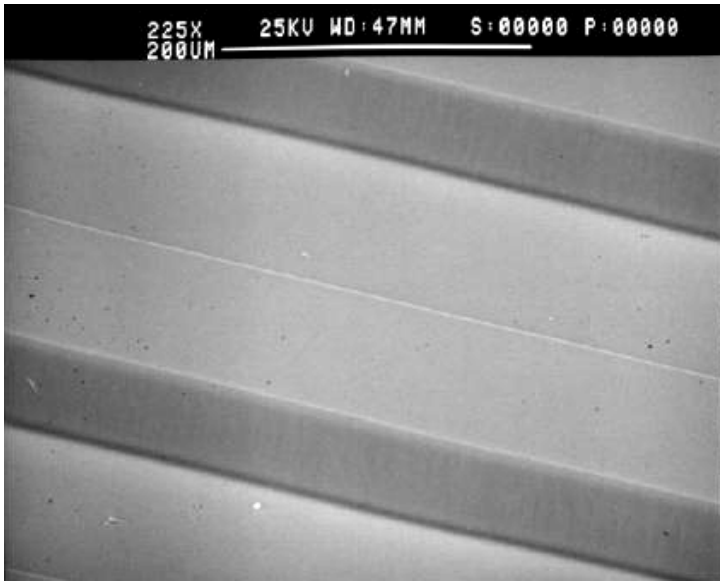


Figure 21. SEM of microchannels fabricated with residence and embossing times of 15 min.

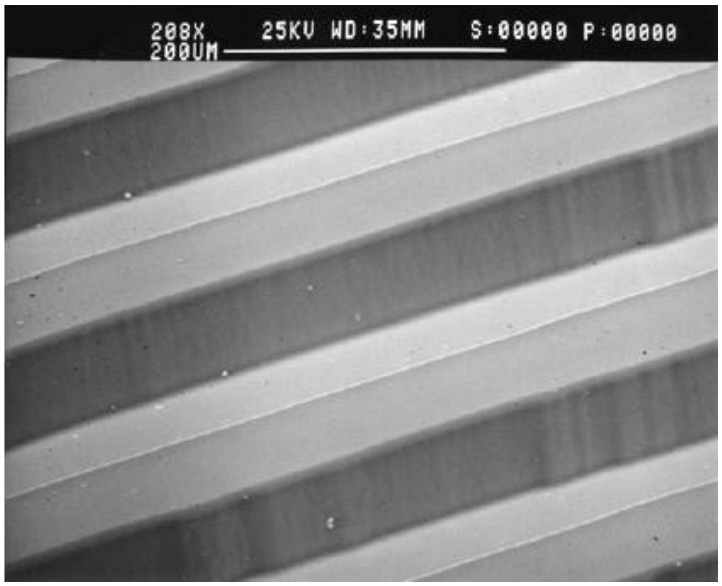


Figure 22. SEM of an array of 150 μm wide channels with 250 μm center-to-center spacing. The residence time was increased to 25 min.

Table 1. Material properties of hot embossing materials.

Property	Nickel	Silicon	PDMS	PMMA
Density (Kg/m^3)	8,900	2,330	920 – 970[3]	1,170 – 1,200
Young's Modulus (Pa)	2×10^{11}	4.7×10^{10}	3.6 – 8.68 x 10^{5} [4]	-
Thermal Expansion Coefficient, at 25°C (K^{-1})	1.3×10^{-5}	2.6×10^{-6}	9×10^{-4}	6×10^{-4}
Thermal Conductivity (W/m-K)	91	150	0.15 - 0.2[4]	0.186
Poisson's Ratio	0.31	-	0.5	0.35

1. Data for nickel and silicon are from [60].
2. Data for PDMS and PMMA are from [62], except where noted otherwise.
3. The lower value was reported in [61]; the higher value was given in [62].
4. The lower value was given in [62]; the higher value was stated in [19].
5. From [61]

at different embossing cycle on both the tool and the resulting channels. We observed that cross-sections of the 20 µm deep channels were identical to that of the tool for all 25 embossing cycle. However, the 70 µm deep channels showed a loss of approximately 4% of in channel depth. While the reason for this loss of depth is not clear, one possible explanation is that the thicker PDMS tools displace more thermoplastic material reaching a point at which forces generated by the relaxing tool are equilibrated by the resistance forces due to rearrangement of the thermoplastic polymer chains. The tools exhibited no damage after 20 cycles of embossing, as evidenced by the profilometer readings shown in Figure 23, with minor damage occurring in the later cycles.

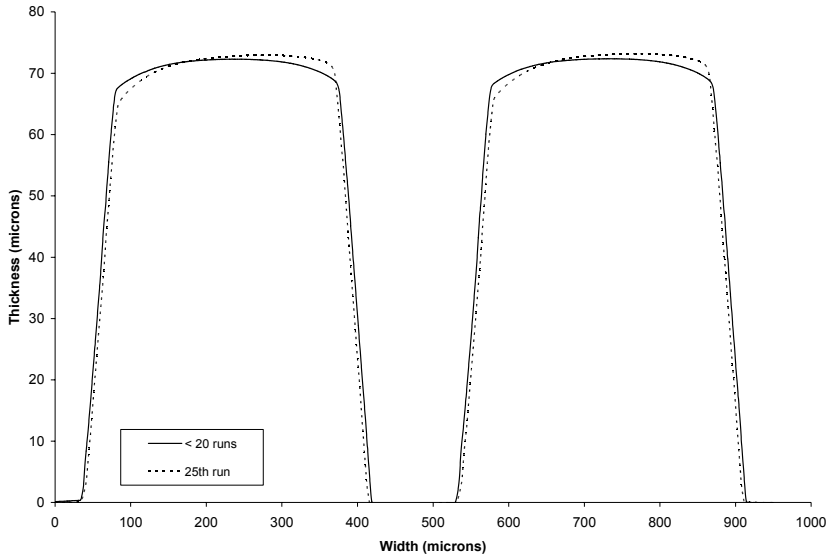
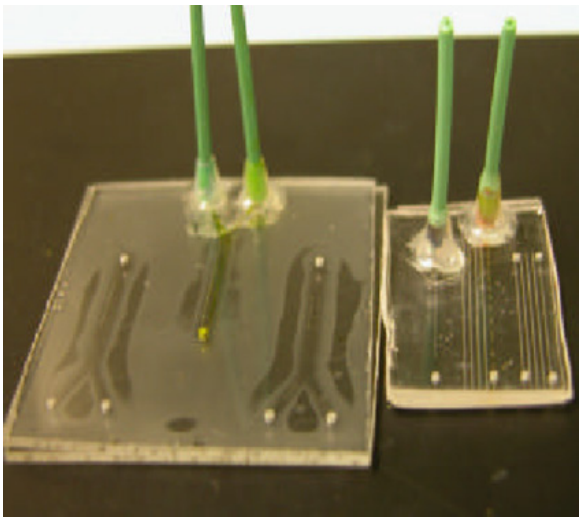


Figure 23. Comparison of PDMS tools after 1, 20, and 25 embossing cycles.

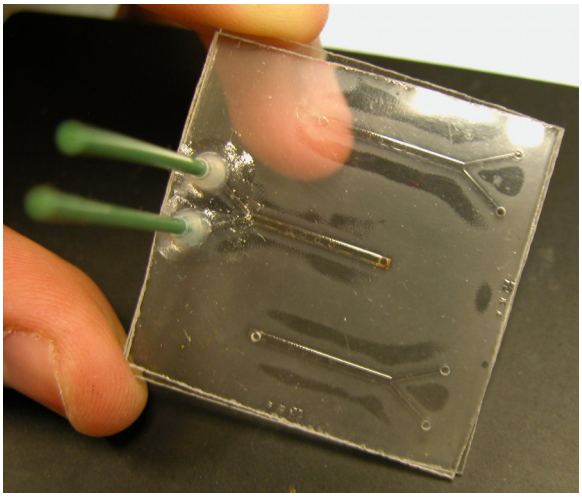
As mentioned in the earlier chapter, fusion bonding of two PMMA substrates was done at a temperature just below the T_g of the polymer in the same machine used for embossing. The temperature used during fusion bonding is the most vital parameter as the other parameters can be altered depending on it. As the bulk polymer softens at the T_g, it was inappropriate to bond the substrates at a temperature very close to the T_g or at T_g of the polymer. Experiments were conducted starting from 90^0C to 100^0C, where the surface of the polymers just softens enough to be fused with the other bare substrate and it showed that the optimum temperature range for bonding PMMA substrates was between 98^0C to 100^0C. The other parameters such as force and cycle time were kept constant and the experiments proved that a degree centigrade variation in temperature resulted in the collapse of the channels or incomplete bonding. Although the bonding was done at the same temperature, the cycle time and the force applied during bonding were altered depending on the depth of the channels. The complete process parameters were

optimized by a trial and error procedure, where the samples bonded with various combinations of bonding parameters were packaged and tested for liquid flow.

Packaging was done exactly the same way as described in the earlier chapter. Care should be taken not to block the fluid ports with the adhesive applied. The viscosity of the adhesive used was 5000 cp, which was high enough to prevent an easy flow into the ports. Improper curing of the adhesive resulted in the loss of adhesion between the ferrules and the bonded PMMA chips. Figure 24 shows a bonded and packaged orthogonal 3-D PMMA microfluidic



(a)



(b)

Figure 24. Photographs of bonded and packaged PMMA orthogonal 3- D microfluidic systems.

device.

Summary

An optimized fabrication technique for rapid prototyping of microfluidic systems, using PDMS embossing tool was successfully developed. The described approach was used to fabricate microchannels in PMMA of aspect rations up to two, with depths ranging from 5 to 250 μm and features as small as 20 μm in width.

The technique was also applied to fabricating orthogonal 3-D microfluidic systems using multiple lithography steps. Parameters involved throughout the fabrication procedure were carefully varied to finalize the optimum conditions. Profilometer measurements and scanning electron microscopy were used to assist the optimization of the various embossing parameters and lifetime of the PDMS tool. Table 2 summarizes the properties of the PDMS tool.

Scanning electron micrographs showed high embossing fidelity for both shallow and deep channels. Vertical compression of the soft tool was minimized by increasing the overall tool thickness, embossing temperature, and pressure. The use of a soft tool material increases cycle time and limits the tool usefulness to about 20 cycles. Overall, this approach is particularly well suited for rapid prototyping, where fast processing and low cost are important and the number of samples is relatively low.

Table 2. Summary of PDMS tool properties.

	PDMS Tool
Aspect ratio (AR)	~2
Feature size (AR limited)	≥20
Cycles (AR limited)	~20
Adhesion	No
Roughness	Moderate
Fabrication Time	~ 4 hrs for any AR

CHAPTER 5

CONCLUSIONS

We have successfully demonstrated an optimized embossing process to fabricate both planar and 3-D microfluidic systems using an elastomer tool (master or mold). Overall, the described method has tremendously reduced the time needed to fabricate embossing tools facilitating the production of prototype devices in an inexpensive procedure. Further, this method does not require any specialized equipments apart from the standard photolithography systems to fabricate the embossing tools. This process is an alternative to the current techniques of fabricating tools using silicon etching, CNC machining, X-ray or UV LIGA. This technique was also extended to fabricate orthogonal 3-dimensional microfluidic systems in thermoplastics in a rapid and inexpensive way.

We used single layer of SU-8 2000 series or AZ 4620 photoresist to define a template for casting PDMS to form the embossing tool. The PDMS tool was then used to emboss the microchannels in PMMA, substrates. We formed the orthogonal 3-D microfluidic devices using a second photolithography step to define features inside the main channel before casting PDMS. Overall, the fabrication steps involved in this process were conventional photolithography, PDMS casting, embossing PMMA, and bonding the microchannels with a capping PMMA wafer using heat and pressure.

Casting PDMS on various polymeric materials without adhesion problem is the key advantage for the success of this technique. The embossing tools showed no signs of damage upto 20 cycles and can be used with wide variety of thermoplastics. Shallow (5 μm) microchannels using AZ4620 and deep (250 μm) microchannels using SU-8 have been successfully fabricated in PMMA. Aspect ratio as high as two and minimum feature size of 20 μm wide channels have been fabricated. A simple Y-shaped passive mixer with 500 μm wide inlets channels and 1 mm wide mixing channel with obstructions of different shapes in the mixing channel were fabricated. The table below shows the properties of an embossing tool fabricated using PDMS.

Compared with the overall time reduced in fabricating the tool, increase in the embossing cycle time due to the low thermal properties of PDMS is negligible. Since PDMS is an inert material, the problem of adhesion with PMMA is avoided. This was vital in this work as the de-embossing was done manually by peeling the PDMS off from the PMMA. This technique has tremendously reduced the complexity involved in fabricating both planar and orthogonal 3-D embossing tools. Combined with a high-resolution mask printing on transparencies, a complete microfluidic device can be fabricated within 24 hours. Since PDMS retains it physical characteristics up to 200^0C, the tools may be extended to emboss other polymer substrates such as polycarbonate, polypropylene, or cycloolefin copolymer.

Future Work

The fabrication process described in this work predominantly focused on reducing the time, complexity, and cost involved in fabricating prototype microfluidic chips. Using PDMS has resulted in the reduction of the parameters mentioned but might be applicable only to certain feature size and aspect ratio. Applications involving high aspect ratio with small feature size will

pose some problems with the current technique. Therefore more work is needed in optimizing the procedure for such applications.

Compression of the tool during embossing for applications involving high aspect ratio will be have to be addressed more carefully as it would be more prominent in such an application. Bonding PDMS base to a thick, flat metal or depositing metal onto the features might enhance the strength to the tool and minimize the compression. A number of castable polymers are commercially available used in various applications that could be used as an embossing tool. More research is needed in exploring such stronger polymers that could be fabricated with the same ease and time. However, it should be noted that the polymer used as the tool would interface different polymers like photoresist and thermoplastics. Therefore, adhesion is a key issue that should be considered in selecting the polymer.

The fabricated tool in this work was used only in hot embossing, which is a relatively slow replication method. The use of polymer tools in injection molding is the next logical step, as it would facilitate mass production in less time. The temperature and force used in injection molding is much higher than those used in hot embossing, which should be considered in using polymer tools. Edwards et al. [49] used negative resist SU-8 as a tool for injection molding and replicated parts in polycarbonate and polypropylene.

The embossing time used in this work was much higher than the conventional embossing with metal tools. Future work should focus on reducing the overall time of the embossing process. The bonding technique optimized in this work using force and pressure at appropriate temperature might not be necessary in certain applications where adhesive bonding is a suitable alternative. Medical grade UV-curable adhesives can be used to bond two polymer substrates but might require an UV-source of high intensity to cure the adhesive.

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