LOW-STRESS WAFER-LEVEL TRANSFER BONDING OF POLYMER LAYERS USING FLOATATION

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ABSTRACT

We introduce and demonstrate a method for low-stress demolding and transfer of polymer microstructures from their mold to a destination wafer. This method has the advantage of not involving stress-inducing handling steps present in traditional demolding and transfer bonding procedures. The mold is coated with a sacrificial layer which is dissolved in an ultrasonication water bath, leading to that the polymer sheet floats to the water surface. This generic method facilitates transfer of large area, thin layers and is here demonstrated for demolding and transfer bonding of wafer-sized layers of microstructured PDMS.

KEYWORDS

Transfer bonding, poly(vinyl alcohol), PVA, PDMS, floatation

INTRODUCTION

In soft polymer replication, a prepolymer is polymerised on top of a mold, after which the polymerised structure, typically polydimethylsiloxane (PDMS), is demolded and transferred to a destination substrate. Several methods involve the use of a carrier during the transfer of structures from a mold to a destination surface [1-4]. A common limitation for these methods lies within the need of control of relative adhesion properties between the polymer and the mold, the carrier and the destination surfaces [5]. Also, as the transferred structure is mechanically contacted during the entire transfer process, stress induced during the polymerisation is never fully released. For transfer of fragile structures, such as PDMS membranes, it is crucial to limit the amount of mechanical stresses induced in the polymer material to avoid deformations and structural damage. While a carrier offers protection of a membrane during demolding and transfer, the carrier debond process after transfer has to be mild to avoid ruptures. The use of a sacrificial layer [6] can help reducing the stress during this step, but the layer and the 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 no strong reagents are involved [7]. Poly(vinyl alcohol) (PVA) is a water dissolvable polymer that has been used for structure release [8,9]. Recently, a method for fabrication of large-area, thin PDMS membranes was described, where PVA film was used as a temporary carrier to provide a low-stress release after transfer bonding [10]. However, due to the manual handling, this process suffers from poor yield for wafer-level transfer of thin, fragile structures.

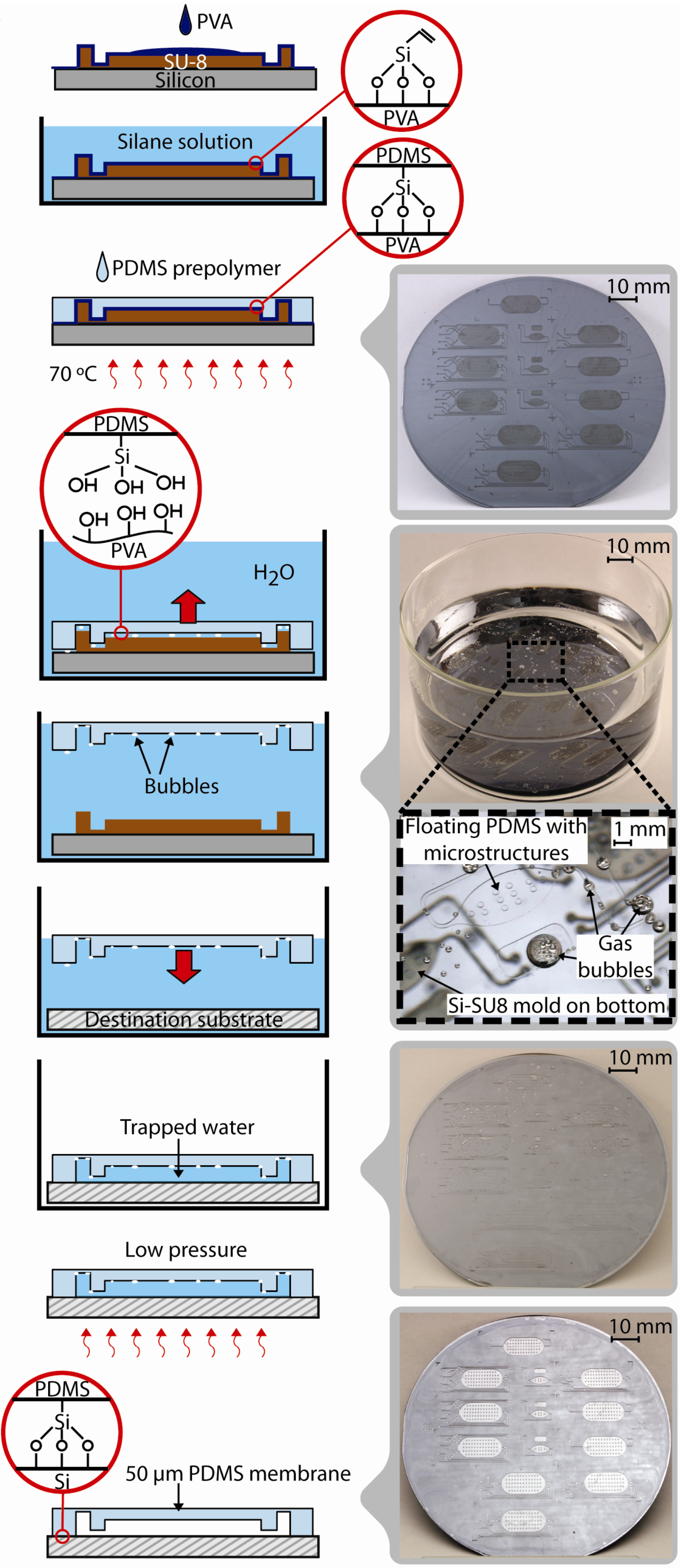
A technique using a water bath for “float-off” delamination of unpatterned polymer sheets from a glass slide, with subsequent “scoop-up” of the polymer onto a target substrate, has been described as a transfer method in thin-film fabrication [11,12].

NOVEL TRANSFER METHOD

Here we present a novel method combining the “float-off” technique with micropatterning to obtain a process for fabrication of polymeric microstructures. The use of floatation to transport the polymer from the mold to the destination substrate omits stress-inducing mechanical handling steps. The process is illustrated for the wafer-scale fabrication of suspended thin, large-area PDMS membranes. PVA is used as a sacrificial layer for mold release, which allows the polymer to detach from the mold under low-stress conditions. Ultrasonication treatment in a water bath leads to bubble formation [13] between the mold and the PDMS, which causes the released polymer sheet to rise to the surface of the water bath due to buoyancy. Removing the water from the bath causes the PDMS to sink on to the target substrate. This method does not induce any significant amount of stress during transfer and allows for releasing any potential stress induced during the polymerisation process on the mold.

EXPERIMENTAL

First, tests were made to find the optimal concentration of PVA in water for the mold coating process. PVA (The Fishing Bag Ltd, UK) was dissolved in DI water to obtain solutions of varying concentrations. The different PVA solutions were thereafter spun (60 s at 800 rpm, 100 rpm/s) onto 4” silicon wafers, which thereafter were baked on a hotplate for 1 h at 70 ºC. PDMS (Sylgard 184, Dow Corning, US) prepolymer (ratio 1:10, curing agent:base) was spun (60 s at 400 rpm, 100 rpm/s) on top of the PVA-coated wafers and cured for 1 h at 70 ºC. Each polymer-coated wafer was thereafter immersed in a water bath that was lowered in an ultrasonication bath. The PDMS was released from the silicon wafer as the PVA was dissolved. Figure 1 shows release times for different PVA concentrations in water. A concentration of 2% (w/w) PVA in water resulted in the fastest release time of 26 min.



a) Prepare a mold, here a 4” silicon/SU-8 wafer mold. Pour on liquid PVA and spin 60 s at 800 rpm. Bake for 10 min at 70 ºC.

b) For bonding: put the mold in 2 % Z-6518 silane (Dow Corning®, US) in methanol ~1 h, rinse with methanol, bake 10 min at 105 ºC. The silane reacts with the hydroxyl groups of PVA and the vinyl groups remain for further reactions.

c) Cast PDMS prepolymer on the PVA-covered mold. Spin at requested speed. Bake for 1 h at 70 ºC. The vinyl groups tethered to the PVA react with the silylhydride groups of PDMS creating covalent bonds betweeen the two layers.

d) Put the stack in an ultrasonication bath with water. As the PVA dissolves, bubbles are formed below the PDMS.

For bonding: a basic (~pH 9) bath will hydrolyse the silane bond and create reactive hydroxysilane groups bound to the PDMS.

e) When the PVA layer is dissolved, the PDMS is released from mold. The bubbles make the PDMS rise to the surface.

f) Replace the mold with the destination substrate, here a 4” wafer. Lower the water level such that the PDMS falls onto the substrate, alt. pull up the wafer out of the bath with the PDMS on top.

g) With the size of the beaker fitting the substrate size, the PDMS and destination wafer are automatically equicentred and can be further aligned 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. If the silane treatments were made, covalent bonds are formed between the PDMS and the silicon via the hydroxy silane groups bound to the PDMS.

i) Transfer bond result. *Right:* PDMS layer with sixteen suspended, 50 µm thin membranes successfully transfer bonded to silicon wafer.

Figure 2: Process flow for the fabrication and low-stress transfer bonding of the PDMS devices. The middle column shows schematic cross-sections of the steps, with corresponding photografts of results in the right column.

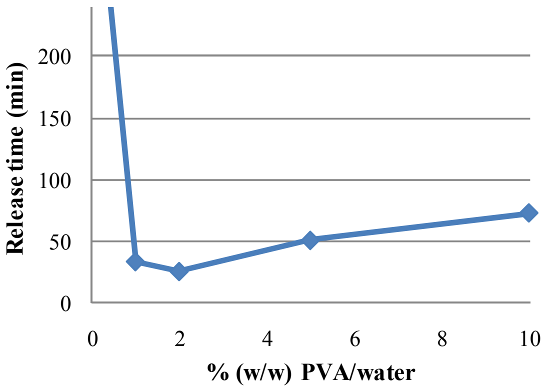


Figure 1: Release time of thick PDMS sheets on PVA films generated using different PVA solution concentrations. Low concentration leads to very thin film and slow release due to diffusion limitations. The reason for slower release at higher concentrations needs further investigation. 0% of PVA resulted in no release after 240 min.

Thereafter, the floatation method was used for transferring microstructures, as described in Figure 2. 2% (w/w) PVA solution was deposited onto an SU-8/silicon mold using spin-coating (60s at 800 rpm, 100 rpm/s) with subsequent baking on a hotplate (10 min at 70 ºC). To obtain covalent bonding between the PVA and the PDMS after polymerisation, the PVA-coated mold was immersed into a bath of 2% vinyl silane (Z-6518, Dow Corning, US) in methanol for 1 hour. Subsequent rinsing with methanol and baking on a hotplate for 10 min at 105 ºC resulted in a mold with vinyl functional PVA surface capable of reacting with the silyl hydride functional group present in the PDMS prepolymer. PDMS prepolymer mix (ratio 1:10) was thereafter casted onto the mold and spun (60 s at 1500 rpm, 100 rpm/s) in order to obtain a 50 µm thick film. The PDMS was thereafter cured on a hotplate for 1 h at 70 ºC.

The entire structure was then immersed into a glass beaker with a slightly larger diameter than the wafer, and that was filled with a low concentration solution of NaOH in DI water with pH 9. The glass beaker was in turn lowered into an ultrasonication water bath. This treatment dissolves the PVA, in which the basic conditions of the solution speed up the hydrolysis of the silane-PVA bonds to create reactive hydroxysilane groups on the PDMS surface. During the dissolution of PVA, gas bubbles form between the PDMS and the mold through the process of cavitation [14]. After 30 min, the PVA layer was entirely dissolved and the PDMS sheet freed from its mold. The bubbles underneath the PDMS then caused the PDMS sheet to rise up to the water-air surface. The bottom surface of the PDMS still contains a monolayer of PVA, covalently bonded to the PDMS surface via the vinyl silane groups.

Thereafter, the mold on the bottom of the beaker was replaced by the destination substrate; for demonstration purposes a plain 4" silicon wafer. Vinyl silane was added to the water in the beaker to obtain 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 until most water was removed. This lowered the PDMS sheet until it rested on a thin water film on the target substrate. This thin water film allows for manual alignment of the PDMS sheet, if such would be desired, by gently sliding the PDMS into the wanted position on the destination substrate without inducing significant stress. To remove this remaining thin water film, elevated temperature (50 ºC) and vacuum treatment (-40 kPa relative atmospheric pressure) were used. While the water evaporates, capillary forces pull the PDMS in contact with the surface. After the water was removed, additional heating (1 hour at 70 degrees) was applied to form a covalent bond between the PDMS and the silicon via silane-silane coupling. An attempt to peel off the PDMS from the silicon resulted in ruptures formed in the PDMS bulk, indicating that the PDMS-silicon bond interface was strong.

In an alternative version of the method, the silane treatment of the PVA-coated mold and the addition of sodium hydroxide and silane to the water bath were excluded from the process, resulting in a PDMS sheet that was easy to peel off from the destination wafer after the transfer.

Multiple layers

A multi-layered PDMS stack on a silicon wafer was also manufactured with a similar process. For the bottom PDMS layer, a mold was spin-coated with first a 2% PVA (w/w) solution and thereafter a PDMS prepolymer, similarly as in steps a-c in the single layer method (Figure 2). A second PDMS layer was then made from a second mold, from which demolding was done using a flexible foil (9742 Scotchpak, 3M, US) as the temporary carrier material. Oxygen plasma treatment (4 kW for 15 s) of the top and bottom PDMS layers prior to their bonding created a covalent bond between the layers. The result was a two-layered PDMS structure resting on a PVA-coated mold (Figure 3). Thereafter, the floatation technique for mold release and transfer bonding to a silicon wafer was used according to the single layer process (Figure 2d-i). This resulted in a 4" wafer-sized PDMS structure with sixteen integrated suspended membranes resting on a silicon wafer. Figure 3 shows one of the structures on the wafer, containing three 50 µm thin integrated membranes.

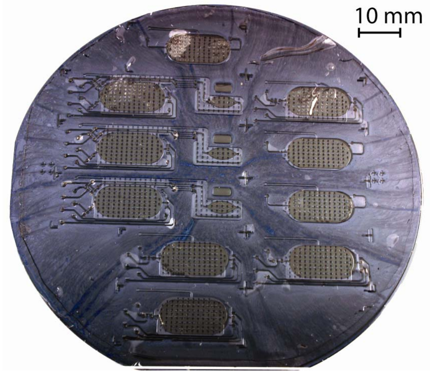


Figure 2: Two plasma-bonded layers of PDMS resting on a PVA-coated 4"-sized silicon/SU-8 mold.

CONCLUSION

We show a novel, low-stress method for demolding, transfer and bonding of a 4”-sized PDMS layer, containing 50 µm thin large area membrane structures, onto a 4” silicon wafer. This method has the benefit of not inducing significant levels of stress to the polymer material during the entire transfer process, and releases potential stresses in the polymer material caused by the polymerisation. Also, the transfer process itself does not require any prerequisites on the surface energy of the destination substrate, as is the case for conventional transfer methods using carriers. The method results in an almost perfect contact between the polymer and the destination substrate, since no manual transfer handling is needed, and since surface tension pulls down the polymer to the wafer surface. Also, both a temporary bond and a covalent bond between the PDMS and the destination silicon wafer were demonstrated, depending on the addition of chemicals to the water during floatation.

We also demonstrated the plasma bonding of additional PDMS layers to the bottom PDMS layer before demolding, thus enabling wafer-level transfer of multi-layered PDMS structures, with similar accuracy as conventional PDMS alignment methods.

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ACKNOWLEDGMENT

This work was performed as part of the EU sponsored FP7 project InTopSens

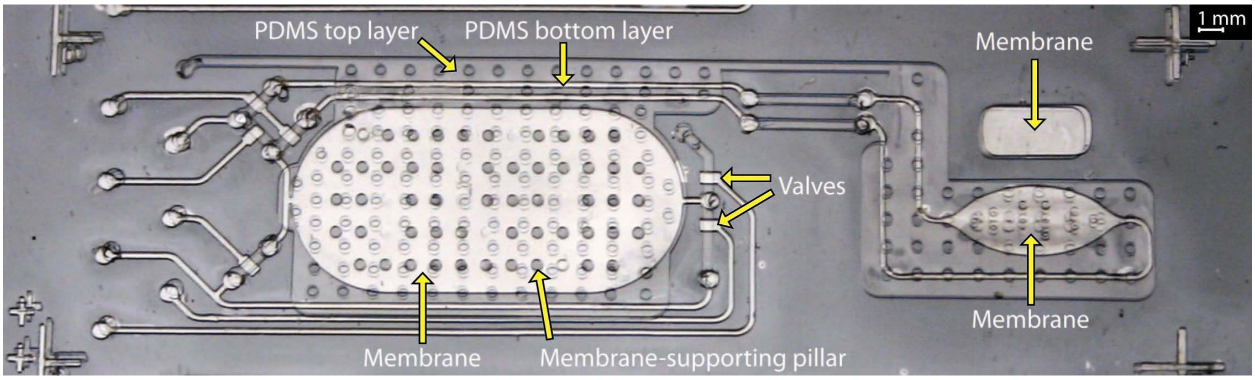

Figure 3: Close-up picture of a two-layered PDMS structure on silicon.