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Sealing SU-8 microfluidic channels using PDMS

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A simple method of irreversibly sealing SU-8 microfluidic channels using PDMS is reported in this paper. The method is based on inducing a chemical reaction between PDMS and SU-8 by first generating amino groups on PDMS surface using N_2 plasma treatment, then allowing the amino groups to react with the residual epoxy groups on SU-8 surface at an elevated temperature. The N_2 plasma treatment of PDMS can be conducted using an ordinary plasma chamber and high purity N_2, while the residual epoxy groups on SU-8 surface can be preserved by post-exposure baking SU-8 at a temperature no higher than 95 °C. The resultant chemical bonding between PDMS and SU-8 using the method create an interface that can withstand a stress that is greater than the bulk strength of PDMS. The bond is permanent and is long-term resistant to water. The method was applied in fabricating SU-8 microfluidi-photonic integrated devices, and the obtained devices were tested to show desirable performance. [doi:10.1063/1.3659016]

I. INTRODUCTION

SU-8 photoresist SU-8 is widely used to prepare the master molds for replication of PDMS (polydimethylsiloxane) microfluidic channels,[1] but it is also directly used for fabricating microfluidic channels. When the material is directly used for channel fabrication, it is simple to integrate the channel with sensors and other components through standard mask alignment and photolithographic processes. Additionally, SU-8 channel fabrication process can be easily scaled up for mass production. Many devices have been fabricated using SU-8 to take these advantages. SU-8 microfluidic channels were integrated with SU-8 optical waveguides in a single SU-8 layer fabricated through a one-shot process to create devices capable of microfluidic-photonic integrated flow cytometry,[2,3] and chemical assay.[4] Such devices were also directly integrated with optical fibers for the online monitoring of lactate,[5] and with electrochemical sensors for the detection of neurotransmitters.[6] Other functions, such as magnetic bead separation,[7] fluid injection and extraction,[8] and micromanipulation,[9] were all successfully demonstrated using SU-8 microfluidic devices.

Unfortunately, while open SU-8 microfluidic channels can be easily fabricated, the channels are difficult to seal. SU-8 films deposited on rigid substrates,[4,6,9] PMMA (polymethyl methacrylate) sheets,[10] were used as lids to seal open SU-8 channels. Irreversible sealing, however, was previously only achieved using SU-8-based lids. Since the SU-8 lids-based process involves the contact of two rigid surfaces and is not suitable for the bonding of large devices, there has been a demand to use a soft PDMS to seal SU-8 channels.[2,5]

It is impossible to bond PDMS to SU-8 using any physical bonding method through a heat or solvent-based process because both cured PDMS and SU-8 are thermoset. Their molecular chain segments are constrained by their crosslinked networks and cannot diffuse into each other

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to get entangled and thus to establish a physical bonding between the two materials. The only possible way to bond PDMS to SU-8 is through a chemical reaction at their interface. Unfortunately, PDMS does not have any chemical groups to react with epoxy groups on SU-8 surface, and it is chemically impossible to directly bond PDMS to SU-8. The popular oxygen plasma activation of PDMS does not change the nature either since the silanol groups generated on PDMS surface do not react with epoxy groups. A special chemical modification on PDMS surface or SU-8 surface has to be done to make this happen. Our previous work showed that oxygen plasma-activated PDMS surface can be aminized using 3-aminopropyltrimethoxysilane through silanol-silanol reaction, and the amino groups attached on PDMS surface can react with the epoxy groups on SU-8 surface through popular amine-epoxide reaction.[11] This method was successfully used to bond PDMS to SU-8 and seal SU-8 microfluidic channels using PDMS. Talaei *et al.* silanized SU-8 with 3-aminopropyltrimethoxysilane in a vapour chamber, and successfully bonded the silanized SU-8 to the oxygen plasma-activated PDMS through silanol-silanol reaction.[12] While both of the methods can result in irreversible bonding between PDMS and SU-8, they need three steps to achieve the bonding, rely on the difficult attachment of 3-aminopropylthiethoxysilane to PDMS or SU-8 surface and have to deal with the short-lived and sticky oxygen plasma-activated PDMS. This work reports a two-step method for sealing SU-8 channels using PDMS. It eliminates the molecular attachment process and avoid the use of oxygen plasma-activated PDMS.

II. EXPERIMENTAL

27 μm- thick SU-8 films were spin coated on 4" silicon wafers and glass wafers using SU-8 2015 from Microchem Corporation, soft baked at 65 °C, exposed to UV light at a dose of 180-220 mJ/cm^2, and then post-exposure baked at 95 °C for 5 min. Thereafter, they were developed to create open microfluidic channels using an SU-8 developer from Microchem Corporation and then dried in a vacuum oven at room temperature for 5 h. Each obtained SU-8 microfluidic device was brought into close contact with a N$_2$ plasma-treated PDMS sheet and then treated at 100 °C for 30 min to drive the reaction and seal the channels. The PDMS sheets, 1 mm thick, were prepared by first casting and gelling via a 1 part curing agent to10 part resin mixture of the Sylgard® 184 kit from Dow Corning in a flat mold at room temperature, and then curing them at 110 °C for 3 h. The N$_2$ plasma treatment was conducted for 2–4 min in a plasma chamber from Harrick Plasma Inc using very pure N$_2$ (99.9995%) from Praxair.

Lap sheer testing specimens were prepared by first bonding PDMS to SU-8 coated glass slides using the process described above, and then, sandwiching them between two steel sheets using RTV silicone adhesive from Dow Corning to hold the structure. The bonding area of PDMS to SU-8 was controlled at 625 mm^2 and the steel sheets were in the size of 100×25 mm^2, according to ASTM D-1002-99 standard. The bonding between PDMS and steel and the bonding between glass and steel using the silicone adhesive were covered in an area over 1200 mm^2 to avoid their failure during testing. An Instron mechanical testing machine (model 1123) was used to pull the two steel sheets in opposite direction at a crosshead speed of 2 mm/min to measure the shear strength of the bonding between PDMS and SU-8.

PDMS–sealed SU-8 straight channels fabricated on a silicon 4''wafer were also prepared for fluidic testing. Fifteen-isolated straight channels, 5 cm long, 27 μm high, and 20 to 160 μm wide (10 μm increment between adjacent channels) were fabricated on each wafer. Stainless tubings (20 ga $\times$ 15 mm) were inserted into the pre-punched holes in PDMS to establish a pressure sealing-based fluidic connection between the microfludic channels and external fluid system. DI water (distilled water) was then pumped into the inlet of each channel using a syringe pump from Harvard apparatus (Model 33), while its outlet was kept open. For the testing of each channel, the flow rate of DI water was stepwise increased from a low value with a 2 min holding period at each step. The test was stopped when the channel or its connection with the external tubings failed at a certain flow rate. A DSC (differential scanning calorimeter, model 2010) from TA Instrument was used to analyze the SU-8 structure and its effect on the bonding process.

In the testing of the PDMS–sealed microfluidic-photonic integrated devices fabricated on glass, a fluorescent laser dye (Nile Blue 690 Perchlorate) from Exciton, Inc., was pumped into the flow channel and subsequently excited by a 630 nm laser beam brought into the channel by the integrated waveguide. The generated image was filtered with a 660 nm bandpass filter and then captured by using a CCD camera (Lumenera Infinity 2–3).

III. RESULTS AND DISCUSSION

SU-8 is an epoxy photoresist and could be still reactive if it is partially cured and still carries sufficient residual epoxy groups. In the fabrication of SU-8 microfluidic channels, SU-8 film undergoes a UV exposed, a post-exposure bake, a development, and then is hard baked. The first three steps are necessary for channel formation and the last one is to make the obtained structure stronger. It was found that the post-exposure baked SU-8 is only partially cured and still carries significant amount of residual epoxy groups that are reactive. As shown in Fig. 1, the post-exposure baked SU-8 released significant amount of reaction heat when it is heated, and the heat is diminished when the material is reheated. The proposed method is to utilize the residual epoxy groups to bond PDMS to SU-8.

Although PDMS does not carry any chemical groups that can react with epoxy groups, its surface can be chemically modified to become reactive to epoxy. Our previous work showed that amino groups can be introduced onto PDMS surface by the silanol-silanol reaction between 3-aminopropyltrimethoxy and oxygen plasma-activated PDMS, and the attached groups are then able to react with the SU-8 films deposited on glass.[11] This amine-epoxide reaction at the solid-to-solid interface between PDMS and SU-8 was investigated with FTIR and is useful for bonding PDMS to SU-8 and sealing SU-8 microfluidic channels with PDMS. However, the process to chemically attach 3-aminopropyltrimethoxy to any surface is difficult to control since the molecule is quite long and only one of its two ends is reactive to the targeted surface. To improve the bonding procedure, N_2 plasma treatment, which was reported to be able to introduce amino groups onto the surfaces of PDMS and other polymers,[13] was applied to achieve the equivalent PDMS surface modification. Fig. 2 shows the SU-8 microfluidic channels sealed using N_2 plasma-activated PDMS. The attempt to peel PDMS from SU-8 surface only results in the local fracture of PDMS as seen in the area indicated by arrow (Fig. 2(a)). When the wafer was cleaved to break the device, there was no debonding observed between PDMS and SU-8, and the fracture pattern of PDMS (as seen by the arrow pointed region) indicate that the bonding is stronger than PDMS itself (Fig. 2(b)). The bonding between PDMS and SU-8 was completely irreversible and remained intact even after the sealed devices were soaked in water for many months.
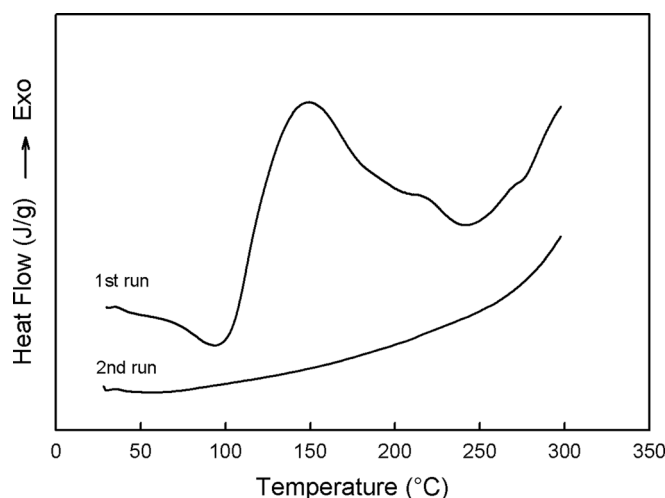

FIG. 1. DSC trace of post-exposure baked SU-8. The bake was done at 95 °C for 5 min.
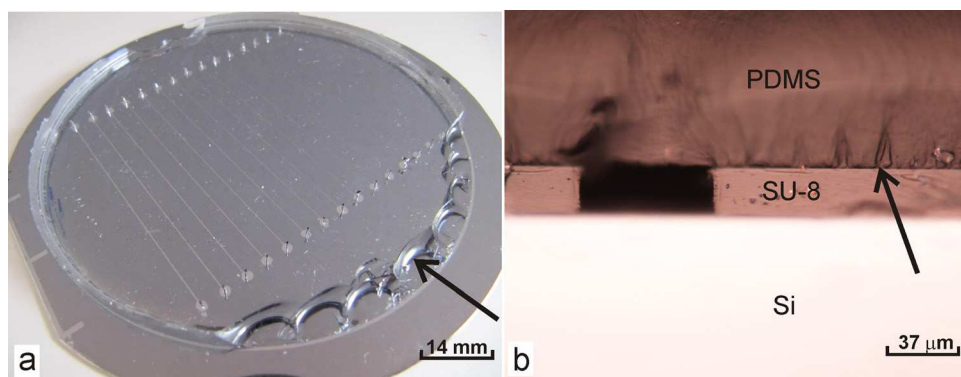
FIG. 2. The SU-8 straight channels fabricated on 4'' silicon wafer and sealed using N_2 plasma-activated PDMS. (a) the whole device; (b) the cleaved cross-section of one of the channels in the device. SU-8 was post-exposure baked at 95 °C for 5 min.

Standard lap shear testing was conducted to measure the bonding strength between PDMS and SU-8 using the specimens prepared with the nitrogen plasma activated method described above. The two steel sheets of each specimen (as shown in Fig. 3(a)) were pulled in opposite direction at a constant speed until they were separated. For all the tested specimens, the fracture only happened in PDMS (as seen in Fig. 3(b)) rather than at the interface between PDMS and SU-8, disqualifying the obtained data as a meaningful measure of the bonding. The test, however, does confirm that the bonding strength between PDMS and SU-8 is greater than the mechanical strength of bulk PDMS.

The involved SU-8 channel sealing process can be summarized in a process flow chart as shown in Fig. 4. Here, a PDMS sheet is activated with N_2 plasma to introduce amino groups onto its surface, and then brought into a close contact with a SU-8 device that contains sufficient residual epoxy groups for the interfacial amine-epoxide chemical reaction (1) at an elevated temperature. The chemical bonding via N-C bond is established between the two materials. For the N_2 plasma treatment of PDMS, PDMS preparation and especially gas purity play important roles in the process. While PDMS cured by a conventional process at around 110 °C usually works fine, the post thermal treatment at 150 °C for 24 h or the extraction with a triethylamine solution would definitely favour the process. The reason is that PDMS is not fully cured in the conventional process and still carries some residual hydrophobic oligomers, which may quickly diffuse to the surface of the plasma-activated PDMS and reduce its reactivity. The above post thermal treatment allows further curing of the PDMS to reduce its residual oligomers, while the chemical extraction simply removes the oligomers from PDMS.[14,15] Our experiment showed that the post thermal and chemical extraction could increase the shelf life of N_2 plasma-activated PDMS to several weeks and even one month.
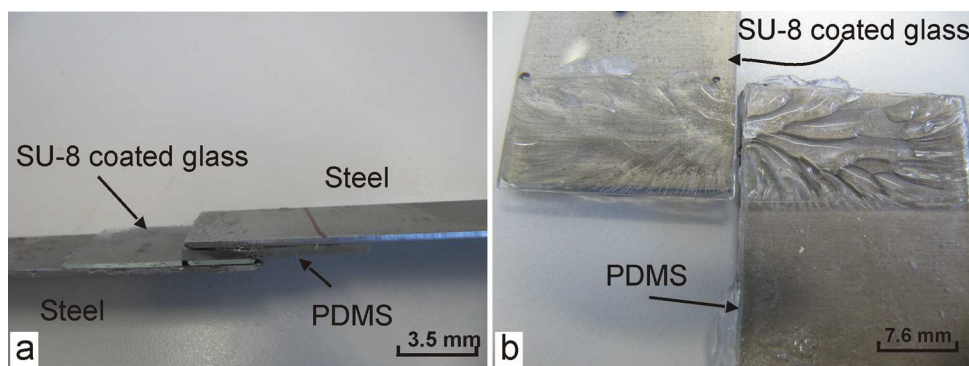

FIG. 3. Lab sheet specimen for testing the bonding between SU-8 and PDMS. (a) before the testing; (b) after the testing. The SU-8 was post-exposure baked at 95 °C for 5 min.
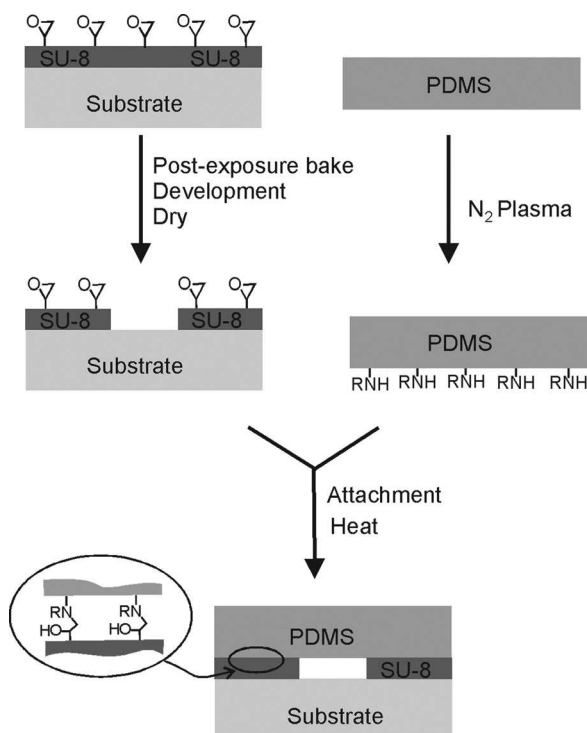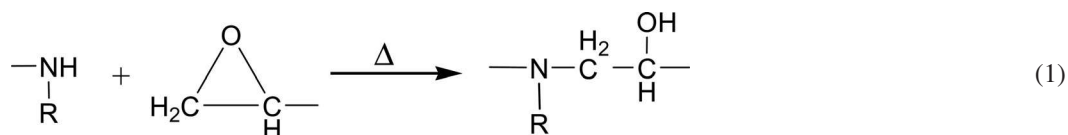
FIG. 4. The process for sealing SU-8 channels using PDMS. Chemical bonding is achieved between PDMS and SU-8.

$$\text{(1)}$$

N$_2$ plasma process requires high-purity nitrogen to generate sufficient amino groups on PDMS surface because Si-O bond is chemically very stable and the presence of oxygen would favour the oxidation over the nitrogenization of PDMS. In addition, pre-cleaning the plasma chamber with N$_2$ plasma is also helpful in removing the residual oxygen-containing molecules resting on the chamber surface. For SU-8 device fabrication, the key is to preserve sufficient residual epoxy groups in the material by controlling the post-exposure bake process, in which epoxy crosslinking reaction occurs. While the post-exposure bake at the manufacturer-recommended 95 °C is good to preserve sufficient amount of residual epoxy groups for the bonding, the process at a lower temperature would definitely preserve more epoxy groups and thus favour a stronger bonding. The subsequent development process would not affect the level of residual epoxy groups, but its involved solvent has to be removed from the devices, in order to achieve a good bonding. In addition, SU-8 surface should be kept free of SU-8 particles. The reason is that the SU-8 dissolved in the developer may precipitate onto device service as fine particles during the conventional isoproponal rinse process. These particles would prevent the molecular contact and thus the molecular reaction between the PDMS surface and SU-8 surface. A simple way to avoid the problem is to rinse the developed devices with fresh developer before rinsing them with isoproponal.

The chemical reaction between N$_2$ plasma-activated PDMS and SU-8 can be controlled at 100 °C or higher for 30 min. During the process, the residual epoxy groups in the material also continue their corsslinking reaction, resulting in a certain degree of SU-8 hardening. If further hardening of the material is required for a specific application, the sealed devices can be subsequently heated by following the standard hardening procedure. This post process is harmless to

the above bonding between PDMS and SU-8. In the case that the involved device is very large, a small compression may be applied on PDMS using a weight to keep its full contact with SU-8 during the reaction. The force can be released after the bonding is established.

Fig. 5 shows the effects of post-exposure bake temperature on the residual epoxy groups in SU-8 and the maximum fluidic holding pressure of PDMS-sealed SU-8 straight microfluidic channels. Quantifying the epoxy groups in SU-8 was calculated via $(\Delta H_o - \Delta H_f)/\Delta H_o$ by measuring the reaction heat ΔH_o of unbaked SU-8 and the reaction heat ΔH_f of post-exposure baked SU-8 using DSC. UV-exposed but unbaked SU-8 was assumed to have 100% residual epoxy groups because the crosslinking reaction of epoxy groups only starts when the UV-exposed material is subsequently baked. The maximum fluidic holding pressure was tested by pumping DI water into the sealed straight microfluidic channels (as seen in Fig. 2(a)) until they were fractured under a certain flow rate, and then estimated from the corresponding flow rate, channel dimension, and water viscosity using the well-known Hagen-Poiseuille's equation.[11] This comprehensive performance is related to the channel sealing, the mechanical strength of PDMS and SU-8, and the connection between PDMS with external metal tubings. With an increase of its post-exposure bake temperature, the amount of residual epoxy groups in the SU-8 is decreased dramatically. When the temperature is below 130 °C, the sealed channels can still hold a small fluidic pressure while the maximum allowable pressure increases as the temperature is decreased. Debonding between PDMS and SU-8 happens in the inlet area when the bake temperature is in the range of 110 °C to 130 °C. In this case, it was observed that PDMS bubbled and water could travel to the adjacent channels to release the pressure. A very high pressure of 0.94 MPa can be achieved when the post-exposure bake is conducted at 95 °C to preserve 43% residual epoxy groups in the SU-8. In this case, material fracture in PDMS itself or sealing failure between PDMS and metal tubings was observed, and water was seen to rapidly leak from the broken PDMS lid or the interface between PDMS and metal tubings. No debonding between SU-8 and PDMS was observed. Even stronger bonding can be obtained when the post-exposure bake temperature is further reduced to preserve more residual epoxy groups.

N_2 plasma-activated PDMS surface has a very long shelf life. It is still reactive and can still establish a strong and irreversible sealing with SU-8 after it has been stored under normal atmospheric conditions for several hours to as long as one or two days. This is clearly different from the fact the oxygen plasma-activated PDMS which only has a few minutes of self life for establishing irreversible bonding. The difference is possibly related to the surface rearrangements that would bring hydrophobic groups to material surface.[1] Amino groups are less hydrophilic than silanol groups, and the surface energy of N_2 plasma-activated PDMS is lower than that of oxygen plasma-activated PDMS. Consequently, such a surface rearrangement in N_2 plasma-activated PDMS is slower and less significant than that in oxygen plasma-activated
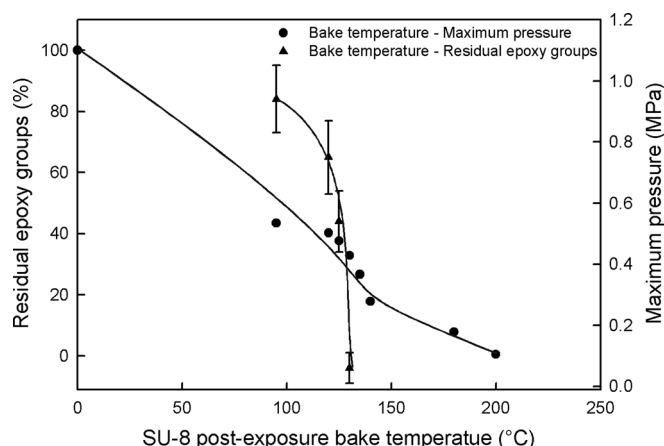

FIG. 5. The effects of the post-exposure bake temperature on the residual epoxy groups in SU-8 and the maximum fluidic holding pressure of the PDMS-sealed SU-8 straight channels.
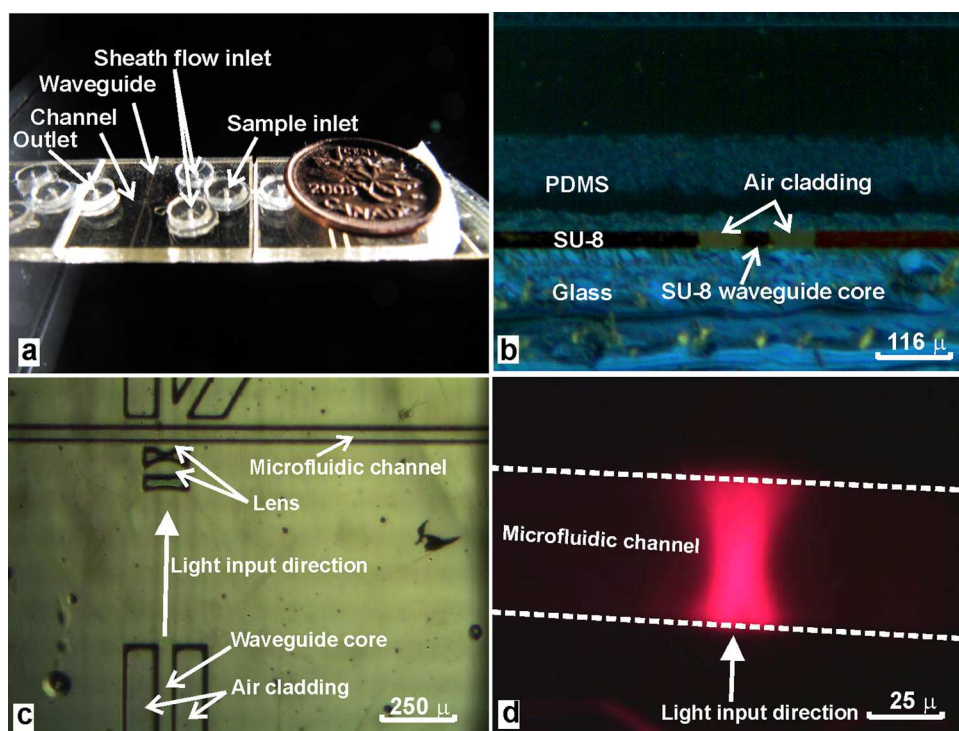
FIG. 6. SU-8 microfluidic-photonic integrated device sealed with PDMS. (a) the whole device; (b) the diced cross-section of waveguide; (c) top view of the device; (d) fluorescent image excited by the input laser.

PDMS. In addition, amine-epoxide reaction used in bonding N_2 plasma-activated PDMS to SU-8 is a polyaddition with no by-products and thermodynamically should not be sensitive to the surface-absorbed moisture. Silanol-silanol reaction used in bonding oxygen plasma-activated PDMS to glass and like surfaces is a polycondensation with water as by-product and thermodynamically is not favoured by the moisture absorbed on the material surface.

At room temperature, N_2 plasma-activated PDMS can be also moved around on SU-8 surface for a proper alignment, and can be attached, removed, and then reattached on SU-8 surface for many cycles without affecting the final bonding performance. This nature is attributed to the weak physical attraction between amino groups and epoxy groups, and the slow amine-epoxide chemical reaction at room temperature. It allows a large process tolerance in device alignment process and device mass production. Oxygen plasma-activated PDMS, on the other hand, is sticky to glass and like surfaces at room temperature because of the strong physical interaction (i.e., hydrogen bonding) between silanol groups. It loses its bonding capability if it is attached to the surfaces and then removed. The reason is that the force used to break the hydrogen bonding would stress the PDMS, resulting in an accelerated surface arrangement in PDMS.

In comparison with the two reported methods described earlier, this newly developed method is simpler and is easier to control. It eliminates the difficult attachment of 3-aminopropylthiethoxysilane to PDMS or SU-8 surface in the reported methods, and only requires two steps, including N_2 plasma activation of PDMS and amine-epoxide reaction-based bonding. It also avoids the use of short-lived and sticky oxygen plasma-activated PDMS required in both the reported processes and avoids the use of vapour deposition chamber required in one of the reported processes. This developed method can be easily adopted in most laboratories and is suitable for mass production, given that both N_2 plasma activation and amine-epoxide reaction are very easy to implement and control, and the N_2 plasma-activated PDMS has a very long shelf life and is easy to handle.

The above described process was applied in fabricating the SU-8-based microfluidic-photonic integrated flow cytometry devices [2,3] as shown in Fig. 6. Here, the PDMS acts not only as the ceiling of the SU-8 microfluidic channels but also as the upper cladding of the SU-8 waveguide cores because PDMS is optically transparent and has a refractive index smaller than that of SU-8. This type of device was previously sealed by mechanically attaching PDMS to SU-8 using a mechanical clamp,[2] due to the lack of a bonding method. The devices fabricated in this work were able to withstand harsh dicing (as seen from the resultant surface shown in Fig. 6(b)). When a fluorescent laser dye was pumped into the microfluidic channel and a 630 nm laser beam was guided through the waveguide into the channel (Fig. 6(c)), the dye was excited in the intersection of the beam and the channel, as seen in Fig. 6(d). No fluidic leaking and light leaking was observed between PDMS and SU-8 even after the test was continued for months. In these devices, the strong chemical bonding between PDMS and SU-8 was critical to hold the fluidic pressure, and the molecular-level contact between PDMS and SU-8 was critical to ensure that PDMS plays its desired cladding role on SU-8 waveguide cores.

IV. CONCLUSION

It is desirable but difficult to seal open SU-8 microfluidic channels using PDMS. The molecular chain segments in both of the materials are constrained by their crosslinked networks and can not diffuse into each other to establish entanglement and thus physical bonding through any heat or solvent-based process. By generating amino groups on PDMS surface using N_2 plasma treatment and utilizing the residual epoxy groups on SU-8 surface, however, amine-epoxide chemical reaction can be introduced at their interface to establish a strong chemical bonding between the two materials. This method was successfully applied in irreversibly sealing SU-8 microfluidic channels using PDMS and fabricating microfluidic-photonic integrated devices. The sealed channels can hold a larger fluidic pressure than the involved PDMS lid or its connection with tubings can withstand. The involved process is simple and easy to control, and the obtained sealing is long-term resistant to water.

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