

# Vapor-assisted bonding of poly(dimethylsiloxane) and silicon-based substrates

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## ABSTRACT

We present a novel method to reliably bond PDMS to glass, Si, SiO<sub>2</sub> and PDMS. In this vapor-assisted method the surface of the PDMS is first brought into contact with the substrate. The PDMS-substrate structure is then exposed to a vapor that acts as the bonding agent. In our first paper we used fluoroalkyl trichlorosilane to generate the vapor. The vapor molecules diffuse through the permeable PDMS and assist in the formation of covalent bonds at the interface. We explain the mechanism of this novel bonding method through a series of experiments which use eight different silanes. The method is suitable for the mass production of lab-on-chip microfluidic devices.

**Keywords:** polydimethylsiloxane, PDMS, glass, bonding, vapor-assisted method, lab on a chip

## 1 INTRODUCTION

Poly(dimethylsiloxane) (PDMS) and glass are nowadays the material of choice for the fabrication of microfluidic prototypes. Two general approaches have so far been used to increase the adhesion strength of PDMS and glass. The first one relies on the oxygen plasma to oxidize the surfaces [1], and the second one is based on using interlaminar adhesives or uncured PDMS [2]. The bonding enhancement obtained by the conventional plasma method is either permanent (irreversible) or negligible, while only few strength levels are offered by the second method for different adhesives [3].

Elastomeric PDMS is made by the crosslinking of chains of alternating silicon and oxygen atoms. Each silicon in the chain bears two methyl groups, except for the terminal units, which are trisubstituted [4]. The surface of bulk PDMS can also contain OH groups. It is widely accepted that the oxidization of PDMS either by oxygen plasma or acidic solutions can increase the density of OH sites on the surface. If these activated surfaces are brought into contact with another surface that also contains silanol groups (e.g. glass), strong Si-O-Si bonds can be formed at the interface. The plasma or acid treated PDMS, however, loses its reactivity through a phenomenon called hydrophobic recovery [5]. Therefore the treated surfaces must be brought into contact in a few minutes or, otherwise, no bonding takes place.

The conventional processes of bonding PDMS, although applicable in the laboratory, are inappropriate for the mass

production of lab-on-a-chip devices, where large number of chips need to be made at the same time with low cost. In this regard, we developed a reliable, inexpensive and straightforward method, *the vapor-assisted method* [6]. This method is equally suitable for laboratory research and manufacturing of lab-on-a-chip devices. In the vapor-assisted method the surface of the PDMS is first brought into contact with the substrate and the resulting PDMS-substrate structure is then exposed to a vapor.

In order to understand the mechanism of bonding we performed the vapor-assisted method with eight different silanes including two fluoroalkyl trichlorosilanes, three alkyl trichlorosilanes, one alkyl dichlorosilane and one alkyl monochlorosilane [7]. We demonstrated that the hydrogen chloride gas as a by-product of the hydrolysis and polymerization of these silanes in the reactor plays an important role in the bonding.

## 2 MATERIALS AND METHODS

Transparent PDMS sheets (BISCO® HT-6240) were obtained from Rogers Corporation (Binghamton, NY, USA) in different thickness ranging from 0.25 mm to 1.6 mm. Different silicon-based substrates were tested: PDMS, glass, silicon wafer, and silicon wafer with thermally grown oxide. Glass microscope slides were purchased from Efton Science (Toronto, Canada). Boron-doped polished silicon wafer with 100 mm diameter and 431-483  $\mu\text{m}$  thickness were purchased from Nova Electronic Materials Ltd (Flower Mound, TX, USA). Boron-doped polished silicon wafer with thermal oxide on the surface with 75mm diameter and 356-406  $\mu\text{m}$  thickness were also purchased from Nova Electronic Materials Ltd. Hydrochloric acid solution (37wt%) was purchased from Sigma. All silanes used in this work (Table 1) were purchased from Gelest, Inc. (Morrisville, PA, USA).

The PDMS sheets were cut in the shape of 15mm  $\times$  60mm strips and were placed on the substrate after removing their plastic cover without any further treatment. Care was taken to avoid trapped air at the interface. Each PDMS-substrate sample was then placed inside a 0.5 L sealable glass reactor such that the PDMS layer remained on the top of the substrate [6, 7]. The substrate was elevated about 5mm from the bottom of the reactor to avoid contact with the added chemicals at the bottom. Two methods were used in this work to generate the hydrogen chloride gas. First, 0.3-0.4 mL of a liquid silane (Table 1) was distributed in each reactor. Second, 2 mL of hydrochloric acid solution was placed inside the reactor for vaporization at room

temperature. The reactors were sealed and kept at  $25\pm 1^\circ\text{C}$ . The mole fraction of the water in the air just before the sealing of the containers was 0.023. After 24 hours, the reactors were opened in a ventilated place and the samples were taken out for examination.

Name	Formula
Octyltrichlorosilane	$\text{C}_8\text{H}_{17}\text{Cl}_3\text{Si}$
Butyltrichlorosilane	$\text{C}_4\text{H}_9\text{Cl}_3\text{Si}$
Ethyltrichlorosilane	$\text{C}_2\text{H}_5\text{Cl}_3\text{Si}$
(Heptadecafluoro-1,1,2,2-tetrahydrodecyl) trichlorosilane	$\text{C}_{10}\text{H}_4\text{Cl}_3\text{F}_{17}\text{Si}$
(Tridecafluoro-1,1,2,2-tetrahydrooctyl)dimethylchlorosilane	$\text{C}_{10}\text{H}_{10}\text{ClF}_{13}\text{Si}$
(Tridecafluoro -1,1,2,2-tetrahydrooctyl)methylchlorosilane	$\text{C}_9\text{H}_7\text{Cl}_2\text{F}_{13}\text{Si}$
(Tridecafluoro -1,1,2,2-tetrahydrooctyl) trichlorosilane	$\text{C}_8\text{H}_4\text{Cl}_3\text{F}_{13}\text{Si}$
(Tridecafluoro -1,1,2,2-tetrahydrooctyl)triethoxysilane	$\text{C}_{14}\text{H}_{19}\text{O}_3\text{F}_{13}\text{Si}$

Table 1: Silanes used in this study for the vapor-assisted bonding of PDMS.

The resulted bonding strength between PDMS and the substrates was qualitatively examined by manual peeling of the PDMS.

### 3 RESULTS AND CONCLUSION

In our first experiment [6], (tridecafluoro-1,1,2,2-tetrahydrooctyl) trichlorosilane was used in the vapor-assisted method to bond PDMS and glass. The obtained PDMS-glass bonding is explained by the hydrogen chloride gas generated as a by-product of the hydrolysis and polymerization of the silane in the reactor. The hydrogen chloride gas molecules reacted with the PDMS and assisted in the formation of covalent bonds at the interface of PDMS and glass substrates. It could be argued that the evaporated silane in the sealed reactor might indeed be responsible for the bonding by forming a bridge at the interface through the silane's multi-functional group (a trichloro group). However, that possibility was rejected in our latest work [7] since a tight sealing of PDMS-glass samples was also achieved in a posterior experiment where a monofunctional silane, (tridecafluoro-1,1,2,2-tetrahydrooctyl) dimethylchlorosilane, was used, suggesting that the multifunctionality is not the main cause of bonding.

Another possible explanation for the bonding could be that the fluorine in the alkyl chain might react with the surfaces and result in the adhesion. But, the examination of samples after vapor-assisted treatment showed that

irreversible bonding on a glass substrate was also obtained for three non-fluoro silanes: ethyltrichlorosilane, butyltrichlorosilane and octyltrichlorosilane. When a silane is distributed inside a reactor with the PDMS-substrate samples, it hydrolyzes by the moisture in the air, at the bottom of the reactor. The silane can also be polymerizes in the reactor. HCl gas is produced by both of the above reactions and participate in the bonding of the PDMS and the substrate [7].

To support the role of hydrogen chloride gas in the bonding, we vaporized hydrochloric acid in the reactor instead of using any silane. It was found that exposing the PDMS-glass samples to HCl vapor increased the work of adhesion [7]. This observation proves the role of hydrogen chloride gas in the bonding.

The silane in Table 1 evaporate at the room temperature to some extent. As a result, a silane deposit on the sample can be obtained after the vapor-assisted treatment in some cases. This silane deposit can have a negative effect on the transparency of the samples. Amongst the different chlorosilanes in Table 1, octyltrichlorosilane is the least volatile. As a result this silane makes the least deposit on the sample compared to other trichlorosilane that were tested. Therefore, octyltrichlorosilane is proposed in this work as a suitable bonding agent.

It was observed in this study that the PDMS bonded to different substrates with different strength. The adhesion strength obtained from treatment of the samples with 0.4 mL of octyltrichlorosilanes in a 0.5L container for 24 hours can be roughly put in order from stronger to weaker as: PDMS-glass > PDMS-PDMS > PDMS-silicon/silicone oxide. More work is under way to quantify the adhesion of PDMS to the above substrates.

A very important and novel outcome of the vapor-assisted method is that the desired interfacial strength can be arbitrarily selected from the range of weak reversible bonding to permanent bonding by controlling the duration of exposure [6]. This is prominent because an increased strength of bonding to a level just below the permanent bonding is sufficient for most of the lab-on-a-chip applications. Unlike the permanent bonding (which does not allow the re-using of the PDMS layers after debonding) the PDMS layers in this method can be reused, eliminating the long microfabrication processes during research.

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