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Polymer Microfluidics Chip Fabrication and Its Energy Applications: A Mini Review

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***Abstract*— Microfluidics is a technology that manipulates fluids at a microscale and has shown great potential in various fields, including energy. This mini-review discusses common microfluidic materials and the main techniques in microfluidic chip fabrication, such as photolithography, soft lithography, and 3D printing-based fabrication methods. Furthermore, several applications of microfluidic chips in the energy sector, such as solar energy and fuel cell systems development, are also discussed. The use of microfluidic chips in energy systems offers high efficiency, low material consumption, and good system integration. This review aims to provide an overview of the progress of microfluidic chip fabrication and its energy potential applications.**

Keywords*— M*icrofluidic chips, microfabrication, renewable energy, solar energy, fuel cells

I. Introduction

Microfluidics is a chip device consisting of channels with a size of micrometers and nanometers and specific geometries that have many applications, especially relating to scale-lab testing. It is usually in the field of biomedical, healthcare, and even in energy applications.

II. MATERIALS

In the first studies, silicon and glass were used to fabricate microfluidic devices. However, those two kinds of material were expensive and difficult to manufacture. The materials were then replaced by polymers because they are easy to fabricate and have a low cost. The polymers in microfluidic fabrication are divided into three types based on the glass transition temperature (T_g), which is the temperature at which the polymer will soften above T_g and harden below T_g[1].

A. Thermoset

Thermoset, often called resins, can be liquid or solid at room temperature[2]. If the material is heated or exposed to high light or other radiation doses, the molecular polymer chains start to crosslink (called curing) and generate an inflexible/hard molecular network[3]. Further, if the curing process has occurred, the polymer remains stiff even if reheated, but it cannot be reshaped anymore. If heated at a higher temperature, it does not melt but decomposes or burns. The T_g value is close to the decomposition temperature (T_d). This kind of polymer, usually used for microfluidic applications, is the photoresist SU-8[3, 4].

B. Thermoplastic material

This material shows a distinct softening at T_g, making it processable around T_g. Besides, T_g and T_d values are much more separated than the thermoset material, so it is possible for large process windows[5, 6]. In thermoplastic materials, there is no curing at high temperatures, so reheating can reshape the molded parts often. However, reprocessed material will not be of the same quality as virgin material[6]. The kinds of this material for microfluidic fabrication are usually poly(methyl methacrylate) (PMMA), cyclic olefin copolymer (COC), poly(styrene) (PS), poly(carbonate) (PC), poly(ethyleneterephthalate glycol) (PTEG).

C. Elastomer material

The molecular chains of this material are longer than those of other materials. The chains do not show a chemical interaction but are physically entangled. The chains will disentangle and stretch elastically if an external force is applied to the polymer[2, 7]. If the external force is removed, it will immediately return to its original shape. The common elastomer polymer used in microfluidic fabrication is poly(diimethylsiloxane) (PDMS)[8].

Thermoplastic and elastomer materials are commonly used for microfluidic devices (microfluidic substrates), while thermoset is usually used as a photoresist[7]. The polymers have their own properties that can affect the fabrication method used.

III. FABRICATION METHODS

Fig. 1 is the outline of the microfluidic fabrication. It includes the selection of polymer material, the fabrication, and the bonding, which are the closing steps. All of these depend on the application of microfluidics, and the low cost can be reached.

Fig. 1. The outline of microfluidic fabrication

There are many common fabrication methods used to manufacture microfluidic devices. They are hot embossing, injection molding, soft lithography, laser photoablation, lithography, stereography, Computer Numerical Control (CNC), etc. This article will only review some of those methods.

A. Stereolithography

The stereolithography method for microfluidic fabrication is illustrated in Fig. 2. The microfluidic channel is formed by exposing liquid resin locally to two high-intensity light beams, usually from one (with a split beam) or two laser

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sources. Using two beams allows the light of each single beam to penetrate the liquid without generating a photo-induced crosslinking. Only at the location where the two beams meet is the light intensity high enough to cross-polymerize the photoresist. In practice, a vessel containing the liquid resin is placed on a stage that can be moved in the z-direction. Movement in x and y is usually realized by scanning the laser beam. By computer-controlled motion, the desired structure is thus built up volume element by volume element (so-called voxel)[1].

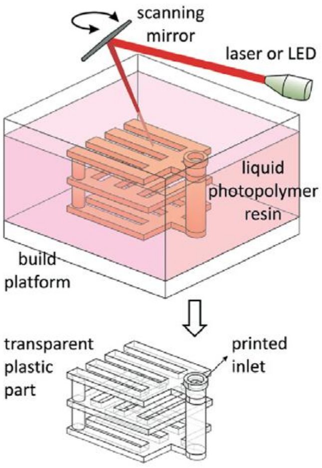

Fig. 2. Stereolithography method for microfluidic fabrication [9]

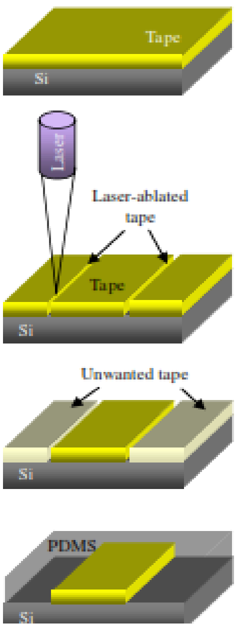

Fig. 3. Laser ablation is for the manufacturing master on the Si substrate. Tape is coated onto Si, the laser ablation is applied to the tape as the desired pattern, the unwanted area is removed and becomes a master, and finally, PDMS is cast onto it [10].

B. Laser Photo Ablation

This method applies a high-powered pulsed laser to break polymer molecule bonds, resulting in an ablation region (as a microfluidic structure) based on a given geometry and removing decomposed or unwanted regions (Fig. 3) [11]. The depth and width of the ablated channels rely on the laser's pulse rate or intensity and the substrate material[11, 12]. This method can be conducted by exposing the polymer substrate with a mask, generating the area to be ablated, or a direct-writing process that directly creates the microfluidic structure on the polymer substrate without a photomask[12, 13]. Recently, photo ablation has been used to create a master/mold as an alternative to the soft-photolithography method shown in Fig. 4. After the master is obtained, the PDM is cast onto the master and cured.

C. Computer Numerical Control (CNC) Micromilling

Fig. 4 outlines the manufacturing steps for microfluidics using CNC milling. The pattern is created by Computer-Aided Design (CAD) to control the channel size [14]. The axis (x, y, z) must be set up to achieve the desired pattern and size, determining the microfluidic structure's length, width, and height[15]. It is then applied to the milling tool. The polymer is placed on the sample holder (under the cutting tool). The working principle of this tool is that the cutting tool removes the area of polymer material (workpiece) referred to as the pattern[16]. The x-axis and y-axis represent left-right and forward-backward movement, respectively, while the z-axis represents up-down movement. The milling time depends on the complexity of the microfluidic structure[15, 17]. After the milling is done, the microfluidic device can be obtained.

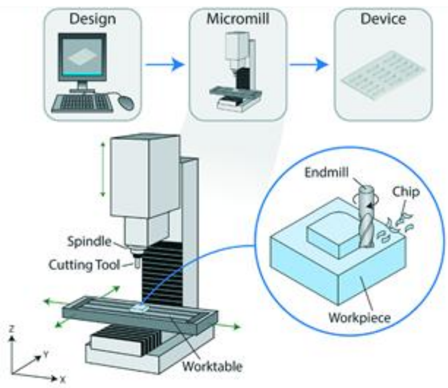

Fig. 4. CNC process of microfluidic fabrication[16]

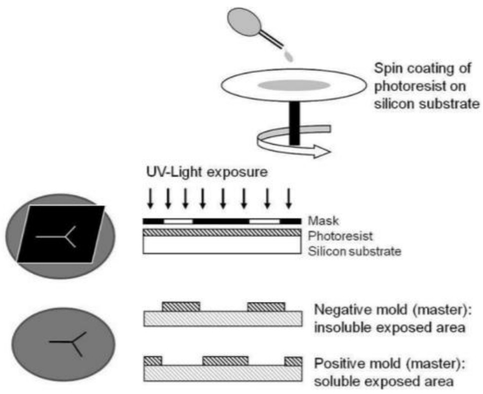

Fig. 5. Mold or master fabrication process using the lithography method[11]

D. Replication methods

This method involves polymer as a microfluidic material, and the geometry of the microfluidic is replicated from a master/mold. Therefore, the first thing to be done in this fabrication is to create the mold/master itself. Meanwhile, several replication methods are commonly used in microfluidic fabrication.

1. Fabrication of the master

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A master or mold is necessary for the replication method. It is usually fabricated using the lithography method. The SU-8 photoresist is generally used as the mold coated on the silicon wafer substrate using spin coating. It is then baked (soft baking) at a specific temperature using a hot plate, irradiated by UV, and finally post-baked[18]. The 2D pattern is imprinted onto the PR layer by exposing it to UV through a photomask to make a PR design. Photomask is drawn in AutoCAD (Autodesk, Inc.) software and then printed [19]. The photoresist consists of negative SU-8 photoresist and positive SU-8 photoresist, the difference of which can be seen in Fig. 5 as mold negative and mold positive[11, 20].

3. Hot Embossing

The hot embossing process is shown in Fig. 6. It is a technique involving thermoplastic materials, such as PMMA, PC, COC, PS, or PETG, in which the pattern is stamped into the substrate (polymer material) using pressure and heat [12, 21]. The polymer substrate is placed in the chamber and heated in a vacuum above T_g [18]. The master structure is also heated to the same temperature or slightly higher. The master structure is pressed into the polymer substrate (The pressure value depends on the polymer and master material. The pressure and the time pressure can be varied)[22]. Master and substrate are isothermally cooled to a temperature below T_g and separated [1, 21].

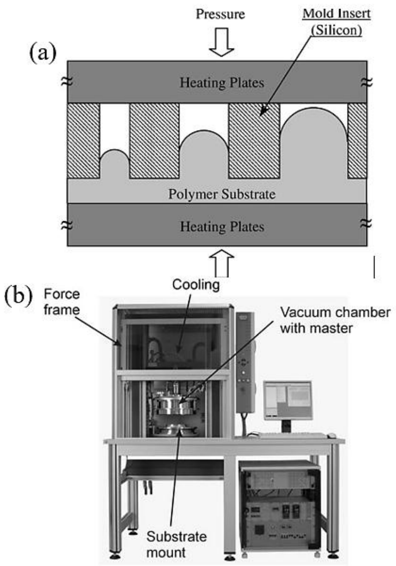

Fig. 6. (a) The mechanism of the hot embossing process[23] and (b) The hot embossing tool[24]

2. Soft Lithography

It is one of the replica molding techniques besides hot embossing and injection molding. The polymer is cast onto the mold (master) and cured. The curing process is conducted at a specific temperature and time (40 °C and 80 °C for 20 min to 2 h for PDMS)[12]. Finally, after the PDMS is cured, the mold is peeled off from the mask (casted PDMS). This process is schematically presented in Fig. 7. The connections, such as channels and reservoirs within the layer, are often manually fabricated with needles placed before pouring the PDMS or by hole-punching in the finished microfluidic device[11].

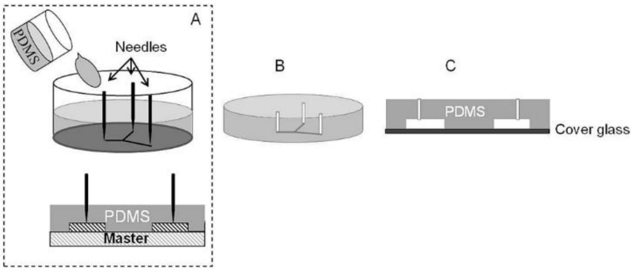

Fig. 7. Soft lithography process[11]

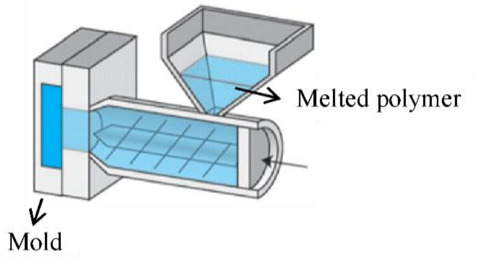

Fig. 8. Injection molding method[16]

E. Injection Mold

As shown in Fig. 8, the polymer is melted and injected into the mold. This process is conducted under high pressure and in a heated mold. After that, the injected sample is cooled and released from the mold. The polymer usually used in this method is a thermoplastic polymer, especially PMMA or PC[12].

F. Bonding

Bonding aims to create closed fluid channels, sealed cavities, and complex 3D structures. Furthermore, it can strengthen mechanical stability and generate a thermal coupling or decoupling, an electrical contact, a galvanic separation, and the interface to the surrounding margin[20]. Depending on the materials of the bond partner, the common bonding methods used are silicon direct bonding, anodic bonding, thermal bonding, plasma-activated bonding, and bonding with intermediate layers, including silicon–liquid interdiffusion bonding, adhesive bonding, and glass frit bonding[1, 9, 20].

IV. APPLICATIONS

A. Microfluidics in Solar Energy

Microfluidics has several opportunities in solar energy. Fluids and fluidic-lensing can be a track to capture solar energy. Therefore, microfluidics can drive photo-catalysis or photosynthesis in a fluid environment [25]. One of the most attractive research areas related to this topic is microfluidic biological solar cells.

Wei *et al.* developed a novel microfluidic biological solar cell that harvests light energy and delivers electricity. The biological solar cell used the photosynthetic and respiratory activities of the Cyanobacterium Spirulina Platensis to generate a maximum power density in a microfluidic reactor compared to previous research. The device consisted of five different functional layers (Fig. 9): (i) a top PMMA layer, which is transparent for solar energy capturing, (ii) a PMMA microfluidic chamber layer, (iii) a rubber gasket, (iv) an anode/proton exchange membrane (PEM)/air-cathode sandwich layer, and (v) a bottom PMMA layer [26]. All layers were carefully aligned and clamped with screws. Two

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tubes for the inlet and outlet were plugged into the holes to form a fluidic channel[27].

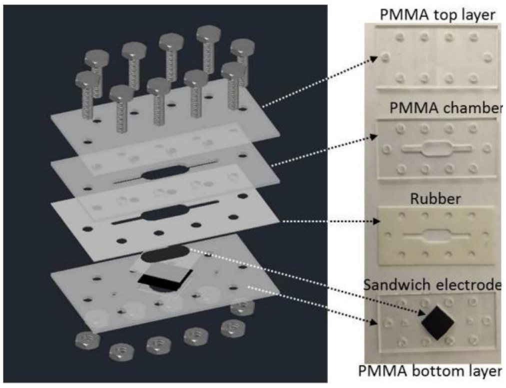

Fig. 9. A single layer of microfluidic biological solar cell

B. Microfluidics in electrochemical energy conversion and storage – fuel cells

A fuel cell is a device that converts chemical energy stored in the fuel (hydrogen) and the oxidant (oxygen) into electrical energy through an electrochemical process involving an oxidation-reduction reaction [28, 29]. Fuel cells consist of the electrode, which includes an anode and a cathode, electrolytes, and catalysts that coat a membrane[26].

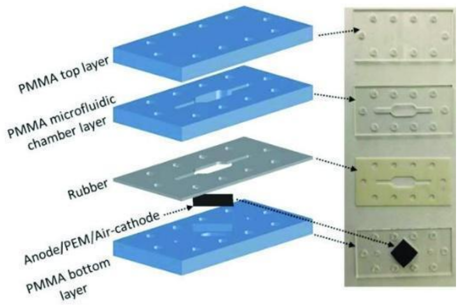

Fig. 8. Schematic of an individual device of a microfluidic biological solar cell[27]

The challenges faced by the fuel cell industry are related to cost and lifetime. The lifetime of the fuel cell is often limited by membrane degradation due to chemical and physical damage occurring during cyclic operation[30]. The membrane must also be hydrated to provide adequate ionic conductivity, which requires complex water management systems or limits the operational range[31]. Too much hydration generates a flooding effect, preventing reactants from reaching the active sites. Importantly, the cost of the membrane layer is relatively high[26, 28].

Microfluidic fuel cell is defined as a fuel cell with fluid transport, reaction sites, and electrode structures all confined to a microfluidic channel[31, 32]. This type of fuel cell operates without a physical barrier, such as a membrane to separate the anode and the cathode, and can use both metallic and biological catalysts. The microfluidic fuel cell operates in a co-laminar flow, which can delay the convective mixing of fuel and oxidant[29].

V. Conclusion

Microfluidic chips are a promising technology in the development of future energy systems that are more efficient, large-scale, and environmentally friendly. Various fabrication techniques, such as soft lithography, photolithography, and 3D printing, allow the manufacture of chips with high complexity and precision according to application needs. In the energy sector, microfluidic chips have shown great solar energy potential and are a key component in miniature fuel cells. Although there are still challenges in production scale, cost, and system integration, technological and material developments continue to open up opportunities for the optimization and commercialization of microfluidic chips on a large scale. Therefore, further research and multidisciplinary collaboration are key to driving the application of microfluidic chips as an integral part of sustainable energy technology solutions.

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