8th INTERNATIONAL SCIENTIFIC CONFERENCE
ON DEFENSIVE TECHNOLOGIES
OTEH 2018
Belgrade, Serbia, 11 – 12 October 2018

EXPERIMENTAL STUDY OF PDMS MEMBRANES FABRICATED EITHER BY SPIN COATING OR TRANSFER BONDING TO A SILICON CHIP WITH ETCHED CAVITY

VESNA JOVIĆ
Institute of Chemistry, Technology and Metallurgy, University of Belgrade, Serbia, vjovic@nanosys.ihtm.bg.ac.rs

JELENA LAMOVEC
Institute of Chemistry, Technology and Metallurgy, University of Belgrade, Serbia, jejal@nanosys.ihtm.bg.ac.rs

MARKO STARČEVIĆ
Institute of Chemistry, Technology and Metallurgy, University of Belgrade, Serbia, mstarcevic@nanosys.ihtm.bg.ac.rs

ZORAN ĐINOVIĆ
Austrian Center for Medical Innovation and Technology, Wiener Neustadt, Austria, zoran.djinovic@acmit.at

MILČE SMILJANIĆ
Institute of Chemistry, Technology and Metallurgy, University of Belgrade, Serbia, smilce@nanosys.ihtm.bg.ac.rs

ŽARKO LAZIĆ
Institute of Chemistry, Technology and Metallurgy, University of Belgrade, Serbia, zlazic@nanosys.ihtm.bg.ac.rs

Abstract: *Nowadays, with no doubt, PDMS, poly(dimethylsiloxane) elastomer is material of choice for microfluidic fabrication because of its unique chemical, optical and mechanical properties. Unfortunately, it is not photo-definable (i.e. not a photoresist) and fabrication of PDMS MEM (micro-electro-mechanical) devices is typically done using soft lithography. Some steps of the process are difficult to perform without manually handling PDMS layers. Next problem to be considered in patterning PDMS membranes is bond strength between membrane and silicon substrate. To investigate this, we fabricated PDMS membranes on silicon either by spin coating Si wafer or transferring previously fabricated PDMS membrane to Si chip with bonding layer on it. PDMS network samples for this research were synthesized with the same composition, which are Sylgard 184 (Dow Corning, USA) silicone elastomer base and silicone elastomer curing agent, volume ratio 10:1. Fabrication of test structures is based on bulk micromachining on ⟨100⟩ oriented Si wafers to fabricate square cavities on which PDMS membranes were realized by one of mentioned procedures. Mechanical testing of PDMS membranes, elastic properties and adhesion strength of membranes with different thicknesses were investigated applying pressurized bulge testing. Pressure was applied to the PDMS membrane via nitrogen gas and the resulting load-deflection curves were monitoring.*

Keywords: *Polydimethylsiloxane (PDMS), proccesing PDMS membranes, PDMS membrane spin coated on bulk machined silicon, PDMS membrane transfer, bulge test, adhesion strength.*

1. INTRODUCTION

Polydimethylsiloxane (PDMS) has been widely used in flexible electronics, optics and microsystem applications [1] including microfluidic systems and lab-on-a-chip (LOP) or micro total analysis systems (μTAS), mainly owing to its unique properties. Furthermore, due to their elastic properties, PDMS structures can function as active mechanical components in MEMS devices [2].

Some physical and chemical properties which make PDMS unique are [3]: a low glass transition temperature, usability over a wide temperature range at least from -100°C up to +100°C), very high flexibility (the shear modulus G may vary between 100kPa and 3 MPa), very low loss tangent ($\delta << 0.001$), small temperature variations of the physical constants (except for the thermal expansivity, $\alpha \approx 20 \cdot 10^{-5} K^{-1}$), high dielectric strength (~$14 V \cdot \mu m^{-1}$), high gas permeability, high compressibility, low chemical reactivity except at extrems of pH and essentially non-toxic for humans. In most higly unpolar liquids it swells, but it is entirely hydrophobic.

PDMS is not photodefinable, i.e. it is impossible to patterning PDMS layer applying spincoating with photosensitive resists.

Fabrication of PDMS devices is typically done using soft lithography [4]. Some fabrication steps of PDMS devices are difficult to perform without manually handling PDMS films. These are usually fragile and very sticky structures and even low levels of strain will damage or deform structures during transfer. Some transfer processes [5] utilize a carrier to provide protection and control of spatial position [6, 7]. Sometimes film structures are produced inserting sacrificial layers that dissolve in appropriate

solvent and release PDMS film [8]. Generally speaking, every structure needs distinct solution which includes a lot of "know how" and depends on large-scale on available equipment.

We here report on methods to fabricate PDMS membranes on silicon chips. Silicon chips have been micromachined to obtain microcavities with defined dimensions. PDMS membranes have been formed on top of cavity so that manufactured structure can be used as pressure indicator [9] or deformable membrane in any MEMS device [10], or integral part of chemical microreactor [11], e.g.

Bonds strength between silicon substrate and PDMS obtained either by spin coting or transfer bonding, and mechanical properties of PDMS membranes itselves have been investigated by bulge testing [12, 13].

2. EXPERIMENTAL

2.1. Fabrication of Si chip with cavity and PDMS membrane formation by spin coating

N-type {100} oriented Si wafers, 400 ± 25 μm thick, both sides mirror polished, with the resistivity 5-3 Ω·cm have been used for fabrication of proposed structure, cavity in Si chip. Process flow diagram is schematically shown in Figure 1. (a-g). The first step is Si oxidation since SiO_2 is used as masking material during further wet etching [14]. Thick SiO_2 (at least 1.4 μm) has been thermally grown at 1100 °C in atmosphere of water saturated oxygen (a). In the next step (b) thick SiO_2 was removed from one side, and thin oxide (0,2 μm) have been grown. This thin oxide from the side of cavity orifice which would be covered with membrane, is necessary because PDMS has better adhesion on oxidized silicon surface than on the bare one [15]. Thin oxide as adhesion layer for future PDMS deposition is indispensable because, as we should see, chemical wet etching in small cavities, step (f), was diffusion limited, and etching layer as thin as possible was desirable.

In the step (c) oxide from the side of chemical etching, has been lithographically patterned and removed at defined regions. All orientation alignments of cavities have been done toward primary flat direction ⟨110⟩ ± 0.5°C.

Anisotropic wet etching of Si wafer [14] was carried out in thermostated Pyrex vessel containing about 0.8 dm^3 solution allowing the temperature stabilization within ± 0.5°C. The vessel is sealed with a screw on lid which included a tape water cooled condenser, to minimize evaporation during etching. The solution is electromagnetically stirred during etching with 300 rpm and the Si wafer was held vertically inside the solution. Si wafer was in wafer holder which protected the wafer's back side and the edge from the etchant solution. Cavity etching in Si wafer was performed in KOH 30 wt.% solution at 80°C. During the first stage, cavity was etched to 350 μm depth (d).

After finishing etching, the SiO_2 have been removed in buffered oxide solution (BOE, 7 vol. (34.8 wt. % NH_4F):1 vol (6.4 wt. %HF), (d) in Fig.1. During oxide removal wafer's back was protected in wafer holder (d).

In step (e) PDMS layer was applied on the wafer side with thin oxide.

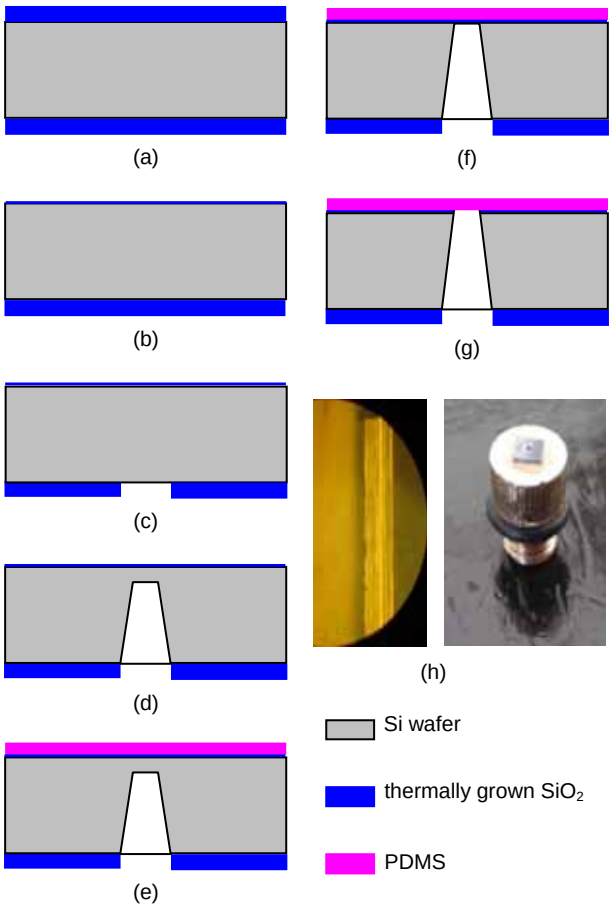


Figure 1. Process flow for fabrication of spin coating PDMS membrane on Si chip with cavity.

Before applying PDMS, the SiO_2 surface was treated with primer to prepare silylated surface and improve bond strength between this dissimilar materials (PDMS / SiO_2 on Si wafer) [16]. A 95% ethanol-5% water solution is adjusted with few drops of acetic acid to pH 4.5-5.5 with acetic. Then silane (ATMS – allyltrimethoxysilane) has been added with stirring to yield a 2% final concentration. For silanol formation five additional minutes must be waiting before dipping wafer into solution, agitated and removed after 2 minutes. After rinsing in ethanol primer layer have been cured for 10 minutes at 100 °C at air.

The PDMS that have been used for film preparation consisted of a base (component A) and a curing agent (component B) named Sylgard 184 from Dow Corning. Components have been mixed in a 10(A):1(B) (weight:weight) ratio and steered. Homogeneous mixture was placed in vacuum desiccator for degassing for at least 30 minutes. Prepared liquid is free of gas bubbles and with high viscosity. PDMS thin film coating has been realized on spin coater. For such prepared uncrosslinked polymer the final thickness of a PDMS membrane mainly depends of spin speed and spinning duration. This dependence was established in our previous work [17]. Polymerization of PDMS was performed at 100°C during 60 minutes at air.

After preparation of PDMS film on top of Si wafer, cavities have been defined by anisotropic wet etching from the bottom (e). During this ultrasound-assisted etching PDMS film was protected in wafer holder.

Since both PDMS and SiO_2 are clear, moment when all Si is etched away is not so hard to notice. Thermally grown SiO_2 has high internal stress [18] and since PDMS is a rubber elastic polymer, this composite membrane becomes deformed with different patterns [17]. This enables that catching sight when oxide is completely removed and PDMS membrane become flat without any patterns.

Last step in fabrication is separation on single dies. This is done by dicing silicon wafer using ″Tempress GS″, dicing saw, model 602M with ″Disco″ diamond blades. Dicing direction is compatible with ⟨110⟩ direction on {100} Si wafer. Depth of cut is one third of wafer thickness so that single dies have been made by wafer cleveage along cuts. Cutting is performed from the wafer side with PDMS film. During cutting surface of PDMS have been covered with sellotape which serves as protecting film. Sellotape can be easily removed from the non-sticking PDMS leaving clean surface of membrane.

Photography from the metallurgical microscope presenting the cut through Si wafer and PDMS film on it is shown in Figure 1. (h). On the right side, the chip with cavity on which the PDMS membrane was fabricated with spining is mounted with epoxy paste on chip holder rady for bulge test.

2.2. Formation of PDMS membrane by release, transfer and bonding

The PDMS film od desired thicknes was fabricated by spin coating on Si wafer. Since we want to remove PDMS film easy, Si wafer must provide bad adhesion toward applied PDMS film. First step in this fabrication scheme, Figure 2.(a) is obtaining Si surface free of oxide. This is practically impossible when working in air atmosphere [14], but dipping Si wafer in $HF:H_20$=1:10,vol. solution for 40 s, drying in high purity nitrogen gas, and applying immediately prepared mix of PDMS (Sylgard 184, base:curring agent=10:1, wt.%) according to established procedure (b).

Cured PDMS film from wafer surface iz pulled out. It is important not to deform film during realizing. Since the film is very thin and sticky, immersing in water during removing film can be helpful.

PDMS film was transferred to the flat slab from PTFE (Polytetrafluoroethylene) and 2x2 mm^2 square have been cut with scalpel, shown in (c).

PDMS squares would be used as PDMS membranes on manufactured silicon chips with cavity and thin SiO_2 on surface to promote adhesion strength between PDMS film and Si chip.

On separate silicon wafer the uncured PDMS film (Sylgard 184, base:curring agent=10:3, wt.%) had been preapred (d). Uncured PDMS film is prepared on Si surface without oxide (pooar adhesion) by spin coating, and it had very small thickness. PDMS squares were placed on uncured PDMS film and slightely pressed by applying gentle pressure with a tweezer-tip, (e) and photograph (h). PDMS squares quickly pulled out and transfered to prepared surface of oxidized Si chip with cavity. Alignment is relativelly simple, since PDMS squares are transparent and dimenssions are fairly high. As mixed PDMS has a working time of about 2 hours at room temperature and sufficient time is available for soaking and aligning PDMS squares, (f).

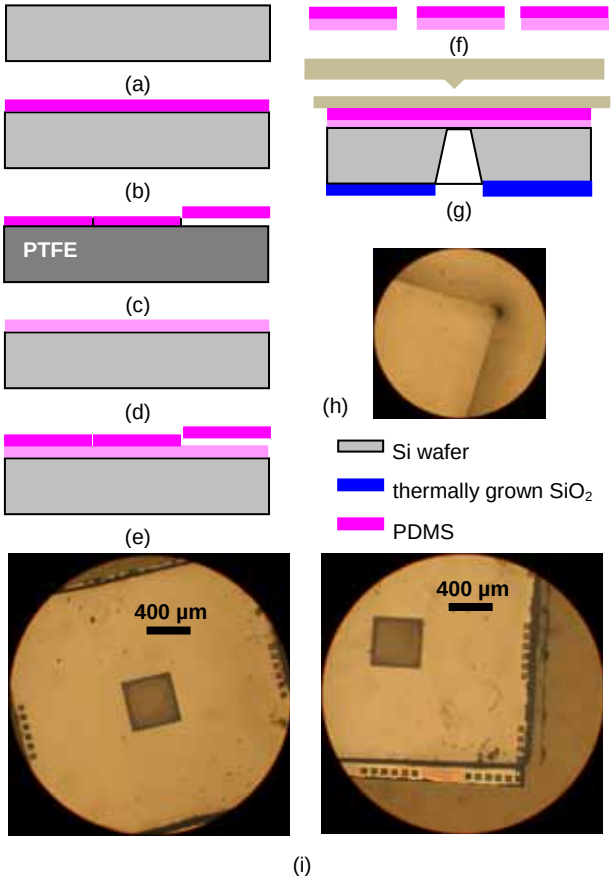


Figure 2. Fabrication sequences of fabrication Si cavity with PDMS membrane fabricated by release, transfer and bonding.

In Figure 2.(i) photographs of bonded PDMS membranes are given. It can be said that PDMS membrane on the left is aligned excellent. Alignment on the chip shown on the right, is not good enough but this chip still be in function.

Final polymerization and bonding of transferred PDMS membrane onto SiO_2 covered Si chip, was done during night. Some load producing pressure of approximately 4,2 Pa, Figure 1.(g), was applied on bonding surfaces.

2.3. Bulge test as method for PDMS membranes characterization

In the past the bulge test has become a standard technique for measuring thin film mechanical properties [20]. The test involves clamping thin film to be tested over an cavity and applying pressure to one side. This test allows determination of different mechanical properties of film, such as film modulus, yield strength, fracture strength and residual stress as well. Many models exist to convert the pressure–displacement experimental data into stress and strain in the film. Since the solutions are based on different bulge shapes and boundary conditions , this test predit soewhat different deformation behaviours. In our case, this test is used to compare PDMS membranes fabricated either by spin coating or bonding transfered membrane.

Single dies have been mounted by epoxy paste on brass holder, Figure 1.(h), which can be connecting to the

nitrogen gas instalation for performing bulge test [12,13,19].

Photograph of the experimental setup that was used to perform bulge testing of PDMS membranes is schematicaly shown in Figure 3. (1) in this figure is sample under testing placed on a special stage connected with gas line, (2) is microscope working in reflected light and it was used to measure the precise deflection of the PDMS membrane deformation, (4) is Automated Pressure Calibrator - APC 600, MENSOR used to set predefined pressure value and to keep it on a set value during the measurements, (5) is nitrogen gas source. Nitrogen is supplied from high pressure cylinder, not shown in this photograph.

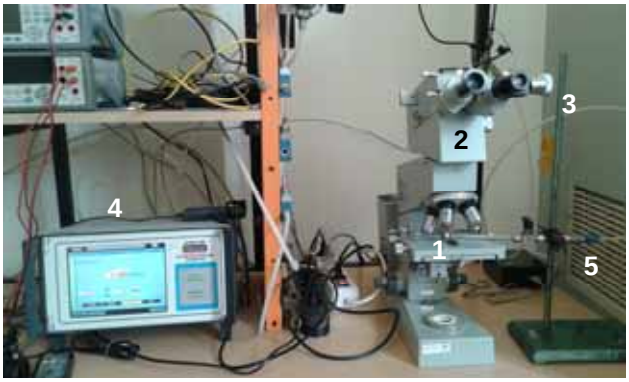
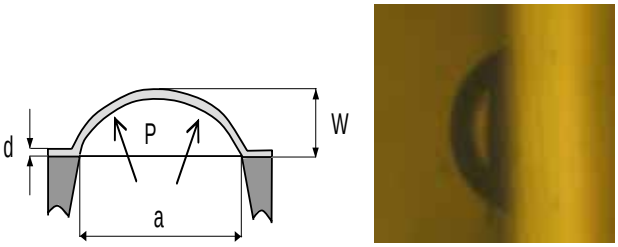


Figure 3. Photograph of an experimental set up to perform bulge test (1) is Si chip with PDMS membrane mounted on brass carrier, (2) is optical microscope in reflected light with measuring capabilities of lateral lengths (3, 4) is APC (automatic pressure calibrator) 600 Mensor and (5) is nitrogen supply from pressurized N_2 cylinder (not shown).

In the next Figure 4(a) schematic of deflected under applied pressure for square membrane is given. Next photograph, Figure 4(b) is what we see in reality during bulge test.



(a) (b)

Figure 4. (a) Schematic diagram of the clamped square membrane with a uniform pressure applied from one side. (b) Photographs showing what we realy see under the microscope. This is square membrane with 400 μm side length pressurized with 4.8 bar.

In this shematic *P* is applied pressure, a is side length of square membrane with the PDMS film thickness *d*. *W* is maximum deflection measured at the centre of the membrane.

3. RESULTS AND DISCUSSION

The membrane properties can be obtained from analyzing the load deflection relation in a pressure bulge experiment. It is a classical mechanics problem to solve this relation for a thin membrane (deflection is larger than the thickness) under uniform pressure. The analytical solution for the deflection problem of a square membrane with an edge length is as follows [12]:

$$P = 13.6\frac{W\cdot d}{a^2}\left(\sigma_o + 1.61\cdot\frac{W^2}{a^2}\cdot\frac{(1.446-0.427\cdot\nu)\cdot E}{1-\nu}\right) \quad (1)$$

This equation can be simplified by introducing geometrical coefficients: C_1=13.6, C_2=1.61 $f(\nu)$=(1.446-0.427·ν):

$$P = C_1\frac{W\cdot d}{a^2}\sigma_o + C_1\cdot C_2\cdot\frac{d\cdot W^3}{a^4}\cdot f(\nu)\cdot\frac{E}{1-\nu} \quad (2)$$

where *P* is pressure applied in bulge test, *W* is the deflection of membrane, a is the side length of the square membrane, d is membrane thickness, σ_o is the residual stress which is already present when there is no deflection of the membrane, *E* is Young's modulus for membrane material and ν is its Poisson's ratio.

To calculate the residual stress (σ_o) on the membrane and Young's modulus of the material, we have to divide both sides of eq. (2) by maximal deflection (w):

$$\frac{P}{W} = C_1\cdot C_2\cdot\frac{d}{a^4}\cdot f(\nu)\cdot\frac{E}{1-\nu}\cdot W^2 + C_1\cdot\frac{d}{a^2}\sigma_o\,. \quad (3)$$

Eq. (3) is a linear one of the form P/W=AW^2+B. A plot of (P/W) versus W^2 gives straight line which slope (A) can be used to calculate the Young's module of the membrane materials, while the intercept (B) is used to calculate the residual stress.

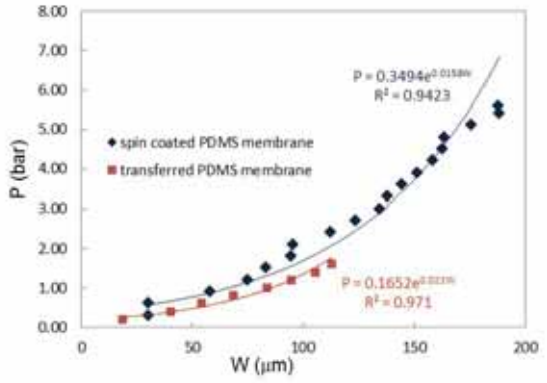


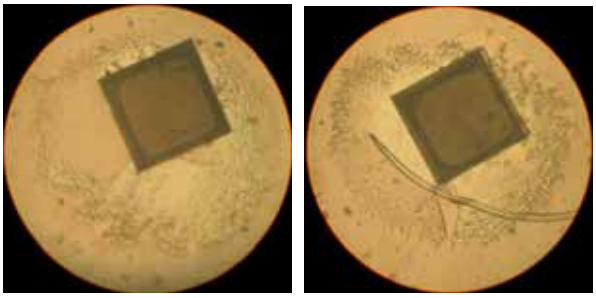
Figure 5. Load-deflection curves for membranes with the same size (400x400 μm^2) and thicknesses (50 μm). Membranes were fabricated either by PDMS spin coating or transfer bonding.

In Figure 5 dependence of the maximum deflection (w) of PDMS membranes (dimensions 400 x 400 μm^2, thickness 50 μm) caused by applied pressure (P) is shown. Results for PDMS membrane fabricated by spin coating and results for membrane obtained by transfer fabrications are given in the same graph.

It is obvious that spin coated membrane supports higher loads and accordingly can tolerate higher applied pressure without leaking. Transferred and bonded membrane with the same dimensions and PDMS thickness, can support

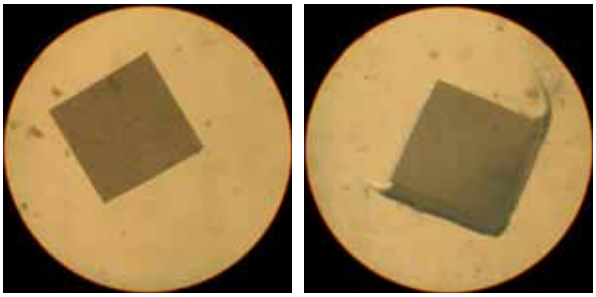
maximum pressure about 2 bar comparing with pressure higher than 5 bar supported by spin coated membrane.

In Figures 6 and 7 microscopic photographs of membranes fabricated by transfer bonding (Figure 6) and spin coated (Figure 7.) after they experienced maximum pressure load before leakage.



(a) (b)

Figure 6. Appearance of PDMS membranes obtained by transfer bonding after maximum pressure load (when membranes started to leak). Both membranes lost their adhesion, and membrane (b) suffered breaking.



(a) (b)

Figure 7. Appearance of spin coated PDMS membrane before bulge experiment (a), and after maximum pressure load, when membrane started to leak.

Main conclusion is lower adhesion force between transfers bonding membrane comparing with spin coated membrane. It seems that transfer bonding membrane explodes under maximum pressure. Spin coated membrane shows small cracks around square orifice edges.

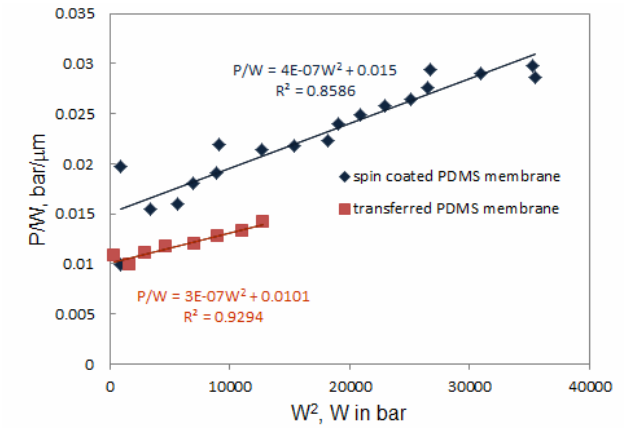


Figure 8. Dependence of P/W on W^2, where P is applied pressure load in bar, and W is maximal deflection in μm, for membranes whose load-deflection curves are given in Figure 5.

In Figure 8, a linear dependence of P/W on W^2 is shown. From these dependences the Young's modulus and residual stress for both membranes are obtained.

The Young modulus for spin coated membrane is 0.93 MPa, and such fabricated membrane has residual stress of 0.35 MPa. For the transfer bonded membrane with the same thickness, the Young's modulus is 0.70 MPa and residual stress is 0.24 MPa. Elastic properties of both membranes are similar. It can be explained with the facts that both membranes are fabricated by the same spin coating process [21]: 5 s spin rate was 500 rpm, next 55 s spin rate was increase to 1000 rpm, which resulted in PDMS membrane thickness of 50μm. During farther processing transferred membrane is somewhat relaxed during releasing from Si substrate and transferring to thin, unpolymerized PDMS film with smaller density fabricated at higher spin rate (3000 rpm).

5. CONCLUSION

This work is about fabrication of PDMS membranes on silicon chip with cavity. Cavities have been microfabricated by Si bulk chemical wet etching. One type of PDMS membrane on Si chips orifice are fabricated by PDMS spin coating on silicon surface with thermal oxide which have been specially treated to obtain good adhesion between PDMS and substrate. Second type of membranes have been fabricated by release spin coted PDMS membrane and farther transfer bonding using uncured PDMS as an adhesive for bonding PDMS to silicon oxide.

Both types of membranes have same thickness, and have been on orifices with the same dimensions.

Membranes elastic properties and adhesion have been investigated by bulge test.

It was shown that spin coated membrane can be pressurized up to 5 bar, and transfer bonded membrane starts to leak on 2 bar applied pressure.

Membranes elastic properties are similar. Second type membrane has smaller residual stress.

These membrane systems envisioned to be used as further microfabricated devices as is, e.g. microfluidic reactor and its components.

ACKNOWLEDGEMENT

This work was funded by the Republic of Serbia – Ministry of Education, Science and Technological Development through the project TR 32008 named: “Micro and Nanosystems for Power Engineering, Process Industry and Environmental Protection – MiNaSyS” and by Integrated Microsystems Austria GmbH – Austrian Center for Medical Innovation and Technology from Wiener Neustadt, Österreich, through the research and development project named “Phase Change Actuator (PCA) for Steering Catheter”.

References

[1] Quake,S.R., Scherer,A.: "*From micro-to nanofabrication with soft materials*", Science, 290(2000), pp. 1536-40.

[2] Rosset,S., Niklaus,M., Dubois,P., Shea,H.R.: "*Metal*

ion implantation for the fabrication of stretchable electrodes on elastomers", Advanced Functioanl Materials, 19(3) (2009), pp. 470-78.

[3] Lötters,J.C., Olthius,W., Veltink,P.H., Bergveld,P., "*The mechanical properties of the rubber elastic polymer polydimethylsiloxane for sensor applications*", Journal of Micromechanics and Microengineering, 7 (1997), pp. 145-47.

[4] Kim,P., Kwon,K.W., Park,M.C., Lee,S.H., Kim, S.M., Suh,K., Yang, "*Soft Lithography for microfluidics: a Review*", BioChip Journal, 2(1) (2008), pp. 1-11.

[5] Karlsson,J.M., Haraldsson,T., Carlborg,C.F., Hansson,J., Russom,A., Wijangaart,W.: "*Fabrication and transfer of fragile 3D PDMS microstructure*", Journal of Micromechanics and Microengineering, 22 (2012) 085009 (9p).

[6] Ryn,K.S., Wang,X., Skaikh,K., Liu,C.: "*A method for precision patterning of silicon elastomer and its applications*", Journal of Microelectromechanical Systems, 13(4) (2004), pp. 568-75.

[7] Sivakumarasamy,R., Nishiguchi,K., Fujiwara,A., Vullaume,D., Clément,N.: "*A simple and inexpensive technique for PDMS/silicon chip alignment with sub-µm precision*", Analytical Methods, 6 (2014), pp.97-101.

[8] Linder,V., Gates,B.D., Ryan,D., Parviz,B., Whitesides,G.M.: "*Water-soluble sacrificial layers for surface micromachining*", Small 1 (2005), pp. 730-36

[9] Cui,J., Zhang,B., Duan,J., Guo,H., Tang,J.: "*Flexible Pressure Sensor with Ag Wrinkled Electrodes based on PDMS substrate*", Sensors, (16) (2016), pp. 2131-40.

[10] Rossat,S., Niklaus,M., Dubois,P., Shea,R.H.: "*Large-stroke dielectric elastomer actuators with ion-implanted electrodes*", Journal of Microelectromechanical Systems, 18(6) (2009), pp.1300-08.

[11] Hua,Z., Xia,Y., Srivannavit,O., Rouillard,J-M., Gulari,E.: "*A versatile microreactor platform featuring chemical-resistant microvalve array for addressable multiplex syntheses and assays*", Journal of Micromechanics and Microengineering, 16 (2016), pp. 1433-43.

[12] Schomburg,W.K.: *Introduction to Microsystem Design*, RWTHedition, Springer-Verlag, Berlin, Heidelberg, 2011.

[13] Yoon,S-H., Reyes-Ortiz,V., Kim,K-h., Seo,Y., h., Mofrad,M.R.K.: "*Analysis of circular PDMS microballons with ultra lage deflection for MEMS design*", Journal of Microelectromechanical Systems, 19(4) (210), pp. 854-64.

[14] Lindros,V., Tilli,M., Lehto,A., Motooka,T.: *Handbook of Silicon Based MEMS Materials and Technologies*, Elsevier Inc., USA, 2010.

[15] Gajasinghe,R.W.R.L., Senveli,S.U., Rawal,S., Williams,A., Zheng,A., Datar,R.H., Cote,R.J., Tiglil,O.: "*Experimental study of PDMS bonding to various substrates for monolithic microfluidic applications*", Journal of Micromechanics and Microengineering, 24 (2014) 075010 (11pp)

[16] http://www.gelest.com,Gelest-Hydrophobicity, hydrophilicity and silane surface modification

[17] Jović,V., Đinović,Z., Radovanović,F., Starčević,M., Lamovec,J., Smiljanić,M.M., Lazić,Ž.: *"Characterization of PDMS membranes fabricated by bulk'micromachining on silicon"*, 6th Internaional Scientific Conference on Defensive Technologies, OTEH 2014, Belgrade, 9-10 October 2014, Proceedings, pp. 674-679.

[18] Yen,J-Y., Hwu,J-G.: "*Enhancement of silicon oxidation rate due to tensile mechanical stress*", Applied Physics Letters, 76(14) (2000), pp. 1834-1835.

[19] Thangawng,A.L., Ruoff,R.S., Swartz,M.A., Glucksberg,M.R.: *An ultra.thin PDMS membrane as a bio/micro-nano interface: fabrication and characterization*, Biomed Microdevices, 9 (2007), pp. 587-95.

[20] Small,M.K., Nix,W.D.: *Analysis of the accuracy of the bulge test in determining the mechanical properties of thin films*, Journal of Materials Research, 7(6) (1992), pp. 1553-63.

[21] Liu,M., Sun,J., Sun,Y., Bock.C., Chen,Q.: "*Thickness-dependent mechanical properties of polydimethylsiloxane membranes*", Journal of Micromechanics and Microengineering, 19 (2009), pp. 035028-32.