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CHARACTERIZATION OF PDMS MEMBRANES FABRICATED BY BULK-MICROMACHINING ON SILICON WAFERS

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Abstract: *In this paper we proposed microfabrication scheme for PDMS (Polydimethylsiloxane) thin membrane fabrication on Si micromachined cavities with square cross section. 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. Mechanical testing of PDMS elastic properties and bond strength between membranes and oxidized Si wafers, were investigated applying pressurized bulge testing In this paper experimentally determined dependence of the PDMS membrane deflection on pressure load for different membrane thicknesses and sizes of square cavities in Si wafers are given. Also, the influence of different types of Si wafer structuring by anisotropic wet chemical etching on membrane bonding strength were considered.*

Keywords: *Polydimethylsiloxane (PDMS), bulk silicon micromachining, silicone elastomer membrane, bulging test, bonding strength*

1. INTRODUCTION

Silicone based materials have been widely used in coatings, sealants and adhesives for different technological fields and industrial applications [1]. Cross-linked Poly(dimethylsiloxane) (PDMS) in particular, is well known for its biocompatibility, good resistance to relatively high temperature, UV light irradiation and chemical attack with highly polar solutions. It is known as a polymer that swells in non-polar solvents [2,3]. It is optically transparent to wavelengths down to near 256 nm.

PDMS is non porous to the liquids but still causes the infiltration phenomenon for gas molecules due to its intrinsic porous nanostructure [4]. The permeability of PDMS with N_2 is 3.1 $cm^3(STP)\cdot cm/(cm^2\cdot s\cdot cm\cdot Hg)$ while with O_2 is even higher [5]. Gas permeability to PDMS is dependant on temperature and on the amount of crosslinking. This characteristic prevents it application in pressure sensors to precise measurements of static gas pressure and can be used only for gas pressure monitoring.

Also, it is hyperelastic polymer [6,7] and can withstand very big distortions without deteriorating and has been extensively used in the field of different microfluidic and micro electro mechanical (MEM) systems. Microfluidic lab on a chip (LoC) device typically encompasses components for fluid flow as channels, valves and micro pumps with PDMS as applied material [8]. Different types of sensors and actuators [9,10] have integrated parts which have been made from this polymer.

In spite of these advantages, the strong hydrophobicity of PDMS surface for some applications seeks activation step

for cleaning or oxidization of PDMS surfaces to render surface hydrophilic and make it suitable for different types of bonding [11].

It is not photo-definable (i. e. not a photoresist) and its patterning for application in MEM devices is typically done using soft lithography [12], different transfer processes accompanying with bonding and debonding PDME film [13] with intermediate films and using different substrates. Integrating and bonding PDMS components to complete systems remains a challenge. Although fabricating for e.g. PDMS membrane is simple, integrating and bonding it to complete system remains a challenge.

It seems that every application of PDMS film needs some knowledge of "know how" having in mind experimental equipment.

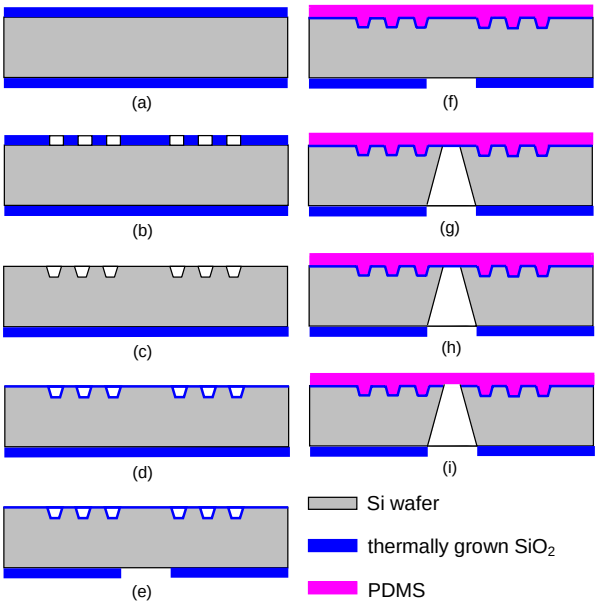
In this paper, a general method for realizing thin film PDMS covering Si cavity with precise feature dimensions, together with PDMS membrane characterization by bulging test is presented.

2. EXPERIMENTAL

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. Process flow diagram is schematically shown on Picture 1. The first step is Si oxidation since SiO_2 is used as masking material during further wet etching. Thick SiO_2 (at least 1.4 μm) has been thermally grown at 1100 °C in atmosphere of water saturated oxygen (a). Oxide from the top side has been lithographically patterned using double side alignment (b). There are three types of patterning. Some elements are flat and some have grooves with or without applied convex corner compensation (CCC) [14]. Fabrication scheme is shown for elements with grooves. Meaning of the grooves is to enlarge contact surface between PDMS membrane and substrate. All orientation alignments of grooves and cavities have been done toward primary flat direction ⟨110⟩ ± 0.5 °C.

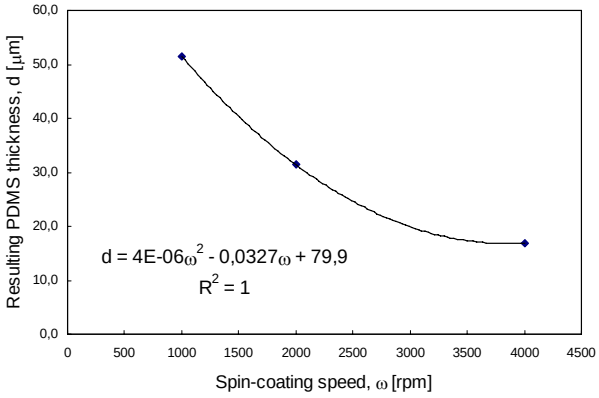
In the step (c) grooves are anisotropic wet etched in 30 wt. % KOH at 80 °C through the SiO_2 mask to the depth of 30 μm. Anisotropic wet etching was carried out in thermostated Pyrex vessel containing about 0.8 dm^3 solution allowing the temperature stabilization within ± 0.5 °C. The vessel is sealed with a screw on lid which included a tape water cooled condenser, to minimize evaporation during etching. During etching, the solution is electromagnetically stirred with 300 rpm and the Si wafers were held vertically inside the solution in wafer holder which protects the wafer's back side and the edge from the etchant solution. After etching completion, the SiO_2 have been removed in buffered oxide solution (BOE, 7 vol. (34.8 wt. % NH_4F):1 vol (6.4 wt. %HF). During oxide removing wafer's back was protected in wafer holder (c).

Wafer with etched grooves were additionally thermally oxidized for a short time till SiO_2 thickness of 0.12 μm have been reached (d). This thin oxide from the side of PDMS membrane is necessary because PDMS has better adhesion on oxidized silicon surface than on the bare one [11].



Picture 1: Fabrication sequence of cavity coated with PDMS membrane. Structure is fabricated by bulk micromachining on {100} oriented Si wafers with cavity edges oriented in ⟨110⟩ direction.

Next step (e) is opening cavity windows in masking material from the bottom side using photolithography and two side alignments. Such prepared wafer was coated with PDMS thin film (f).

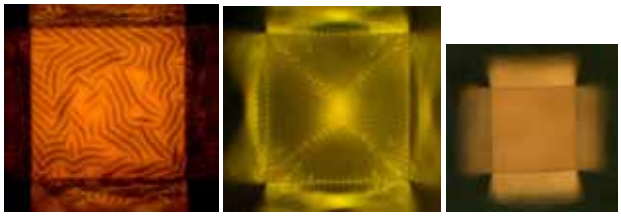


Picture 2: Dependence of the PDMS layer thickness as a function of spin speed for a rotation time 60 s (5 s 500 rpm + 55 rpm).

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) [15]. 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 desicator 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. On Picture 2. experimentally obtained dependence between resulting PDMS thickness and spin-coating speed is shown. Thicknesses are measured after polymerization of PDMS at 100 ^{o}C during 60 minutes at air.



(a) (b) (c)

Picture 3. Photographs from microscope showing the bottom of processed cavities on PDMS coated Si wafer.

(a) PDMS membrane covered with 0.12 μm thin thermally grown SiO_2. **(b)** PDMS membrane covered with thin thermally grown SiO_2 film and so thin, that is transparent, layer of Si from wafer where cavity is not completely etched. **(c)** PDMS membrane where SiO_2 is completely removed.

After preparation of PDMS film on top of Si wafer, cavities have been defined by anisotropic wet etching from the bottom (h). During etching PDMS film was protected in wafer holder. Si wafer is relatively thick, so first step of etching have been performed in 25 wt. % TMAH solution at 80 ^{O}C, and final step in the KOH water solution according to previously described way. Reasons for such selection of etching solutions, is high difference in etching rates of masking material in these two solutions [14].

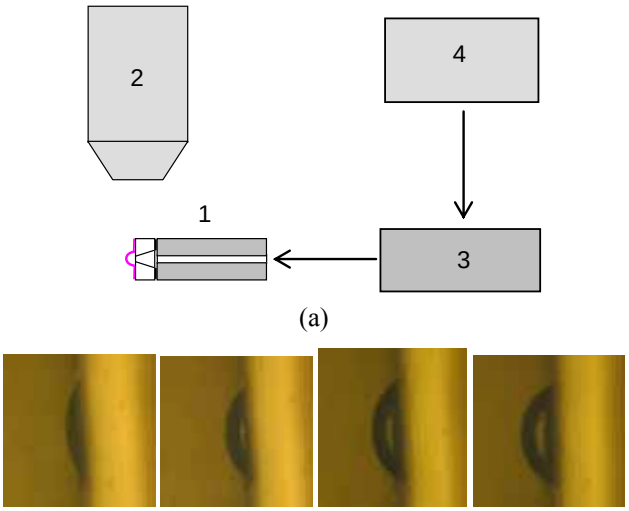
(a) (b) (c)

Picture 4. PDMS membrane on Si cavity: **(a)** Si surface is flat, **(b)** Si surface is corrugated with square grooves, **(c)** same as previous but with applyng CCC to obtain convex corners.

Since both PDMS and SiO2 are clear, moment when all Si is etched away is not so hard to notice. Thermally grown SiO2 has high internal stress [16] and since PDMS is a rubber elastic polymer, this composite membrane becomes deformed as can be seen on Picture 3. During wet anisotropic etching in cavities centers of exposed areas etch with a seemingly lower speed compared with the borders of the areas. This is called notching effect or pillowing [18] and it is seen on Picture 3 (b) for silicon etching.

To remove thin layer of thermally grpwn SiO_2 from the bottom of cavity, wafer is ultrasonicaly chemicaly etched in BOE solution, step (i) on Picture 1. During etching wafer is in holder to protect PDMS film on the top of Si wafer. On Picture 3.(c) is shown microscopic photograph of the realized PDMS membrane closing cavity on Si wafer. On Picture 4. is shown microscopic photograph of PDMS membrane taken from the top of processed Si wafer.

Last step in fabrication scheme 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 film of PDMS leaving clean surface of membrane.



(a)

1.2 mbar 2.7 mbar 3.6 mbar 4.8 mbar

(b)

Picture 5.: Schematic representation of an experimental set up to perform bulge test

(a) 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 is APC (automatic pressure calibrator) 600 Mensor and 4 is nitrogen supply from pressurized N_2 cylinder. **(b)** Photographs taken from microscope during bulge test of PDMS membrane under different pressures. Cavity dimensions on flat Si plane on which PDMS membrane adheres are 400 x 400 μm^2.

Single dies have been mounted by epoxy paste on brass holder which can be connecting to the nitrogen gas instalation for performing bulge test [17].

The experimental setup that was used to perform bulge testing of PDMS membranes is schematicaly shown in Picture 3. (a). 1 on this picture 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, 3 is Automated Pressure Calibrator - APC 600, MENSOR used to set predefined pressure value and to keep it on a set value during the measurements, 4 is nitrogen gas source (high pressure cylinder).

In Picture 3. (b) photographs from the microscope of what is seen during pressurizing PDMS membrane are given. Values of corresponding pressures are given for each deformed membrane.

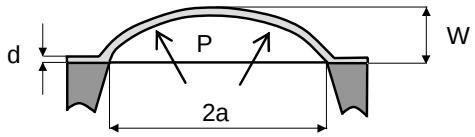
3. RESULTS AND DISSCUSION

The material properties can be obtained from analyzing the load deflection relation in a pressure bulge experiment. It's 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 membranewith an edge length 2a is as follows [19]:

$$P = C_1 \frac{w \cdot d}{a^2}(\sigma_o + C_2 \frac{w^2}{a^2} \cdot \frac{f(\nu) \cdot E}{(1-\nu)}), \qquad (1)$$

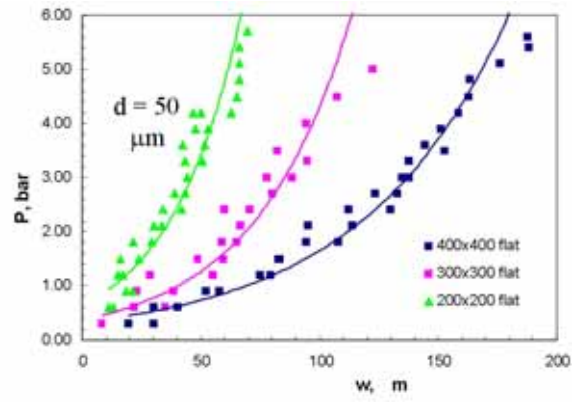
where P is the uniform pressure applied to the membrane, d is PDMS membrane thickness, w is the maximum deflection measured at the center of the membrane, σ_o membrane's residual stress, E its Young's modulus, and ν its Poisson's ratio [19, 20]. The geometrical coefficients C_1, C_2 and $f(\nu)$ for square membranes are 13.6, 1.61 and (1.446-0.427ν) respectively [19].

Schematic of a square PDMS membrane realized in this work is shown on Picture 6.



Picture 6.: Schematic diagram of the membrane with a uniform pressure applied to one side.

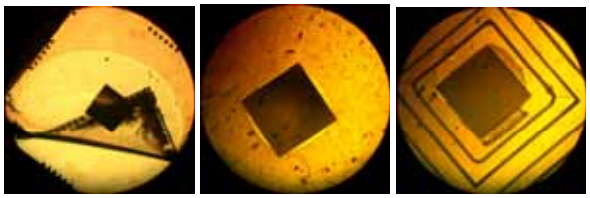
Representative load-deflection experimental data are plotted in Picture 7. The membrane thickness was 50 μm and three different sizes of square membranes, namely 400 x 400 μm^2, 300 x 300 μm^2 and 200 x 200 μm^2 were tested.



Picture 7. Load-deflection curves for square membranes with 50 μm PDMS thickness and with different sizes indicated on the diagram

Within the range of deflections tested, higher deflections were observed for larger membranes under same applied pressure. During pressurizing at high enough pressures the membrane starts to peel of from the substrate. Since the PDMS membranes are extremely flexible and can withstand very high relative strains, improvement of adhesion between PDMS and SiO_2 coated Si wafer is necessary if we want to apply this kind of membranes at higher pressures. Membranes can be reproducibly loaded and unloaded without showing any hysteresis.

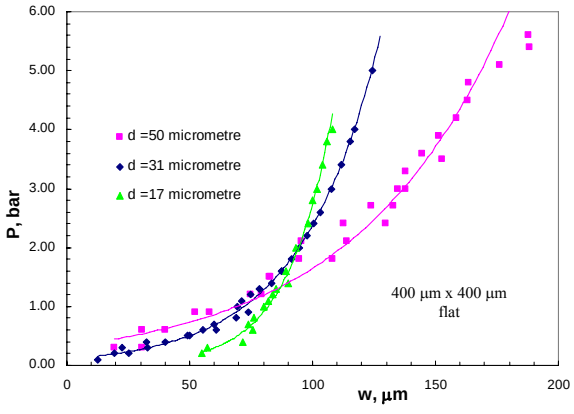
In Picture 8. are shown PDMS square membranes after their adhesion with substrates are destroyed under the influence of high applied pressure.



(a) (b) (c)

Picture 8. Photographs from microscope (first is under two times smaller magnification) of 400 x 400 μm^2 PDMS membranes 50 μm thick, after they lost adhesion with substrate under the applied pressure.
(a) membrane on the flat Si substrate which is partially blow up,
(b) more common case where membrane lost it adhesion around cavity perimeter,
(c) same as in (b), but membrane peeling is stopped on substrate corrugations.

In Picture 9. Dependence of the maximum deflection (w) of PDMS membranes (dimensions 400 x 400 μm^2, flat substrate) with thicknesses of 50, 31 and 17 μm, caused by applied pressure (P) is shown. It can be seen that below the pressure of 1,5 bar, thicker membranes have smaller deflections. Above this pressure opposite is truth according with experimental results.

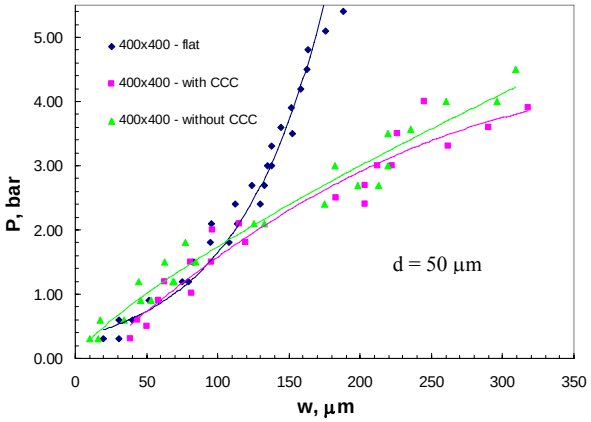


Picture 9. Load-deflection curves for square PDMS membranes (400 x 400 μm^2) with different thicknesses

To explain obtained resistance to deformation of PDMS membranes as a function of thickness, dependence of mechanical properties of PDMS (e.g. Young's modulus) and internal stress in the membrane must be considered [22,23]. Mechanical properties are strongly dependant on

the status of cross-linked networks in polymer chains of PDMS. Fabrication method, especially coating substrate with PDMS membrane material on spin-coater with grate angular velocity produce greater shear stress in material which is not cross-linked and more pronounced to deformation, stretching and breaking of polymer chains.

Since PDMS is very sticky and viscous, extensive mechanical work must be applied during membrane fabrication and achieving desired cross-linked networks and the resulting PDMS structure which enhance desired properties.



Picture 10. Experimental results on the measured maximum deflection (w) as a function of applied pressure (P) for square membrane with 400 x 400 µm^2 dimensions and 50 µm PDMS thickness for membranes fabricated on flat Si substrate, and Si substrates with purposely made corrugations with or without convex corners compensations

Diagram with experimental results on Picture 10. compares load - deflection properties of square PDMS membranes (400 x 400 µm^2), with the same membrane thickness, fabricated on the flat substrate and two types corrugated substrates, with and without CCCs. It should be noticed that below approximately 2 bar, membranes on all kinds of surfaces have the same deflection. Above this pressure it is clearly apparent that membranes on corrugated substrates exhibited larger deflections. To explain this, we need further studies on investigation of internal stress influence on membrane mechanical properties. Also we must consider in our further studies the mode of loosing adhesion of pressurized membranes. It seems that there are micro leeks along the bonded surfaces of PDMS and oxidized silicon wafers. In [24] authors reported the average bond strength for PDMS (mixing ratio 10:1, cured at room temperature for 48 hours, thickness 30 µm) on Si with thermally grown SiO_2 of 2,4 bar.

4. CONCLUSION

In this paper microfabrication of square PDMS (Polydimethylsiloxane) membranes with different thicknesses have been presented. PDMS is fabricated from Sylgard 184 (Dow Corning, USA) silicone elastomer base and silicone elastomer curing agent, volume ratio 10:1. Curring temperature was 100 ^oC, and curing time 10 min. The fabrication process is based on applying bulk silicon wet etching for cavities fabrication and spining uncured material to obtain PDMS membrane. Cavities are oriented on ⟨110⟩ direction on {100} oriented Si wafers.

Membranes on three types of silicon wafer surfaces are investigated: membranes on flat surfaces and membranes on two types corrugated surfaces (with and without convex corners compensations).

Testing of membrane mechanical properties are performed by bulge testing.

Experimental results for load – deflection dependances for square membranes of different sizes and thicknesses are given. Also, bonding strenght and deflection properties of membranes fabricated on flat and corrugated silicon surfaces are compared.

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REFERENCES

[1] Moretto, H., Schulze M., Wagner G., *Silicones in Ullmann's Encyclopedia of Industrial Chemistry*, Wiley-VCH, Weinheim, 2005.

[2] Ortiz, G. C., "The study Of polydimethylsiloxane (PDMS) thin-film surface roughness properties and its resistance in elevated temperature and UV light resistant applications", *Proceedings of The National Conference On Undergraduate Research (NCUR)*, Ithaca College, New York, March 31-April 2, 2011.

[3] Lee, J. N., Park, C., Whitesides, G. M., "Solvent Compatibility of Poly(dimethylsiloxane)-Based Microfluidic Devices", *Anal. Chem.,* 75 (2003) 6544-6554.

[4] Yang, L-Y., "On gas permeation in PDMS", J. Micromech. Microeng. 20 (2010) 115033 (7pp).

[5] Boscainia, E., Alexanderb, M. L., Prazellerb, P.,. Märk, T. D., "Investigation of fundamental physical properties of a polydimethylsiloxane (PDMS) membrane using a proton transfer reaction mass spectrometer (PTRMS)", *Int. J. of Mass Spec.*, 239, (2004) 179–186.

[6] Schneider, F., Fellner, T., Wilde, J., Wallrabe, U., "Mechanical properties of silicones for MEMS", *J. Micromech. Microeng.*, 18 (2008) 065008 (9pp).

[7] Löttersy, J. C., Olthuis, W., P H Veltink, P. H., Bergveld, P., "The mechanical properties of the rubber elastic polymerpolydimethylsiloxane for sensor applications", *J. Micromech. Microeng.*, 7

(1997) 145–147.

[8] Eddings, M. A., Gale, B. K., "A PDMS-based gas permeation pump for on-chip fluid handling in microfluidic devices", J. Micromech. Microeng. 16 (2006) 2396–2402.

[9] Kudo, H., Sawada, T., Kazawa, E., Yoshida, H., Iwasaki, Y., Mitsubayashi, K., "A flexible and wearable glucose sensor based on functional polymers with Soft-MEMS techniques", *Biosensors and Bioelectronics* 22 (2006) 558–562.

[10] Rodríguez G. A. A., Rossi, C., Zhang, K., "Multi-physics system modeling of a pneumatic micro actuator", *Sensors and Actuators A*, 141 (2008) 489-498.

[11] Gajasinghe, R. W. R. L., Senveli, S. U., Rawal, S., Williams, A., Zheng, A., Datar, R. H., R J Cote, R. J., Tiglil, O., "Experimental study of PDMS bondingto various substrates for monolithicmicrofluidic applications", *J. Micromech. Microeng.,* 24 (2014) 075010 (11pp)

[12] Kim, P., Kwon, K. W., Park, M. C., Lee, S. H., Kim, S. M., Suh, K. Y., "Soft Lithography for Microfluidics: a Review", *Biochip Journal*, 2(1) (2008), 1-11.

[13] 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) 587-595.

[14] Jović, V., Lamovec, J., Mladenović I., Smiljanić M. M., Popović, B., "Prevention of convex corner undercutting in fabrication of silicon microcantilevers bz wet anisotropic etchnig", *Proc. 29th International Conference on Microelectronics* Belgrade, Serbia, 12-14 May (2014) 163-166.

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

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

[17] Small, M. K., Nix, W. D., "Analysis of the accuracy of the bulge test in determining the mechanical properties of thin films", *J. Mater. Res.,* 7(6) (1992) 1553-1563.

[18] Madou, M., *Fundamentals of microfabrication*, CRC Press, Boca Raton, FL, 1997.

[19] Schomburg, W., K., *Introduction to microsystem design*, Springer, 2011.

[20] Thangawng A., L., Rouff R., S., Swartz M., A., Glucksberg M., R., "An ultra-thin PDMS mambrane as a bio/micro-nano interface: fabrication and characterization", *Biomed Microdevices*, 9 (2007) 587-595.

[21] Klein, E., *Mathematical Methods in Theoretical Economics*, Academic Press, New York, 1973.

[22] Liu, M., Sun, J., Sun, Y., Bock, C., Chen, Q., "Thickness-dependent mechanical properties of polydimethylsiloxane membranes", *J. Micromech. Microeng*., 19 (2009)035028 (4pp).

[23] Lötters, J., C., Olthuis, W., Bergveld, P., "The mechanical properties of the rubber elastic polymer polydimethylsiloxane for sensor applications", *J. Micromech. Microeng.*, 7 (1997), 145-147.

[24] Gajasinghe, R., W., R., L., Senveli, S., Rawel, S., Williams, A., Zheng, A., Datar, R., H., Cote, R., J., Tigli O., Experimental study of PDMS bonding to various substrates for monolithic microfluidic applications, *J. Micromech. Microeng.*, 24 (2014) 075010 (11 pp).