FABRICATION OF MASTERS FOR MICROFLUIDIC DEVICES USING CONVENTIONAL PRINTED CIRCUIT TECHNOLOGY

A Thesis

by

ARJUN PENUBOLU SUDARSAN

Submitted to the Office of Graduate Studies of
Texas A&M University
in partial fulfillment of the requirements for the degree of

MASTER OF SCIENCE

August 2003

Major Subject: Chemical Engineering

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Approved as to style and content by:

Victor M. Ugaz (Chair of Committee)	M. Sam Mannan (Member)
Paul S. Cremer (Member)	Kenneth R. Hall (Head of Department)

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ABSTRACT

Fabrication of Masters for Microfluidic Devices Using Conventional Printed Circuit Technology. (August 2003)

Arjun Penubolu Sudarsan, B.E., Bangalore University

Chair of Advisory Committee: Dr. Victor M. Ugaz

The capability to easily and inexpensively fabricate microfluidic devices with negligible dependence on specialized laboratory equipment continues to be one of the primary forces driving the widespread use of plastic-based devices. These devices are typically produced as replicas of a rigid mold or master incorporating a negative image of the desired structures. The negative image is typically constructed from either thick photoresists or etched silicon substrates using conventional photolithographic fabrication processes. While these micromachining techniques are effective in constructing masters with micron-sized features, the need to produce masters rapidly in order to design, fabricate, and test microfluidic devices, is a major challenge in microfluidic technology.

In this research, we use inexpensive photosensitized copper clad circuit board substrates to produce master molds using conventional printed circuit technology. The techniques provide the benefits of parallel fabrication associated with photolithography without the need for cleanroom facilities, thereby offering a degree of speed and simplicity that allows microfluidic master molds to be constructed in approximately 30 minutes in any laboratory. These techniques are used to produce a variety of

microfluidic channel networks using PDMS (polydimethylsiloxane) and melt-processable plastic materials.

DEDICATION

To my parents, Rathna and P. Sudarsan and my brother, Vikram

for all their love, encouragement and support.

ACKNOWLEDGEMENTS

I would like to express my sincere gratitude to my advisor Dr. Victor M. Ugaz for all his guidance and unwavering belief in me. I am truly grateful to Dr. Sam Mannan not only for serving on my committee, but also for all his indispensable advice and encouragement over the past couple of years. I would like to thank Dr. Paul S. Cremer for his invaluable advice and for agreeing to serve on my committee. This work would not have been completed without all the help and facilities provided by Dr, William M. Lackowski. I thank my group members, Roger, René, Ruchi, Faisal, Nitin, Steve and Jian for all their support and encouragement. Finally, I would like to thank the Department of Chemical Engineering for giving me the wonderful opportunity of pursuing my studies in this reputable university.

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CHAPTER I

INTRODUCTION

The field of microfluidics, encompasses the entire process of designing and constructing devices for the management of liquids and gases in channels with cross-sectional dimensions on the order of 10-100 μm. These devices are becoming a key technology in a myriad of miniaturized systems that are being developed for biological, chemical and medical purposes. The design of miniaturized fluidic systems presents many challenges owing to the extremely high surface to volume ratios, in which fluids are subjected an environment quite different from typical macro-scale applications. The flow of fluids in micro-scale channels, surface chemistry of fluidic channels and materials of construction, viscosity of fluids, volatility of fluids, temperature and pressure ranges in which fluids and devices are stable, bonding of substances to create hermetic systems, are only a few examples of critical parameters to be considered in the design and construction of microfluidic systems. Furthermore, fabrication of micron scale structures requires the use of specialized techniques like micro-contact printing, selective etching, replica molding and injection molding, which are different from fabrication processes for hardware in macro-scale systems.

This thesis follows the style and format of *Electrophoresis*.

The potential applications of microfluidic devices are vast. These range from electrophoresis [1] to the study of receptor binding interactions on the surface of phospholipid bilayers [2] to protein crystal growth [3] to rapid and high density sequencing of DNA [4] to rapid analysis of bodily fluids [5] to devices for *in vivo* drug delivery [6]. Miniaturization of devices has many advantages which include decreased cost in manufacture, use and disposal; decreased time of manufacture and analysis; reduced consumption of reagents; reduced production of potentially harmful by-products; and increased portability to conform with lab-on-a-chip standards.

For microfluidic devices to be successful, the fabrication procedures and techniques, environment under which devices are made, materials used for fabrication, and other attributes have to be compatible to accommodate micro-scale features. Manufacturing costs, time, facilities available, physical and chemical properties of devices made are all important considerations in any efforts to commercialize microfluidic technology. Conventional fabrication techniques used in microfluidics can be complex and expensive, and are suitable only for small-scale production runs and specialized applications. Since microfluidic systems are becoming more and more mainstream, there is a great need to shorten the duration of time between design-fabrication-testing cycles. Consequently, there is significant interest in finding new ways to optimize and simplify techniques to quickly produce robust working microfluidic devices that can aid in the design of systems to satisfy more complex applications. In this work, we address this need by developing a new technique for constructing masters using conventional printed circuit technology. These masters can be fabricated in

approximately 30 minutes, and are used for casting against poly(dimethylsiloxane) (PDMS) or melt-processable plastic materials to form working microfluidic devices.

Soft lithography

Soft lithography is one of the primary fabrication techniques for making micro-scale devices. This method involves replication of structural features on a rigid master mold in a plastic substrate like PMMA (polymethylmethacrylate) or PDMS (polydimethylsiloxane). When used for making microfluidic devices, soft lithographic techniques satisfy many of the requirements of microfluidic fabrication such as high-fidelity reproduction of structures from a mold, sturdy devices with considerable tear resistance, stable devices at elevated temperatures, easy maneuverability of fluids in channels of micro- and nano-scale dimensions, optical transparency for easy visual monitoring, and at the same time being inexpensive, simple to produce.

Soft lithography offers several advantages over conventional micromachining techniques. One of the principal advantages is that routine access to a cleanroom facility is not required. Further, soft lithographic techniques can be used in virtually any laboratory without the need for expensive and complicated equipment. Structures with size ranges as small as a few microns can be fabricated with good quality. Microfluidic structures can be patterned on planar or non-planar surfaces and are generally easy to release from the mold without causing any damage to the device or master. Additionally, a large number of devices can be made from a single master depending on the size of the

master and devices. As an example, on a 6" x 6" master, we are able to fabricate 32 usable microfluidic devices at once. A larger master would allow more devices to be produced without compromising quality.

Overview of process

The main goal in soft lithography is to obtain an elastomeric block with patterned relief structures on its surface. The most commonly used elastomer is PDMS. The elastomeric block or structure is prepared by a cast molding technique [7], where a prepolymer of the elastomer is poured on the surface of a rigid mold or master that has relief structures patterned on its surface. The prepolymer is then cured thermally in an oven, after which the cured elastomer is removed and mounted on a support surface, typically glass, silicon or PDMS, to form closed structures. Figure I-1 illustrates the procedure for fabricating PDMS stamps from a rigid mold or master.

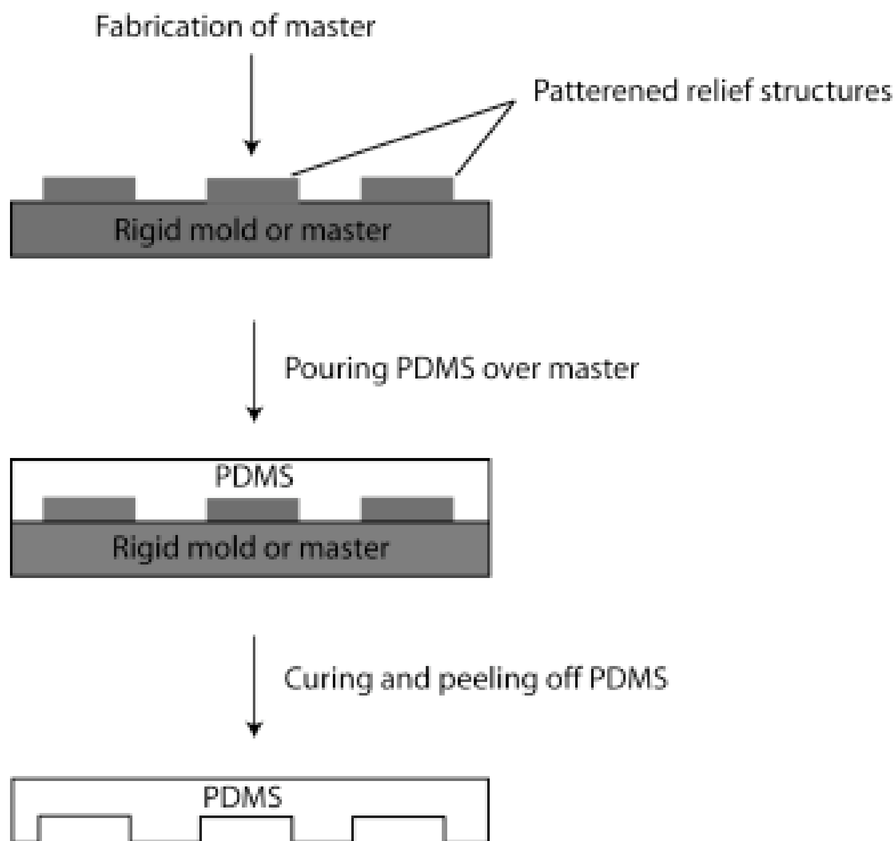


Figure I-1. Fabrication of a PDMS structure from a rigid mold or master.

At the molecular level, PDMS is characterized by the presence of an inorganic siloxane backbone with organic methyl side groups [8]. One formulation of PDMS commonly used is Sylgard™ 184 obtained from Dow Corning. It is composed of a liquid silicon rubber base (vinyl-terminated PDMS) and a catalyst or curing agent that includes cross-linking siloxane oligomers containing at least three silicon-hydride bonds (mixture of a platinum complex and copolymers of methylhydrosiloxane and dimethylsiloxane). Both components contain siloxane oligomers with vinyl-terminated groups. The

chemistry that leads to the cross-linked polymer is summarized in Figure I-2 [9]. Once mixed (10:1 base to curing agent by weight), poured over the master, and cured either thermally or at room temperature for a longer period of time, the material becomes a solid cross-linked elastomer. The cross-linking siloxane oligomers and silicon-hydride bonds of the curing agent react with the platinum-based catalyst. The addition of the Si-H bonds across the double bonds of the cross-linking oligomers results in the formation of Si-CH_2-CH_2-Si linkages. This process is also referred to as the hydrosilation between vinyl (SiCH=CH_2) groups and hydrosilane (SiH) groups. The multiple reaction sites on the Si-H bonds allow for three-dimensional cross-linking. A major advantage of this type of addition reaction is that no by-products are generated.

The exact mechanism of the hydrosilation has not been completely determined. The nature of the catalyst and of the molecular species undergoing reaction influences the hydrosilation. One possible mechanism for hydrosilation is described as follows. The metal atom can be considered to be a site to which the SiH and the SiCH=CH_2 can bond in the proper proximity and stereo-chemical configuration for addition to occur [10]. For the catalyst to be effective, the olefin ligands attached to the metal atom must be labile enough to permit substitution of vinyl groups attached to silicon, and at the same time, small enough to permit oxidative addition of SiH without steric hindrance.

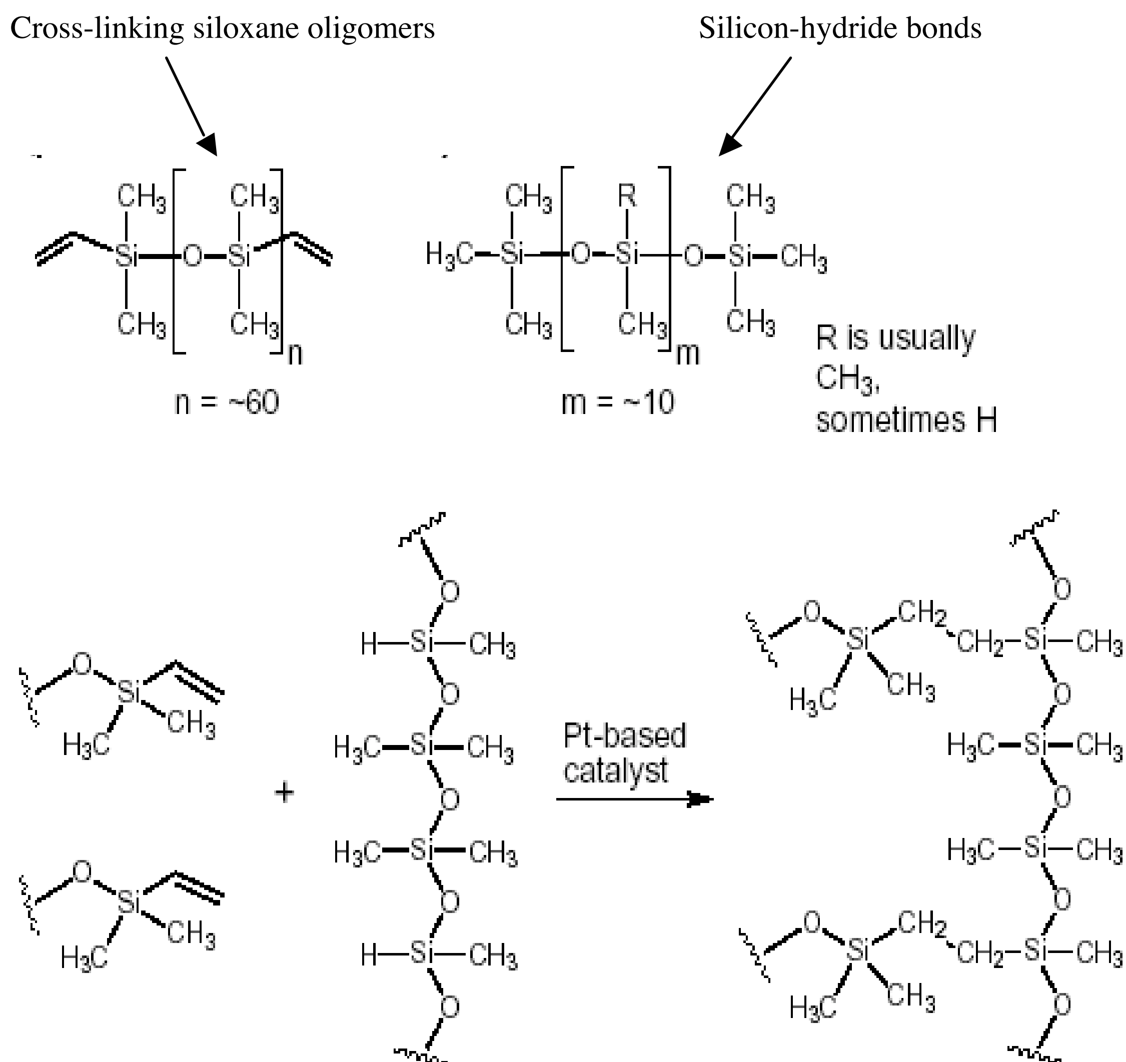


Figure I-2. Cross-linking mechanism of PDMS [9]. The addition of Si-H bonds of the curing agent across the double bonds of the cross-linking oligomers results in the formation of Si-CH_2-CH_2-Si linkages.

Varying the base to curing agent ratio will change the properties of the resulting cured elastomers. As the base to curing agent ratio decreases, the resulting elastomer will be more rigid. An increase in curing temperature will also alter the viscoelastic properties by accelerating the cross-linking reaction. The versatility of changing the base to curing agent ratios can be easily demonstrated by making bouncing balls made from PDMS (see for example http://mrsec.wisc.edu/edtec/cineplex/PDMS.html). A PDMS ball made with a higher ratio of curing agent to base will bounce more than a ball made with a lesser ratio.

Elastomers in general are advantageous for use in microfluidic applications because they can make conformal contact with planar and non-planar surfaces. They can be used over large surface areas and can be easily released from rigid masters or molds, or even from complex, three-dimensional structures. The following are other properties of PDMS elastomers that make them extremely useful in soft lithography of microfluidic structures [11]:

a) PDMS is not hydroscopic and does not swell with humidity
b) PDMS is elastic and provides a surface that has low interfacial free energy (~21.6 dyn/cm) with good chemical stability. Most molecules or polymers being patterned or molded do not adhere irreversibly to, or react with, the surface of PDMS.
c) The elastomer is optically transparent down to ~300 nm. Prepolymers being molded can also be cured by UV cross-linking.

d) Due to its isotropic and homogeneous nature, molds from this material can be deformed mechanically to manipulate the patterns and relief structures in their surfaces.

e) PDMS membranes are permeable to gas flow.

f) A PDMS stamp or mold can be used repeatedly with minimal degradation.

Fabrication of masters

In the past few years, significant progress has been made in the field of rapid prototyping of microfluidic devices. As described earlier, soft lithographic techniques are often used to fabricate devices as replicas of a rigid mold or master containing a negative image of the required structures. The rigid mold or master is constructed from either dense photoresists or etched silicon substrates produced using conventional photolithographic fabrication processes [12,13]. These processes are effective in producing masters with micron-scale features, but the speed of making masters is limited as routine access to a cleanroom is required. Consequently, the rate at which new fluidic designs can be tested is limited as it is heavily contingent upon the fabrication speed of masters.

An alternative process for the fabrication masters for use in the manufacture of injection-molded devices requires serial processes associated with cumbersome UV curing protocols [14]. An epoxy is pipetted onto a brass block and a pretreated polyester grating film is placed on top of the epoxy. The pretreatment involves, dipping of the

polyester grating film in sodium dodecyl sulfate and then drying in nitrogen under vacuum in an oven for 30 minutes. A mask is then placed on top of the grating film and the epoxy is cured for 30 s. Undeveloped material is removed by immersing the master in acetone at –20 ºC in a stream of CO_2. The master is then dried under nitrogen, post cured for a further minute and then treated at 50 ºC for 2 hours in a vacuum oven, before it can be used.

Another process recently developed requires high precision milling to fabricate master templates [15]. The templates, made out of an aluminum alloy, consist of negative features of the channel structures created by the use of a high-precision milling machine. A piece of acrylic is then pressed on top of the aluminum-alloy mask and heated in an oven at 205 ºC for 2 hours to allow the acrylic to sink into the channels and generate a positive feature in the acrylic surface. While this process is capable of producing channels with heights ranging from 7 to 20 μm, the milling machine may not be capable of producing complex curved structures, and the entire process takes about 8 hours to prototype microfluidic devices.

Techniques using liquid phase photopolymerization have also been developed for microfluidic systems [16]. These require serial processes that are associated with injection and removal of UV cross-linkable polymers. Masters for PDMS molding are fabricated by placing a small amount of the prepolymer on a silicon substrate, placing a mask on the prepolymer, and then exposing to a UV light source. Unexposed polymer is washed away using methanol, and the master is baked for one hour to harden the material. A similar method for fabrication of individual microfluidic devices consists of

introducing the prepolymer in a glass or plastic cartridge that is attached to a microscope slide with an adhesive gasket. The cartridge is then filled with the prepolymer using a pipette tip and a mask is placed on the surface of the prepolymer before exposure to a UV light source. After exposure, the uncured polymer mixture is extracted from the channels using a syringe. Any remaining unpolymerized monomer is removed using methanol. Channels are then dried before being used.

Another recently developed method to fabricate fluidic device masters involves spin casting of thin polystyrene films on glass and plastic substrates and pressing a mold onto the thin film [17]. While this technique is capable of producing sub-micron scale features, the pressing of the mold before the film dries might limit the use of this technique, as there is a certain amount of trial and error involved. Firstly, if the film dries too quickly, it will not be capable of incorporating the structures on the mold and spin casting needs to done again. Secondly, the pressing of the mold has to be done extremely carefully without any sideways movements as this will cause the master structures to become deformed.

Objectives

While the above-mentioned processes have provided useful contributions to microfluidics, none of them offers highly parallel fabrication capabilities that are of extreme importance. The main objective of this research is to address this difficulty by demonstrating that master molds can be constructed using presenstitized printed circuit boards (PC boards) in a fast and efficient way so that PDMS (and other plastic)-based

microfluidic components can be quickly built and tested at minimal expense. The PC boards are commercially available with different copper thicknesses, allowing the fabrication of channel structures at a variety of heights. With this capability, and without the need for specialized and expensive laboratory equipment, we are able to manufacture microfluidic devices in less than two hours. This time accounts for both fabrication of new masters (approximately 30 minutes), and casting of the microfluidic devices using PDMS.

The techniques employed here combine the advantages of soft lithography and rapid prototyping to offer the highly parallel level of fabrication associated with photolithography without the need for expensive laboratory equipment. Using these techniques, microfluidic structures as small as 15 μm in height can be easily fabricated in virtually any laboratory. The masters are capable of being used repeatedly for casting microfluidic devices with minimal material degradation.

CHAPTER II
PC BOARD FABRICATION

Printed circuit boards, or PC boards, are one of the most important parts of any type of electronic equipment. They are used for bearing the load of smaller components and also to supply the wiring that interconnects various individual components to create an integrated system. Generally, PC boards incorporate three primary constituents: a resin system, reinforcement and a conducting foil layer (usually copper). The resin system and reinforcement together form an insulating substrate on which electrical connections can be made by patterning the conducting foil.

Since etching is the most economical way to produce a desired wiring pattern on the conductive copper layer, an etch-resistant material must first be applied on the surface to serve as a mask for the required pattern. During etching, the resist-covered areas are protected from chemical degradation while unwanted copper is removed from the exposed areas. Further washing and stripping of the remaining resist renders a clean copper pattern on the surface of the PC board. The different materials used in the construction of PC boards and the different methods of applying resists for pattern transfer are discussed in this chapter.

Overview of construction

As there is a substantial degree of variability in the three substances that make up a PC board, plenty of permutations are available for manufacture. In general, it is

desirable for PC boards to be compatible with different manufacturing processes and to have good physical and electrical properties, while at the same time keeping the cost of manufacture as low as possible.

In the past, PC board insulating substrates were constructed from a laminate of paper and a synthetic resin thermally bonded under pressure. The resulting material was called synthetic resin bonded paper (SRBP). Unfortunately, this material was brittle in nature and could be broken easily. It was also hydrophilic in nature and absorbed moisture, often leading to short-circuiting problems. PC boards constructed using this process are seldom used today, except in some mass-produced consumer equipment, as manufacturing cost is cheap.

Currently, most PC boards are made of an epoxy resin with woven glass as the reinforcement. Base materials for PC boards are classified according to the following schemes based on the details associated with the type of reinforcement used, the resin system, the glass transition temperature T_g of the resin system, and other material properties [18].

1. National Electrical Manufacturers Association (NEMA) grades
2. IPC-4101 specification for base materials for rigid and multilayer boards

Glass transition temperature

The glass transition temperature of the resin system indicates the temperature at which the material changes from a fairly rigid or glassy state to a more deformable or softened state. As a material's temperature nears this transition point, its physical

properties are affected owing to an increase in intermolecular segmental mobility. The T_g of the resin system is of extreme importance in PC board manufacture because of its influence on the thermal expansion properties and the degree of cure of the resin system.

The thermal expansion behavior in the vicinity of T_g is of particular interest. For the purposes of PC board manufacture, it is convenient to define T_g as the intersection formed by a linear extrapolation of the high- and low-temperature volumetric expansion behavior. Figure II-1 shows a measure of the glass transition temperature as determined by thermo mechanical analysis or TMA [17]. Here, T_g is defined as the point where extrapolations of the linear portions of the curve intersect. The resulting slopes of the linear portions of the curve can then be taken as a measure of the coefficients of thermal expansion in the respective temperature ranges, which are important properties to determine the environmental operating parameters of the fabricated printed circuit boards.

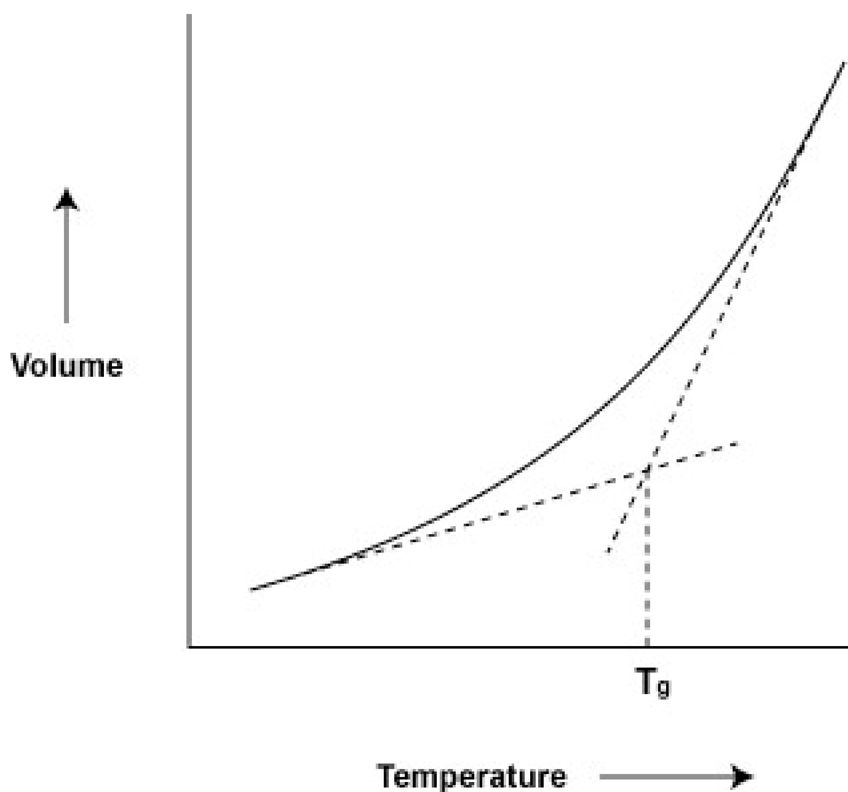


Figure II-1. Schematic illustration of estimation of T_g by TMA [18]. T_g is the point where extrapolations of the linear sections of the curve intersect.

Most resin systems incorporate subcomponents containing reactive sites that, when combined with a curing agent, cross-link under the influence of heat. The cross-linking reaction induces a dramatic change in the physical properties of the material, characterized by an increase in T_g. The magnitude of this change is directly related to the extent of cross-linking. The degree of cure can be determined by carrying out successive TMA on the same sample at various stages during the course of the curing process. The resulting difference between glass transition temperatures obtained from subsequent

TMAs can be taken as a measure of the degree of cure. Figure II-2 illustrates how the curing process can be characterized by an increase in T_g.

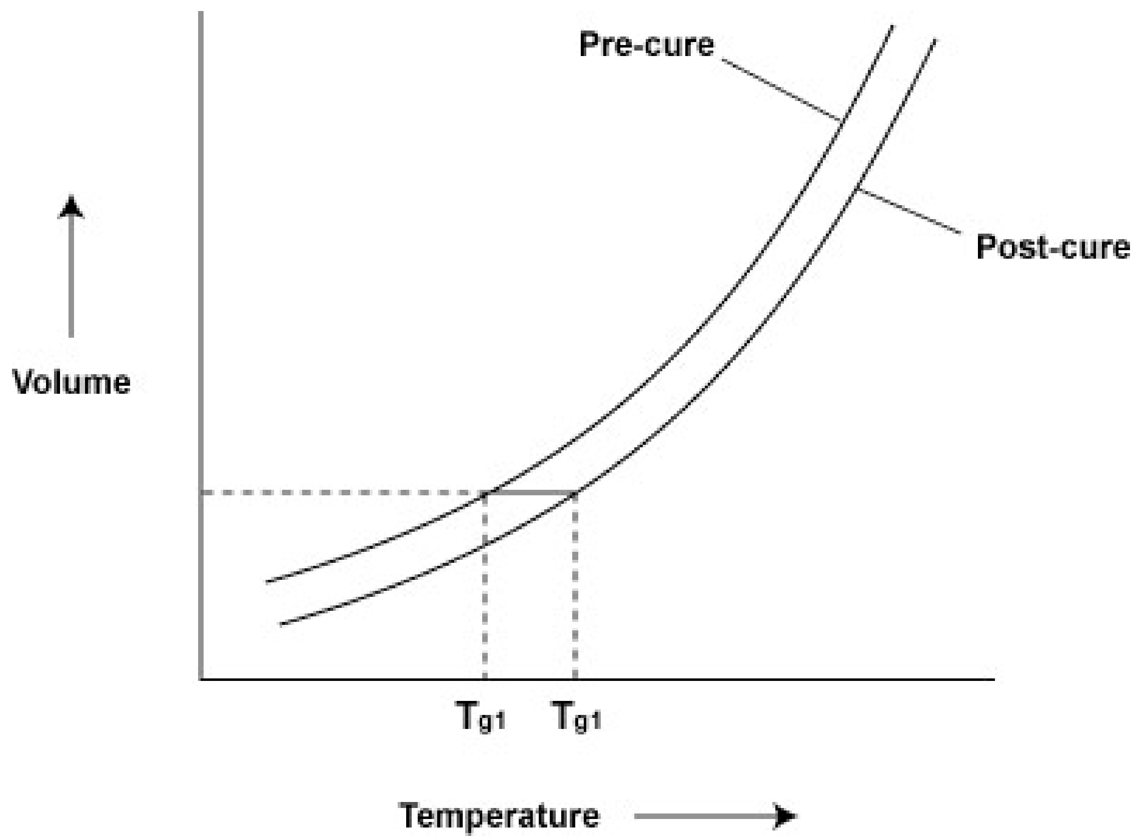


Figure II-2. Schematic illustration of estimation of degree of cure [18]. Difference between T_g's is a measure of the degree of cure.

A higher glass transition temperature implies a low overall degree of thermal expansion until higher temperatures are reached, although the magnitude of this expansion varies with different materials. High glass transition temperatures are characterized by harder and more brittle mechanical properties. The T_g also affects the strength and delaminating characteristics of the conductive copper layer. Hence, the glass transition temperature is a critical parameter when choosing a resin system.

Classification schemes

The most widely used PC board base materials are classified according to one of two schemes. These classifications are used to identify the base material when purchasing PC board components. They are also useful when designing PC board systems to have desired mechanical properties under specific operating conditions.

One of the oldest classification schemes for PC board base materials and other electrical components is the *NEMA* classification system. The classification grades from this scheme are shown in Table II-1.

Table II-1. NEMA classification [18]

Grade	Resin	Reinforcement	Flame retardant
XXXPC	Phenolic	Cotton paper	No
FR-2	Phenolic	Cotton paper	Yes
FR-3	Epoxy	Cotton paper	Yes
FR-4	Epoxy	Woven glass	Yes
FR-5	Epoxy	Woven glass	Yes
FR-6	Polyester	Matte glass	Yes
G-10	Epoxy	Woven glass	No
CEM-1	Epoxy	Cotton paper/woven glass	Yes
CEM-2	Epoxy	Cotton paper/woven glass	No
CEM-3	Epoxy	Woven glass/matte glass	Yes
CEM-4	Epoxy	Woven glass/matte glass	No
CEM-5	Polyester	Woven glass/matte glass	Yes
CRM-6	Polyester	Woven glass/matte glass	No
CRM-7	Polyester	Matte glass/ glass veil	Yes
CRM-8	Polyester	Matte glass/ glass veil	No

IPC-4101 is an alternate classification scheme applicable to base materials for rigid and multilayer PC boards. In this system, a specification sheet number designates property requirements for each material. A few examples from this classification are illustrated in Table II-2.

Table II-2. IPC-4101 classification [18]

Specification Sheet Number	**Resin**	**Reinforcement**	**T_g Range (ºC)**
00	Phenolic	Cellulose paper	N/A
01	Modified phenolic	Cellulose paper	N/A
02	Modified phenolic, flame resistant	Cellulose paper	N/A
04	Modified epoxy, flame resistant	Cellulose paper	N/A
20	Epoxy, non-flame resistant	Woven E-glass fabric	≥ 100
21	Epoxy, flame resistant	Woven E-glass fabric	≥ 110
25	Epoxy/PPO, flame resistant	Woven glass	150-200
40	Polymide	Woven E-glass	≥ 200
53	Polymide	Nonwoven aramid	≥ 220
70	Cyanate ester	Woven S-2 glass	≥ 230
71	Cyanate ester	Woven E-glass	≥ 230

Physical properties of manufactured PC Boards

PC boards are manufactured with different thicknesses of copper foil to accommodate various electrical requirements. Thicknesses are specified in terms of ounces/square foot, which represents weight of the copper foil per square foot of the base material. Copper foils are typically laminated or electrodeposited on the surface of the base material in standard thicknesses, as shown in Table II-3.

Table II-3. Copper weight and thickness [18]

General terminology	Area weight (oz/ft^2)	Thickness (μm)
1/2 oz	0.50	17.2
3/4 oz	0.75	25.7
1 oz	1	34.3
2 oz	2	68.6
3 oz	3	103.0
4 oz	4	137.0
5 oz	5	172.0
10 oz	10	343.0

The most commonly used foil thicknesses are 1 oz and 2 oz. 1/4 oz boards can also be obtained, but usually must be custom made.

Manufacturing process

Once the resin and reinforcement systems are chosen, the manufacturing process of a PC board consists of two primary stages, prepreg manufacturing and laminate manufacturing [18,19]. The former stage is sometimes referred to as 'B' stage while the latter is referred to as 'C' stage. B stage represents a state of partial cure while C stage represents a total cure. In reality, total cure is not possible as all reactive sites on the resin molecules do not cross-link, but this term can be used to characterize an "almost" total cross-linking of the active sites. Most popularly, epoxy is chosen as the resin system while fiberglass cloths or phenolic papers are chosen as the reinforcement systems.

The prepreg manufacturing stage consists of coating the resin system on the chosen reinforcement type. Rolls of reinforcement material are first passed through treaters where they are pulled through plates containing the resin system. The reinforcement cloth or paper then passes through a set of metering rolls that monitor the amount of resin to be transferred. The next step is to pass the reinforcement through successive thermal zones that normally consist of infrared heating and forced-air convection systems, or a combination of the two. Here, any solvent used to carry the resin is evaporated before the B-staging or partial curing process occurs. After curing, the prepregs must be stored carefully to avoid thermal or moisture attack, as this can adversely affect the lamination process.

In the laminating process, desired thicknesses of copper foils are placed on top of the prepregs and subjected to pressure, temperature and vacuum. Typically, a number of

prepregs can be laminated with copper by stacking them one on top of the other using stainless steel or aluminum sheets as separating mediums. The amount of pressure and heat applied depends on the degree of cure required. Figure II-3 summarizes the PC board manufacturing process. After lamination, the PC boards are cut to the desired dimensions, inspected and then either sold or taken for resist coating depending on the customer needs.

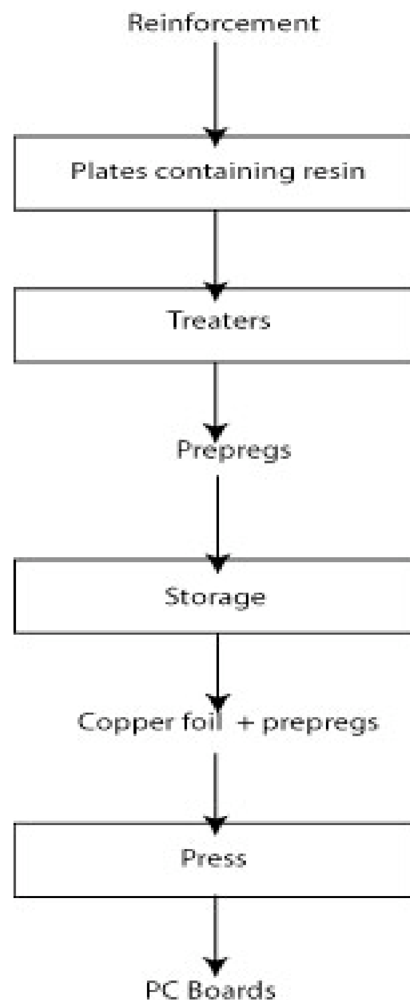


Figure II-3. Overview of PC board manufacture.

More sophisticated lamination techniques use copper foils stacked in rolls and pushed through the press along with the prepregs to create a continuous manufacturing process. Here, direct current is used as the means to heat the laminate and prepregs. Monitoring the amount of current provides a way to precisely control the temperature in the stack. The advantage of direct current is that a uniform heat is disseminated throughout the stack as opposed to heating the interior plates solely by conduction from the top and bottom plates. Other benefits include resin consistency and laminate stability with good surface quality.

Coating of resists

PC boards are sold with a bare copper foil surface or "presensitized" with a photosensitive resist coating covering the copper foil. Presensitized boards can be coated either positive or negative tone resists depending on the users requirement. A photoresist coating is used to transfer the desired circuit pattern to the copper foil using photolithography. After exposing the photoresist coated PC board to a light source using a mask containing the desired pattern the resist can be selectively removed in the unmasked areas. This step is called development of resist and is followed by an etching process to selectively remove copper from areas not coated with photoresists. After etching, the remaining photoresist is stripped from the board leaving behind the copper circuitry pattern on the surface.

Whether the resist is positively or negatively coated, it has to provide sufficient resolution for image transfer during exposure, needs to be highly etch-resistant, and has

to have good stripping capabilities when the resist needs to be removed. During etching, the resists need to adhere well to the copper layers to avoid excessive under-cut (etching under the photoresist layer). Resists need to be void of pinholes, oil and resin bleeding and should not damage the substrate or circuitry when removed. Figure II-4 provides an overview of producing circuits with a photo-defined resist.

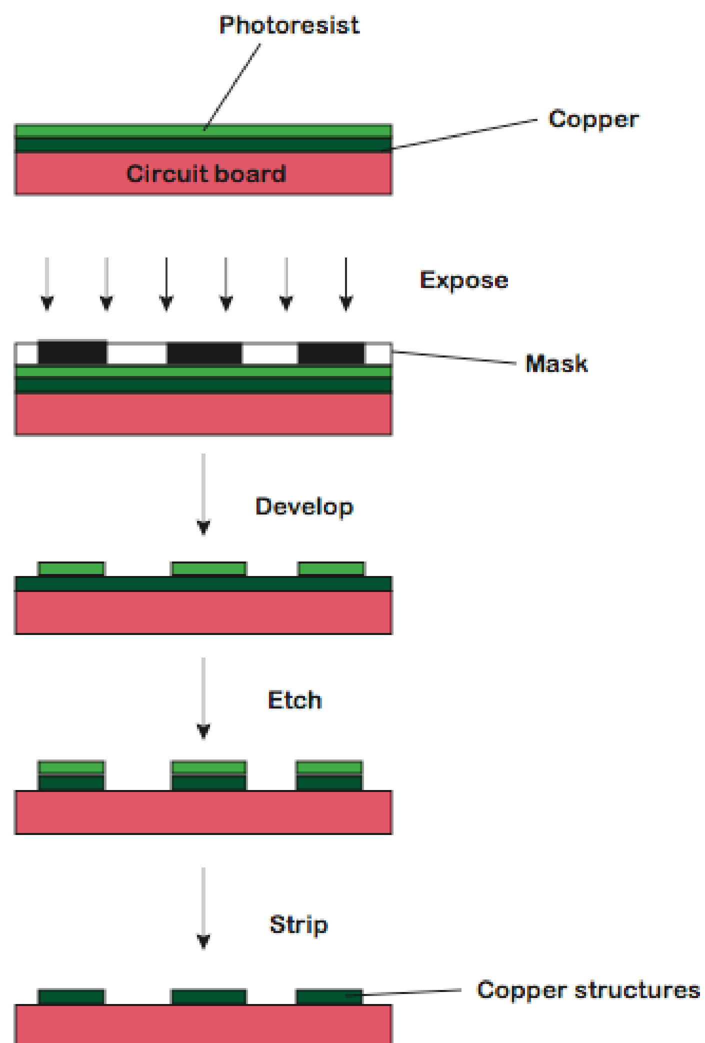


Figure II-4. Overview of producing circuits with a photosensitive resist.

Dry-film and liquid photoresists are capable of producing fine-line, 76 to 127 μm (0.003 to 0.005 in), circuits needed for production of surface-mount circuit boards [18]. Both positive and negative tone resists offer better protection in acidic solutions as compared to alkaline solutions, although negative acting resists are more tolerant towards alkaline solutions [18]. After exposure and development, positive resists remain sensitive to light and must be protected from ambient white light. On the other hand, negative resists become immune to light and can be handled in white light. The different methods of applying resists are discussed here.

Dry-film photoresist

Dry-film photoresist is becoming a prominent resist technology for both inner and outer layer fabrication [19]. Sodium hydroxide or potassium hydroxide is used for developing the resist while acetone is used for resist stripping. Chlorinated solvents are no longer used for processing dry-film resists. The dry-film resists, which are available in different thicknesses, are supplied in rolls with the photoresist sandwiched between a polyester cover sheet and a polyethylene separator. To laminate the resist on the surface of copper, the polyethylene separator is removed and the resist with the cover sheet is placed on top of the copper board. Using heat and pressure, the resist is laminated onto the copper layer. Care must be taken to ensure that the copper surface is free of contaminants prior to lamination. Generally, cleaning of the copper surface is done using caustic solutions followed by water and acid rinses. Application of dry-film resist to a drum-sided foil surface is advantageous as cleaning before lamination is minimized. The

lamination process is usually accomplished using an automatic cut sheet laminator that uniformly applies photoresist to one or both sides of the board in a single step. The temperature, pressure and speed of lamination depend on the resist chemistry in order to achieve proper resist conformation and adhesion to the copper surface. This technique is sometimes referred to as *postage stamp lamination* as the resist is applied within the edges of the board to reduce resist waste.

Liquid photoresist

Liquid photoresist was the popular choice of resists for fine-line imaging before the advent of dry-film resists [19]. Liquid resists have many flaws as compared with dry-film resists. The resists are not covered by any protective sheets and serve as a source for contamination before the development stage. They are easily damaged during handling, stacking and transporting after the imaging stage. During imaging, the pattern transfer can be highly sensitive to contaminants. Nowadays, only a small number of PC board manufacturers use liquid photoresists for inner layer production, although they are still popular for production of small quantities of PC boards. Imaging liquid resists is similar to dry-film processes. The resist is applied onto the copper surface and dried before photoimaging. The following methods are used for coating liquid resists.

<u>Dip coating</u>

PC boards are immersed completely in deep tanks that contain liquid photoresists maintained at constant temperatures. The immersed boards are then withdrawn at a

constant rate to achieve a uniform coating on the surface. Once coated, the boards are dried in a series of convection ovens.

Roller coating

In this technique liquid photoresists are metered onto rollers of double-sided coating equipment for application to the PC board surface at a predetermined wet thickness. Coated boards are then transported to ovens on a conveyor belt and then cooled before photoimaging. This technique is suitable for large volume production and generally produces a uniform dried thickness of approximately 0.025 mm [19]. However, a cleanroom environment is required with continuous filtration of the liquid photoresist. Operating parameters need to be altered with different board thicknesses, and roller surface chemistries must be compatible with the liquid resist.

Spray coating

Spray coating of liquid photoresists from nozzles used to be a viable technique for thin film coating. Coating could be either single or double-sided, and the resist was subsequently dried in ovens. Due to the excessive use of liquid photoresists and the high maintenance costs of the spray heads, this technique has now become obsolete.

Curtain coating

In curtain coating, liquid is pumped from a reservoir to flow down like a curtain across the width of the coating areas. The boards are passed on conveyor belts through

the curtains, where they are coated on one side, and then into drying ovens before being taken for coating on the other side. This technique offers the highest productivity of liquid systems as it uses high-speed conveyor belts for transporting boards. The conveyor speed, liquid temperature and viscosity play a role in determining the coating thickness. Initial installation of the coating equipment is expensive and disposal or recycling of the liquid resist is a liability.

Electrophoretic deposition

In this technique, liquid resist is held in a tank and the board to be coated is immersed in the tank and connected as the anode to the rectifier. Stainless steel plates are connected to serve as cathodes. When an electric potential is applied, negatively charged photoresist components in solution migrate to the anode forming a resist layer on its surface. The coating thickness is controlled by immersion time, resist temperature, current density and resist formulation. This technique is usually capable of producing a dried coating thickness of 0.013 mm [19]. The coated resists have a high-resolution capability. For a high-volume production, the initial investment is high.

Photoresist development

Photoresist removal or development is another key step in the fabrication of PC boards. The method used for developing the resist must be carefully selected to account for the effect on board materials, cost and production requirements, and safety and pollution issues. If the resist is underdeveloped, unwanted copper will remain on the

surface of the board, ruining the design on the finished boards. On the other hand, overdeveloping will cause too much resist to get washed away leaving more areas of copper exposed to the etchant than required. Solvent-based developing solutions are under continual environmental pressure while chlorine-based solvents, xylenes, toluenes and other cyclic compounds have been banned. As a result, aqueous solutions are extensively used for resist removal [18].

Dry-film resist development

Dry-film resists have been modified to simplify development in aqueous solutions. Resist removal can be either a batch process in a tank or a continuous using conveyor belts. The continuous process uses a spray technique that assists in separating the resist from the copper and rinsing away the removed material. When aqueous-alkaline resist removal solutions are used, they give rise to partially dissolved debris of softened resist films. This debris is removed using a filter system and then disposed in accordance with waste-disposal requirements.

Positive acting liquid resist development

The easiest way to remove this resist is by rinsing in an aqueous-alkaline solution such as sodium hydroxide. If the boards are subject to light baking prior to development, then it is necessary to use commercial organic or inorganic strippers. Excessive baking will make the removal of the resist difficult and also damage the insulating substrate.

Sometimes, machine stripping is employed using a 0.5*N* sodium hydroxide solution with nonionic surfactants and defoamers.

Negative acting liquid resist development

Commercial solvents or strippers easily develop negative acting liquid resists, after light baking. Here, the resist may not dissolve, but will soften and swell, breaking the adhesive bond to the substrate. After this is accomplished over the entire surface, the resist is washed away using a water spray.

Copper etching

Copper etching is another major step in the construction of PC boards. Etching refers to the chemical processing of subtractive printed boards or the selective removal of copper to achieve desired circuit patterns. As with developers, the choice of etchants has been limited by environmental, economic and operational concerns. Alkaline ammonia is now becoming the most commonly used etchant due to its capacity for continuous operation and compatibility with metallic and organic resists. Ferric chloride, ammonium persulfate, and chromic-sulfuric acid have historically been the most common etchants. However, their use has diminished in recent years due to environmental concerns. Nevertheless, ammonium persulfate and ferric chloride remain popular for small scale PC board production.

A number of factors must be considered when choosing an etchant chemistry. Some of the primary considerations include [18]:

- Etch rate
- Compatibility with resist
- Operating conditions and environment required
- Disposal of by-products and pollution control
- Equipment maintenance

Ammonium persulfate

Continuous and batch systems of ammonium persulfate are widely used for copper etching in PC board manufacture. Persulfates in general are compatible with most commonly used photoresists, although environmental restrictions often limit their use. Sometimes ammonium persulfate is used in combination with mercuric chloride, which functions as a catalyst.

Ammonium persulfate is a stable salt of persulfuric acid ($H_2S_2O_8$). The persulfate ion ($S_2O_8^{2-}$) is formed when these salts are dissolved in water. In the etching process, persulfate oxidizes metallic copper to cupric ions. The standard reaction for ammonium persulfate etching is [18]:

$$Cu + (NH_4)_2S_2O_8 \rightarrow CuSO_4 + (NH_4)_2SO_4$$

Persulfate solutions hydrolyze to form peroxy monosulfate ion (HSO_4^-) followed by hydrogen peroxide and oxygen. This hydrolysis is acid catalyzed and accounts for any instability of acidic persulfate etching solutions. Ammonium persulfate solutions,

usually made up to 20 percent by weight, are acidic in nature and their pH is reduced from 4 to 2 as a result of the hydrolysis reaction. In addition, the concentration of persulfate is lowered resulting in the formation of hydrated cupric ammonium sulfate precipitate [$CuSO_4.(NH_4)_2SO_4.6H_2O$], which might hinder the etching process [18].

Ammonium persulfate is stable in the solid state and can be stored under dry conditions in closed containers without material degradation. Solution compositions can include various catalysts such as organics and transition metals like Cr, Fe, Cu, Ag, etc. It forms a clear solution that enables easy visualization of the etching process. It is the likely choice of etchants for research laboratories. However, there are a few drawbacks associated with using ammonium persulfate.

Ammonium persulfate should not be allowed to interact with oxidizable organics and reducing agents, and should be stored carefully. The etching rate produced using ammonium persulfate is somewhat low. Generally increasing the temperature can influence the etching, although ammonium persulfate has the tendency to decompose above 65 ºC. Salt crystallization can occur on the surface of the board leaving behind streaks on the surface. This can damage the board and block holes if present. The solution should be used immediately after it is prepared in order to avoid spontaneous decomposition, especially at elevated temperatures. During etching, ammonia vapor is produced and can cause eye watering and nasal irritation. Hence, etching needs to be carried out in well-ventilated areas.

Ferric chloride

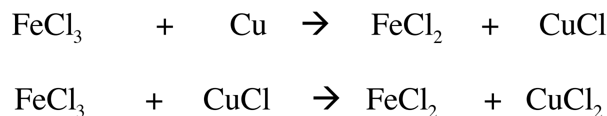
Ferric chloride solutions are used as etchants for copper, copper alloys, Ni/Fe alloys and steel in PC applications, electronics, photoengraving arts and metal finishing. It is ideal for spray etching due to its easy handling and high capacity to hold copper. Ferric chloride can be used on an intermittent batch application basis.

Etchant solutions with ferric chloride are generally around 30 to 40 % by weight. A major advantage of ferric chloride is that it is relatively inexpensive. Heating of the solution during etching is not required. The natural acidity is compensated by adding up to 5 percent of HCl to prevent formation of insoluble precipitates of ferric chloride. Commercial formulations are roughly 4.0 lb/gal $FeCl_3$ for copper etching. Antifoam and wetting agents may also be present.

When ferric chloride is mixed with water, some free HCl is produced through hydrolysis.

$$FeCl_3 + 3H_2O \rightarrow Fe(OH)_3 + 3HCl$$

The basic etching mechanism involves three stages. First, ferric ions oxidize copper to form cuprous chloride, which is further oxidized to cupric chloride.



$$FeCl_3 + Cu \rightarrow FeCl_2 + CuCl$$

$$FeCl_3 + CuCl \rightarrow FeCl_2 + CuCl_2$$

The final reaction takes place between cupric chloride and copper.

$$CuCl_2 + Cu \rightarrow 2CuCl$$

One of the problems associated with ferric chloride as an etchant is that it is not compatible with resists containing tin and lead. Its use is declining due to expensive disposal of etchant waste and increase commercial support for ammonical and cupric chloride etchants [18]. Ferric chloride forms a dark and ‘soupy’ etching solution that makes viewing of the etching process difficult. Ferric chloride solutions can also become messy and produce dark and almost irremovable stains on almost any surface.

Photoresist Stripping

After etching is complete, unwanted resist is usually stripped away using acetone. Continuous etching processes are replacing batch type operations to obtain constant etch rates. Batch type operations can be characterized by variable etch rates and periodic downtimes. In the future, alkaline etching with ammonium hydroxide may become the etchant of choice due to its compatibility with most metallic and organic resists, high capacity for dissolved copper and faster etch rates [18]. Easy control and replenishment, improved pollution control and constant etch rates are additional desirable attributes of alkaline ammonia solutions.

Summary

The entire process of fabricating PC boards, from the design stage, to photolithography, to etching and stripping of resists is analogous to the fabrication of masters for microfluidic applications. This is because the standard copper thicknesses available in PC boards are of the same order of the channel heights present in microfluidic devices. Consequently, the process can be adapted to make masters for microfluidic applications, which serve as molds for casting structures using soft lithography. A casting material like PDMS can then be used to make devices replicating the images on the masters.

By using PC boards with different thicknesses of copper, structures on the finished PC boards with different heights can be easily produced. For example a 1 oz/ft^2 copper board will produce masters with structures approximately 34.3 μm height, while a 1/2 oz/ft^2 board should produce structures with a height of 17.2 μm. Similarly, a 4 oz/ft^2 copper board can be used to make structures with a height of 137 μm. Such easy and precise control of the structure height is difficult to achieve without the use of silicon and glass micromachining techniques. Considering that the entire process of fabricating a PC board takes only 30 to 45 min, this technique can provide a major impetus in the ability to produce rapid prototypes of microfluidic devices.

CHAPTER III
MAKING MASTERS FROM PC BOARDS

This chapter discusses the use of PC boards to make master molds for microfluidic devices. The different stages involved are exactly the same as that used for making a printed circuit design. Circuit boards presensitized with a positive acting photoresist are used to make microfluidic channels. Channels are designed using ordinary drawing software and printed on transparency film. The transparency mask is then placed on top of the circuit board and exposed to a UV light source, after which the pattern is developed in a in sodium hydroxide solution and unwanted copper is etched away using an ammonium persulfate solution. Finally the remaining photoresist is stripped using acetone. Figure III-1 summarizes the master fabrication procedure. Channel geometries are characterized using a stylus profilometer. The fabricated masters can then be used for casting against a polymer to make microfluidic channels.

By using PC boards with different copper thicknesses, we are able to easily produce structures on masters with various well-controlled heights and with a high degree of surface uniformity. The height of structures ranges from approximately 15 to 122 μm, corresponding to the standard copper foil thicknesses. Boards with copper thicknesses of 1/2, 1, 2 and 4 oz/ft^2 are used in this work. The etching process is extremely critical as structures made from thinner copper layers can be quickly etched away while structures made from thicker foils may exhibit a higher degree of under cut.

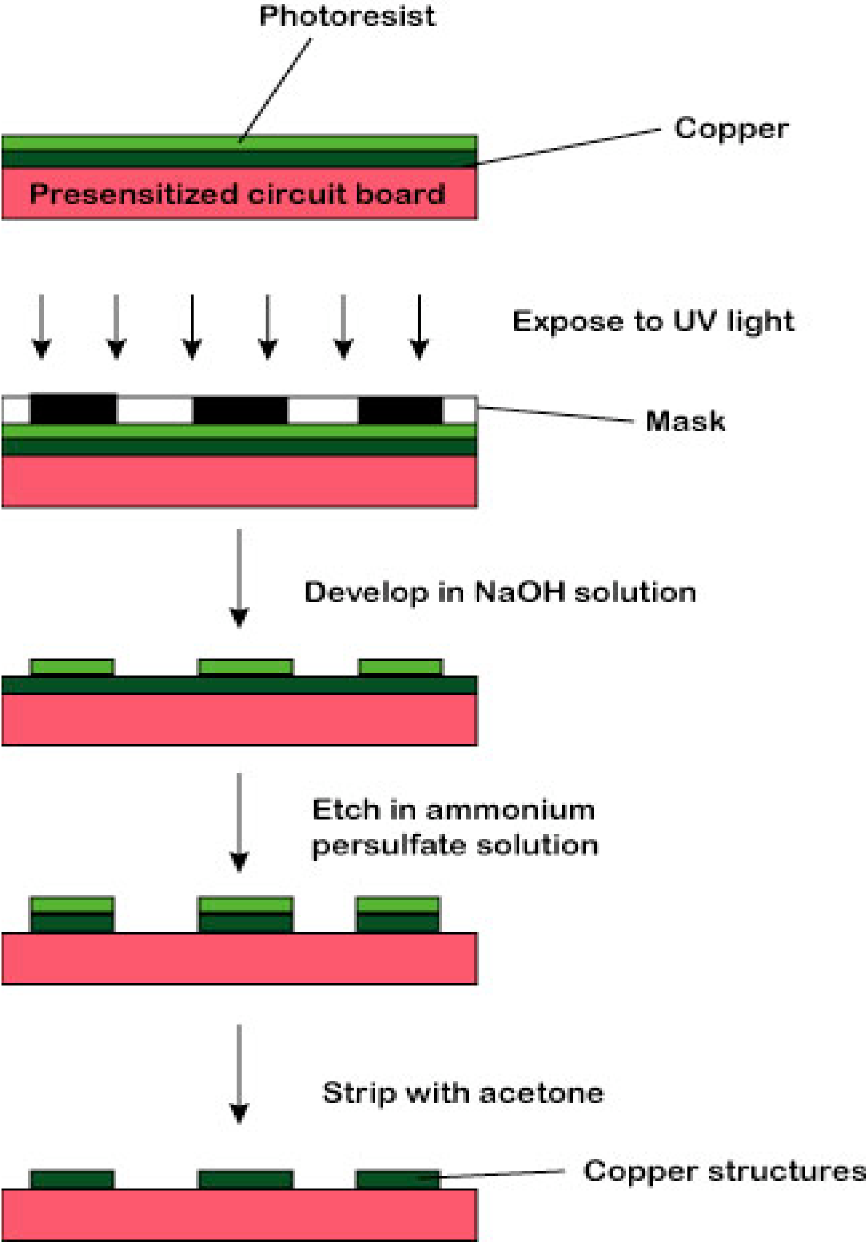


Figure III-1. Fabrication of masters.

To a certain extent, the under cut can be compensated by making channels of greater widths as compared to the widths of structures in thinner foils. The most uniform sidewall profiles are obtained in thinner copper foils as long as the etching conditions are optimized.

Imaging

The drawing tool used for designing channels is Adobe Illustrator 10 (Adobe Systems Inc.; San Jose, CA). A wide variety of channel designs can be produced ranging from straight-line geometries, to curved channels, and even complex spiral shaped channels. Channel line widths were varied from 200 microns to 600 microns. Figure III-2 shows a few of the designs used to make masters. Once the design is ready, the layout is printed on a transparency using a high-resolution (3166 dpi) printer (Mika Color; Los Angeles, CA). For simpler patterns, a laser printer or an ink-jet printer can be used as well. The transparency film serves as a mask for transferring images onto PC boards.

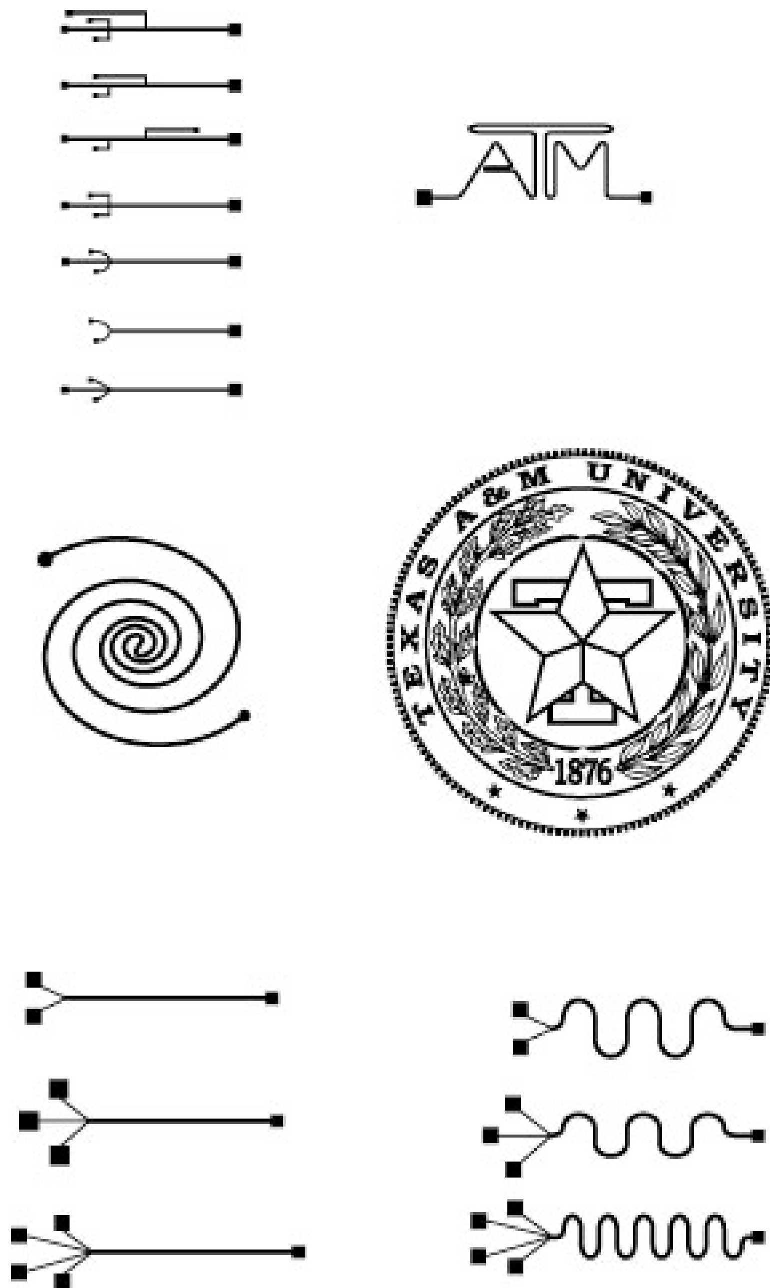


Figure III-2. Examples of fluidic channel designs used for making masters. (Patterns are shown actual size)

The mask is placed on top of a pre-sensitized positive tone PC board (1 oz. boards are purchased from Circuit Specialists Inc.; Mesa, AZ while the others are purchased from Injectorall Electronics Corp.; Bohemia, NY) and exposed to UV light using a conventional laboratory UV lamp (Reproset; Amersham Biosciences; Piscataway, NJ) for 90 s to transfer the image onto the PC board. During exposure, it is desirable to maintain close contact between the mask and the PC board. To enable this, a clean glass plate (approximately 3.5 mm thick) is placed on top of the mask to hold it down firmly. Care should be taken to ensure that both the mask and the PC board surfaces are clean and free of any scratches.

Developing

After exposure, the PC boards are immersed in a sodium hydroxide solution, prepared by mixing 3 – 3.5 ml of a 50% w/w aqueous NaOH solution (Fisher) in 500 ml of DI water. Areas of the PC board that were exposed to UV light are subsequently dissolved in the developer solution, leaving behind clear images of channels. The developing process usually takes 90 to 120 s and is carried out in a shallow glass tank. Rocking the tank or gently agitating the solution will accelerate the process. It is essential to remove all unwanted resist to obtain clean etching; however excessive developing may dissolve photoresist on the unexposed areas.

Once clear images of the desired layouts are obtained after developing, the PC boards are thoroughly rinsed with DI water to remove remaining residues and visually

inspected to ensure the integrity of the transferred pattern. The developed PC boards are then taken to the etching tank and subject to copper etching.

Etching

This by far is the most critical step in making masters. Etching is carried out in a fume hood in order to comply with pollution and safety regulations. Developed PC boards are etched in a solution made of ammonium persulfate prepared by mixing 150 g of ammonium peroxydisulfate powder (certified A.C.S., Fisher) in 1 liter of DI water. Although we arrived at this etchant concentration empirically, it is within the range of concentrations (140-150 g/l) typically used [19].

The ammonium persulfate solution is prepared in a vertical tank and heated on a hot plate with constant stirring until the powder is fully dissolved and a clear solution is obtained. The stirrer bar is then removed and a developed PC board is inserted into the tank using a plastic carrier. The holder is attached to an air pump that provides continuous agitation to the etching solution. The etching is normally carried out in the temperature range of 40 to 55 ºC. The etching setup is shown in Figure III-3.

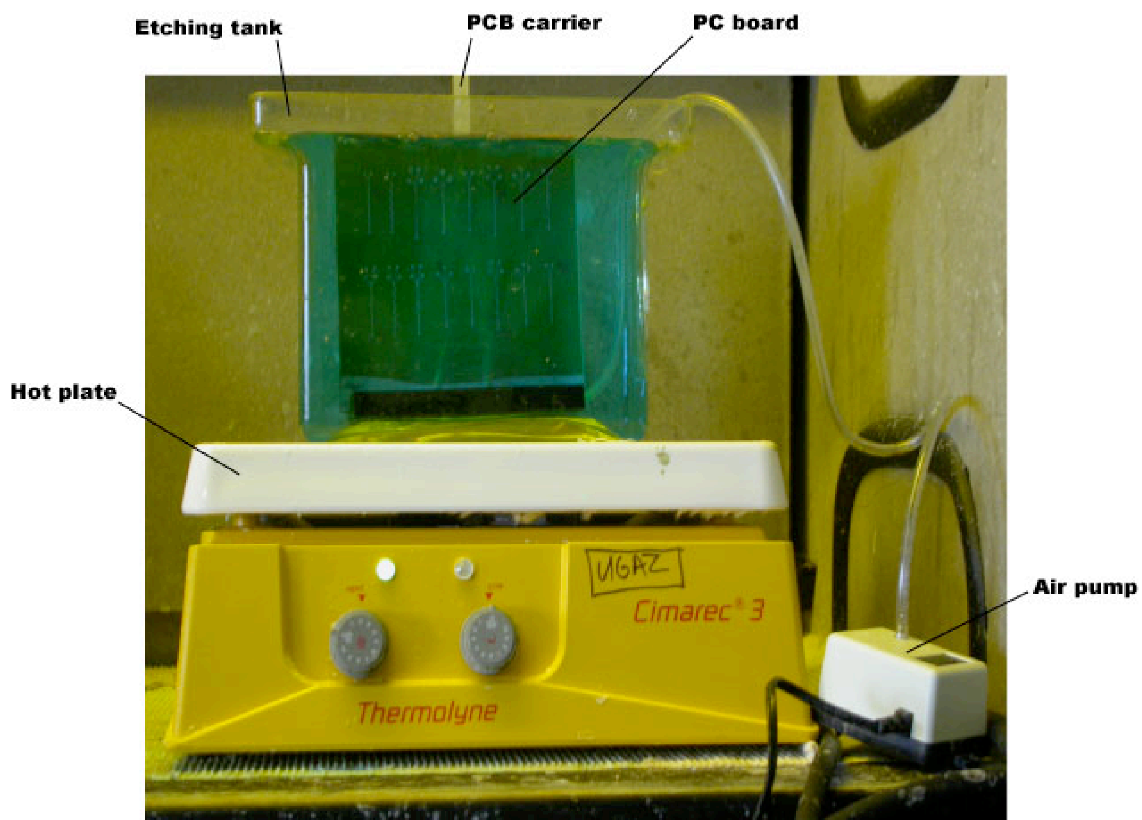


Figure III-3. Etching setup. The PC board is inserted in the etchant solution that is continuously agitated by means of the air pump. Etching is usually carried out in the temperature range of 40 – 55 ºC.

At the start of our experiments, etching was carried out in a shallow tank with a stirrer to create agitation. Unfortunately, this setup produced non-uniform etching over the PC board surface, i.e., parts of the board closer to the stirrer experienced faster etching. By the time etching was complete on areas farthest from the stirrer, channels closer to the stirrer began to show a great amount of under-cut, and ultimately were getting etched away completely. Hence this setup was not feasible for copper etching on boards with large surface areas. By using the vertical tank setup, better agitation can be

achieved over a larger area, and a more uniform etching rate is observed over the entire surface of the board. This setup allows boards with dimensions of up to 6" x 6" to be etched uniformly over the entire surface. After etching unwanted copper, the PC boards are rinsed with water to remove any remnants of etchant solution. The remaining photoresist is then stripped using acetone to obtain clean copper structures on the surface of the PC boards. The PC boards are now ready to use as master molds for soft lithographic fabrication. Figure III-4 shows a photograph of a fabricated PC board master.

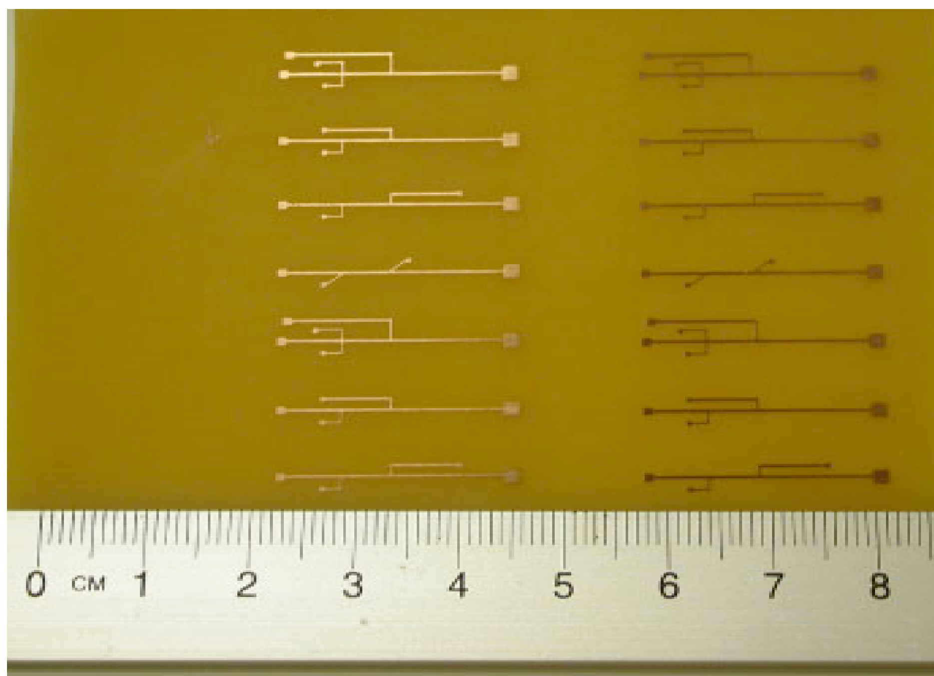


Figure III-4. Fabricated PC board master having an array of electrophoresis channels. The length of the main horizontal channels is 21.8 mm and its cross-sectional dimensions are 400 x 29.5 μm.

The overall resolution achievable using the PC board process was characterized by constructing masters using a mask incorporating the Standard USAF 1951 Resolution Test Pattern (Edmund Industrial Optics; Barrington, NJ) on a 1 oz. copper board. Photographs of the fabricated master are shown in Figure III-5. Etching was carried out at 55 ºC.

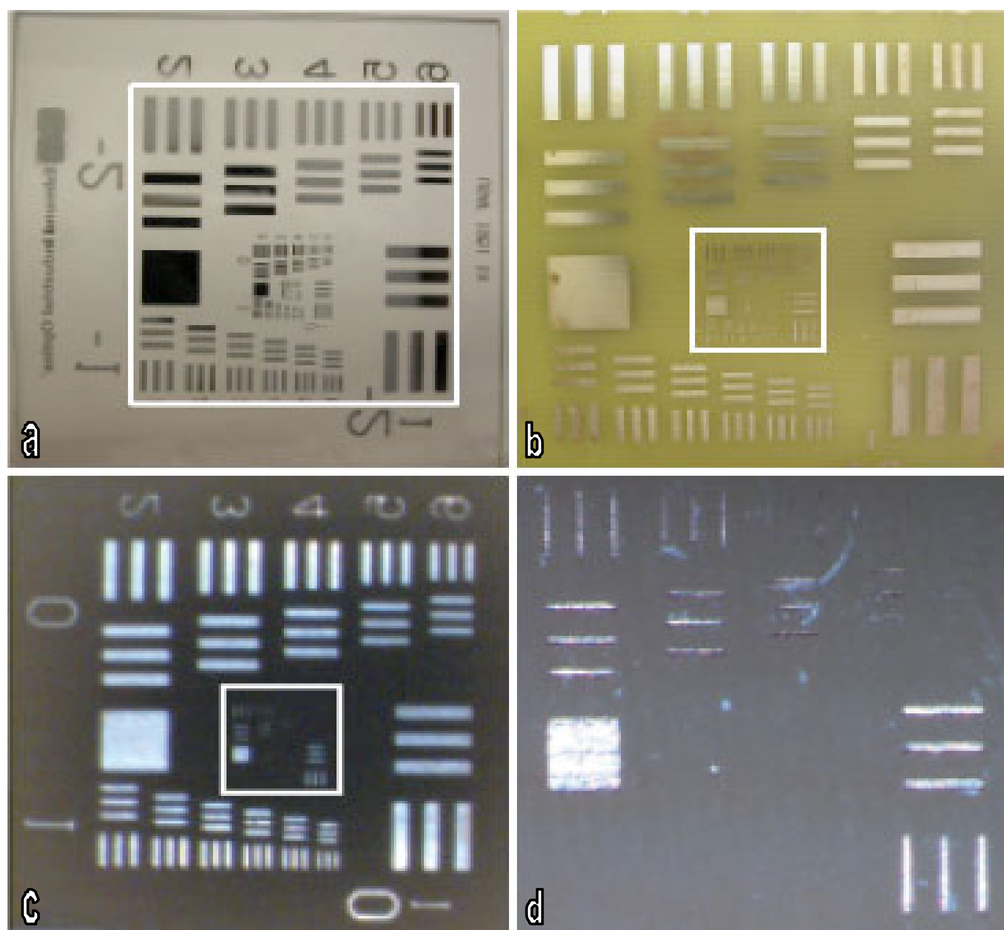


Figure III-5. Characterization of test pattern. Figure III-5a is a photograph of the original mask. Figures III-5b,c,d are zoomed in levels of the fabricated master. Boxed regions correspond to the full field of view in the subsequent figure.

The test pattern is composed of five concentric levels of line spacing (cycles/mm). Figure III-5a shows a photograph of the original test pattern. Figures III-5 b, c, d are corresponding zoom levels of the first, second and third concentric layers. The fourth and fifth concentric layer patterns were too small to be patterned by this setup as they got etched away. The smallest spacing that could be patterned completely under these conditions was 10.1 cycles/mm, which corresponds to approx. 49.50 μm wide lines.

Determination of etching rate

The etching rate at different temperatures was characterized by using PC boards that had not been patterned with channel structures. These bare PC boards were cut to reasonable sizes (approximately 7.5 x 5.0 cm), exposed to UV light without a mask and developed in sodium hydroxide solution in order to mimic the master fabrication process. After developing, the PC boards were thoroughly rinsed with water and completely dried. The dried PC boards were weighed before immersion in the copper etchant. After a period of time, the PC boards were removed from the etchant solution and rinsed with water. The clean PC boards were then dried completely and weighed again to determine the weight of copper lost during etching. Etching rates were then determined from the difference between the weights before and after etching with respect to the etching duration. PC boards were etched at different temperatures in order to determine ideal etching conditions for our standard ammonium persulfate etchant solution (150 g/lt H_2O). The results are tabulated in Table III-1.

Table III-1. Determination of etching rate

Temp. °C	Weight in grams		Time sec	Etch rate	
	Before etching	After etching		gram/min	μm/min
24.2	8.9271	8.5226	1075	0.023	0.703
35.1	9.2134	8.7782	631	0.041	1.205
46.2	9.1221	8.3453	540	0.086	2.527
54.1	9.0434	8.2993	451	0.099	2.967
60.3	9.0182	8.3019	425	0.101	3.068
65.4	9.1878	8.3471	485	0.104	3.117

The variation of etching rate with temperature is shown in Figure III-6. It can be observed that the highest etching rates are is obtained in the temperature range of around 55 – 65 ºC. However, at these temperatures we find that it is not possible to reliably make structures with widths below 100 μm. This is probably due to the difficulties in producing sufficient agitation to maintain a perfectly uniform etch rate over the entire surface of the PC board using our setup. A temperature range of 40 – 55 ºC is suitable for making channels greater than 100 μm wide. Modifications to the etching process to produce structures less than 100 microns in width are discussed later in this chapter.

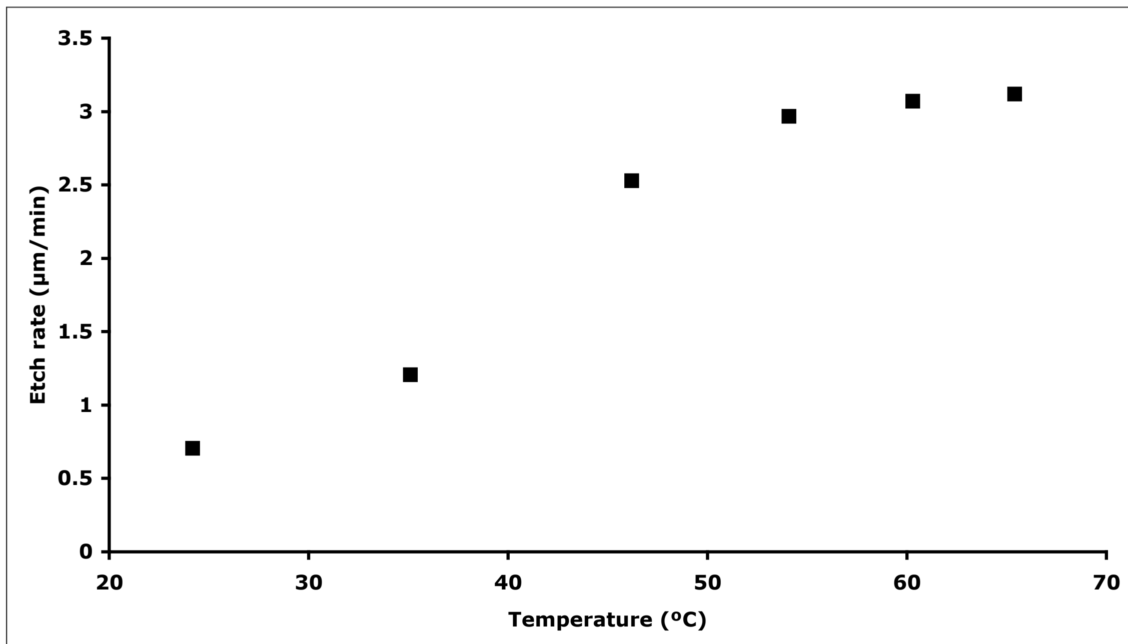


Figure III-6. Variation of etching rate with temperature. Data are shown for an unpatterned 1 oz. PC board.

Determination of etching time

The required etching time depends on the thickness of copper foil on the PC board. We carried out etching using 1/2, 1, 2 and 4 oz/ft^2 copper boards. Average etching times for different copper thicknesses, as determined by visual inspection of the PC boards during the etching process, are shown in Figure III-7. Data are shown for rectangular boards with dimensions of 3" x 6". As expected, the etching time increases linearly with copper foil thickness. Etching for longer times results in degradation of the patterned structures, ultimately resulting in them being etched away completely.

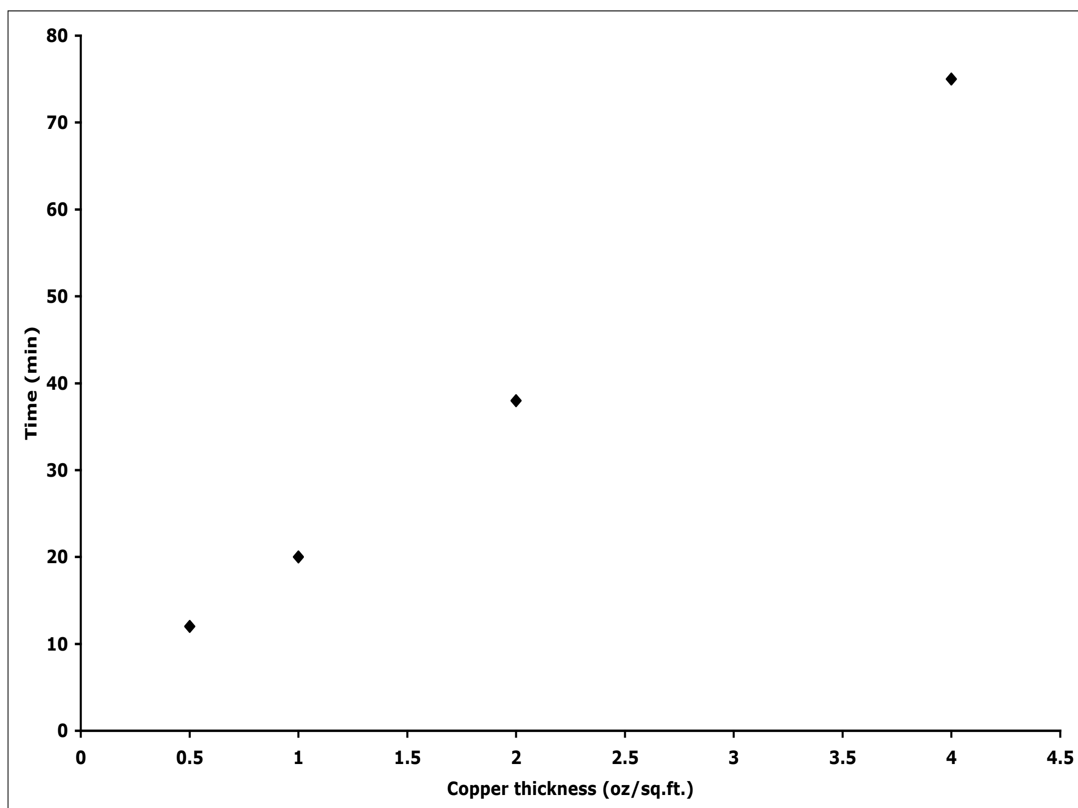


Figure III-7. Variation of etching time with copper thickness. Data are shown for PC boards of dimension 3" x 6" and an etching temperature of 50 ºC.

Variation in channel heights

By using PC boards with different thicknesses of copper foil, it is possible to easily vary the heights of structures on the masters in a precisely controlled fashion. We have successfully used boards with copper thicknesses of 1/2, 1, 2 and 4 oz/ft^2 to produce fluidic channel structures. The channel profiles of the 1/2 and 1 oz. copper boards were characterized using a Dektak 3 Stylus Profilometer. The heights on the 2 and 4 oz. copper boards were outside the range of the profilometer, and were instead determined using calipers with 0.001 mm accuracy. Data were collected at various

locations over the entire surface of the board and used to compute average heights (Figure III-8). Figure III-9 shows photographs of channel structures for the different copper foil thicknesses. Photographs are taken using a Hirox 3-D microscope. Channel heights corresponding to the foil thicknesses are lesser than those indicated in Table II-3. This might be due to slight variability in the copper deposition process, or even impurities in the copper. However, the reproducibility between PC boards used is excellent.

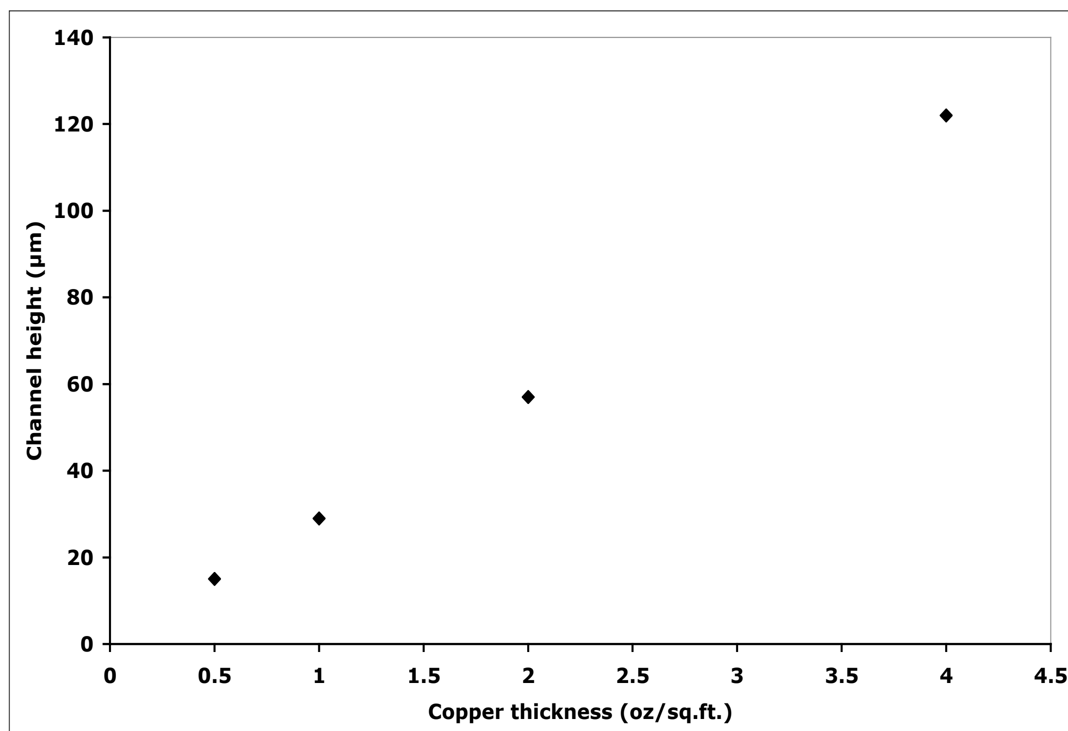


Figure III-8. Channel heights for different copper thicknesses. Data are shown for 600 μm wide channels and an etching temperature of 50 ºC.

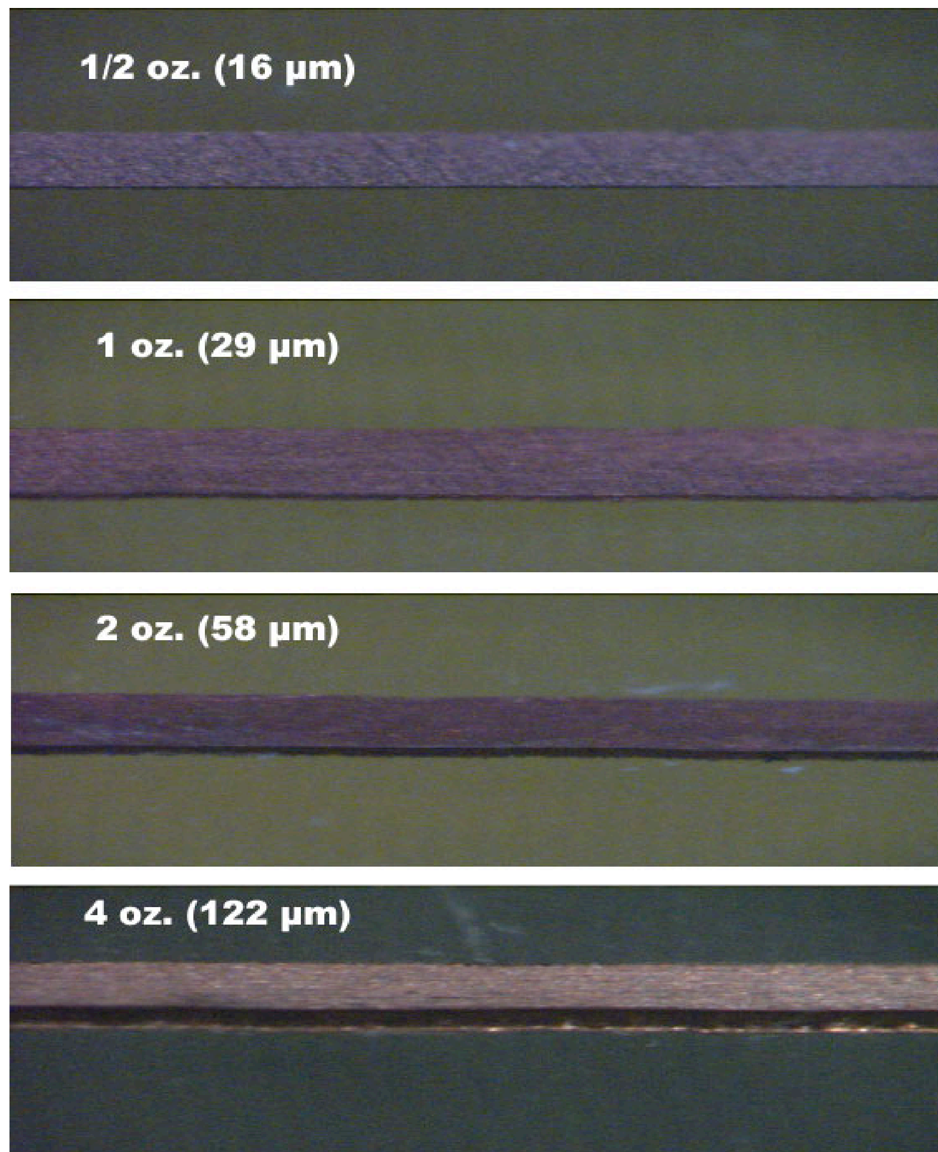


Figure III-9. Photographs of channel heights for different foil thicknesses.

Determination of ideal etching temperature for narrow line widths

As stated earlier, etching temperatures in the vicinity of 60 ºC provide high etching rates, but cannot be used to reliably produce structures with line widths below approximately 100 μm. Lower temperatures, however, can be used to produce structures less than 100 μm in width. For a 1 oz/ft^2 copper clad board, masters with line widths ranging from 400 microns down to 20 microns were used to study the effect of etching temperature. As shown in Figure III-10, an etching temperature of 38 ºC yielded a well-defined 50 μm line while this line showed a slight degree of undercut or was even etched away at temperatures near 60 ºC. The 100 μm line was stable at all temperatures and showed consistent profiles. Therefore, an ideal etching temperature would be around 50 ºC and higher for line widths above 100 μm. At 38 ºC, the 20 μm that line, visible at the start of the etching was ultimately etched away. It is possible for this line and maybe even thinner structures to be produced by adjusting other parameters such as the etchant formulation and degree of agitation.

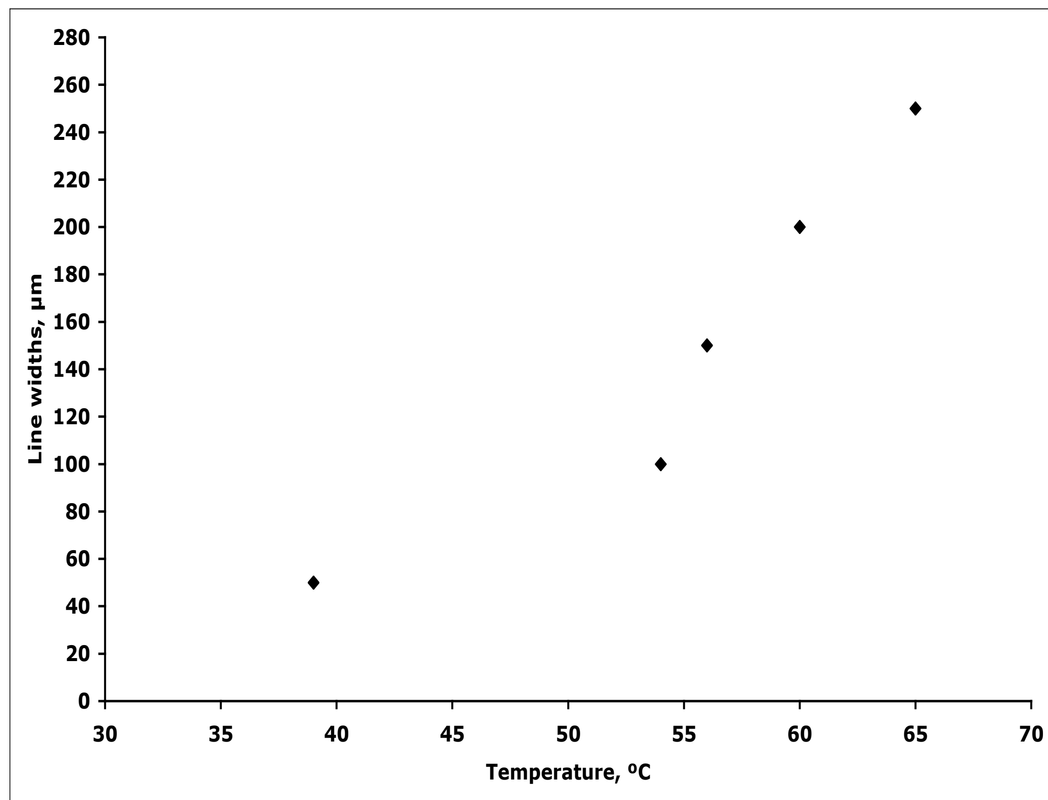


Figure III-10. Minimum resolvable line width as a function of etching temperature. A 1 oz. copper board is used.

Surface characterization of etched structures

The geometries of the etched copper structures were characterized using a Dektak 3 Stylus Profilometer. Figure III-11 shows the profile of a 600 μm wide line on a 1oz. copper board. The difference in width between the base and top of the channel structure is about 60 microns and is characteristic of a trapezoidal etch profile. During etching, channels are shielded from the etchant by the photoresist material. However, since the copper structures exhibit a finite thickness, their sides are exposed to the etchant solution. Consequently, the sidewall surfaces of the copper structures experience

some degree of etching. This isotropic etching process causes the width at the top of the copper structures to be less than the bottom, thereby causing a trapezoidal profile. If the widths of channel lines are too thin, this process may cause the channels to become completely etched away. The minimum channel width that can be produced depends on the thickness of the copper foil. As the thickness of copper on the surface of the PC board increases, a greater sidewall surface of the channels is exposed to the etchant, causing increased deviation from a vertical profile. Table III-2 shows the dimensions of visible line structures obtained from etching at 38 ºC.

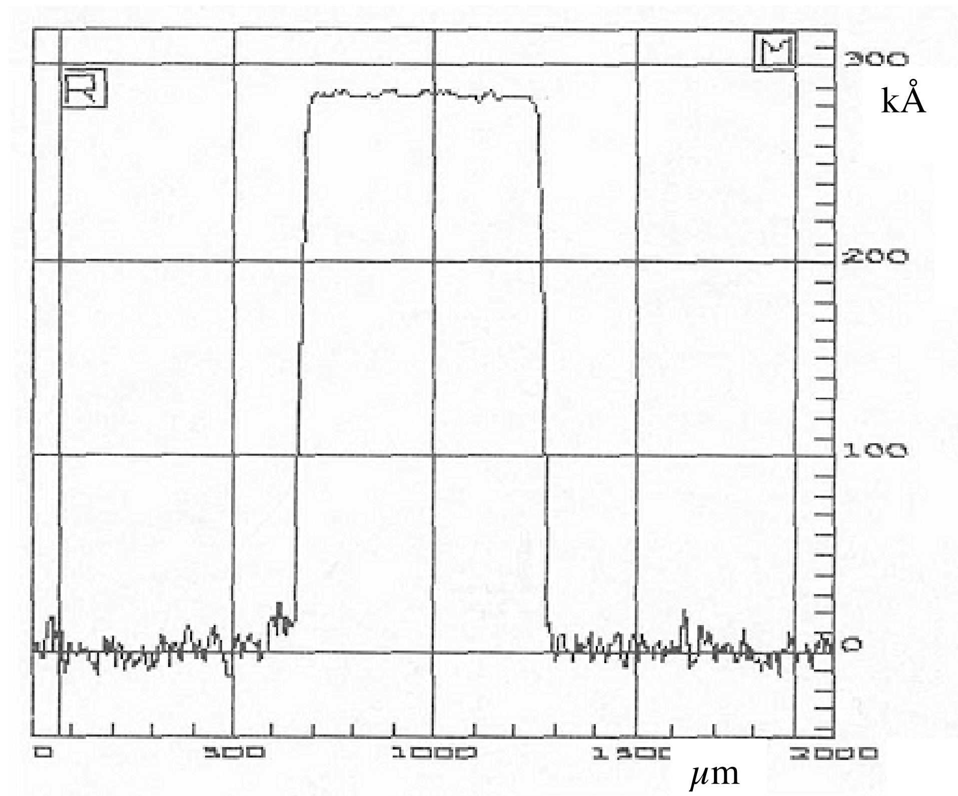


Figure III-11. Height profile of a 600 μm wide channel line from a stylus profilometer. The master used is a 1 oz copper board. The channel height is 29.5 μm, and its widths at the top and base are 553.1 and 613.4 μm respectively.

Table III-2. Line dimensions in microns for 38 ºC etching for a 1oz copper board

Line width on mask	Line width on master (base)	Line width on master (top)	Line height on master
50	58.7	22.4	26.9
100	111.3	61.5	26.9
150	156.4	106.2	28.2
200	207.9	156.4	30.2
250	257.0	206.7	28.7
300	307.3	244.4	28.8
350	360.1	284.9	28.4
600	613.4	553.1	29.5

Summary

As described above, PC boards can be used to make masters for microfluidic devices using conventional printed circuit technology. Masters with a wide variety of channel geometries can be fabricated rapidly without the need for expensive laboratory equipment. Whether channel structures are simple straight-line channels or complex curved structures, master molds can be fabricated in less than 30 minutes. The fabrication techniques neither require serial processes associated with cumbersome UV

curing protocols, nor do they require any micromachining equipment. The fabricated PC board masters can be used repeatedly to cast plastic microfluidic devices with minimal material degradation, as described in the following chapter.

CHAPTER IV
FABRICATION OF MICROFLUIDIC DEVICES

PDMS devices

To test the PC board prototyping process, we made a variety of microfluidic devices using the PC board masters to cast PDMS replicas. The PDMS formulation used, Sylgard™ 184 (Dow Corning; Midland, MI), is composed of a liquid silicon rubber base and a liquid catalyst or curing agent. The base and curing agent are measured in a 10:1 ratio by weight and mixed thoroughly by hand for about 5 minutes. The mixture is then degassed under vacuum for about 10 minutes to remove any entrapped air. After degassing, the mixture is poured over the master mold and cured in an oven. Different curing protocols can be used as directed by the manufacturer (Table IV-1). However, in this work we used the 60-minute protocol at 90° C.

Table IV-1. Curing protocols for PDMS (Source: Manufacturer documentation)

Temperature (C)	Curing time (min)
115	30
90	60
60	180
Room temperature	24 – 48 h

After curing, the devices are released by peeling from the master and fluidic access holes are punched using syringe needles with an internal diameter of 1.15 mm. The devices are then mounted on glass microscope slides and filled with a colored dye solution (Nucleic acid sample loading buffer, Bio-Rad; Hercules, CA) to test their ability to hold liquid without leakage. A few examples of PDMS devices fabricated from PC board masters are shown in Figure IV-1.

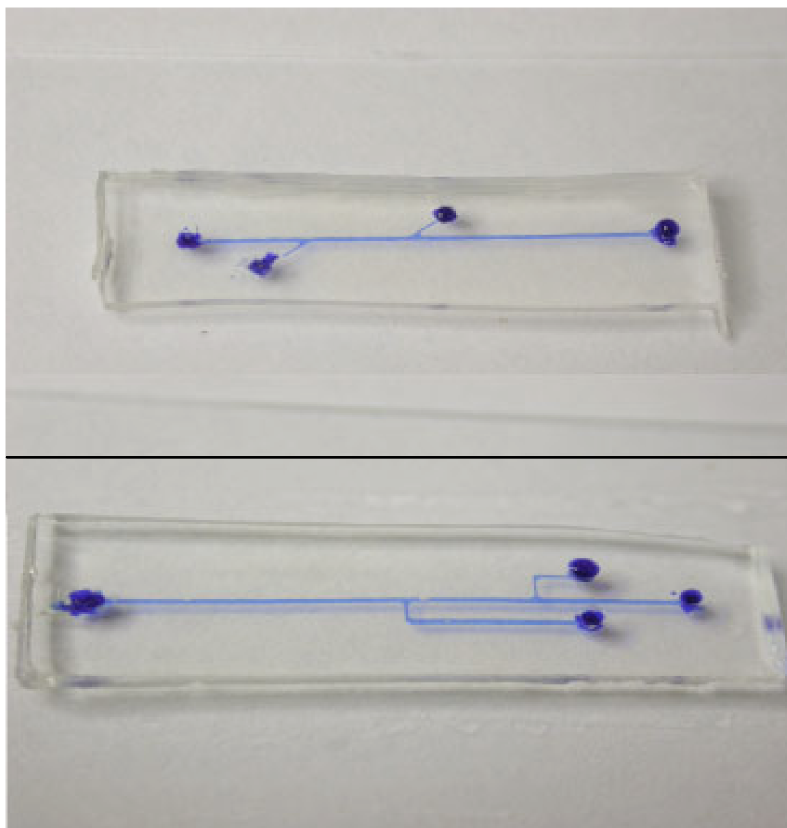


Figure IV-1. PDMS microfluidic devices fabricated from PC board master mold. The length of the main horizontal channel is 21.8 mm and its cross-sectional dimensions are 400 x 29.5 μm. Channels are filled with a dye to enable visualization of the fluidic arrangement.

A problem encountered with this process was that the surface of the PC board exhibits a slight degree of roughness, making it difficult for the PDMS devices to make a uniform bond with glass so that no fluid leaks out of the channels. By reducing the curing time by approximately 10% and immediately releasing the devices from masters, a degree of tackiness can be retained on the PDMS, allowing a better bond to be achieved on glass. However, this bond may not be strong enough for applications where large pressures are generated within the channel.

Many microfluidic devices, however, are constructed from multi-layer PDMS structures [20]. Here, it is necessary for the bonding to be done between individual PDMS structures to construct enclosed channels, in which all inner surfaces are PDMS. The process of bonding PDMS channels on a PDMS surface is not as sensitive to surface roughness and can be performed using PC board masters. A flat mounting surface for the devices was made using a 20:1 ratio of base to curing agent while the devices are fabricated using a 5:1 ratio of base to curing agent. The two mixtures were partially cured for 45 minutes at 80 ºC and the device was then mounted on the flat surface and further cured for 45 minutes at the same temperature. Uniformly bonded microfluidic channels surrounded by PDMS on all sides could then be obtained.

It is important to mention that the resulting bond between the microfluidic device and the mounting surface is not permanent. However, it is strong enough to be used for many microfluidic applications, even those that generate moderate internal pressures. As a test of this bond, microfluidic channels were filled with dye and the holes were

plugged and kept aside for several days. The device showed no signs of leakage as no amount of dye seeped in between the two layers.

Test for residual copper on cast PDMS surfaces

Since the PDMS is in close contact with the copper PC board structures while curing, it is useful to find out whether the copper influences the cross-linking of the PDMS or whether any residual copper becomes deposited on the surface of the PDMS when peeled off from the master mold. To determine this, we cured PDMS on a 5 x 5 cm bare copper PC board surface and performed surface analysis using X-ray photoelectron spectroscopy (XPS). The spectrometer used was an Axis HSi 165 and Ultra (Kratos Analytical Ltd.; Manchester, England). XPS analysis involved irradiating the sample to be tested with monoenergetic soft x-rays under vacuum, and analyzing the energy of the emitted electrons [21]. The emitted electrons have measured kinetic energies given by:

$$KE = h\nu - BE - \phi_s$$

where $h\nu$ is the energy of the photon, BE is the binding energy, and ϕ_s is the work function of the spectrometer. The binding energy is the difference in energies between the initial and final states after the photoelectron has left the atom. An energy spectrum, basically a plot of the number of electrons detected per energy interval as a function of their kinetic energy, is then obtained. As each element has its own characteristic energy spectrum, it was easy to determine whether copper was present on the surface of the PDMS sample. As a control, we also tested a sample of PDMS cured on a glass microscope slide. The emitted spectra for both samples are shown in Figure IV-2. Figure

IV-3 shows the profile that copper would typically exhibit in the binding energy range of 930 – 970 eV if present. As can be inferred from these figures, no amount of trace copper was detected on the surface of the PDMS. The spectra generated correspond to the electrons detected due to the presence of carbon, oxygen and silicon.

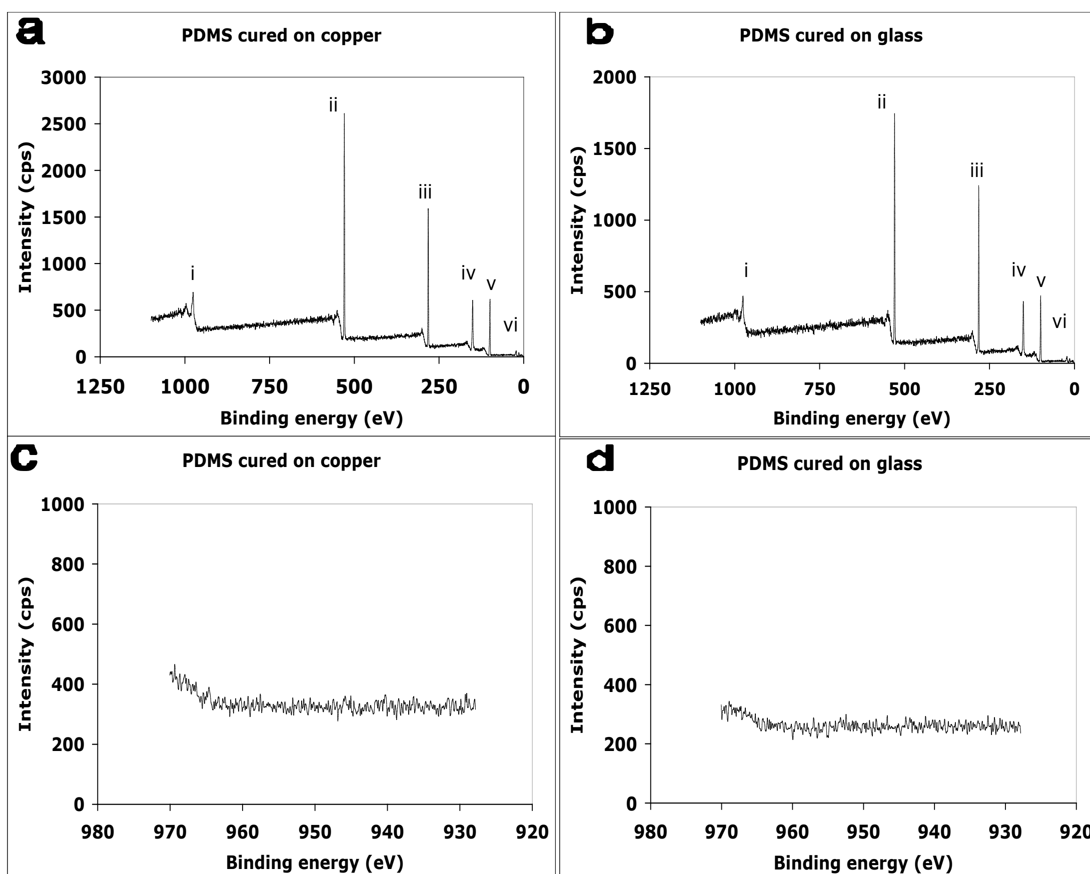


Figure IV-2. XPS spectra to detect the presence of residual copper. Figures IV-2a,b show spectra over binding energy range of 0 – 1250 eV. Figures IV-2c,d are the corresponding spectra within the range of 920 – 980 eV. The numbered peaks correspond to orbital shells as follows: (i) O_{KLL} (Auger), (ii) O_{1S}, (iii) C_{1S}, (iv) Si_{2S}, (v) Si_{2P} and (vi) O_{2S}.

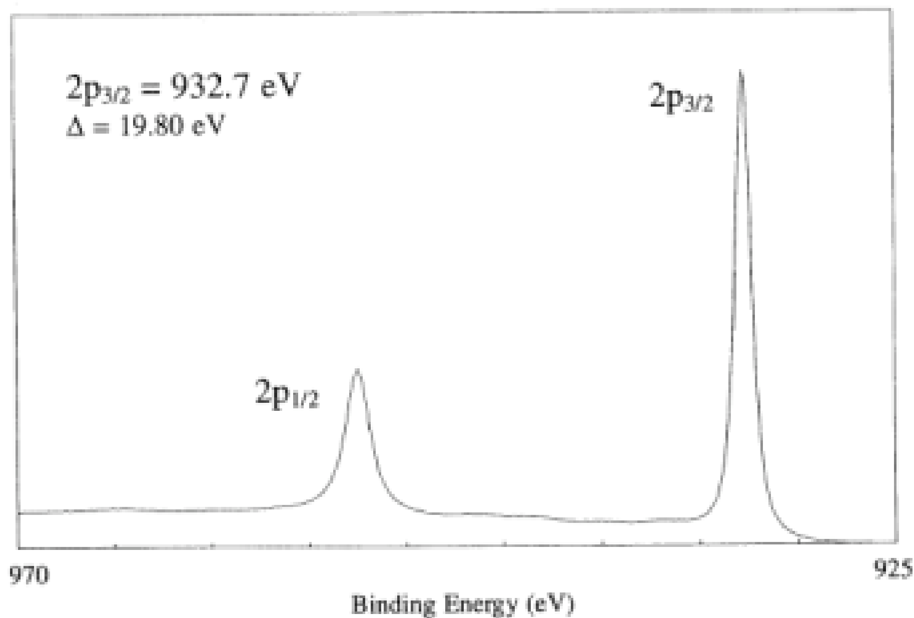


Figure IV-3. Typical copper profile [21]. The two distinct peaks correspond to the electrons of the 2p orbital of copper atom.

Melt processable plastic devices

PC board masters can also be used to construct microfluidic devices from melt processable plastic materials. We demonstrated this by constructing a variety of microfluidic devices using an optically transparent thermoplastic elastomeric material with a melting temperature around 95 ºC. The devices were constructed by placing a piece of the elastomer on top of the master mold and heating it to 120 ºC on a hot plate. On melting, a glass plate was placed on top of the elastomer and gentle pressure was applied by hand to ensure complete contact with the structures on the mold. After

cooling, the gel is solidified while incorporating the shape of the structures on the master.

For meltable materials, the surface roughness present on the PC board surface is not a problem because the devices can be placed on a glass slide and heated to the vicinity of the melting temperature for a few seconds. The cloudiness on the device that was formed due to the surface roughness disappears and the device makes a good bond with the glass surface. Instead of using glass microscope slides, these devices can also be bonded with a flat layer of the gel itself to obtain microfluidic devices enclosed by the same material.

The use of meltable plastic materials not only helps in overcoming the surface roughness problem, but also provides additional advantages. As devices are fabricated by melting the material on the mold and then cooling to solidify it, new devices can be fabricated and tested extremely rapidly. The melting and cooling steps can be completed in only a few minutes, compared to the hour required to cure PDMS. Further, devices can be cleaned and re-melted for subsequent use. An example of a microfluidic device made from a thermoplastic elastomeric material is shown in Figure IV-4. Figure IV-5 shows a photograph of a spiral microfluidic device fabricated from this gel. The master used is a 1 oz. copper board.

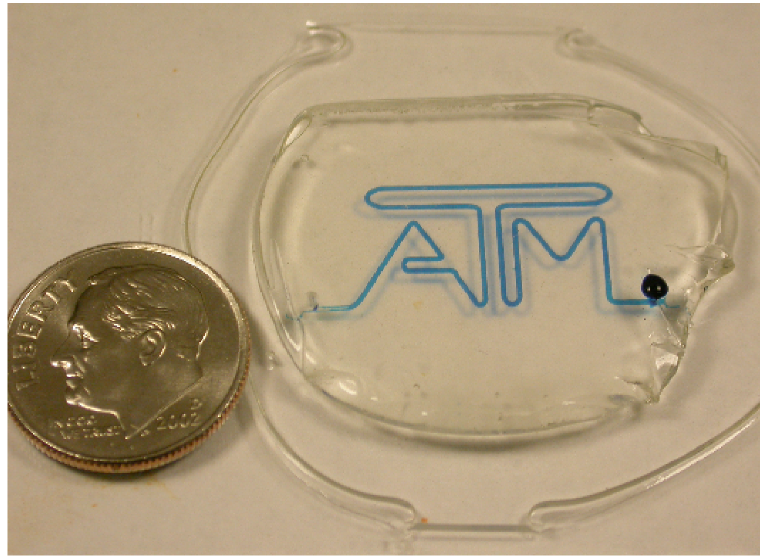


Figure IV-4. Microfluidic device made from a thermoplastic elastomer. Channel is made from a 1 oz. copper board and the channel width is 400 μm. It is filled with a dye to enable visualization of the fluidic network.

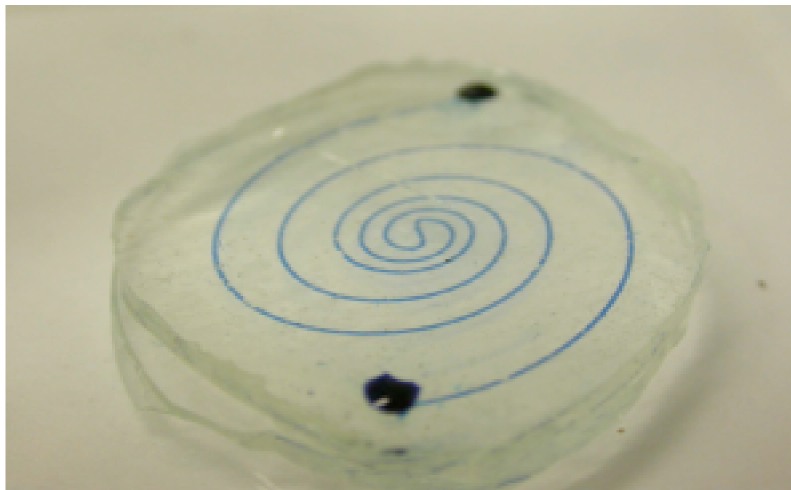


Figure IV-5. Spiral microfluidic channel. Channel is made from a 1 oz. copper board and the channel width is 400 μm.

Photographs of devices constructed using masters with different channel heights are shown in Figure IV-6. Channel heights are indicated on the figure. The widths of the main channel lines are 600 μm. Channels are filled with a dye to enable visualization of the fluidic network.

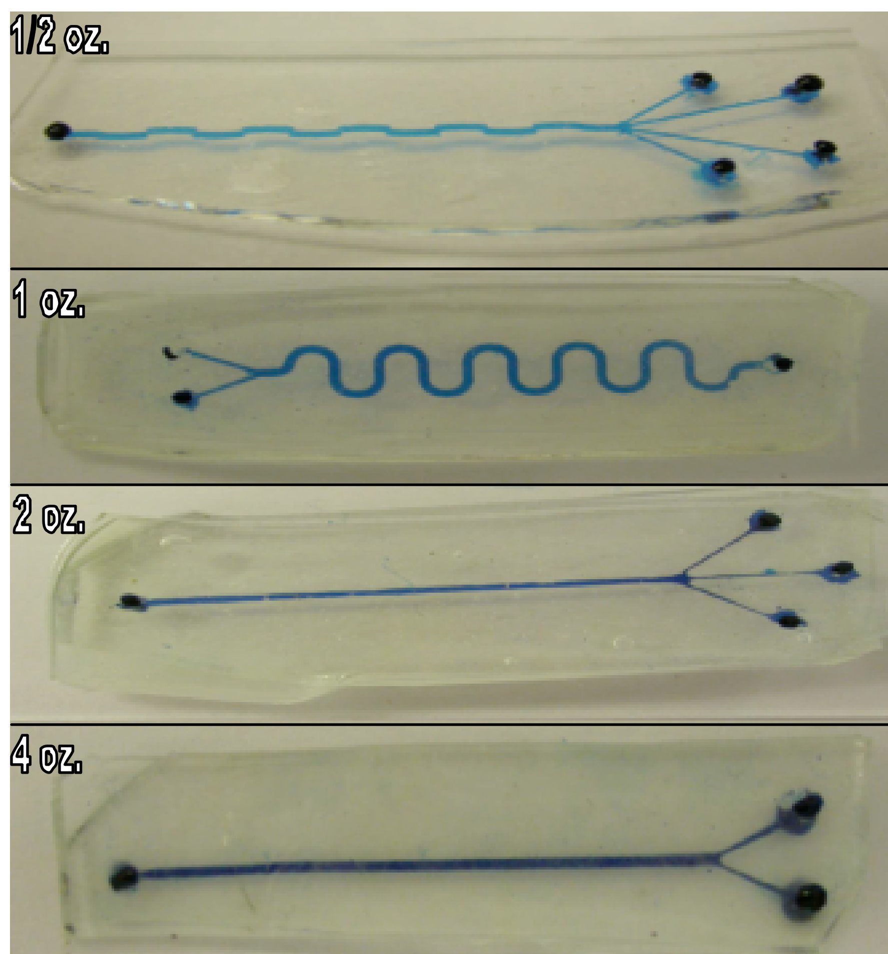


Figure IV-6. Devices with different channel heights. Channel heights of the devices correspond to the copper thickness as indicated on the figures.

By using our fabrication techniques, a number of microfluidic devices can be fabricated at the same time using a single master. After melting down the gel to take the shape of the mold and subsequently cooling it down, the gel allows for easy release just like PDMS. A single master can be used to make a number of microfluidic devices as shown in Figure IV-7.

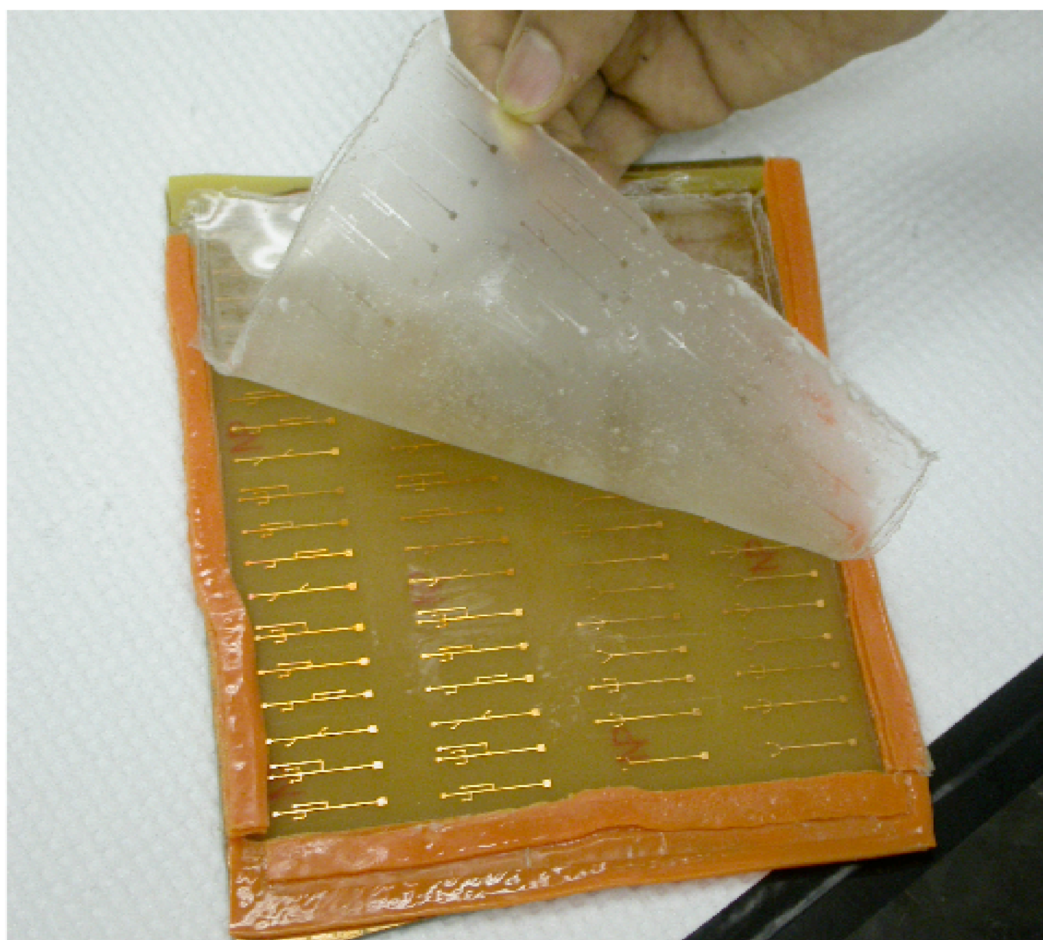


Figure IV-7. Release of microfluidic devices from master. The master is a 1 oz. copper board showing an array of electrophoresis devices. The main horizontal channels are 400 μm wide with an average height of 29.5 μm.

Summary

In this chapter, we have demonstrated how fabrication techniques using PC board masters allow for a number of microfluidic devices, with a variety of channel geometries, to be fabricated at once. The production time is not contingent upon the complexity of the channel structures. Fabrication can be carried out without the need for dense photoresists or cumbersome UV curing protocols associated with serial processes. Casting of devices can be carried out either by heat curing or melt-processing with equal ease. The PC board masters are compatible with both materials and can be used repeatedly for casting with minimal material degradation. There is no element of trial and error involved in producing channels with a variety of heights. The surface roughness problem associated with PDMS devices can be completely overcome by the use of melt-processable materials, which have optical properties similar to PDMS. The only problem associated with these devices is they become unstable in the vicinity of their melting point.

CHAPTER V

CONCLUSIONS

Summary

This research has demonstrated that masters for microfluidic devices can be fabricated using conventional printed circuit technology. Channels with a wide range of lengths, widths and channel heights can be fabricated quickly and efficiently under normal laboratory conditions without the use of complicated and expensive equipment. Using these techniques, masters can be fabricated in less than 30 minutes. Fabricated masters can be used repeatedly to make microfluidic devices without showing any signs of material degradation. The masters are compatible with both cross-linked plastics (PDMS) and melt processable materials (thermoplastic elastomers). These techniques are simple and can be carried out in any research laboratory to reliably construct features above 50 microns in width, with heights ranging from 15 to 120 microns.

When using PDMS to make fluidic devices, the surface roughness on the PC boards makes it difficult to bond them to glass substrates. This problem can be overcome to some degree by bonding two layers of PDMS together with different ratios of base to curing agent. However, devices made this way do not always show good bonding between the two layers, and the bond is not a permanent one. This will limit its use when applications require large pressures to be generated inside the fluidic channels. The best way to overcome this surface roughness problem would be to use PC boards that are made from a smoother substrate of insulating material. The smoother substrate could be

glass, silica, aluminum, or some polymer composite that would be stable enough for a layer of copper to be laminated on its surface. Polyimides, for example, are used in the construction of flexible circuit connectors and may provide better results for fabrication of masters. The use of meltable plastic materials, however, eliminates many of these problems. Heating to near the melt transition temperature during the bonding process can eliminate residual surface roughness.

Recommendations and future work

As mentioned earlier, alternative substrate materials with smoother surface properties would allow problems associated with residual surface roughness to be overcome completely. This would allow devices made from PDMS to be bonded permanently to glass, silica or PDMS itself. A current advantage of our process is that we make use of readily available copper clad boards that are pre-coated with a photoresist. But, resist could easily be applied manually if necessary. The thickness of the resist layer does not have to be perfectly uniform since the channel height is defined by the thickness of copper and not the resist. This control over the height of channel structures is a major advantage of our process.

Further optimization of the etching solution mixture, might allow the fabrication of masters lesser cross-sectional dimensions below 50 μm. Use of copper foils with other thicknesses will also expand the capabilities of these techniques with respect to channel geometries. Additionally, improved techniques for generating uniform agitation of the etching solution would allow larger masters to be fabricated.

In this work, we have demonstrated a fabrication technique that has the potential to contribute significantly to microfluidics technology. This processes is effective in constructing devices with micron-scale features without the need for expensive and complicated laboratory equipment. The heights of channel structures are controlled by the thickness of the copper foil, thereby eliminating the need for precise control of photoresist thickness. Etching of channel structures provides the flexibility of parallel fabrication of master molds with a number of channels and a variety designs, without the need for high-precision micromachining equipment. Furthermore, the fabrication steps are straightforward and do not require serial processes associated with cumbersome UV curing protocols, UV cross-linkable polymers or liquid phase photopolymerization techniques that might require additional steps to remove uncured polymers. The casting of plastic devices takes 60 minutes for PDMS and only a few minutes for melt-processable elastomers, and is not contingent upon resist materials drying up or carefully pressing of the molds on resist layer, which are characterized by a certain degree of trial and error. The master molds can be used repeatedly for casting with minimal surface degradation and the entire fabrication procedure, from channel design to loading of dye in the fluidic channels, can be completed in approximately one hour.

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