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Microfabrication of plastic-PDMS microfluidic devices using polyimide release layer and selective adhesive bonding

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Abstract: In this paper, we present an improved method to bond poly(dimethylsiloxane) (PDMS) with polyimide (PI) to develop flexible substrate microfluidic device. The PI film is fabricated on a silicon wafer by spin-coating followed by a series of thermal treatment processes to avoid surface unevenness of the flexible substrate. In this way, we can integrate flexible substrate into standard MEMS fabrication. Meanwhile, the adhesive epoxy is selectively transferred to the PDMS microfluidic device by a stamp-and-stick method to avoid epoxy clogging the microfluidic channels. To spread out the epoxy well on the transferring substrate, superhydrophilic vanadium oxide film coated glass is used as the transfer substrate. After the bonding process, the flexible substrate is peeled off from the rigid substrate easily. Contact angle measurement (CAM) is used to characterize the hydrophilic property of the vanadium oxide film. X-ray photoelectron spectroscopy (XPS) analysis is conducted to study the surface morphology of the epoxy. We further evaluate the bonding quality between the PDMS microfluidic device and the polyimide substrate by a set of peeling tests. A maximum bonding strength of 100 kPa is obtained. By injecting liquid with dyed liquid, the plastic microfluidic device is confirmed to be well bonded with no leakage for a day under 1 atm. The proposed versatile method could bond the microfluidic device and various substrates together and be applied in the fabrication of biosensors and lab-on-a-chip systems.

Keywords: microfluidic device, flexible substrate, polyimide(PI), polydimethylsiloxane (PDMS), adhesive bonding, superhydrophilic, stamp-and-stick

1 Introduction

Microfluidic structures all need sealing to form hollow embodiment. PDMS (Polydimethylsiloxane) has been widely used in microfluidic systems due to its optical transparency, biocompatibility[1], and more importantly, it can be easily bonded to glass after oxygen plasma treatment to formulate the microchannel[2] [3]. Recently, there has been growing interest in developing plastic-based microfluidic devices. Various polymer materials have been used as the substrate, such as polyimide (PI), polystyrene (PS) [4], polyethylene terephthalate (PET) [5], polycarbonate (PC) [6] and polymethylmethacrylate

(PMMA) [7, 8]. These materials have a lot of attractive properties such as low mass, high chemical resistance, low thermal conductance, high optical transparency, and good biocompatibility, which make them potential candidate materials for electrochemical lab-on-a-chip[9], bio-MEMS (Micro-electromechanical systems) calorimeter[10], and other biosensors[11] applications. However, the bonding of PDMS on these plastic materials is still challenging.

Previously reported bonding techniques can be divided into two categories: direct bonding and indirect bonding. Thermal bonding [12], laser bonding [13, 14] are the two commonly seen direct bonding methods. They may need oxygen plasma or

UV ozone treatment [15] for surface modification during the bonding process. Yet direct bonding often requires high temperature or voltage and thus might introduce unwanted problems like channel deformation during heating. Meanwhile, indirect bonding, which required an intermediate layer to bond the two incompatible surfaces, could circumvent such issue. These adhesives could be based on chemical effects like polymerization (e.g. acrylics), polycondensation (e.g. silicones) or polyaddition (e.g. epoxies)[16] and could often be cured at elevated temperatures or by UV light. Recently, (3-Aminopropyl)triethoxysilane (APTES)[17], (3-Mercaptopropyl)trimethoxysilane (MPS)[18] and low-temperature co-fired ceramics (LTCC) [19] have also been demonstrated effective to bond PDMS to plastic material.

While adhesive bonding enables high strength bonding at much lower temperature, this technique also confronts several challenges. The uncured adhesive might flow into the microfluidic channel and cause clogging [5]. Minimizing the contact area at the interface between the adhesive and the fluid could also be crucial when labile biomolecule or cell culturing is involved. As a result, stamp-and-stick, a selective bonding method, has been used to address the problem. It solves the above problem by transferring an intermediate adhesive layer to other surfaces using a patterned stamp [20]. However, the ununiformed topography of the thin flexible plastic substrate might be a challenge for the stamp-and-stick method[20]. Direct laminating a thin layer of flexible plastic substrate on a rigid substrate could easily introduce unwanted bubbles, and such uneven surface might cause troubles for sealing. However, few papers reported solutions to this problem. Another challenge during the stamp-and-stick process is the adhesive might not spread out on the transferring substrate, especially when the substrate is not hydrophilic enough. This is because when a substrate has low surface energy compared to the adhesive, the adhesive will be attracted to itself rather than to the substrate, so that the adhesive will bead up on the surface rather than wet the surface. Previous reported superhydrophilic substrates were obtained from UV-irradiated titanium oxide film[21]. Based on the similar principle, we found argon annealed vanadium oxide could also achieve superhydrophilicity.

This paper used the release layer of PI flexible substrate [22] to produce a highly uniform PI surface so that the leakage phenomenon could be avoided. Also, this method can integrate flexible substrate into standard MEMS fabrication. We used adhesive epoxy and implemented selective bonding to prevent clogging while increasing the bonding strength between PI and PDMS. The superhydrophilic vanadium oxide layer is used as the transferring substrate to prevent epoxy beading up. We have demonstrated the adhesive bonding method could obtain irreversible and robust bonding by performing peeling test and leakage test. We also used X-ray photoelectron spectroscopy (XPS) to characterize the surface functionalities so that the bonding mechanism could be better understood. To summarize, this improved bonding method provided a strategy to develop flexible substrate microfluidic device and could be applied to biosensors or other lab-on-a-chip systems.

2 Experiments

2.1 Materials and chemicals

SU-8 100 and SU-8 developer were purchased from MicroChem (Newton, MA, USA) , Poly(dimethylsiloxane) (PDMS) prepolymer (Sylgard 184) and a curing agent was purchased from Dow Corning (Midland, MI, USA). PI2611 was purchased from HD Microsystems, Chlorotrimethylsilane was bought from Sigma-Aldrich (MO, USA). The epoxy (EPO-TEK 301-2) was supplied by Epoxy Technology.

2.2 Polyimide layer fabrication

The polyimide, PI 2611, is firstly spin coated on the cleaned silicon wafer.. The PI film is then cured on the hotplate by setting the temperature ramping up from room temperature to 350 °C at low heating rate (2-3 °C per minute) to ensure fully heat distribution thus avoid bubbles generation during the curing process.. After staying at the targeted temperature for 30 minutes, the temperature of the hotplate is slowly reduced to room temperature to prevent excessive

thermal stress in the PI film during the cooling. Eventually, the thickness of the fully cured PI film is 5-10 μ m. The PI can be easily peeled off with the aid of a scalpel. Since the adhesion at the edge is mildly larger, sometimes we may need to cut the corner part to help to release.

Figure 1. PI layer peeled off from the wafer using a scalpel. Lithography, thin film deposition or etching could be applied on the substrate to fabricate the sensing elements before peeling off.

2.3 PDMS microfluidic chamber and master pattern fabrication

The designed pattern is a microfluidic chamber (diameter 0.6 cm) with inlet and outlet (width 100 μ m). The master pattern is fabricated by patterning the SU8 100 photoresist on a silicon substrate using lithography method. The SU 8 master could reach 200-250 μ m with high profile aspect ratio (10:1). To protect the master mold from damages during demolding, we placed a bottle containing 10 μ L of chlorotrimethylsilane and the master mold together in a vacuum desiccator for 10 minutes, so that a thin layer of chlorotrimethylsilane is coated on the surface of the SU8 mold. After that, the mixed PDMS (10:1 portion) is poured onto the mold and then degassed in the vacuum chamber. Finally the PDMS is cured at 80 $^{\circ}$ C for 1 hour. The solidified PDMS microfluidic device is peeled off from the master before we puncture the holes on the PDMS to form inlets and outlets.

2.4 Superhydrophilic vanadium oxide layer fabrication

Vanadium oxide is deposited on a glass substrate by sputtering the pure vanadium target in the mixture of argon and oxygen (argon and oxygen mixed ratio=69:2). After deposition, the sample is annealed in the RTP (rapid thermal processing) furnace with 3

SCCM (Standard Cubic Centimeters per Minute) of argon flow at 300 $^{\circ}$ C for 2 minutes.

2.5 Stamp-and-stick bonding process

The epoxy is a two component adhesive. We first mixed the A and B part (ratio=10:3.5) in a temporary container. The transfer process started from spin coating the epoxy adhesive on the glass substrate covered by a deposited vanadium oxide thin film. The PDMS microfluidic device is treated with oxygen plasma for 30 seconds to generate hydroxyl groups on the surfaces at the same time. The adhesive is then transferred to the PDMS by pressing the PDMS onto the epoxy layer. The PDMS is then bonded to the PI substrate. We cured the bonded sample on the hotplate at 60 $^{\circ}$ C for 2 hours. At last the bonded sample is peeled off from the silicon wafer.

Figure 2. Stamp-and-stick bonding process (a) PDMS stamped on the epoxy. The epoxy was spin coated on a vanadium oxide deposited glass substrate. (b) adhesives transferred to the PI-wafer substrate (c) PDMS-PI bonding and curing (d) PDMS-PI delaminated from the silicon wafer to form flexible microfluidic system

2.6 Surface characterization and bonding strength analysis

XPS is performed in a standard ultra-high vacuum (UHV) chamber, equipped with a hemispherical electron energy analyzer and an Al/Mg twin anode X-ray source. The XPS spectra is obtained using unmonochromatized Mg Ka (1253.6 eV) radiation. All atom-specific core level spectra is taken at analyzer pass energy of 50 eV, with a step size of 0.05 eV, and dwell time of 0.1s. Each region signal is averaged for 3 scans. Analysis of the XPS spectra is

performed using CasaXPS. The C 1s peak at 284.8 eV is used to calibrate the energy scale to which all the measured binding energies are adjusted. A Shirley background is applied to the spectra which is then fit with an appropriate number of peaks. The fits are allowed to be optimized without constraints as long as a reasonable FWHM (Full width at half maximum) and goodness of fit are obtained. In cases where an FWHM greater than 3 eV occurred, widths and/or known peak separations were fixed to one another, until an acceptable fit was achieved.

The peeling test is carried out with MTS mechanical tester (C43). The PI films and PDMS are clamped firmly without slippery. We applied the load at a constant speed of 1mm/min and recorded the load. Three samples are tested and the average load is then determined.

3 Results and discussion

Sample	Glass (non-treated)	Vanadium oxide on glass (non-treated)	Vanadium oxide on glass (annealed in Ar)	Epoxy coated glass
Contact angle(°)	67	41	Almost zero	20

Table 1. contact angles measurement for different surfaces

To verify the argon annealed vanadium oxide's feasibility to serve as the transferring substrate during the stamp-and-stick process, hydrophilicity study is needed, since the adhesive could not wet the surface with lower surface energy substrate or larger contact angle. We measured the contact angles of 10 μ L water droplets on the four different substrates and summarized the results in table 1. The epoxy coated glass is smaller than non-treated glass, which is the reason why the epoxy could not wet the glass substrate. We also found that after annealing the vanadium oxide thin film in argon, the contact angle was significantly lower, from 41° to almost zero, forming superhydrophlic surface (Figure 3). This result is similar to the superhydrophilicity of UV-irradiated titanium oxide [23]. A potential explanation could be related to the production of oxygen vacancy during annealing in argon, and furthermore, the conversion of relevant V^{5+} sites to V^{3+} sites also promoted the dissociation of water molecules into surface OH groups[23]. Therefore, when the glass surface is

deposited the argon annealed vanadium oxide could serve as the transferring substrate of the epoxy, and no beading up phenomenon were seen.

Figure 3. (a) 10 μ L water placed on vanadium oxide coated glass substrate (b) after annealing the vanadium oxide under argon, the surface became superhydrophilic. The 10 μ L water spread on the surface

Normally, the excellent adhesive properties of epoxy are due to the attractive forces between the epoxy resin and the surface of the substrate. Therefore, a surface analysis was needed to examine whether polar forces or direct bonds is formed between the resin and the surface of the substrate.

Figure 4. XPS spectra (a) C1s peaks of the untreated PI film (b) C1s peaks of PI film coated with epoxy (c) O1s peaks of the untreated PI film (d) O1s peaks of PI film coated with epoxy

We did the XPS study of the epoxy deposited substrate and PI substrate respectively for the surface analysis. Figure 4(a) showed the C1s peaks of the untreated PI film. The peak centered at around 285 eV corresponded to C-C bonds and the smaller one near 288 eV corresponded to C=O bonds. After coated with epoxy, C-O-H bonds depicted by a peak centered at 287 eV is shown in figure (4.b). Similarly, when comparing the O1s peaks of the PI with and without epoxy (Figure 4 (c), (d)), additional C-O-H bonds at around 534 eV was found. This indicates the introduction of epoxy resulted in pendant hydroxyl (-OH) groups along with their chain. These (-OH) groups could form bonds or strong polar attractions to the oxide and hydroxyl surfaces of the PDMS and PI film. The schematic view of the chemical structures of the bonded microfluidic device is shown in Figure 5.

Figure 5. chemical molecular chains of the bonded microfluidic device

To further examine the bonding microstructure of the PDMS-PI assembly, we cut the device with a scalp and observed it with a scanning electron microscope (SEM) (Figure 6). The assembly was turned upside down for better observation. The thickness of the epoxy is around 1 μm and the amount of epoxy flow into the channel is almost negligible, and in this way, the clogging could be further prevented. To achieve low thickness, we used the epoxy with low viscosity. Also, peeling off the PI-PDMS assembly from the silicon wafer did not cause any damage to the bonding. In addition, we found the PI (7 μm thick) had high uniformity, which could further help to prevent leakage.

Figure 6. (a) a scanning electron microscope (SEM) image of the PI-PDMS assembly. (b) magnified image of the square part in figure (a) to show the microstructure of the bonding interface.

To study the integrity of the sealed microfluidic chamber, a solution with light blue dye was injected into the chamber by a syringe. We saw no dyed solution flow to the surrounding air gap (Figure 7). The distance between the air gap and chamber was 200 μm , meaning the PI surface was homogeneous and even sealed with thin walls could prevent leakage at the bonding interface. Moreover, sealing the inlet and outlet with the waterproof gel to minimize the evaporation, we observed that no leakage happened in 24 hours under 1 atm. In this way, the PI-PDMS assembly could be applied in sensors that measured the liquid sample in static for a prolonged time.

Figure 7. (a) PI-PDMS bonded microfluidic device. (b) an optical microscope image of the microfluidic chamber filled with dyed solution (light blue) and no leakage was shown.

The bonding strength could be crucial when the microfluidic device is applied in situations where heating or rotating induced pressure is involved. We measured the bonding strength of the PI-PDMS assembly by peeling test. After the delamination, part of the PDMS residue was still attached on the PI and the ruptured surface indicated permanent bonding was achieved. The measured peeling force was on average 5 N and the bonding strength was calculated to be around 100 kPa considering the area of the PI-PDMS assembly ($10 \times 5 \text{ mm}^2$). This peeling force was affected by the size of the contact area, the geometry of the PDMS and the thickness of the adhesive epoxy. Control experiments showed that PDMS bonded by Kapton PI tape had a 3 N bonding strength. And using the plasma treated PDMS and PI after the same thermal treatment had a maximum of 0.5 N bonding strength. This meant the method can improve the bonding strength by one order or more.

Figure 8. optical image of PI and PDMS after delamination test. The PDMS and PI were bonded and is then subjected to peeling test.

4 Conclusions

We report an improvement to the flexible microfluidic device fabrication by selective adhesive bonding. PI and PDMS are selected to construct the microfluidic device due to their biocompatibility, good thermal and optical properties. The uniformed PI surface is achieved by spin coating on silicon wafer and post annealing. The adhesion between PI and silicon wafer is just moderate for peeling off. In this way, we could obtain highly uniform PI surface for bonding and ensure the bonding quality. Meanwhile, this method could be integrated into the MEMS fabrication so that patterning on it could also be achieved. To prevent the epoxy from beading up during the stamp-and-stick process, we discovered a novel way to obtain highly hydrophilic substrates: by sputtering the vanadium oxide thin film on glass substrates followed by post-annealing in argon. This improved selective adhesive bonding method has been proven to be highly effective to improve the sealing and the bonding strength of the plastic microfluidic device. It enhances the reliability of the stamp-and-stick method. Further research is expected to expand the scope of the material to other plastic materials and apply the method to some flexible biosensors or bio-MEMS devices that required the biocompatibility, chemical inertness, good thermal and optical properties.

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