SHORT COMMUNICATION

Microstructured reaction areas for the deposition of silica

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Abstract Patterned films with hexagonal structures were prepared by photochemical grafting of hydrophobic poly (acrylic acid 2-ethyl-hexylester) (PEHAA) as barrier and poly(ethylene imine) (PEI) as reaction area. The films have been characterized by ellipsometry, contact angle measurements, and scanning electron microscopy (SEM). These patterned films have been used in silica mineralization experiments by dipping them into a silica precursor solution. Silica deposition occurs only in PEI-coated areas, resulting in regular arrays of lens-shaped silica particles. The deposited silica was investigated by SEM and atomic force microscopy (AFM).

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Introduction

Silica sol-gel chemistry allows the preparation of interesting materials. In the 1960s, alkylammonium ions were used to control the pore size, shape, and periodicity of zeolites [1]. Kresge et al. [2] used longer-chain alkylammonium ions in an attempt to increase the maximum pore size of zeolites beyond ~1.2 nm. This templating has been further developed, and many interesting materials can be prepared in this way [3].

The silica formation on surfaces was reported by Kim et al. [4]. A 140-nm thick film of poly(2-(dimethylamino)ethyl methacrylate) was created on a surface by a grafting from polymerization. Upon contact with silicic acid solution, silica formation within the swollen polymer film was observed resulting in ~700-nm thick hybrid films. Using microcontact printing for applying the polymerization initiator to the surface, micropatterned polymer and hybrid films were obtained [5]. The features of the polymer film were 10 μm in diameter, with a thickness adjustable by the polymerization conditions between 40 and 130 nm. Silica formation in the swollen polymer film resulted in hybrid films approximately twice as thick. Brott et al. [6] used holographic two-photon-induced photopolymerization to create peptide-enriched lines on a polymer surface. When these nano-patterned structures are exposed to a silicic acid solution, an array of silica nanospheres is deposited onto the polymer substrate. Coffman et al. [7] studied the silica deposition on surfaces patterned with poly(L-lysine) by reagent jetting (spots of approximately 500 μm in diameter). By bringing the surfaces into contact with a solution of sodium

orthosilicate in borate buffer (pH=8.5) or sodium phosphate buffer (pH=7.0), silica particles of approximately 30 nm diameter were deposited on the poly(L-lysine) coated areas. Kim et al. [8] fabricated microstructures of silica on silicon wafers or glass slides by using the MIMIC procedure (micro-molding in capillaries) and subsequently converting the siloxane precursor film by heating. Xu et al. [9] used direct ink writing to assemble 3D polyamine-rich scaffolds. By exposing to silicic acid, these templates allow to create synthetic diatom mimetic hybrid structures (~100–200 μm in size).

Compared to the method described by Xu et al. [9], the photochemical "grafting onto" is less extensive, almost universal, and enables to bind all kinds of different polymers to a surface in an easy and fast way [10, 11]. A photoreactive anchor is immobilized as self-assembled monolayer on the surface. Upon illumination with UV light, it reacts with C–H bonds in a polymeric overcoat, resulting in an immobilized polymer [10]. Another advantage of this method is that by using a mask during illumination, a laterally structured polymer film is available on the surface by repetition of the illumination-reaction sequence with a second polymer [12, 13]. In this study, we report on the fabrication of two-dimensional reaction areas on silicon wafers where poly(ethylene imine) (PEI) is present, separated from each other by an inert polymer. These structures have been used as reaction areas in silica deposition experiments. The resulting highly ordered arrays of lens-like silica structures have been investigated by scanning electron microscopy (SEM) and atomic force microscopy (AFM).

Materials and methods

Chemicals

All solvents were distilled. Poly(acrylic acid 2-ethyl-hexylester) (PEHAA; Mw=92 000 g/mol, Tg=−55 °C, Aldrich) was used as received. PEI (750,000 g/mol, 50 wt% solution in water, Aldrich) was freeze-dried. Tetramethoxysilane (TMOS, 99%, Acros), hydrochloric acid (37% p.a, Riedel-de Haen), and Millipore water (~17.5 MΩ cm) were used for the preparation of silica precursor solutions.

Preparation of patterned polymer films

Preparation of the anchor layer. 4-(3′-chlorodimethylsilyl) propyloxybenzophenone was synthesized according to Prucker et al. [9]. Cleaned silicon wafers [2.5×2.5 cm, cleaning: acetone, chloroform in an ultrasonic bath, "piranha"-solution (3:7 vol.% 30% H_2O_2/conc. H_2SO_4)] were covered with a solution of 4-(3′-chlorodimethylsilyl) propyloxybenzophenone ($3.1×10^{-3}$ mol) in 7 ml abs.

toluene together with 1 ml dried triethylamine for 18 h. After reaction, the modified silicon wafers were rinsed with chloroform.

Preparation of structured polymer layers

For spin-coating, 10 mg/ml solutions of the polymers were prepared. PEHAA was dissolved in petroleum ether, poly(vinylidene fluoride) in dimethylformamide, PEI in ethanol, and poly(styrene) in chloroform. The first polymer in solution was spin-coated onto the silicon wafer at a speed of 2,000 rpm for 30 s. The substrates with the anchor layer and the polymeric overcoat were illuminated using a 350 W high-pressure mercury UV lamp with a filter UG 1 (Spindler and Hoyer, Germany) λ=360±50 nm. The mask was placed directly on the sample to spatially pattern the film. The light intensity at the sample was 100 mW/cm². Subsequently, the silicon wafer was washed with the solvent for 20 h in a soxhlet extractor to remove unbound polymer. The second polymer was analogously spin-coated, illuminated, and extracted. However, in this case, no mask was used. The illumination time for PEHAA, poly(vinylidene fluoride), and poly (styrene) was 3 h, for PEI 35 min. After illumination, the samples were extracted in a soxhlet extractor with the appropriate solvent for 20 h to remove any non-bound polymer. For PEI, the extraction in ethanol must be done immediately after the illumination.

Condensation of silicic acid

For carrying out silica condensation reactions on the polymer-coated substrates with its hexagonal reaction areas, TMOS was added to 0.01 M hydrochloric acid to prepare a 4.0 M silicic acid solution. Subsequently, the structured silicon wafer was dipped into the silicic acid solution for 10 min and withdrawn at a speed of 100 cm/min.

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 tilting 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. AFM measurements were performed with a DME 95–50 scanner (DME, Denmark) in the AC mode using a silicon cantillever (tip curvature radius<10 nm, NanoWorld, Switzerland). SEM investigations were done employing a JEOL-JSM-6400 (JEOL, Germany) or a Phillips 30XL ESEM (Phillips, Germany).

Results and discussions

For photochemical grafting of polymers onto silicon surfaces, two different photochemically active anchor systems have been established [10, 12]. The photoactive benzophenone anchor introduced by Prucker et al. [10] and Jeyaprakash et al. [13] appears to be the simpler system with respect to synthesis and handling when compared to the azide derivative used by Bartlett and Yan [12], Keana et al. [14], and Yan [15]. Although Bartlett has reported good experiences with the preparation of structured surfaces, we have chosen the benzophenone derivative as photo-active group because of the diversity of applied polymers [10, 11, 13, 16]. The preparation of the 4-(3′-chlorodimethylsilyl)-propyloxybenzo-phenone (BP) and the formation of the self assembled monolayer have been carried out according to literature procedures [10]. The typical thickness of the monolayer obtained by ellipsometry was 0.8 ± 0.3 nm, which is in line with the literature (~1 nm) [10, 13].

Polymer films can be attached onto the anchor monolayer by illumination (see Fig. 1). The maximum film thickness that can be obtained by the photochemical grafting is determined by the radius of gyration of the polymer molecules and to a minor extent by parameters like monolayer graft density, spin cast film thickness, and illumination intensity and time [17]. The thickness of the polymer overcoats obtained by spin coating is influenced among other parameters by the spin coating process, the concentration of the polymer solution, and the temperature.

For this reason, the overcoats vary somewhat in thickness for the different samples and polymers PEI (72–81 nm) and PEHAA (59–114 nm). However, the thickness of the overcoat is always significantly larger than the maximum thickness of the bound polymer film as given by the radius of gyration (a few nanometers depending on the molecular weight).

The irradiation with UV light causes the covalent bonding of the polymer molecules in the overcoat, which are in direct contact with the anchor monolayer. The binding occurs due to the photo-induced formation of radicals, which then react with CH_2-groups in the polymer chain [18]. This reaction is unspecific and therefore very universal. After the illumination, non-bound polymer is removed by soxhlet extraction of the wafers with a good solvent for the polymer. This extraction secures that only covalently bound polymer remains at the surface.

By using a mask in the illumination step, laterally structured surfaces are available (see Fig. 1) [13]. The polymer is bound to the surface only in the illuminated areas, and after extraction, areas with and without polymer are obtained. In the polymer-free area, the anchor groups remain active. After spin casting of a second polymer onto this structure, illumination results in binding of the second polymer in those areas where it is in contact with the still active anchor groups. Removal of the non-bound parts of the second polymer results in a surface with different polymers in well-defined areas.

Employing this chemistry, many different polymers can be tethered to a silicon surface; however, every polymer

Fig. 1 Schematic drawing of the preparation of a surface with two polymers in different surface areas by photochemical grafting onto
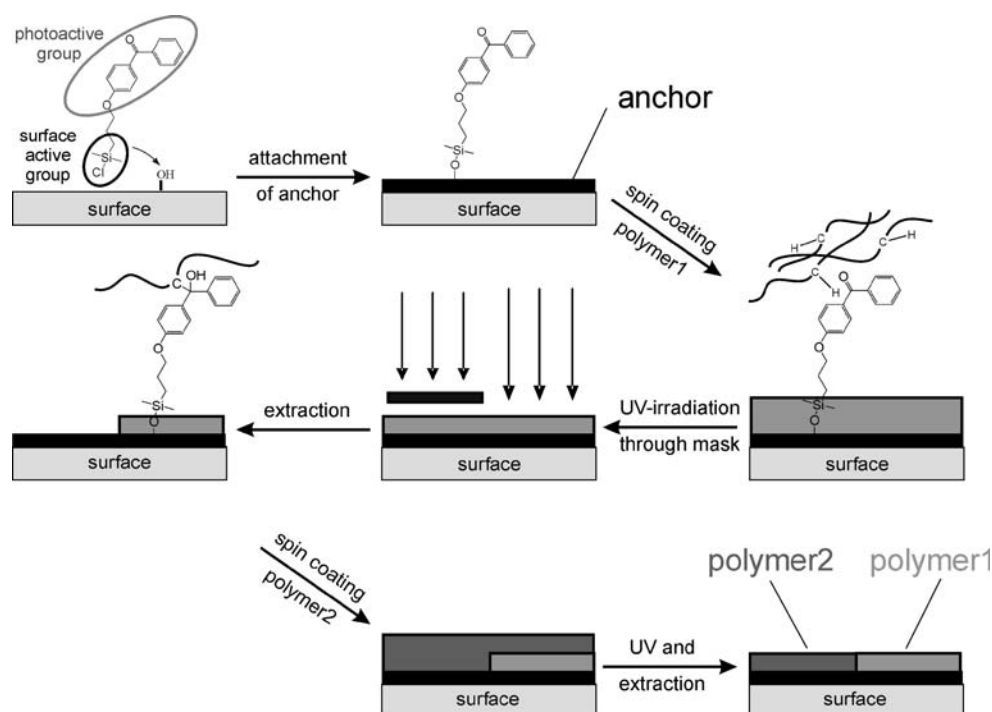
Table 1 Attachment of PEHAA and PEI to the benzophenone anchor layer: contact angles and thicknesses

Anchor		Anchor/polymer1				Polymer2/polymer1			
$\theta_{Ad/Re}$ (°)	d (nm)	$\theta_{Ad/Re}$ (°)		d (nm)		$\theta_{Ad/Re}$ (°)		d (nm)	
Anchor	Anchor	Anchor	PEHAA	Anchor	PEHAA	PEI	PEHAA	PEI	PEHAA
64±4	0.8±0.2	81±3	106±3	1.7±0.3	6.1±0.5	54±5	98±5	5.2±1.1	6.6±2.3
33±4		46±5	63±6			26±4	52±3		

combination has to be tested, and, for example, the sequence of binding the polymers can be very important. For the polymer that is present within the reaction area, PEI was chosen because similar polyamines have shown to be involved in the silica biomineralization process [19], influencing the silica precipitation [20], and the flocculation of the primary particles to form larger aggregates [21]. PEI has a strong tendency to adsorb [22, 23] and cannot be removed by soxhlet extraction from the wafers even if not bound by the photochemical reaction (see Supporting Info). Therefore, PEI always has to be applied as second polymer.

Among others, poly(styrene) (PS) and poly(vinylidene fluoride) (PVF) were tested as hydrophobic barrier; however, it can be shown that the PEI covers the already coated hydrophobic areas, suggesting that the polymer layers are not completely homogeneous and not free of defects (see Supporting Info).

To prevent the adsorption of the PEI, hydrophobic polymers with a low Tg have to be employed, which can form a more homogeneous and defect-free coating on the anchor monolayer. In preliminary experiments for PEHAA (Tg=−55 °C), poly(acrylic acid isobutylester) (PiBuAA, Tg=−59 °C) and poly(methacrylic acid octadecylester) (POdMA, Tg=−105 °C), an efficient blocking of PEI adsorption was found. Therefore, all of them would be suited as barrier material. The results for PEHAA are shown in Table 1 because it was chosen for the further experiments.

Employing the procedure described above and using a mask during the first illumination step, structured surfaces with hexagonal areas of PEI of four different dimensions (64, 32, 16, and 10 μm width) surrounded by PEHAA were obtained (see Fig. 2a). For three of the four different sizes, the hexagons are clearly visible in SEM; only the smallest structures are not resolved in the resolution chosen. The contrast mechanism is not absolutely clear, as the two polymer films do not differ significantly in thickness as determined by ellipsometry (see Table 1). Most likely, the contrast is due to a higher conductivity of the polar PEI.

Fig. 2 SEM images of substrates with hexagonal PEI-coated areas **a** before and **b**, **c** after silica deposition, **d**, **e**, and **f** dimensions of the PEI area and the deposited silica
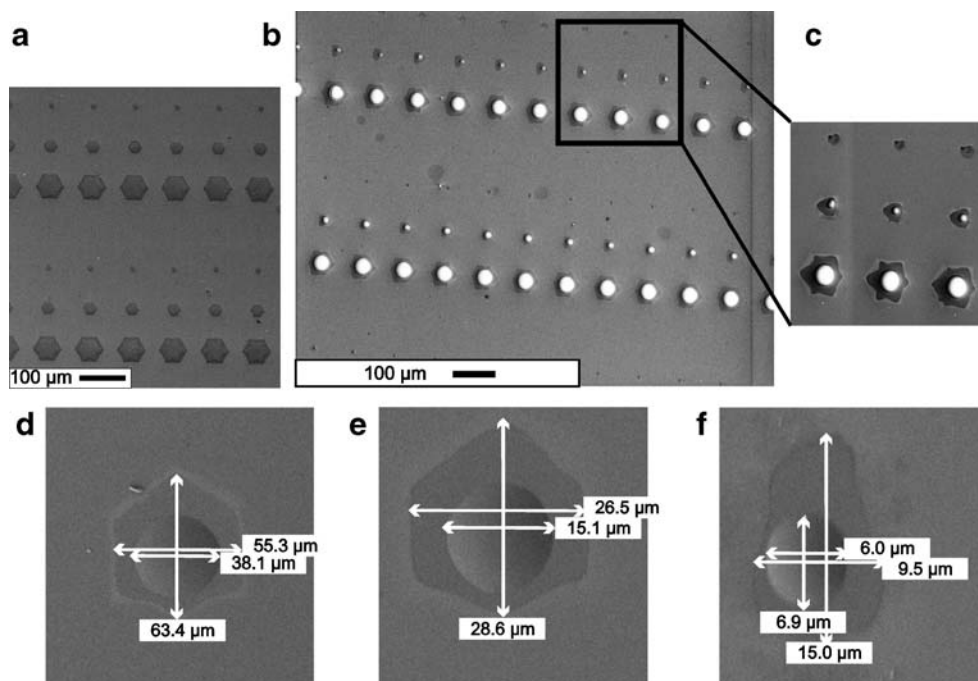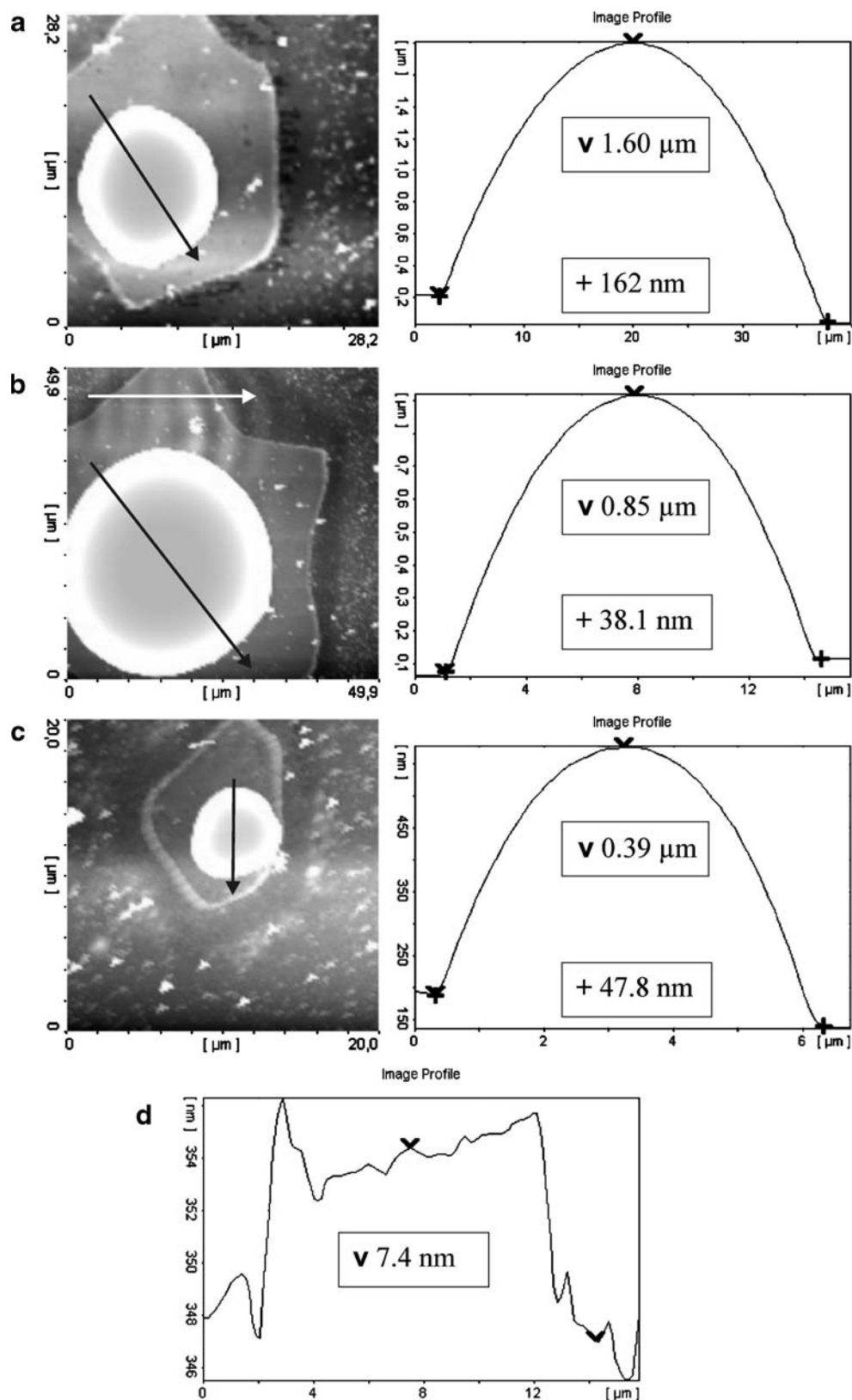
Fig. 3 AFM investigation of PEI-coated areas and deposited silica: Pictures (*without plane correction*) and profiles (*black arrows*) of the deposited silica on PEI hexagons of three dimensions: **a** 64 μm, **b** 32 μm, **c** 16 μm, and **d** of the structured polymer film **b** (*white arrow*)

The dimensions of these areas can be obtained from SEM (see Fig. 2) or AFM measurements (see Fig. 3 and Supporting Information). Comparison of the average width obtained with this method indicates a loss of 10–25%. This loss can be understood as a consequence of light diffraction at the edges of the structures on the mask. It is noteworthy that the smaller structures are not accurately represented on the substrate mostly due to defects of the mask.
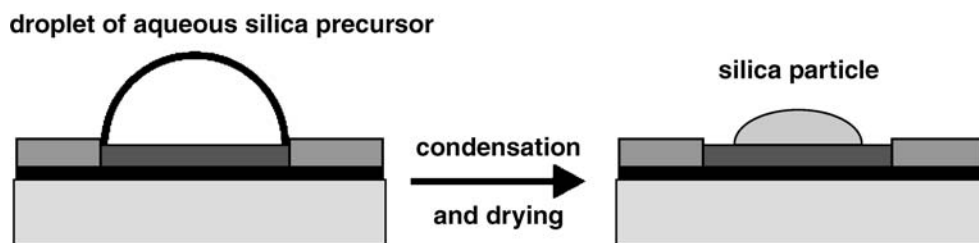
Dipping the wafers with the spatially resolved PEI-covered areas into an acidified TMOS solution results in silica deposition on the surface. The silica is deposited only in the PEI-covered areas of the wafer. This result is in accordance with literature reports by Kim et al. [4], who found silica deposition on poly(DMAEMA)-coated gold surfaces. However, our experiment results in different deposits. We found very regular arrays of small silica particles on the surface. Typical SEM images of such structures of the deposited silica are shown in Fig. 2b–f.

Both SEM (see Fig. 2b–f) and AFM (see Fig. 3a–c) indicate that the particles are round, have a smooth surface, and do not fill the complete reaction area. However, a thin film of silica is covering the remaining surface of the reaction area (compare Fig. 3d and Supporting Information). The film is very thin (~10–15 nm) in comparison with the height of the silica particles (50–100 times larger). The size of the particles clearly scales with the size of the PEI-coated area. By doubling the size of the reaction area (16/32/64 μm), the silica particles become apparently larger in diameter (approximately 6/15/38 μm) and approximately twice as high (~0.4/0.8/1.6 μm for the example in Fig. 3). Despite all experimental variations, the tendency of larger particles formed in bigger reaction areas is obvious. Due to the fact that the average of height of the particles is about 1/15 of their diameter (see Fig. 3), we can speak of lens-shaped particles of silica in the reaction areas.

The dependence of the particle size on the size of the reaction area and the round shapes of the silica particles can be explained to be a consequence of the wetting of the PEI surface and the interaction of the silicic acid with PEI amino groups at the surface. This interaction and the wetting behavior result in the formation of droplets on the top of the reaction areas; in these areas, the silicic acid condensation takes place (see Fig. 4). Upon evaporation of the solvent and condensation, round and smooth particles develop, which are relatively flat due to the strong interaction with the surface.

The photochemical grafting procedure allows also to bind other hydrophilic polymers in the reaction area like poly(acrylic acid) (PAA) or poly(ethylene glycol) (PEG). The surfaces patterned with these polymers were also used in deposition experiments. The resulting silica deposits exhibit in all cases a lens-like shape similar to the structures as found on PEI-coated reaction areas (see Supporting Info). This result supports the hypothesis that the formation

of the lens-shaped deposits is due to droplet formation and wetting phenomena, i.e., the silicic acid solution wets only the reaction areas and forms droplets within them.

Conclusion

Microarrays of areas covered with different ultrathin polymer layers have been generated using a photochemical grafting onto method and appropriate masks for irradiation. PEI was used as a hydrophilic polymer interacting with silicic acid and its condensation products, and PEHAA was used as a hydrophobic polymer that separates the reaction areas from each other. PEI shows a strong adsorption on the silicon wafers covered with a benzophenone anchor layer. Thus, the sequence of the polymer deposition has to start with PEHAA. Furthermore, PEI showed strong adsorption on some hydrophobic polymer films, most likely caused by defects in the films. Such an undesired adsorption can be avoided by employing low Tg polymers like PEHAA, which yield homogeneous and defect-free coatings. The formation of the polymer layers was proven with simple structures by means of ellipsometry and contact angle measurements. The more elaborate microstructures were prepared using masks in the photochemical bonding reaction. The spatially resolved reaction areas can be visualized by SEM and AFM. Employing these structures in silica mineralization experiments by dipping them into freshly prepared silicic acid solution resulted in deposition of silica on the PEI-coated areas only. The deposited silica particles have a lens-like shape and appear in a regular array as dictated by the arrangement of the PEI-coated areas. The size of the silica particles depends among other factors on the size of the PEI-coated areas. The structure formation process is a consequence of wetting phenomena and droplet formation at the surface. Further experiments to investigate the conditions for silica deposition on surfaces with other hydrophilic polymers are reported [24] and with additives present in the silicic acid solution are under way.

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