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Low-stress transfer bonding using floatation

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Abstract

A novel method for transferring thin, large-area polymer layers from a mould and its subsequent bonding to a destination substrate is presented here. Buoyancy is used for transfer via floatation to allow the release of internal stress in the polymer and to avoid induced strain. Additionally, floatation leads to wrinkle-free contact between the polymer layer and its destination substrate, an important feature for the transfer of large-area polymer sheets. Poly(vinyl alcohol) is used as a release film on the mould, from which the device polymer layer is released using ultrasonication. The polymer layer floats from the mould to a destination surface, to which it automatically aligns. Here, the method is demonstrated by the successful manufacturing of a 4" sized, triple microfluidic layer PDMS stack on a silicon wafer, containing a total of 48 large-area, fragile membranes, each with a thickness of 50 μm .

(Some figures may appear in colour only in the online journal)

1. Introduction

Polymeric materials are extensively used for the fabrication of microsystem components, in particular for lab on chip. The transfer of microstructured layers from a source to a destination surface is a critical manufacturing step that is present in the vast majority of microfabrication processes. For example, in micro-replication moulding, also known as soft lithography, a prepolymer, typically polydimethylsiloxane (PDMS), is polymerized on top of a mould, demoulded and transferred onto a destination substrate. The transfer process requires good alignment precision while simultaneously allowing for low material stress, since even a minute amount of stress results in an unacceptable deformation of the layers. This requirement is particularly demanding when upscaling production throughput in microsystem fabrication by using wafer-level rather than chip-level manufacturing techniques since a larger area invariably leads to a larger strain and hence poor alignment of features located far apart on the transferred layer. For the fabrication of large-area polymeric structures, e.g. wafer level, the transfer process becomes a serious bottleneck for the yield, as the above-mentioned requirements on precision and stress are difficult to satisfy using manual handling.

Several reported transfer methods involve the use of a temporary carrier during the transfer of polymer microstructures from a mould to a destination surface [1–4], where the temporary carrier provides support and retained spatial position. A common limitation of these methods is the need to precisely control the relative adhesion properties between the polymer surface and, respectively, the mould surface, the carrier surface and the destination surface [5]. For the transfer of fragile structures, such as thin PDMS membranes, it is crucial to limit the amount of mechanical strain induced in the polymer material to avoid deformation and structural damage. While a carrier offers protection for fragile components during demoulding and transfer, the carrier release process after transfer has to be gentle to avoid rupture. Also, strain of a polymer sheet causes misalignment, and manual handling during the transfer often leads to both induced strain and wrinkles at the bonding stage.

The use of sacrificial layers in transfer processes [6, 7] can help reducing the level of induced strain, but the sacrificial material and its solvent need to be compatible with the other materials used. Water-dissolvable polymers can be used as sacrificial layers in microfabrication and are attractive since only mild reagents are involved [6, 8]. Poly(vinyl alcohol) (PVA) is a water-dissolvable polymer that has been used

(1) Mould coating

(a) Spin-coat a SU8/Si mould with PVA solution (800 rpm, 60 s).

(b) Evaporate the water (70 °C, 10 min).

*(c) Submerge the mold into a silane/methanol solution (60 min). Rinse with methanol and cure (105 °C, 10 min).

(2) Device layer preparation

(a) Cast PDMS prepolymer onto the mould.

(b) Cure the PDMS (70 °C, 60 min).

(3) Transfer using floatation

(d) Submerge the stack in an ultrasonication water bath. As the PVA dissolves, bubbles form underneath the PDMS. *Adding NaOH favours formation of hydroxysilane groups on the PDMS.

(e) The PDMS releases from the mould as the PVA dissolves and floats to the liquid surface.

(f) The mould is replaced with a destination substrate. Lowering the water level causes the PDMS to sink onto the substrate. Alternatively, the PDMS is scooped out of the bath onto a wafer.

(g) Pre-alignment is achieved when fitting the size of the beaker to the substrate. Further alignment can be achieved by sliding the PDMS, gliding on top of a water film.

(h) The trapped water evaporates when the stack is treated with low-pressure and heat.

(i) Transfer bond result. *Covalent bonds are formed between the PDMS and the silicon.

Figure 1. Process flow for the fabrication and low-stress transfer bonding of PDMS microfluidic layers. *Optional treatment to be applied when covalent bonding of the PDMS to the destination substrate is required, with corresponding surface groups illustrated in dotted boxes.

previously for structure release [9, 10]. Recently, a method for the fabrication of large-area, thin PDMS membranes was described, where the PVA film was used as a temporary carrier to provide a low-stress release after transfer bonding [11]. However, due to the manual handling required, this process suffers from poor yield for wafer-level transfer of thin, fragile structures. In contrast, a technique using a water bath for ‘float-off’ delamination of an unbounded polymer sheet from a hydrophilic glass slide, with subsequent ‘scoop up’ of the polymer onto a target substrate has been successfully used for the transfer of unpatterned thin-film layers for photovoltaic devices [12] and transistors [13]. This method uses the difference in wettability between the polymer (hydrophobic) and the glass (hydrophilic), in combination with

the surface tension of the liquid, for the sheet to float off. The method is therefore unsuited for the transfer of moulded layers in soft lithography in which both the mould and the polymer are hydrophobic, such as those required in PDMS processing. Also, the float-off/scoop-up technique requires manual handling during release and retrieval and is therefore problematic for structure alignment.

In this work, we present a low-stress transfer bonding method for the fabrication and assembly of microstructured polymer layers for use in life science applications and microfluidic lab-on-chip systems in particular. The method is designed to minimize the strain induced during (i) mould release, (ii) polymerization stress relaxation, (iii) handling, (iv) movement, (v) alignment and (vi) bonding of the polymer

Figure 2. Process flow of a three-step multilayer assembly using the floatation method.

sheet during its transfer from a mould to a destination substrate. Strainless handling of the polymer sheet is achieved by omitting mechanical contact of solid materials with the polymer and instead using floatation in a water bath. Large-area, fragile microstructured PDMS layers are released from their moulds in a water bath via dissolution of a water-dissolvable PVA release layer. Buoyancy forces then cause the layer to float up in the liquid for transfer, whereafter automatic alignment and bonding to a destination substrate are achieved. Here, a method used for single-layer transfer [14] is further developed into a general method for the transfer and assembly of advanced, large-area and fragile structures consisting of multiple polymer layers aligned to each other.

2. Materials and methods

Figure 1 illustrates the novel fabrication method. We demonstrate the technology by the transfer of microstructured, wafer-sized PDMS sheets from a 4"-sized SU(8)/silicon mould to a 4" natively oxidised silicon wafer.

2.1. Mould coating and device layer preparation

The moulds used in the experiments were made using standard lithography patterning of SU-(8) resist on 4" silicon wafers. To obtain moulds that are easily separated from cured PDMS,

the moulds were coated with a fluorocarbon film formed through C₄F₈ plasma deposition using a reactive ion etch tool at 30 W for 60 s. PVA (The Fishing Bag Ltd, UK) was dissolved in deionized water at a concentration of 2% (w/w), see figure 1(A). The PVA solution was then spin coated (800 rpm, 60 s) on the mould, with subsequent baking on a hotplate (70 °C, 10 min). To obtain covalent bonding between the PVA and the PDMS after polymerization, the PVA-coated mould was immersed into a surface activation mixture, consisting of 2% vinyl silane (Z-6518, Dow Corning, US) in methanol, for 60 min. Subsequent rinsing with methanol and baking on a hotplate for 10 min at 105 °C resulted in a mould coated with a vinyl functional PVA surface capable of reacting with the silyl hydride functional groups present in the PDMS prepolymer. PDMS (Sylgard 184, Dow Corning, US) prepolymer mix (ratio 1:10) was thereafter casted onto the mould and spun (1500 rpm, 60 s) to obtain a 50 µm thick film, see figure 1(B). The PDMS was thereafter cured on a hotplate for 60 min at 70 °C.

2.2. Transfer with floatation

The entire structure was then immersed into a deionized water-filled circular glass beaker with a marginally larger inner diameter than the mould wafer. The glass beaker was lowered into an ultrasonication water bath, a treatment leading to

Figure 3. Transfer bonding process results. (a) PDMS spin-coated and cured on a PVA-covered mould. (b) PDMS floating in a water-filled beaker after release, magnified in (c). (d) One layer of PDMS resting on a water film on a destination wafer. ((e)–(g)) Transfer results showing close-ups at a tilted angle in the left column, a top view close-up in the middle column and a full structure in the left column of (e) one-layer transfer, (f) two-layer assembly and (g) three-layer assembly.

dissolution of the PVA. Separate experiments were performed using a water bath of pH 9 by adding a low concentration of NaOH, in order to speed up the hydrolysis of the silane–PVA bonds and create reactive hydroxysilane groups on the PDMS surface. During the dissolution of PVA, the ultrasonication creates gas bubbles between the PDMS and the mould through the process of cavitation [15]. The PDMS sheet is separated from the mould via PVA dissolution within 1 h of ultrasonication, and the bubbles underneath the PDMS lifted the PDMS sheet to the surface by buoyancy. When using the protocol for bonding, i.e. when including steps marked (*) in figure 1, the bottom surface of the PDMS has a monolayer of PVA covalently bonded to the PDMS surface via the vinyl silane groups.

The mould at the bottom of the beaker was thereafter replaced by the destination substrate; for demonstration purposes a plain 4" silicon wafer with native oxide was used. The water level in the beaker was lowered until most water

was removed. While the water level was lowered, automatic pre-alignment of the polymer sheet to the destination surface was obtained since the size of the water-filled beaker was marginally larger than that of the polymer layer and the destination substrate, thus guiding the polymer layer onto the destination surface. Experiments to obtain covalent bonding of the PDMS to the destination surface utilized an addition of vinyl silane to the water in the beaker to reach a concentration of 4% (w/w) silane/water. After letting the silane react with the PDMS and silicon for 20 min, the water level was lowered and pre-alignment was obtained.

At the end of the floatation transfer process, the PDMS sheet rested on a thin water film on the target substrate. This thin water film allowed for further alignment of the PDMS sheet, passively through surface tension aligning the polymer to the wafer, or actively by gently sliding the PDMS on top of the destination substrate. Manual sliding

with a single mechanical contact point does not induce strain outside the contact region. To remove the remaining thin water film, elevated temperature (50 °C) and lowered pressure (−40 kPa relative atmospheric pressure) were used until all water was removed. Experiments to obtain covalent bonding of the PDMS to the silicon substrate included additional heating (70 °C, 60 min) after the water was removed to complete the silanisation reaction by driving off the by-products. To test the bond strength of the PDMS to the silicon substrate, pressurized gas was applied to channels in the finished structure. A tube with a gasket was fixed to a channel inlet of the device, and connected to a pressure regulator, a pressure sensor and a gas bottle containing pressurised nitrogen.

2.3. Multilayer assembly

The process was further tested for the fabrication of multilayer PDMS stacks on silicon wafer substrates, as illustrated in figure 2. First, a full floatation-based transfer was conducted as described in section 2.2. Thereafter, the second PDMS sheet was prepared and released. While the second sheet was floating on the water surface, the mould was replaced with the silicon–PDMS stack from the first assembly. The water level was lowered such that the second sheet was deposited and aligned to the first. The resulting stack was then used as the destination substrate for the third PDMS sheet, resulting in a silicon wafer with a triple microfluidic PDMS layer.

3. Results and discussion

Successful experiments were made using the floatation method for the fabrication and transfer of 4'' PDMS layers, each containing 16 membrane structures with a thickness of 50 μm , from their moulds to silicon wafers (figure 3). All membranes were intact and non-deformed and the overall polymer layers were wrinkle free after transfer to the destination wafers. Also, a multilayer assembly was successfully performed for producing a three-layer wrinkle-free structure with 48 intact, suspended membranes of 50 μm thickness, 30 of which had an area of 1 cm^2 .

The spin-on deposition of PVA onto the mould required an excess of PVA solution to obtain good coverage of PVA over the mould. No reflow of the solution towards structure corners was observed, which is important for high-resolution patterning. A possible cause of reflow prevention is the evaporation of water that already started at the spinning process, causing an increase in PVA viscosity. Furthermore, low PVA concentration of the PVA solution ensured a thin PVA film, which also reduced the significance of thickness variations since small differences in thickness were easily accommodated by the rubbery PDMS. The PVA film was not dissolved by methanol, so surface treatment with the surface activation mixture was possible. The release of the PDMS sheet from the mould required 30 min of ultrasonication. Bubble formation was abundant and sufficient for transport of the polymer layer to the surface (figures 3(b) and (c)). Once reaching the liquid–air surface, the polymer layer is stretched out by the surface tension of the liquid, $\gamma_{\text{water}} = 0073 \text{ N m}^{-1}$ at 20 °C, and the elasticity of the polymer stretched the polymer

layer, thus avoiding any strain in the form of folds or wrinkles, while inducing only a minimal amount of tension in the sheet.

Pre-alignment is provided by choosing the liquid bath recipient, the mould, the polymer sheet and the destination substrate having an equal footprint shape, for example rectangular. Having the inner beaker dimensions only marginally larger than the outer dimensions of the mould, sheet and destination ensure that the sheet can only move in a vertical direction during floatation, hence ensuring self-alignment through guidance by the recipient walls. The use of circular baths, moulds and destination wafers for the demonstration structures resulted in a rotational freedom during floatation of the polymer layers, which reduced the accuracy of the pre-alignment. Sliding and rotating the PDMS on the destination wafer after the film had settled was used successfully to counteract the process induced alignment errors. The areas of the transferred polymer layers were reduced with a few per cent as compared to the moulds, which probably was caused by polymerization shrinkage. Although this could complicate the alignment of layers of different fabrication processes, there are methods to account for variations of polymerization shrinkage due to layer thickness and polymerization temperature in order to obtain the required alignment [16].

While the water evaporated, the capillary action in the residual liquid film between the polymer and the destination substrate surface ensured a conformal, void-free contact between the layers. Experiments using high temperature ($T = 100 \text{ }^\circ\text{C}$) and vacuum ($P = -90 \text{ kPa}$ relative atmospheric pressure) for water removal from the structure led to rapid removal of water, but membranes were also significantly bended. A slow and mild 4 h treatment of heating at 50 °C and a low pressure of −40 kPa relative to the atmosphere gave slow vapour formation and insignificant bending of the membranes, and resulted in perfectly transferred structures. A programmable hotplate/vacuum chamber would offer a fast and automatic method for drying.

Preliminary tests of the bond strength were performed by trying to peel off the PDMS from the destination surface and inspect the site of rupture. Instead of breaking at the PDMS–silicon oxide bond interface, ruptures were formed in the PDMS bulk, thus indicating that the bond was strong and probably covalent via silane crosslinking. This was further confirmed with the bond tests using pressurized nitrogen. The bond was still intact when a gas pressure of 4 bar was applied, which was the maximum pressure provided by the pressure source. For layer transfer in which the bonding treatments (marked * in figure 1) were omitted, a reversible bond was obtained, with which a PDMS sheet was easy to peel off intact from the destination wafer after the transfer. The latter method was also tested as a transport method for fragile PDMS sheets, in which the destination wafer protects the structure during transportation and for on-shelf storage. The polymer layer was easily released from the destination wafer 280 days after the initial floatation transfer when the structure was submerged into another liquid bath.

The multilayer assembly was performed similar to the first transfer, with the only difference that the water removal was more time consuming due to partial water filling in layers

beneath the top layer. The misalignment between the two first PDMS layers in the multilayer assembly was measured to be 20 μm , whereas a three-layer device had a misalignment of 40 μm , which is in line with manual alignment methods. Since the PDMS rests on the water film and does not bond until water has evaporated, there is time for further improving alignment using microscopy. The topography of the mould leads to a non-planar top surface of the PDMS during the spin-coating process. Even so, we observed no wrinkles, deformation or bond voids in the assembled three-layer structures, except for some small voids at the wafer edges in some of the structures. The successful transfer bonding can be explained by the levelling period [17] on the hotplate before the PDMS polymerizes, which leads to partial top surface planarization, and by the elastomeric behaviour of the PDMS during contacting. Unlike our early unsuccessful attempts to transfer thin wafer-sized PDMS structure using manual and carrier-based methods, the floatation transfer method resulted in a 100% yield of the 48 fragile membranes of 50 μm thickness and up to 1 cm^2 area, all suspended within the three-layer structure (figures 3(e)–(g)).

4. Conclusions

A novel method for stress- and strain-free transfer bonding of polymer sheets is described here. Unlike previous methods, this new approach allows for the release of polymerization stress and does not induce mechanical deformation during handling, allowing for the fabrication of fragile, large-area structures with wrinkle-free deposition of polymer layers onto the destination substrate. Pre-alignment of the transferred layer to the destination substrate is achieved automatically during the transfer itself and is further refined at the end of the transfer, resulting in an alignment accuracy of 40 μm . Successful manufacturing of a 4'' area, triple PDMS multilayer microfluidic structure on silicon is shown, containing 48 fragile membranes that feature 50 μm thickness of which the majority have an area of 1 cm^2 , all of which were intact and non-deformed. It was further demonstrated that both temporary bonding and covalent bonding between the layers could be achieved in a controlled fashion.

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