Colloid Polym Sci (2008) 286:305–311
DOI 10.1007/s00396-007-1743-4

SHORT COMMUNICATION

Influence of shape and surface properties of microstructured reaction areas on the deposition of silica

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Received: 1 June 2007 / Accepted: 13 July 2007 / Published online: 10 January 2008

Abstract Differently shaped reaction areas for silica deposition were created by photochemical grafting of hydrophobic poly(acrylic acid 2-ethyl-hexylester) as barrier and a hydrophilic polymer employing a mask having hexagons, pentagons, squares and stripes. Poly(ethylene glycol), poly(acrylic acid), branched and linear poly(ethylene imine) and linear poly(methylpropylene imine) have been applied as hydrophilic polymer in the reaction area. These patterned films have been used in silica mineralization experiments by dipping them into a silica precursor solution. Investigations of the polymer films and silica depositions have been done by contact angle measurements, ellipsometry and scanning electron microscopy (SEM). Silica deposition occurs only in the hydrophilically coated areas, resulting in regular arrays of lens-like silica particles. There are only minor differences due to the shape of the reaction area. The influence of the different hydrophilic polymers can be explained by their wetting behaviour.

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Keywords Surface patterning · Photochemical grafting · Silica deposition · Hydrophilic areas

Introduction

In nature, silica is found among others in the skeletons of sponges, radiolarians and diatoms. Their beautiful skeletons are of extraordinary complexity [1] and high stability [2] formed by completely amorphous silica [3]. Deposits of ancient shells are mined as diatomeaceous earth and find several technical applications, for example, as adsorbents and in filtration processes. Furthermore, the properties of silica shells attract attention as photonic crystals [4] or new porous materials [5], like zeolites [6]. In the subject of not only classic sol-gel chemistry [7] but also in the setting of biomineralization [8, 9], many investigations were done in solution. However, only few investigations have been done using structured surfaces on a substrate to test the deposition of silica in a restricted geometry. Coffman et al. [10] succeeded in depositing small silica particles on fairly uniform poly(L-lysine) areas. Kim et al. [11, 12] reported the deposition of silica into a poly(DMAEMA) film patterned on gold surfaces. Peptide-enriched lines on a polymer surface were created by a holographic two-photon induced photopolymerization [13]. In contact with buffered silicic acid solution silica nanospheres were deposited along these lines. Silica structures prepared by deposition of silica onto direct ink written 3D polyamine-rich templates appear very similar to diatom biosilica [14]. We have developed a method to prepare delineated reaction areas on a silicon wafer by photochemical grafting [15]. By this method small hexagonal areas (from 10–64 µm) coated with branched poly(ethylene imine) (brPEI) are separated from each other by hydrophobic low T_g poly(acrylic acid 2-ethyl-hexylester)

(PEHAA). Dipping these structures into a freshly prepared solution of silicic acid resulted in highly regular arrays of lens-like silica particles. In this study, we describe experiments in which we investigate the role of the geometric shape of the reaction area—hexagons, pentagons, squares or stripes. Furthermore, different hydrophilic polymers are used. Beside the branched high molecular weight poly(ethylene imine), we have used linear low molecular weight polyamines [14] comparable to the naturally occurring polyamines [16–18], anionic poly (acrylic acid) (PAA) and non-ionic poly(ethylene glycol) (PEG). Up to now, these polymers were only used as additives for silicic acid mineralization experiments performed in solution [19–25].

Materials and methods

Chemicals

All solvents were distilled. Poly(acrylic acid 2-ethylhexylester) (M_w=92,000 g/mol, T_g=−55 °C, Aldrich), PAA (M_w=2,000 g/mol, Aldrich) and PEG (M_w=12,000 g/mol, Alfa Aesar) were used as received. Branched poly(ethylene imine) (M_w=750,000 g/mol, 50 wt% solution in water, Aldrich) was freeze-dried. Linear poly(ethylene imine) (P_n=14) was synthesized by cationic ring-opening polymerization of 2-methyl-2-oxazoline and subsequent hydrolysis [20]. Poly(methylpropylene imine) (P_n=14) was synthesized by cationic ring-opening polymerization of 5,6-dihydro-4H-1,3-oxazine followed by hydrolysis and Leukart–Wallach reaction [20]. Tetramethoxysilane (TMOS, 99%, Acros) and hydrochloric acid (Fixanal, 0.01 M, Riedel-de Haen) were used for the preparation of silica precursor solutions.

Preparation of patterned polymer films

The preparation of patterned polymer films on silicon wafers was done according to Helmecke et al. [15]. For spin coating, 10 mg/ml solutions of the polymers were prepared. Poly(acrylic acid 2-ethyl-hexylester) was dissolved in petroleum ether and PEG in chloroform. Ethanol was used for all other polymers. During illumination, the mask was placed directly on the sample. After the photochemical reaction, the silicon wafer was washed with the corresponding solvent for 20 h in a soxhlet extractor to remove unbound polymer. The second polymer was analogously spin-coated, the wafer was illuminated without mask and extracted with the corresponding solvent. The illumination time for poly(acrylic acid 2-ethyl-hexylester) was 3 h and 35 min for all other polymers.

Condensation of silicic acid

For carrying out silica condensation reactions on the patterned silicon wafers, TMOS and 0.01 M hydrochloric acid in a ratio of 2:1 *v*/*v* were stirred for 2 min to prepare a silicic acid solution. Subsequently, the silicic acid solution was spin-coated onto the surface-patterned silicon wafers at a speed of 2,000 rpm for 30 s.

Characterization

The wettability of the anchor and the polymer layers on the silicon wafers were determined by contact angle measurements (Krüss Type G1, Germany) of water droplets at room temperature using the tilted plate method (tilting angle ~45°). Film thicknesses were determined using a Multiscope (Optrel, Germany) in the ellipsometry mode measuring at four angles at three positions on the wafer. Each silicon wafer was measured as reference before treatment. Scanning electron microscopy (SEM) investigations were done employing a JEOL-JSM-6400 or a JEOL-JSM-6700F (JEOL, Germany).

Results and discussions

In a previous work, it was shown that it is possible to create small reaction areas on the surface of silicon wafers by the attachment of different polymers via photochemical grafting onto [15]. In this process, the silicon wafer is covered with a self-assembled monolayer of 4-(3′-chlorodimethylsilyl)propyloxybenzophenone, which acts as an anchor layer [26]. The first polymer is applied by spin coating and attached by irradiation with UV light. Using a mask during illumination and washing-off non-bound polymer, this procedure can be repeated with a second polymer resulting in a patterned surface (see Fig. 1). In the previous

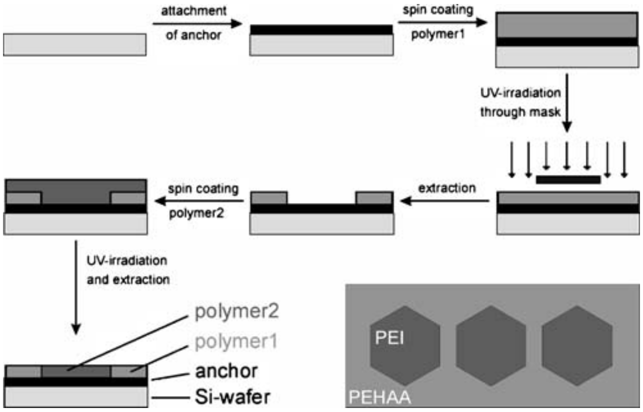


Fig. 1 Schematic drawing of the preparation of structured polymer films on a surface by photochemical grafting onto

work, the reaction areas were covered with high molecular weight brPEI and separated from each other by PEHAA as a hydrophobic and low T_g polymer. Dipping the silicon wafers with the so-produced delineated reaction areas into a freshly prepared solution of silicic acid at pH=2 resulted in the deposition of silica onto the brPEI covered areas and the formation of regular arrays of silica particles [15]. The reaction areas were of hexagonal shape.

The variation of the shape should allow to investigate whether the restricted geometry at the surface can influence the silica deposition and structure formation. The photochemical grafting can also be used for creation of differently shaped reaction areas [26–28]. A mask was produced having beside hexagonal areas also pentagonal and quadratic structures as well as stripes of different width in a range of 10 to 128 μm (see Fig. 2a). Using this mask, reaction areas of different shapes and sizes can be patterned onto silicon wafers by the process described above and using PEHAA and brPEI as polymers. All structures are clearly visible in SEM images (see Fig. 2b,c), although the difference in the height of the polymer layers is only minor (brPEI, 5.2 nm; PEHAA, 6.6 nm; see [15]). The exact contrast mechanism is not clear but might be due to the different electron conductivities of the polar brPEI compared to the hydrophobic and non-polar PEHAA.

For the silica condensation experiments, we have not dipped the patterned silicon wafer into the freshly prepared silicic acid solution, as described previously, but have spin-coated the solution onto the wafer. The spin coating results in basically the same structures as the dipping; however, the reproducibility is much better. The dipping process is more prone to variations of parameters like humidity, temperature, etc. The structures received on the silicon wafers after silica deposition are shown in Fig. 2d–i.

As the different geometries are situated on the same support and the deposition conditions are the same for all geometries, only size and shape should influence the structure of the deposited silica. For hexagons, we have reported an increase in size of lens-like deposited silica [15]. For more precisely formed hexagons including a larger structure (128 μm) and using a different deposition method (spin coating instead of dipping) the results are the same. The larger the reaction area is, the larger are the sizes of the silica particles (see Fig. 2d–h). The particles formed at the surface are very smooth and lens-like (see Fig. 2g). Comparison of the different geometries—hexagons (see Fig. 2d), pentagons (Fig. 2e) and squares (Fig. 2f)—reveals that the resulting silica particles are very similar and that their shapes do not depend significantly on the geometry of the reaction area. Thus, it can be concluded that the

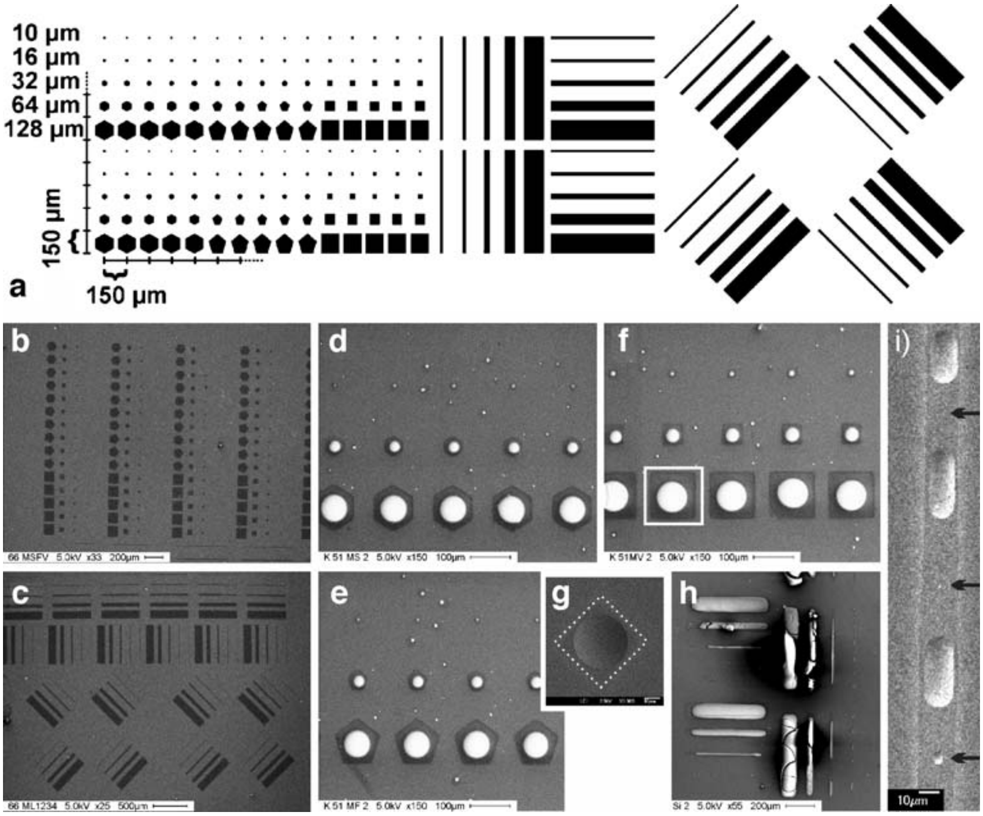


Fig. 2 **a** Schematic drawing of the mask with an arrangement of hexagons, pentagons, squares and stripes in five different sizes. **b**, **c** SEM images of the patterned surface: brPEI is inside the arrays and PEHAA outside (the smallest structures are not visible with the resolution used here). **d**–**i** SEM images of silica deposits in areas of different geometry. **g** HR-SEM image of square filled with silica. **i** HR-SEM of second smallest stripe with big and small (*arrows*) silica particles

geometry does not have a decisive influence on the shape of the silica deposits but that the shape is determined by the formation of a droplet on the surface. The droplet formation depends of course on the wetting properties of the surface and the surface tension of the spin-coating solution. As a result, round-shaped structures are formed. A slightly different behaviour is found for the larger rectangular areas. In this geometry, the silica particles are not completely round but elongated, but still have rounded edges. This finding is in accordance with the hypothesis that the silica structures formed are a consequence of wetting, droplet formation on the surface of the reaction areas and finally the contraction of the droplets upon removal of the solvent. This contraction process in the rectangular reaction areas should result in such elongated structures with round edges. Furthermore, the contraction can result in a very interesting arrangement of silica particles on the smaller rectangular reaction areas. Here, the deposition can be as large and small particles, in some areas in an alternating fashion (see Fig. 2i).

The photochemical grafting method not only allows to vary the shape of the patterns but also to cover the reaction areas with different polymers, that is to exchange branched poly(ethylene imine) against other hydrophilic polymers in the reaction area. So far, we have used commercially available brPEI, which is a polyamine, as are the natural polyamines found in diatoms [16, 18, 29], and has been shown to strongly interact with silicic acid and its condensation products [20, 21]. However, the question arises whether amino groups on the surface are important for the deposition of silica or if only the hydrophilicity is important. Therefore, for further experiments, we have used PEG as a hydrophilic non-ionic polymer and PAA, an acidic polymer with reduced hydrophilicity, at low pH values. Furthermore, brPEI is not a good model for the polyamines found in biosilica due to its high molecular weight and its branched architecture. For this reason, low molecular weight linear poly(ethylene imine) (linPEI) and poly(methylpropylene imine) (linPMPI) are also used [20]. All these polymers have been used in silica deposition experiments in solution. The influence of low molecular weight linPMPI and linPEI on the kinetics of the silica condensation reaction has been studied [20]. Vrieling et al. [21] have found by USAXS investigations that large, smooth spherical or vesicle-shaped particles are formed when PEG is added. However, large fractal particles have been found when brPEI was added [21]. In experiments with PAA, no silica particles are precipitated but rather a gel was formed due to the negative charge of the polymer [23]. Furthermore, it was reported that no silica is formed on electrostatically self-assembled bilayers of PAA and PAH [23].

The different hydrophilically coated reaction areas were prepared as described for brPEI; thus, the conditions for spin coating, illumination and extraction were kept constant. In first experiments, we have covered half of the silicon wafer with the hydrophobic PEHAA and the other side with one of the hydrophilic polymers. However, for all polymers no significant increase in layer thickness compared to the anchor layer was found. This is easily explainable, as all polymers used possess low molecular weight, and thus, their radius of gyration is very small (PEG, 12,000 g/mol; PAA, 2,000 g/mol; linPEI, 602 g/mol and linPMPI, 994 g/mol).

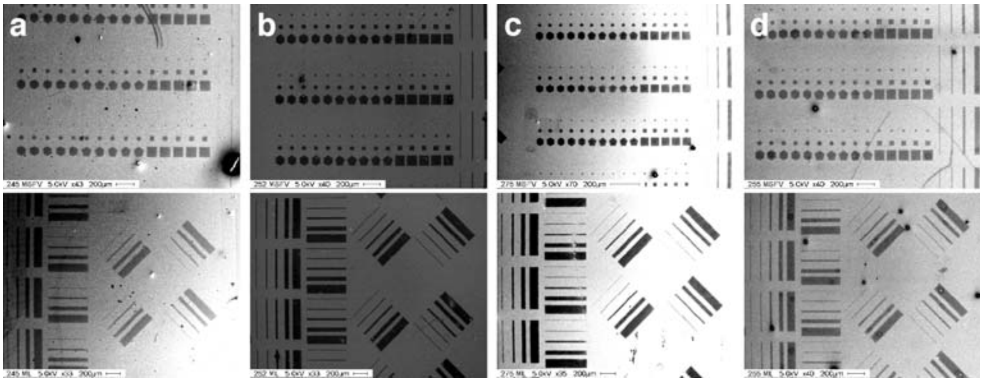
Despite these results, the presence of the applied polymers on the surface can be shown. For all polymers, a significant difference in contact angles compared with the hydrophobic PEHAA layer is found (see Table 1). Furthermore, after spin coating and attachment of PAA and PEG, a significant decrease of water contact angles compared to the anchor layer can be measured (see Table 1). In the case of the merely oligomeric linPMPI and linPEI, the changes in contact angles are only small (see Table 1). This is somewhat expected, as the changes for the high molecular weight branched PEI are also not very large (see Table 1). The results, however, indicate that the surface might not completely covered. On the other hand, the clear contrast in the SEM is indicative that there is polyamine at the surface (see Fig. 3).

Using the above-mentioned mask (see Fig. 2a), the differently shaped reaction areas were prepared with all the four different hydrophilic polymers. Some examples are shown in Fig. 3. The contrast between the hydrophilic polymers in the reaction area and the surrounding hydrophobic matrix is supposed to be due to the different conductivities on the surface of the silicon wafers. This visible characteristic is a strong evidence that the surfaces

Table 1 Advancing (adv)/ receding (rec) contact angles of anchor layer and different polymer layers (compare PEHAA: θ_{adv} 98±5 °/θ_{adv} 52±3 °)

$\theta_{adv/rec}$ [°]	Anchor	Polymer
PAA	74/41 ±3/±3	59/31 ±3/±2
PEG	73/43 ±3/±2	45/22 ±7/±5
linPEI	78/43 ±7/±4	70/36 ±4/±4
linPMPI	69/42 ±2/±3	66/37 ±2/±2
brPEI [15]	64/33 ±4/±4	54/26 ±5/±4

Fig. 3 SEM images of different surface patterns filled with **a** PEG, **b** PAA, **c** linPEI and **d** linPMPI

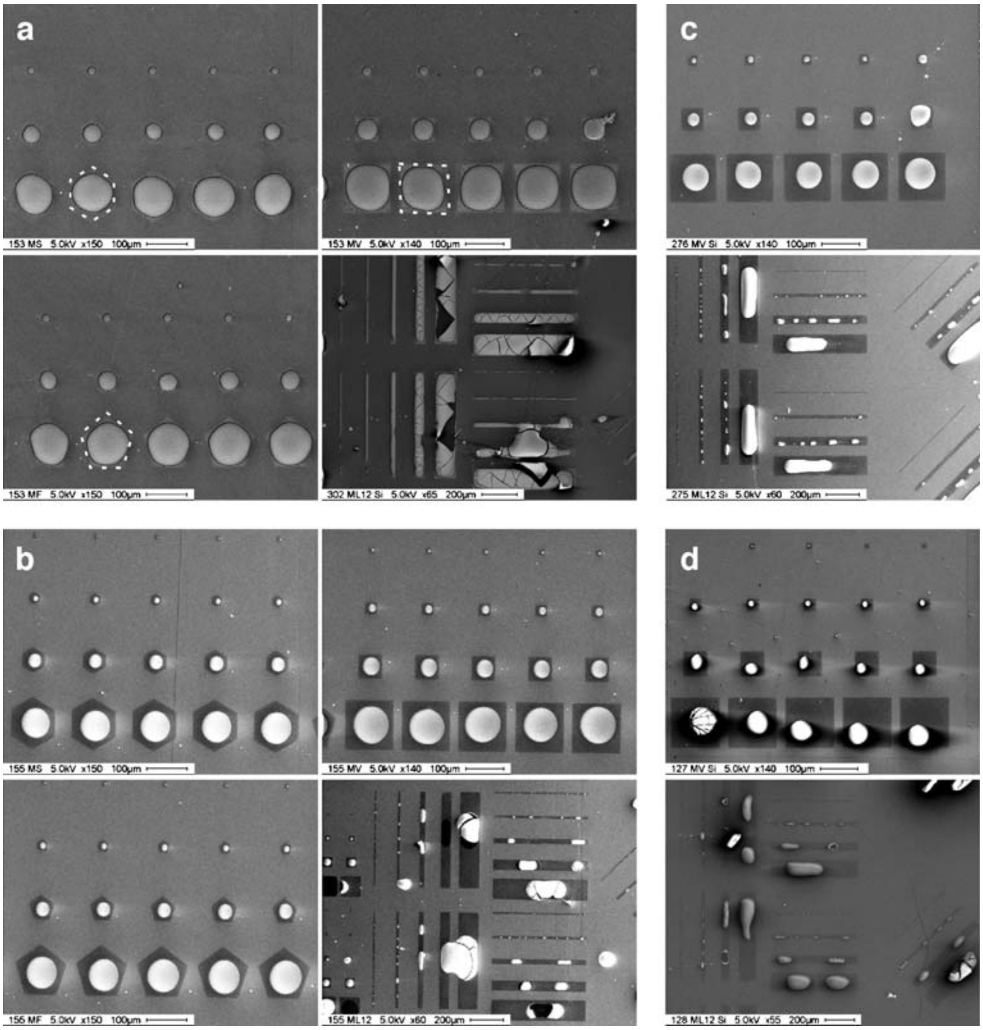


to be used in the silica deposition experiments are in fact patterned by different polymers.

The surfaces patterned with the different polymers were used in silica mineralization experiments by spin coating a freshly prepared silicic acid solution onto the surface. In all cases, silica is deposited on the reaction area. The resulting silica deposits always exhibit a roughly round shape (see Fig. 4) similar to the structures found on brPEI-coated reaction areas (see Fig. 2). However, in the case of the rectangular stripes, no homogeneous deposition was found.

Comparing PAA and PEG (see Fig. 4a,b), a slight difference is visible. On the PEG-coated squares, pentagons

Fig. 4 SEM images of silica deposits on structures filled with **a**) PEG, **b**) PAA, **c**) linPEI and **d**) linPMPI



and hexagons, the particles are typically larger than on PAA, filling not all but most of the reaction area. Furthermore, on PEG, the particles are not perfectly round (as on PAA), and a thin film of silica also appears to have been deposited in the corners of reaction areas as already reported [15]. These difference can be discussed as consequences of the different wetting behaviour of the polymers. Both polymers have very low contact angles with water. PEG seems to be a little bit more hydrophilic under the conditions used (see Table 1). PEG is generally known as a very hydrophilic polymer, and for this reason, the reaction area is probably completely filled upon spin coating. This explains the partially deposition of silica in the corners of the reaction areas (silica left behind during evaporation of the solvent) and the generation of broader particles (due to flatter droplets) shaped slightly similar to the shape of the reaction areas (see Fig. 5). In the case of PAA, the droplets are smaller and almost perfectly round shaped, maybe due to a higher contact angle with water at low pH values (silicic acid solution, pH 2).

The silica deposits on low molecular weight linPMPI and linPEI (see Fig. 4c,d) are very similar to those found on high molecular weight brPEI (see Fig. 2). Apparently, the influence of polymer molecular weight and architecture is only small. However, in case of the low molecular weight polyamines, the deposition is less homogeneous most likely due to the less homogenous polymer coating.

In summary, it can be stated that in contrast to silica mineralization experiments in solution, the functional groups of the macromolecules on the surface have no significant influence on the deposits formed by the silicic acid condensation. In contrast, the results indicate that the formation of the spherical lens-shaped deposits of silica is caused by wetting of the reaction areas and by droplet formation of the silicic acid solution. Consequently, the hydrophilicity of the polymer is of essential importance.

Conclusion

Differently shaped micro-arrays covered with diverse hydrophilic polymers as ultrathin layers have been used to investigate the deposition and condensation of silicic acid in restricted geometries. Squares, pentagons, hexagons and stripes have been fabricated by photochemical grafting. The silica deposits are in all cases round-shaped. Thus, the shape of the reaction area does not have much influence. The different polymers—branched and linear poly(ethylene imine), linear poly(methylpropylene imine), PAA and PEG—also generally result in similar structures of the silica deposits. SEM investigations typically show round-shaped silica particles. However, slight differences can be explained to be caused by differences in the wetting behaviour, due to different hydrophilicities of the polymers. The results suggest that merely the wetting behaviour of the polymer layer governs the silica deposition.

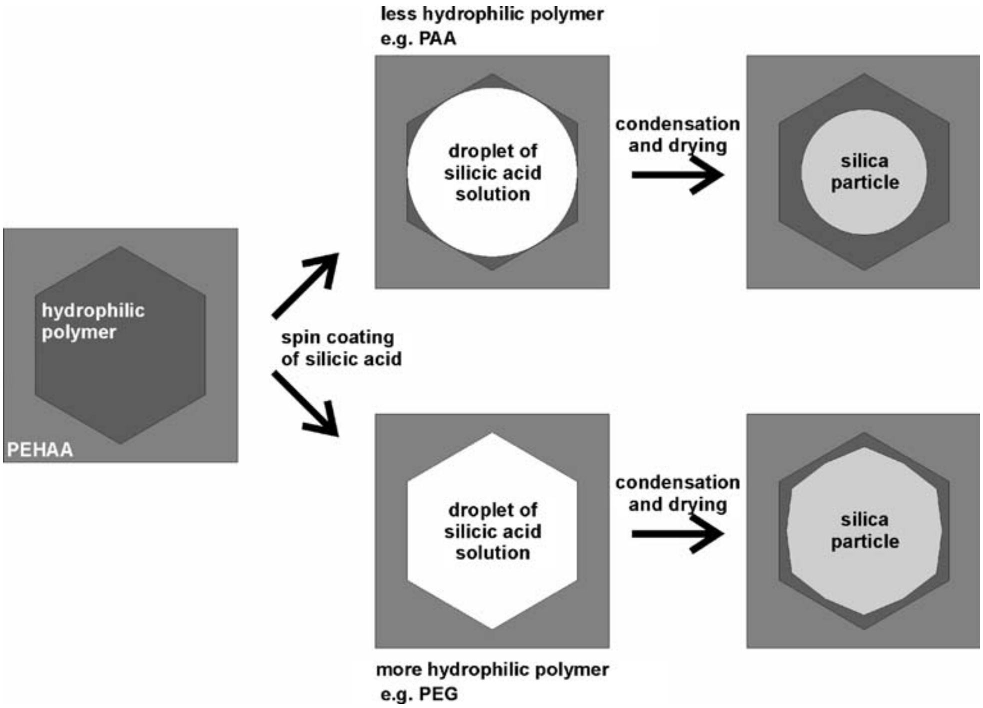


Fig. 5 Different wetting of the PEI-covered and PEG-covered reaction areas by spin coated silicic acid solution and subsequent silica formation

Acknowledgement The authors would like to thank Prof. A. Waag and M. Karsten (Institute of Semiconductor Technology, Braunschweig University of Technology) for the preparation of the mask and A. Scherbarth for SEM measurements. This work was supported in the scope of the Priority Research Program 1117 "Principles of Biomineralization" by the Deutsche Forschungsgemeinschaft (DFG).

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