

Surface functionalization of silicone rubber for permanent adhesion improvement

Siliconelastomere werden aufgrund ihrer hervorragenden mechanischen Eigenschaften, ihrer Beständigkeit gegenüber Temperaturschwankungen, UV-Strahlung, Chemikalien oder wässrigen Medien in sehr vielen Bereichen der Wirtschaft eingesetzt, zunehmend auch in modernen Technologien wie der Mikrofluidik, der Softlithographie oder der Mikroelektronik. Ein entscheidender Nachteil der Silicone in Kombination mit anderen Materialien sind ihre schlechten Adhäsionseigenschaften bedingt durch die niedrige freie Oberflächenenergie und durch das Fehlen reaktiver Gruppen in der Oberflächenregion. Bekannt ist, dass durch eine Niederdruckplasmabehandlung, die Sauerstoff oder Ammoniak als Prozessgase verwendet, zwar Silicone mit hydrophilen Oberflächeneigenschaften erzeugt werden können, dieser Effekt aber nicht über einen längeren Zeitraum stabil ist. Basierend auf einem besseren Verständnis der Mechanismen, die zum Verlust der Oberflächenaktivität führen, wurden neue Strategien entwickelt, um funktionalisierte Siliconschichten mit maßgeschneiderten, langzeitstabilen Oberflächeneigenschaften auszustatten. Die Gültigkeit des Konzeptes wurde am Beispiel der Haftung zwischen Siliconschichten, die im Siebdruckverfahren auf Siliciumwafern hergestellt wurden, und einem photostrukturierbaren Epoxidharz getestet.

Introduction

Poly(dimethyl siloxane) (PDMS, commonly called silicone rubber) is one of the most important high-performance polymers. Besides the favorable properties of PDMS, such as excellent flexibility, durability [1, 2], and high thermal and oxidative stability [2-4], the application of PDMS is limited by its low surface free energy of about $20 \text{ mJ}\cdot\text{m}^{-2}$ [5] and the lack of reactive surface groups, causing poor adhesion joints. Additionally, the relatively high amount of low-molecular weight constituents affect the adhesion of PDMS to other materials. These constituents have a high mobility in the polymer bulk and the tendency to migrate to the PDMS surface [6, 7].

Low-pressure (low-temperature) plasma treatments [8-12], corona discharge treatments [13] and UV-eximer irradiation [3, 14] were applied to modify the PDMS surface by the introduction of functional groups, whereas the bulk composition and properties of the polymer were kept constant. Freshly modified PDMS surfaces show good or moderate wettability by polar liquids, which is a necessary (but not sufficient) requirement for good adhesion. However, this modification effect is not permanently stable and the hydrophilic PDMS surface regains its hydrophobicity partially or completely over time. This well-known phenomenon is called *hydrophobic recovery* [10-12, 15]. It is usually explained by the reorientation of polar groups from the surface to the bulk phase or the reorientation of nonpolar groups from the bulk to the outermost surface and by the diffusion of low-molecular weight silicone fluid from the bulk to the surface [9]. The high mobility of the PDMS chains causes a particularly pronounced *hydrophobic recovery* at a rather short time scale. The *hydrophobic recovery* effect is connected with the loss of wettability and surface reactivity.

Keywords

surface functionalization
poly(dimethyl siloxane)
plasma treatment
hydrophobic recovery
poly(ethylene-*alt*-maleic anhydride)
adhesion
epoxy resin coating

Bearbeiter

K. Grundke
J. Roth
V. Albrecht
M. Nitschke
C. Bellmann
F. Simon
D. Pleul
S. Zschoche
S. Michel
B. Voit

Förderer

Qimonda Dresden GmbH & Co.
OHG
Sächsisches Ministerium für
Wirtschaft und Arbeit
Europäischer Fond für Regionale
Entwicklung

Kooperation

Dr. C. Luhmann
Qimonda Dresden GmbH & Co.
OHG
Dr. M. Schneider, Dr. J. Gehrke
Institut für Korrosionsschutz
Dresden GmbH

Initially stable joints or composites lose their mechanical strength, delaminate, or rupture. To avoid this undesirable behavior efforts were focused on the stabilization of the modified PDMS surfaces.

One promising concept is a two-step modification. At first the PDMS is plasma-treated. In a second step, the surface functionalities introduced by the plasma treatment can act as anchors for a subsequent *grafting from* procedure. In this case, monomers (acrylic and methacrylic acid, glycidyl methacrylate, 2-hydroxyethyl methacrylate, acrylonitril) can be radically polymerized on the functionalized PDMS surface [16-18]. Instead of monomers polymers can also be used to graft them covalently onto the functionalized PDMS surface (*grafting to* procedure) [19].

Here we describe a route to design a stable surface functionalization of PDMS layers that is based on the surface activation by oxygen or ammonia plasma treatments and a subsequent grafting of a thin copolymer layer [20].

To study the effect of the surface modification on the surface properties of the PDMS, we used a combination of various surface-sensitive characterization techniques including X-ray photoelectron spectroscopy (XPS), contact angle, electrokinetic, and roughness measurements.

The influence of the surface modification of PDMS to form stable adhesion joints was investigated with respect to the adhesion of an epoxy resin on the modified PDMS surface.

Design of a stable surface functionalization of PDMS materials

Our approach to design a stable surface functionalization of PDMS materials is outlined in Scheme 1. In the first step, the PDMS surface is activated by oxygen or ammonia plasma treatment.

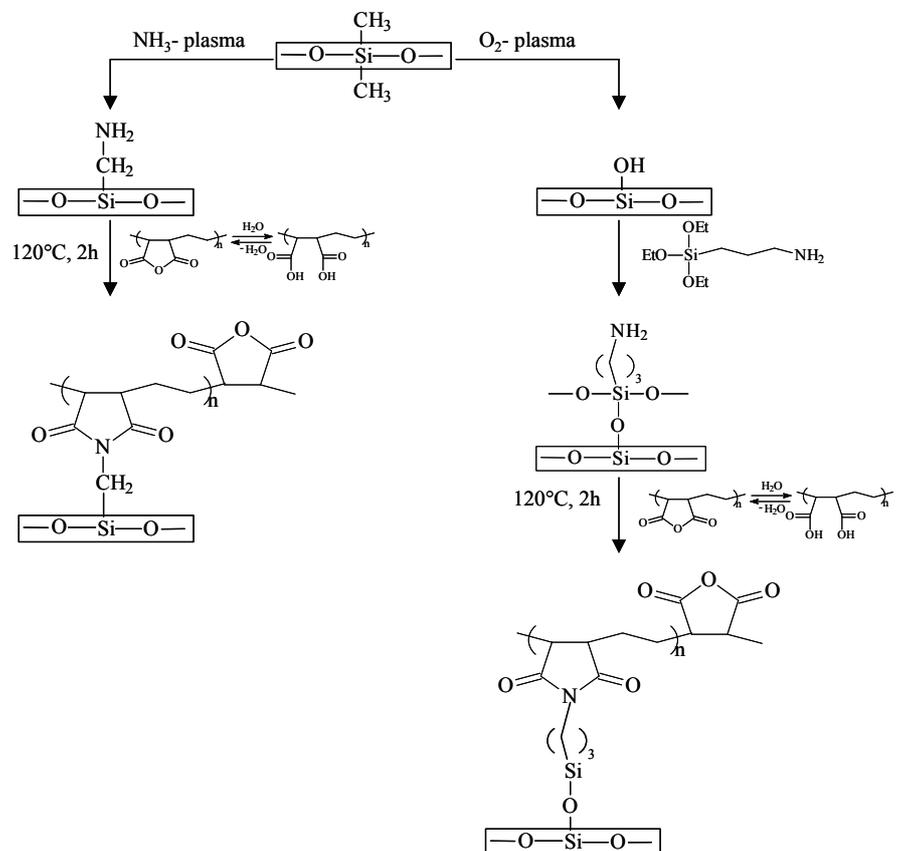


Fig. 1:
Scheme of the grafting procedure of poly(ethylene-alt-maleic anhydride) (PEMA) on plasma-treated PDMS surfaces

For the anchoring of PEMA copolymers by the grafting-to technique, primary amino groups are required at the PDMS surface. They can be created directly by an ammonia plasma treatment. The second route uses oxygen plasma and 3-aminopropyltriethoxysilane (γ -APS) as an adhesion promoter. Outstanding silanol groups (Si-OH) obtained by the oxygen plasma treatment of PDMS should be able to react with γ -APS. The attachment of γ -APS provides primary amino groups for a further modification with PEMA. The primary amino groups can react with the anhydride group of the PEMA copolymer at elevated temperature (120 °C) by the formation of imide bonds. It is assumed that the covalently bonded PEMA top layer contains free, non-bonded, reactive anhydride functionalities for further reaction with an epoxy resin. To validate this concept, the surface properties of the PDMS screen-printed layers were characterized after each modification step.

Surface properties of plasma-treated PDMS samples

The first step in our procedure is the plasma treatment of the PDMS samples. It comprises the generation of reactive surface groups required for further modification steps.

In the case of an *oxygen plasma treatment*, a significant amount of reactive silanol groups can only be created if high doses of an oxygen plasma are applied. Under these conditions, numerous reactive silanol groups are generated, but the surface functionalization is overlapped by strong PDMS degradation processes resulting in the formation of low-molecular weight PDMS species. These oligomers have a high molecular mobility and can easily segregate to the sample surface over time. Furthermore, a high density of silanol groups propagates their condensation to Si-O-Si bridges and a silica-like surface layer can be formed.

Fig. 2a shows the zeta potential as a function of the pH of aqueous KCl solutions for untreated and oxygen plasma treated PDMS surfaces. PDMS samples treated with an oxygen plasma show isoelectric points ($\text{iep} = \text{pH}|_{\zeta=0}$) smaller than the iep of the untreated PDMS sample.

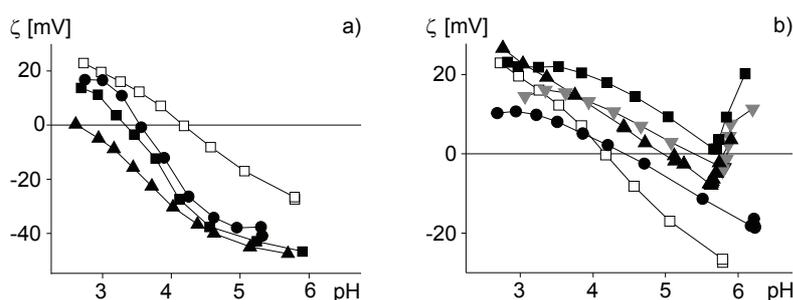
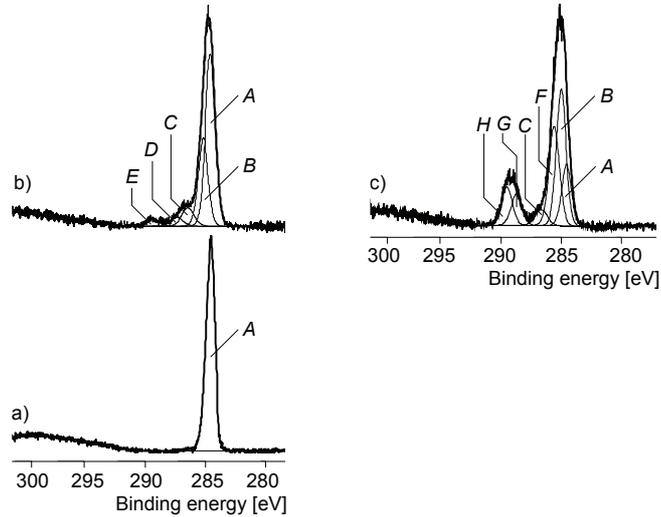


Fig. 2: Zeta-potential of untreated and differently plasma-treated PDMS samples as a function of pH of an aqueous $1 \cdot 10^{-3} \text{ mol} \cdot \text{l}^{-1}$ KCl solution. a) untreated PDMS sample (\square), oxygen plasma-treated sample at 100 W for 15 s (\bullet), oxygen plasma-treated sample at 300 W for 15 s (\blacksquare), and oxygen plasma-treated sample at 600 W for 15 s (\blacktriangle). b) untreated PDMS sample (\square), ammonia plasma-treated sample at 7 W for 120 s (\bullet), ammonia plasma-treated sample at 7 W for 600 s (\blacktriangledown), ammonia plasma-treated sample at 10 W for 120 s (\blacktriangle), and ammonia plasma-treated sample at 10 W for 300 s (\blacksquare).

According to Stern's theory of the electrochemical double layer [21], the iep can be considered as the pH value of the solid surface, that means it is a measure for the number of functional surface groups providing hydronium ions during its dissociation. In the case of oxygen plasma treatments, the Brønsted acid groups can be silanol and carboxylic acid groups. The high-resolution C 1s spectrum of the XPS measurements showed that the number of carboxylic acid groups is rather small (Fig. 3b).

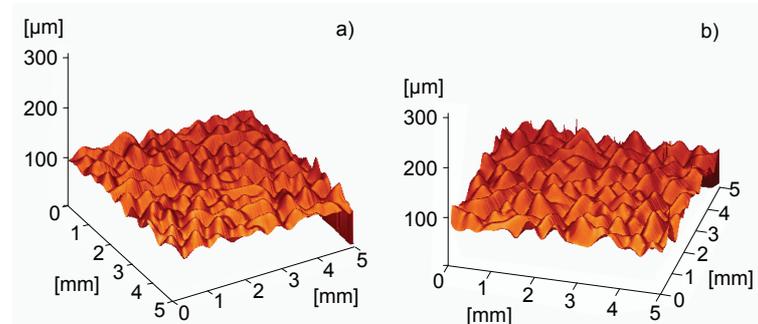
Fig. 3:
C 1s XPS spectra of untreated (a) and (b) oxygen plasma-treated PDMS. The plasma treatment was carried out at a plasma power of 600 W and a treatment time of 15 s. The main component peak A results from intact Si-C bonds. A slightly shifted component peak B shows the presence of saturated hydrocarbons C_xH_y, which are deposited on the PDMS surface by the plasma process. The component peaks C, D, and E show the presence of oxygen-containing functional groups, having C-OH or C-O-C bonds (C), keto groups (C=O, D) and carboxylic groups (O-C=O, E). (c) C 1s spectrum obtained for a PEMA layer grafted onto an ammonia plasma-treated PDMS sample.



Hence, the strong iep shift is mainly caused by silanol groups. These surface groups also contribute to the increased oxygen content in the plasma-treated PDMS surface region [cf. 20]. The higher the plasma power during the oxygen plasma treatment the higher is the iep shift to lower pH values indicating an increase in the number of surface silanol groups (Fig. 2a). These surface groups can be used as anchoring sites for a subsequent functionalization with γ -APS.

Table 1 shows that the functional surface groups generated by the oxygen-plasma treatment significantly decrease the advancing and receding water contact angles on PDMS surfaces. On the untreated PDMS surface, a mean advancing water contact angle θ_{adv} of $116.6^\circ \pm 1.3^\circ$ was measured which is in good agreement with values measured by other authors on such surfaces (e.g., ref [16], $\theta_{adv} = 115^\circ \pm 3^\circ$). These high water contact angles indicate that the pendant methyl groups in PDMS are closely packed at the solid/ air interface. As the main reason for the low receding contact angle of $\theta_{rec} = 44.8^\circ \pm 0.8^\circ$ and, hence, the high contact angle hysteresis ($\Delta\theta = |\theta_{adv} - \theta_{rec}|$), the roughness of the screen-printed PDMS layers was considered. Fig. 4 shows typical images of the surface topography using an optical device (MicroGlider). The vertical roughness values were found to be in the order of several micrometers and were not changed by the oxygen-plasma treatment.

Fig. 4:
Typical images showing the surface roughness of an unmodified screen-printed PDMS layer (a) and an oxygen plasma-treated PDMS layer (b, plasma power 600 W; treatment time 15 s) recorded by the MicroGlider (image size 5 x 5 mm²). The mean roughness parameter R_a was found to be 4.6 μm for the untreated and 4.1 μm for the plasma-treated PDMS sample using a scan size area of 5 x 5 mm².



For such high roughness values, the measured contact angles may not reflect thermodynamically meaningful contact angles that can be applied in conjunction with Young's equation to calculate the surface free energies (γ_{sv}) of the differently treated PDMS surfaces. Nevertheless, the contact angle values seem to be useful to quantify changes in the hydrophobicity/hydrophilicity of the sample surfaces caused by the plasma treatments (Table 1).

PDMS sample	plasma power / treatment time	$t_s = 0$ $\theta_{adv} / \theta_{rec}$	$t_s = 1$ d $\theta_{adv} / \theta_{rec}$	$t_s = 7$ d $\theta_{adv} / \theta_{rec}$
untreated		117° / 45°		
oxygen plasma	100 W / 15 s	38° / 22°	69° / 50°	81° / 55°
	300 W / 15 s	42° / 32°	53° / 39°	68° / 55°
	600 W / 15 s	26° / 15°	74° / 41°	96° / 53°
	600 W / 60 s	0° / 0°	74° / 41°	103° / 75°
ammonia plasma	7 W / 120 s	98° / 70°	102° / 71°	105° / 67°
	7 W / 600 s	64° / 23°	68° / 24°	78° / 37°
	10 W / 120 s	86° / 45°	87° / 49°	97° / 47°
	10 W / 300 s	62° / 31°	62° / 35°	72° / 45°

Table 1: Advancing (θ_{adv}) and receding (θ_{rec}) water contact angles determined on PDMS surfaces before (indicated by plasma power = 0 and treatment time = 0) and after their oxygen and ammonia plasma treatments and the contact angle changes in dependence on the sample storage time in air (t_s)

The decrease in the contact angles of the oxygen plasma-treated PDMS samples depends on the plasma power and the treatment time (Table 1). After an intensive oxygen plasma treatment (600 W for 60 s) the sample surface is completely wetted by water. In the other cases, the oxygen plasma treatment results in low advancing and receding contact angles and in a small contact angle hysteresis. From these results it can be concluded that the polar oxygen containing surface groups mainly control the wetting behavior. The increase of the water contact angle with time is typical of the so-called *hydrophobic recovery* of the PDMS surface. Table 1 shows that the rate and the degree of the hydrophobic recovery can be controlled by the plasma treatment conditions. The higher the plasma power and the longer the treatment time, the higher was the driving force to achieve the original hydrophobicity after a certain storage time. This loss of the plasma modification effect of the PDMS samples is a drawback for the fabrication of long-time stable composites or adhesive joints, because it requires a fast application of the pre-treated samples. There is a permanent risk that low-molecular weight PDMS species segregate to the interfaces and initiate failures.

Ammonia plasma treatments were successfully carried out in a pulsed mode which can be considered as rather mild process conditions [20]. XPS measurements showed that the ammonia plasma introduces nitrogen-containing functional groups in the PDMS surface. The nitrogen content could be increased either by increasing the treatment time or the plasma power. As the number of the primary amino groups cannot be directly determined from XPS measurements labeling reactions with trifluoromethyl benzaldehyde (TFBA) were carried out. It was found that the fraction of primary amino groups relative to the total nitrogen content was rather low, between 9 % and 20 %. A plasma power of 7 W and a treatment time of 600 s were the most favorable conditions for introducing a maximum number of amino groups into the PDMS surface.

In addition, the generation of the basic amino groups can be proved by zeta-potential measurements. After ammonia plasma treatments the isoelectric points are shifted to higher pH values indicating the introduction of Brønsted basic groups into the surface region of PDMS samples (Fig. 2b).

At pH values around 6 the functions $\zeta = \zeta(\text{pH})$ seem to be discontinuous. The charge reversal from positive to negative zeta-potential values can only be explained by the partial dissolution of the functionalized surface layer under the applied shear field of the streaming liquid. The decrease of the pH values causes an increase of the protonation degree of the amino groups. The enrichment of positive charges also increases the solvation of the highly functionalized polymer chains which are not strongly anchored in the PDMS surface region (*weak boundary layer*). Hence, amine-functionalized polymer chains are removed from the PDMS surface, while polymer chains having a lower functionalization degree remain in the PDMS surface region. The further protonation results in isoelectric points which are always higher than the iep measured for the untreated PDMS sample.

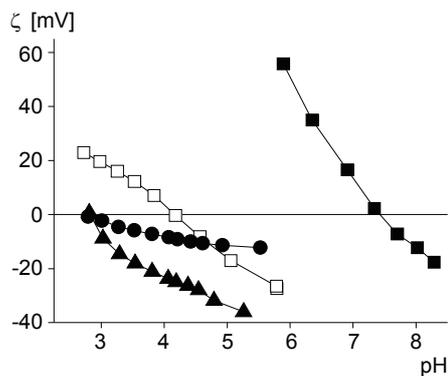
Table 1 shows that the functional surface groups introduced by the ammonia plasma treatment also decrease the advancing as well as receding water contact angles on the PDMS surfaces. In the case of the ammonia plasma, less hydrophilic PDMS surfaces were generated compared to the oxygen plasma treatment.

From these investigations, it can be concluded that oxygen and ammonia plasma treatments result in PDMS surface functionalizations that increase the wettability and reactivity of these surfaces. However, the plasma modification effects were temporarily and mechanically instable. It was, therefore, of great interest to develop strategies for a permanent modification of PDMS surfaces.

Surface properties of PEMA layers grafted onto plasma-treated PDMS surfaces

The silanol and amino functional groups, which have been introduced by the plasma treatments, were subsequently used to graft a thin top layer of PEMA copolymer on the PDMS surface which can act as a barrier to avoid the surface segregation of low-molecular weight species from the PDMS bulk (Fig. 1). Whereas PEMA copolymers can be directly grafted onto amino-functionalized plasma-treated PDMS surfaces, PDMS surfaces with plasma-generated silanol groups require γ -APS as an adhesion promoter for the grafting-to procedure with PEMA. γ -APS is able to react directly with the silanol groups. The attachment of γ -APS provides primary amino groups for imide formation with PEMA. The grafting of γ -APS onto the oxygen plasma-treated PDMS surface introduces numerous amino groups shifting the isoelectric point to a higher value (iep ≈ 7.4 , Fig. 5)

Fig. 5:
Zeta-potential of untreated and differently plasma-treated PDMS samples grafted with PEMA, γ -APS, and γ -APS/PEMA in dependence on pH values of an aqueous $1 \cdot 10^{-3}$ mol.l⁻¹ KCl solution; untreated PDMS sample (\square), ammonia plasma-treated at 7 W for 600 s and grafted with PEMA-h (\bullet), oxygen plasma-treated at 600 W for 15 s and grafted with γ -APS (\blacksquare), and oxygen plasma-treated at 600 W for 15 s and grafted with γ -APS and PEMA-h (\blacktriangle).



The grafted layer remains stable under the shear stress during the electrokinetic experiment which confirms the assumption that covalent bonds are formed between the modified PDMS layer and the γ -APS network. After the subsequent grafting-to procedure with PEMA the iep is significantly lowered. Primary amino groups of the γ -APS are involved in the formation of imide and amide groups and are no longer available for the protonation in acidic solutions. Furthermore, PEMA contains non-reacted maleic anhydride groups, which undergo hydrolyzation reactions producing carbonic acid groups of moderate acidity. The advancing dissociation of those groups with decreasing pH values of the aqueous solution contributes to the negative surface charge shifting the iep to lower values.

The direct grafting of PEMA onto the ammonia plasma-treated PDMS surfaces shifts the iep to the same value that was observed for the γ -APS/PEMA modified PDMS surface (Fig. 5). This indicates that the electrokinetic properties are widely determined by the outermost PEMA layer, while the accessibility of the amino groups for protonation is prevented by their involvement into the covalent binding to PEMA or their shielding by the grafted polymer layer. While the iep of the grafted PEMA layers are identical there is a difference in the course of the zeta-potential versus pH curves (Fig. 5). The absolute values of the zeta-potential are lower when PEMA was grafted on ammonia plasma-treated PDMS surfaces compared to γ -APS/PEMA modified PDMS surfaces. The lower zeta-potential values are an indication for a more hydrophilic PEMA surface. The comparison with the contact angle measurements confirms this assumption (Table 2).

PDMS sample	plasma power/ treatment time	$t_s = 0$ $\theta_{adv} / \theta_{rec}$	$t_s = 1$ d $\theta_{adv} / \theta_{rec}$	$t_s = 7$ d $\theta_{adv} / \theta_{rec}$
ammonia plasma + PEMA-h ^(a)	7 W / 600 s 10 W / 120 s	64° / 21° 75° / 24°	55° / 18° 64° / 20°	59° / 18° 68° / 19°
oxygen Plasma + γ -APS	600 W / 15 s	85° / 33°	96° / 40°	104° / 71°
oxygen plasma + γ -APS + PEMA-h ^(a)	600 W / 15 s	80° / 20°	79° / 19°	81° / 20°

Tab. 2:
Advancing (θ_{adv}) and receding (θ_{rec}) water contact angles measured on plasma-treated PDMS surfaces grafted with PEMA, γ -APS and γ -APS/PEMA and their changes in dependence on the sample storage time in air (t_s).
^(a) The PEMA surfaces were hydrolyzed before the contact angle measurements with water [20].

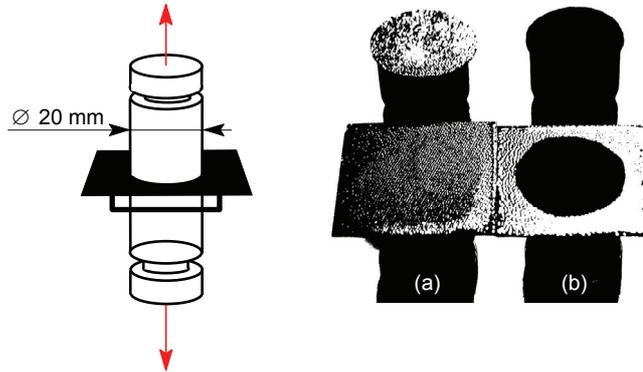
The differences in the hydrophilicity/hydrophobicity of the grafted PEMA layers can be explained by the different amount of primary amino groups available for the grafting-to procedure. In the case of the ammonia plasma-treated PDMS surface, less amino groups are available for the covalent reaction with maleic anhydride groups (cf. Fig. 2 and 5). Hence, the grafted PEMA contains non-reacted maleic anhydride groups that render the PEMA hydrophilic. When the PEMA is grafted onto γ -APS modified PDMS a higher amount of primary amino groups are available for the reaction so that less non-reacted maleic anhydride groups remain in the PEMA layer rendering the surface less hydrophilic. The grafting of PEMA produces stable surface layers, which were not washed off by the streaming liquid during the electrokinetic experiment.

These findings excellently agree with the contact angle data showing that the grafted PEMA prevents the surface segregation of PDMS species and hence the hydrophobic recovery of the modified PDMS samples (Tab. 2).

Adhesion between PDMS-coated silicon wafers and a photo-patternable spin-on epoxy resin coating

The influence of the surface modification of PDMS to form stable adhesion joints was investigated exemplarily for the adhesion of an epoxy resin top coat. The scheme of the adhesion joint used in the pull-off tester is shown in Fig. 6. Details of the experimental procedure are described in [20].

Fig. 6:
Scheme of the fixture used for the pull-off tests (left side). Typical fracture patterns: In the case of the untreated PDMS sample, the adhesion between the PDMS layer and the epoxy resin coating is poor and adhesive failure was observed (a). For surface functionalized PDMS samples, cohesive failure within the PDMS layer takes place (b).



The pull-off test results are summarized in Tab. 3. To estimate the adhesion strength between the PDMS layer and an epoxy top coat the pull-off strength was determined. In general, the adhesion strength of the model coating system is increased when the PDMS layer was surface functionalized. The pull-off strength values for the system with the untreated PDMS substrate were determined to be 0.2 and 0.5 MPa, respectively. When the PDMS surfaces were plasma-treated and grafted with a thin PEMA layer the measured pull-off strength values were an order of magnitude higher. Although this increase in the adhesion strength is significant the mode of detachment upon failure has also to be considered. The poor adhesion of the coating system with untreated PDMS surfaces was caused by an adhesive failure (Fig. 6). In this case, the failure occurs from the interface between the PDMS layer and the epoxy top coat. In all other cases, the mode of failure was cohesive and occurred within the PDMS layer. Obviously, the surface functionalization of the PDMS layer resulted in a very high adhesion strength between PDMS and the epoxy resin top coat that exceeds the cohesive strength of the PDMS layer. It can be assumed that the presence of reactive silanol or amino functionalities at the plasma-treated PDMS samples and anhydride groups in the case of grafted PEMA copolymer, respectively, enables a chemical bonding with the epoxy resin. The measured values for the cohesive strength vary from 2.2 up to 4.7 MPa. The tensile strength of the silicone which can be considered as a measure of the cohesive strength of a material is 3 MPa (given by the manufacturer). Hence, the measured pull-off strength values are in relative good agreement with this value. However, due to the cohesive failure mode for the coating systems with surface functionalized silicone layers, it was not possible to reveal the effect of different surface modifications of PDMS on the adhesion to an epoxy resin top coat.

Surface functionalization of PDMS	Pull-off strength [MPa]	Failure mode ^(a)
Untreated	0.3 0.5	A
O ₂ plasma: 600 W, 15 s	3.6 4.2	C
NH ₃ plasma: 7 W, 600 s	3.3 4.7	C
NH ₃ plasma: 7 W, 600 s + PEMA	3.7 2.2	C

*Tab. 3:
Effect of surface functionalization of PDMS layers screen-printed onto silicon wafers on the pull-off strength of an epoxy resin top coat*
^(a) A = adhesive failure at the silicone/ epoxy resin interface; C = cohesive failure in the silicone layer.

Conclusions

We describe a route to design a stable surface functionalization of PDMS layers screen-printed onto silicon wafers. In a first step, the PDMS surfaces were activated by oxygen or ammonia plasma treatments, respectively. In the case of oxygen plasma, rather intense treatment conditions and long treatment times are required to functionalize the PDMS surface. Reactive silanol groups were generated together with a brittle, silica-like surface layer. Ammonia plasma-treatments were carried out under rather mild conditions. Here, the surface functionalization was connected with the formation of a *weak boundary layer* that can be easily washed off by polar liquids. A strong tendency to recover their hydrophobicity was observed when the plasma treated PDMS samples were stored under ambient conditions. The amino functional groups created directly by the ammonia plasma treatment and by the attachment of γ -APS onto oxygen plasma-treated PDMS surfaces, respectively, were used in a second step to graft a thin layer of PEMA copolymer onto the PDMS surface. It was shown that the grafted PEMA acts as a barrier to avoid the surface segregation of low-molecular weight species from the PDMS bulk and thus, no hydrophobic recovery was observed. The reactivity of the PEMA surface caused by the availability of anhydride groups can be controlled by the amount of amino functional surface groups of the PDMS surface necessary for the covalent binding of PEMA. The higher the amount of the amino groups available for the grafting-to procedure the lower was the hydrophilicity and, hence, the reactivity of the PEMA surface since the number of remaining active anhydride and carboxylic acid groups was reduced.

We could further show that the adhesion between PDMS surfaces, screen-printed as layers onto silicon wafers, and a photo-patternable spin-on epoxy resin coating can be improved considerably by the above described surface functionalization of the PDMS layers.

References

- [1] R. Anderson, B. Arkles: Silicon Compounds, Petrach Systems, Bristol, PA, 1987
- [2] H. Meynen, M.V. Blucke, M. Gonzales, B. Harkness, G. Gardner, J.S. Holt-schlag, B. Vandavelbe, C. Winters, E. Beyne: Microelectronic Eng 76 (2004), pp. 212-218
- [3] V.M. Graubner, D. Clemens: Langmuir 21 (2005), pp. 8940-8946
- [4] T. Meyer, H. Hedler, L. Larson, M. Kunselman: Chip Scale Review 8 (2004), pp. 65-71
- [5] S. Wu in: Polymer Blends / Eds. D.R. Paul, S. Newman ; New York : Academic Press, 1987, pp. 243
- [6] H. Hillborg, S. Karlsson, U.W. Gedde: Polymer 42 (2001), pp. 8883-8889
- [7] A. Toth, I. Bertoti, M. Blazso, G. Banhegyi, A. Bognar, P. Szaplanczay: J. Appl. Polym. Sci. 52 (1994), pp. 1293-1307

- [8] H. Hillborg, J.F. Ankner, U.W. Gedde, G.D. Smith, H K. Yasuda, K. Wikström: *Polymer* 41 (2000), pp. 6851-6863
- [9] M.J. Owen, P.J. Smith: *J. Adhesion Sci. Techn.* 8 (1994), pp. 1063-1075
- [10] M. Morra, E. Occhiello, R. Marola, F. Garbassi, P. Humphrey, D. Johnson: *J. Coll. Interface Sci.* 137 (1990), pp. 11-24
- [11] J. Kim, M.K. Chaudhury, M.J. Owen: *J. Coll. Interface Sci.* 244 (2001), pp. 200-207
- [12] E.P. Everaert, H.C. Van Der Mei, H.J. Busscher: *J. Adhesion Sci. Techn.* 9 (1995), pp. 1263-1278
- [13] H. Hillborg, M. Sandelin, U.W. Gedde: *Polymer* 42 (2001), pp. 7349-7362
- [14] A. Olah, H. Hillborg, G.J. Vancso: *Appl. Surf. Sci.* 239 (2005), pp. 410-423
- [15] J.L. Fritz, M.J. Owen: *J. Adhesion.* 54 (1995), pp. 33-45
- [16] N. Völcker, D. Klee, H. Höcker, S. Langefeld: *J. Mat. Sci. – Mat. Medicine* 12 (2001), pp. 111-119
- [17] S.D. Lee, G.H. Hsiue, C.C. Wang: *J. Appl. Polym. Sci.* 54 (1994), pp. 1279-1287
- [18] Q. He, Z. Liu, P. Xiao, R. Liang, N. He, Z. Lu: *Langmuir* 19 (2003), pp. 6982-6986
- [19] W. Hellmich, J. Regtmeier, T.T. Duong, R. Ros, D. Anselmetti, A. Ros: *Langmuir* 21 (2005), pp. 7551-7757
- [20] J. Roth, V. Albrecht, M. Nitschke, C. Bellmann, F. Simon, S. Zschoche, S. Michel, C. Luhmann, K. Grundke, B. Voit: *Langmuir* 24 (2008), pp. 12603-12611
- [21] O. Stern: *Z. Elektrochemie* 30 (1924), pp. 508-516