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Structured Polymer Brushes on Silicon Carbide

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A straightforward method is presented for the preparation of homogeneous as well as structured polymer brushes on SiC substrates. The self-initiated photografting and photopolymerization (SIPGP) of styrene and *N*,*N*-dimethylaminoethyl methacrylate (MAEMA) allows the preparation of polymer brush layers directly and selectively onto C—OH terminated (000$\bar{1}$) 6*H*-SiC surfaces in a single step reaction. In contrast, the analogous reaction on Si—OH terminated (0001) 6*H*-SiC does not occur. The reactivity contrast between Si—OH and C—OH terminated crystal faces for SIPGP was studied using the density functional theory method which showed a higher SiO—H bond dissociation energy for hydrogen abstraction on the Si-polar relative to the C-polar crystal face. Furthermore, structured polymer brushes on the submicrometer scale could be prepared by the carbon templating (CT) technique on Si—OH terminated (0001) 6*H*-SiC surfaces. First, an ultrathin template layer was formed by electron beam induced carbon deposition (EBCD) on SiC by means of a focused electron beam. Amplification of the template by SIPGP resulted in polymer brush structures with controlled three-dimensional shapes. The effect of the applied electron dose as well as the initial lateral structure size on the brush layer morphology was investigated.

1. Introduction

Silicon carbide (SiC) is a very promising candidate for biotechnology and biosensing applications.[1−5] This wide band gap semiconducting material ($E_{\text{gap}} = 2.4-3.2$ eV, depending on the polytype) is mechanically extremely hard, chemically inert, and biocompatible.[6] Furthermore, SiC has physical properties that allow the fabrication of high temperature, high voltage, and high frequency devices.[7,8] In (bio)-chemical sensor applications, the establishment of a stable organic layer covalently attached to the semiconductor surface is of central importance. Despite the exceptional properties of this material, as well as its promise for use in biosensing, microelectromechanical systems (MEMS), and microfluidic applications, very little work has been devoted to preparation of functional SiC surfaces. Thus far, two approaches have been developed for the formation of dense and well-defined organic monolayers on SiC. Rosso and co-workers reported both photochemical and thermal functionalization of SiC with terminal alkenes.[9,10] The functionalization of SiC with organosilane self-assembled monolayers (SAMs) was reported by the research group of Uvdal.[11] Both approaches have been applied by some of us for biofunctionalization of SiC substrates with proteins.[12,13]

For the immobilization of biomolecules on surfaces, covalent grafting of polymer chains bearing multiple binding sites per chain is highly desirable. Such polymer chains allow the design of biosensors with higher loading capacities and enhanced sensitivities.[14] Furthermore, compared to direct immobilization of molecules on flat

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SAMs, this approach allows fabrication of systems which more closely resemble real biological environments.[15] However, to the best of our knowledge, no study has yet reported polymer coatings covalently attached to SiC substrates.

Surface-initiated polymerization (SIP) on SAMs has been the most widely used approach for the preparation of dense and well-defined polymer brushes on solids and allows control of the functionality, density, and thickness of the polymer brush layer with near-molecular precision.[16] SIP has been demonstrated for all types of polymerization methods including free[17] and controlled[18-20] radical, living anionic,[21] living cationic,[22] and ring-opening metathesis[23] polymerization. However, commonly used SAM approaches have several practical limitations. For example, their low thermal and chemical stability complicates polymerization or subsequent functionalization of the grafted polymer chains under more demanding reaction conditions.[24,25] Furthermore, silane monolayers on oxidized surfaces are prone to hydrolysis and are inappropriate for long-term biomedical applications.[26]

Recently, we have shown that well-defined, homogeneous, and highly stable polymer brushes can be prepared directly on carbonaceous materials such as diamond[27] and glassy carbon[28] by self-initiated photografting and photopolymerization (SIPGP) of vinyl monomers. The formation of defined reactive interlayers, such as SAMs, is no longer necessary and polymer brushes can be prepared in a one-step reaction. Furthermore, the SIPGP approach allows the preparation of micro- and nanostructured polymer brushes on various noncarbonaceous substrates by means of the carbon templating (CT) technique.[29] First, a stable ultrathin template layer of carbonaceous material is locally deposited on an inorganic substrate (e.g., Si, Si_3N_4, Ge, GaAs, GaN, mica, glass, Al) by means of a focused electron beam. Amplification of the carbon template by SIPGP results in polymer brush layers of controlled three-dimensional shapes on the submicrometer scale. Furthermore, the excellent chemical and thermal stabilities of the polymer brush layers allow consecutive polymer analogue reactions, even under drastic conditions. By this approach, stable polymer brushes with different shapes, dimensions, polymer architectures, and chemical functionalities can be prepared on a variety of substrates.[28-30]

Here, we report for the first time on the preparation of homogeneous as well as structured polymer brushes on SiC substrates. Unstructured polymer brushes were synthesized by the SIPGP of styrene and *N*,*N*-dimethylaminoethyl methacrylate (MAEMA) directly onto hydroxylated 6*H*-SiC surfaces in a single step reaction. A reactivity contrast was observed between the C—OH terminated $(000\bar{1})$ and Si—OH terminated (0001) 6*H*-SiC crystal faces, which was interpreted theoretically using density functional theory. Furthermore, we investigated the preparation of structured polymer brushes on the submicrometer scale using the CT-approach on Si—OH terminated (0001) 6*H*-SiC surfaces. The effects of both the locally applied electron dose and the initial lateral structure size on the brush layer morphology were investigated. The results presented here provide access to a broad range of applications; SiC cantilevers and membranes with different functionalities on their two surfaces for (bio)sensing applications, the asymmetric functionalization of SiC nanostructures for hierarchical self-assembly, and selectively functionalized surfaces of microfluidic channels may all be straightforwardly achieved using this method. Furthermore, these findings suggest that a variety of additional technologically important compound materials may exhibit anisotropic reactivity contrasts which could be explored in the future.

2. Experimental Section

All 6*H*-SiC substrates were purchased from SiCrystal AG and chemico-mechanically polished by NovaSiC to a root-mean-square surface roughness of < 0.3 nm on both Si- and C-polar surfaces. Before use, the SiC samples were ultrasonically cleaned in acetone and 2-isopropanol for 10 min each. The native oxide layer was removed by etching in HF (5% vol.) for 5 min. Additional surface cleaning was performed by plasma oxidation in oxygen at 200 W for 5 min. Surface hydroxylation was achieved by a final HF (5% vol.) etch for 5 min.

2.1. Electron Beam Induced Carbon Deposition (EBCD). Direct writing with a focused electron beam was performed with a Zeiss E-Line scanning electron microscope. The electron beam energy was set at 3 keV with a current of 136 pA and a vacuum pressure of $\sim 5 \times 10^{-6}$ mbar. The polymer brush gradient consisted of 100 parallel 10×0.5 μm^2 lines with electron doses linearly increasing between 2 and 10 mC/cm^2.

2.2. Self-Initiated Photografting and Photopolymerization (SIPGP). Freshly prepared SiC samples were added to approximately 1 mL of freshly distilled and degassed styrene or MAEMA. Polymerization was performed for 16 h in styrene and for

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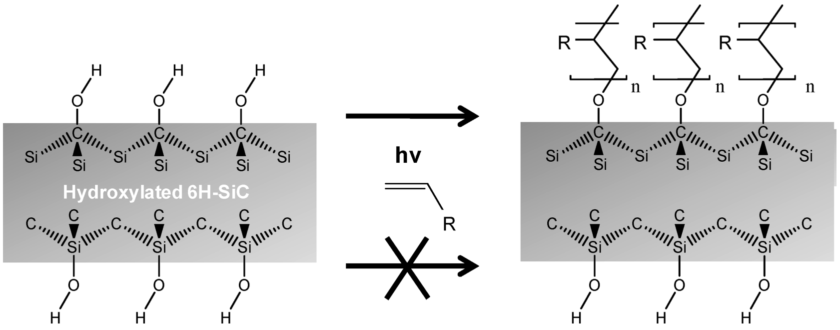

Figure 1. Preparation of polymer brushes on hydroxylated 6*H*-SiC. Polymer brushes are selectively formed on the C—OH terminated (000$\bar{1}$) crystal side by UV-induced SIPGP of styrene or MAEMA.

2.5 h in MAEMA under irradiation with UV light (intensity maximum at λ = 350 nm with a total power of ~5 mW/cm^2) at room temperature. After polymerization, the samples were removed from the reaction solution and immediately rinsed with a good solvent (toluene for PS brushes, ethanol for PMAEMA brushes). To ensure that only chemically grafted polymers remained on the surface, all substrates were additionally cleaned by ultrasonication for 5 min in the same solvent. The samples were then treated by ultrasonication in ethyl acetate and ethanol for 5 min each.

2.3. Atomic Force Microscopy (AFM). AFM scans were preformed with a Nanoscope IIIa scanning probe microscope from Veeco Instruments using standard tips in tapping mode under ambient conditions. The measurement of the unstructured polystyrene brush thickness on the C—OH terminated (000$\bar{1}$) 6*H*-SiC surface was performed by scratching the polymer layer with a metallic needle. The border of the scratch was then imaged by AFM in tapping mode over an area of 10 μm^2. The scanned data were then analyzed by the local depth analysis option of the commercial AFM software by choosing areas within the scratched region and the intact surface around the trench. Due to the extreme hardness of SiC, no scratching of the underlying substrate is possible. Although remnant derbis are observed in the scratched region, the underlying substrate morphology can be resolved in places using AFM, indicating a complete removal of the polymer brush layer within the measurement error.

2.4. Infrared Spectroscopy (IR). IR spectroscopy was performed with an IFS 55 Bruker instrument equipped with a diffuse reflectance infrared Fourier transform (DRIFT) setup from SpectraTech and a liquid nitrogen cooled MCT detector. For each spectrum, 470 scans were accumulated with a spectral resolution of 4 cm^{-1}. For each measurement, background spectra were recorded on unmodified SiC samples.

2.5. Density Functional Theory (DFT). The calculations were performed under periodic boundary conditions with a spin-polarized general gradient approximation (GGA) using the BLYP functional (a hybrid functional where the exchange part is generated by B88,[31] and the correlation part is generated with the LYP functional[32]). A mesh of (2 × 2 × 1) k-points was generated using the Monkhorst-Pack scheme,[33] and the SCF density convergence was set to 1.00×10^{-6}. The numerical basis set of choice included polarization p-functions on all hydrogen atoms, and d-functions on all carbon, silicon, and oxygen atoms.

3. Results and Discussion

The method for preparation of polymer brushes on 6*H*-SiC is outlined schematically in Figure 1. First, a freshly cleaned 6*H*-SiC substrate was etched with HF in order to remove the surface oxide layer. It has been reported that the Si-face of HF-etched 6*H*-SiC crystals is nearly perfectly OH-terminated, whereas the C-face is primarily OH-terminated with a smaller fraction of C—H terminating groups.[34−36] The substrate was successively placed in a phototube and submerged in bulk monomer. For the preparation of polystyrene (PS) brushes, the self-initiated photografting and photopolymerization (SIPGP) of styrene was performed for 16 h by placing the phototube between two UV-lights (maximum intensity at λ = 350 nm) in order to irradiate both C—OH terminated (000$\bar{1}$) and Si—OH terminated (0001) crystal faces. To ensure that only chemically grafted polymer remained on the surface, the substrate was ultrasonically cleaned in a series of solvents.

In order to verify the formation of an unstructured polymer brush layer, both crystal faces were subjected to a so-called scratch experiment. First, the surface was scratched with a metallic needle in order to locally remove the PS brush layer and leave the hard SiC substrate intact. The border of the scratch was then imaged by AFM and analysis of the height difference between the intact and scratched surface areas gave the thickness of the brush layer (Figure 2). Detailed analysis of the scanned data on different analogue scratches showed that a homogeneous 42 ± 5 nm thick PS brush layer was formed on the C-face of the crystal. However, no polymer layer was observed by similar scratch experiments on the Si—OH terminated crystal face.

The formation of PS brushes exclusively on the C—OH terminated crystal side was further confirmed by diffuse reflection infrared Fourier transform (DRIFT) spectroscopy. In the infrared (IR) spectrum of the modified C-face (Figure 3), the characteristic fingerprints of PS are

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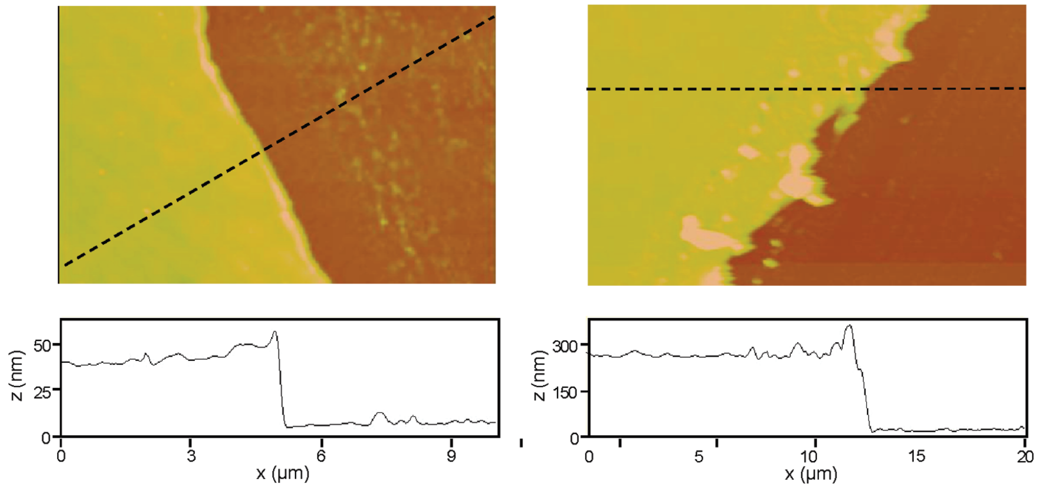

Figure 2. AFM height image and section analysis of trench created by scratching the PS (left) and PMAEMA (right) brush layer on C−OH terminated (0001) 6*H*-SiC surface with a metallic needle. The localized depth analysis yielded an average height difference of 42 ± 5 nm for PS brushes and 230 ± 10 nm for PMAEMA brushes.

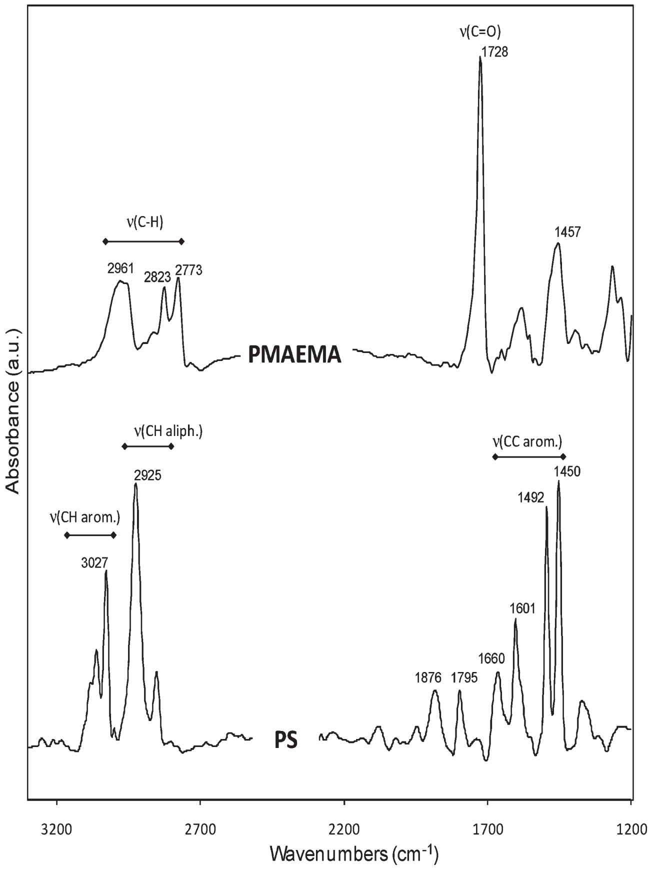

Figure 3. IR spectra of PMAEMA and PS brushes on a C—OH terminated $(000\bar{1})$ 6*H*-SiC surface. The spectra show characteristic fingerprints of PMAEMA (the stretching C—H and C=O vibrational modes) and PS (the stretching vibrational modes of aromatic groups (*ν*(CH aromatic) and *ν*(CC aromatic)) and from methylene groups).

observed: the stretching vibrational modes of aromatic groups (*ν*(CH) at ~3027 cm^{-1} and *ν*(CC) between 1450 and 1601 cm^{-1}) and the methylene groups of the polymer backbone with a maximum at 2925 cm^{-1}.[37] However, no characteristic absorption bands were detected by IR measurements on the other crystal face, thus confirming the absence of PS brushes on Si—OH terminated (0001) 6*H*-SiC surfaces and revealing the reactivity contrast between the two crystal sides for SIPGP.

As reported previously, polymer brush formation occurs via the SIPGP mechanism in which the monomer acts as a photosensitizer that activates a surface functional group by hydrogen abstraction to begin a surface-initiated free radical polymerization.[27,29,30,38] Since the SIPGP relies on hydrogen abstraction by a photoactivated monomer, the grafting efficiency depends on the bond dissociation energy (BDE) of the surface functional group. In previous studies, this has explained the selective grafting of styrene on oxidized and H-terminated diamond substrates.[37]

In order to investigate the reactivity contrast between the two SiC crystal faces, we have calculated the CO—H and SiO—H bond dissociation energies of 6*H*-SiC using density functional theory. For a perfectly OH-terminated (0001) 6*H*-SiC surface, the theoretical BDE of SiO—H was calculated to 121.9 kcal/mol. This value is very similar to the BDE of SiO—H on silica (119.3 kcal/mol).[39] The absence of polymer brushes on the Si-face of SiC due to the high BDE energy of SiO—H groups is in agreement with an earlier report in which we showed that no polymer brushes form on bare silica surfaces during the SIPGP process.[29]

The theoretical BDE of a CO—H group on partially OH-terminated $(000\bar{1})$ 6*H*-SiC surfaces was calculated to between 92.7 kcal/mol for an OH-termination fraction of 75% and 96.3 kcal/mol for an OH-termination fraction of 50%. For both calculations, the remaining surface sites were H-terminated. The SIPGP-induced formation of polymer brushes on surface terminations with BDEs for hydrogen abstraction below approximately 100 kcal/mol is in agreement with earlier reports.[30] Thus, these results

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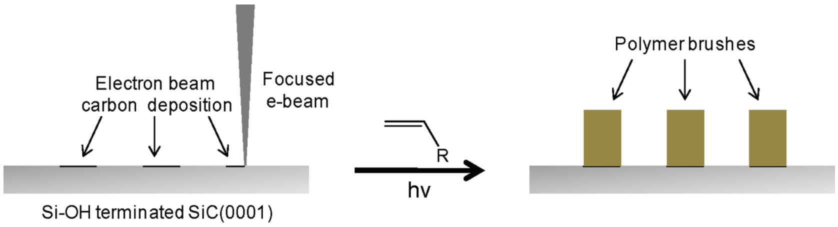

Figure 4. Formation of structured polymer brushes on Si−OH terminated 6*H*-SiC (0001) surfaces by the carbon templating technique. Irradiation of the substrate by an electron beam induces the formation of a carbon template. Amplification of the carbon template by SIPGP results in structured polymer brushes.

show that the selective formation of PS brushes on the C-face can be explained by the proposed SIPGP mechanism, and the energy difference required for hydrogen radical abstraction from the C—OH terminated and Si—OH terminated 6*H*-SiC crystal faces. Despite the room temperature thermal distribution of states of the reacting species, the ~20 kcal/mol higher BDE on the Si—OH crystal face kinetically prohibits polymer layer formation during reasonable reactions times. It is noted here that the C—H groups of the partially hydroxylated C-face most likely do not participate in the SIPGP mechanism since the BDEs were calculated to be between 109.0 and 109.5 kcal/mol, depending on the hydroxyl coverage.

Besides the polymerization of styrene, the SIPGP reaction can be performed with a broad variety of vinyl monomers such as styrene derivatives and (meth)-acrylates.[29,30,38] In order to demonstrate that this approach allows an anisotropic functionalization of SiC with various polymer brushes having different properties and functionalities, we have performed here the SIPGP of *N*,*N*-dimethylaminoethyl methacrylate (MAEMA) resulting in poly(*N*,*N*-dimethylaminoethyl meth(acrylate)) (PMAEMA) brushes. PMAEMA is a weak polyelectrolyte with multiresponsive solution properties (pH, salt, and temperature).[40] The responsiveness of the PMAEMA brushes could be potentially applied in sensor systems or for nanoactuator constructions. AFM-scratch experiments (Figure 2) as well as IR spectroscopy (Figure 3) revealed that also with MAEMA, polymer brushes were selectively formed on the C—OH terminated crystal side. However, it was found that the increase of the thickness of the polymer layer with the irradiation time was specific for each monomer. After 2.5 h of irradiation, SIPGP of MAEMA gave a layer thickness of 230 ± 10 nm.

Recently, we reported on the preparation of highly defined functional and structured polymer brushes on various inorganic substrates by means of the carbon templating (CT) technique.[29] A stable template layer formed by electron beam-induced carbon deposition (EBCD) was locally applied on an inorganic substrate. Amplification of the carbon template by SIPGP resulted in polymer brush layers of controlled three-dimensional shapes. The formation of polymer brushes on EBCD-treated surfaces by the SIPGP mechanism can be explained by the low BDE for hydrogen abstraction from the carbon deposits.[29,41] Since a reactivity contrast between the bare substrate and surface carbon deposits is required during the SIPGP step, the CT-approach was not applied for the preparation of structured polymer brushes on C—OH terminated $(000\bar{1})$ 6*H*-SiC surfaces. However, because no polymer brushes were formed on the Si-face during the SIPGP process, we have investigated here whether the CT-technique enables the synthesis of structured PS brushes on Si—OH terminated (0001) 6*H*-SiC surfaces. The preparation of structured polymer brushes by the CT-technique is schematically outlined in Figure 4.

In a first experiment, a 10×50 μm^2 carbon template gradient was prepared by direct writing with a focused electron beam on a freshly hydroxylated (0001) 6*H*-SiC surface. The electron dose was continuously increased from 0 to 50 mC/cm^2. The structured substrate was subsequently immersed in styrene and irradiated with UV light for 16 h. After rigorous ultrasonic cleaning of the substrate in solvents, AFM measurements were performed and revealed selective formation of PS brushes with a thickness of up to 105 nm on the carbon template region (Figure 5).

Figure 5 also shows that the height of the resulting polymer brush gradient structure is determined by the locally applied electron dose. The dependence of the polymer layer thickness on the electron beam dose is in agreement with earlier work.[29] At low doses, the carbon deposits only partially cover the substrate and the polymer layer thickness is proportional to the surface concentration of potential grafting points.[30] The gradual increase of the PS brush thickness on SiC between 0 and 10 mC/cm^2 can be explained by an increase of the polymer grafting density. However, Figure 5 also shows a polymer layer thickness decrease between 10 and 50 mC/cm^2. A very similar height profile was observed recently under identical CT and SIPGP conditions on Al, Ge, GaAs, and GaN surfaces. In contrast, it was found that the polymer layer thickness remains constant at high electron doses on Si and Si_3N_4.[29] The reason for the layer thickness decrease above 10 mC/cm^2 on certain substrates remains unclear. A possible explanation is that a prolonged irradiation of the carbon deposits may alter the surface chemistry and thus the site density for the photografting, as was reported

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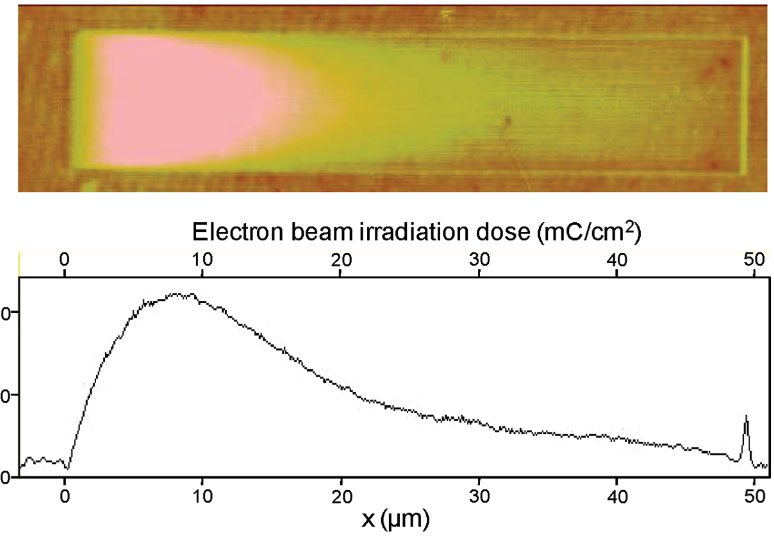

Figure 5. AFM measurement ($52 \times 13\,\mu m^2$) and height profile of a PS brush structure created by the SIPGP of styrene (polymerization time = 16 h) on an EBCD gradient layer on Si—OH terminated 6*H*-SiC (0001). The electron beam dose was linearly increased from 0 to 50 mC/cm^2.

for SAMs.[30,41−45] The elucidation of this intriguing behavior will be the subject of future experimental and theoretical studies.

Nevertheless, this experiment shows that the layer thickness of the polymer brushes can be tuned with CT by controlling the locally applied electron dose. Different experimental and theoretical studies on micro- and nanostructured polymer brushes have demonstrated that the polymer brush morphology and thickness were not only influenced by the polymer chain length and grafting density, but also by the initial pattern size.[44,46−48] In order to study the effect of the e-beam dose and the initial structure size on the resulting brush morphology, an array of isolated “X-structures” was created by varying the electron irradiation dose and the line width over the pattern (Figure 6(a)).

In Figure 6(b), the PS brush layer thickness is plotted as a function of the electron irradiation dose for structures written with different primary line widths. As a comparison, the polymer layer thickness of the PS gradient structure (Figure 5) as a function of electron dose is also displayed. A similar dose/height dependence is observed in both experiments. Between 0 and 10 mC/cm^2, the polymer layer thickness increases gradually with the applied electron dose. Since each X-structure was written by the superposition of two crossing lines, the electron dose at the line intersection is the sum of the dose of each individual line. For the structures written with a line width of 1000 nm, it can be clearly observed in Figure 6(a) that the layer thickness increases at the line intersections for structures with a dose of 2 mC/cm^2 (from 31 to 71 nm) and 4 mC/cm^2 (from 70 to 95 nm), and that the layer thickness decreases at the intersection for lines written with a dose of 8 mC/cm^2 (from 98 to 66 nm) and 10 mC/cm^2 (from 99 to 51 nm). This behavior is in agreement with the grafting gradient experiment and confirms the reduction of the layer thickness above 10 mC/cm^2. Note that the gradient and the array structures depicted in Figures 5 and 6(a) were fabricated on the same substrate and, thus, identical reaction conditions were applied.

Figure 6(b) also shows that for polymer lines created under identical electron irradiation conditions, the polymer layer thickness is strongly influenced by the lateral feature size. The strong dependence of the initial line width on the layer thickness for lines written with identical electron doses is illustrated in Figure 6(c). This behavior is observed because the length of the grafted macromolecules is comparable to the dimension of the lateral structures. Since polymer chains at the edges of the structures can extend to polymer-free surface regions, conformational relaxation of the stretched chains results in a decrease of the polymer layer thickness due to the drop of the local grafting density at the edges.[44,46−48]

The possibility of the brushes extending to polymer-free surface regions also results in a widening of the structures. The line width at half-maximum height ($\omega_{1/2}$) of the X-structures, as measured by AFM, confirmed the widening of the structures; for example, for structures with an electron dose of 10 mC/cm^2, $\omega_{1/2}$-values of 280, 340, 570, and 1150 nm were measured for lines with initial widths of 50, 100, 500, and 1000 nm, respectively. It is noteworthy that AFM measurements systematically overestimate the line width of polymer brush structures due to convolution with AFM tip.[49] Nevertheless, these results show that the CT-technique

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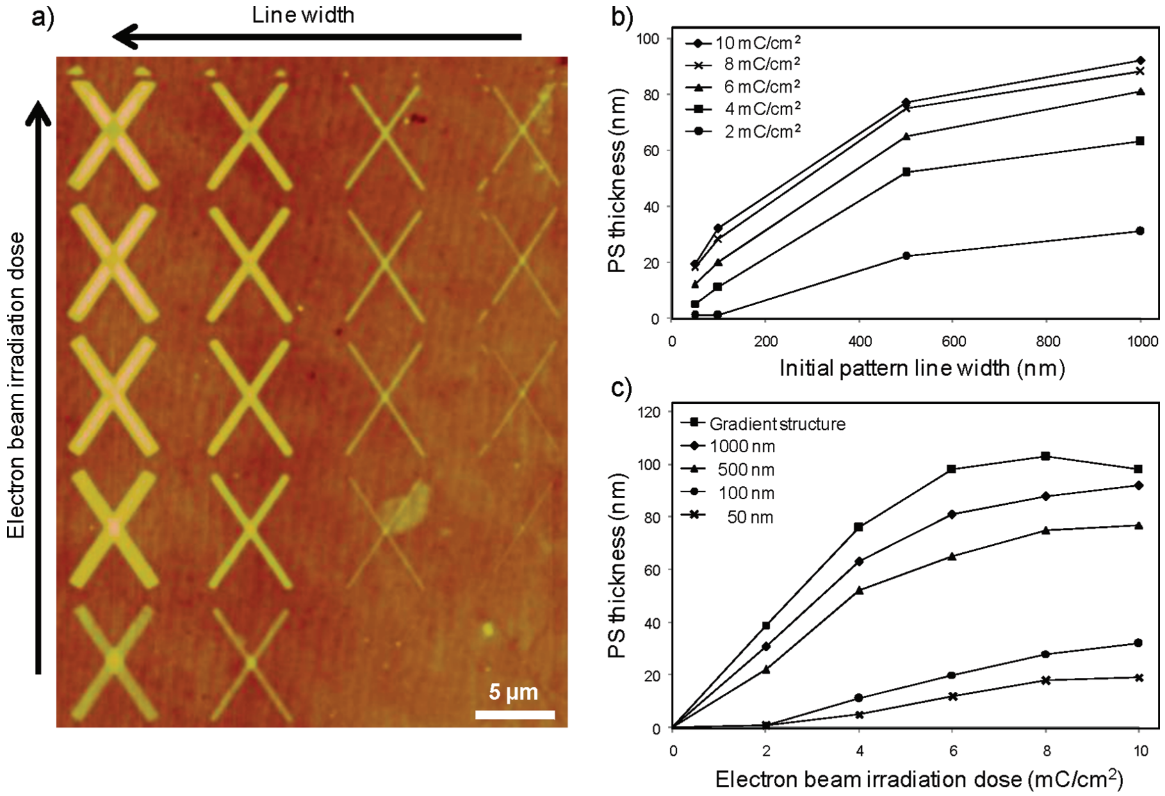

Figure 6. (a) AFM image (37 × 48 μm^2) of an array of structured PS brushes created by the SIPGP of styrene (polymerization time = 16 h) on different carbon template structures on a Si—OH terminated 6*H*-SiC (0001) surface. The X-structures were written with a line width of 1000, 500, 100, and 50 nm and an electron dose of 2, 4, 6, 8, and 10 mC/cm^2. (b) Height of the polymer brush X-structures as a function of the electron irradiation dose for lines with widths of 50, 100, 500, and 1000 nm (polymerization time = 16 h). As a comparison, the polymer layer thickness of the PS gradient shown in Figure 3(b) is also plotted. (c) Height of the polymer brush X-structures as a function of the initial line width for lines written with an electron dose of 2, 4, 6, 8, and 10 mC/cm^2.

allows the preparation of polymer brush structures on Si—OH terminated 6*H*-SiC (0001) on the submicrometer scale.

4. Conclusion

While self-initiated photografting and photopolymerization (SIPGP) of styrene and MAEMA result in homogeneous and stable polymer brush layers directly on C—OH terminated (0001) 6*H*-SiC surfaces, no polymer brushes were observed on the Si—OH terminated 6*H*-SiC (0001) crystal face under identical reaction conditions. The reactivity contrast between the two crystal faces for SIPGP was explained by the differences between the bond dissociation energies for hydrogen abstraction on the two hydroxylated surfaces, as revealed by theoretical calculations using density functional theory. Furthermore, structured PS brushes on the submicrometer scale were prepared using the carbon templating (CT) technique on the Si—OH terminated crystal face. The effect of the applied electron dose on the thickness of the brush layer was studied using a gradient structure. Finally, a structure array was prepared to study the effect of the lateral structure size and the irradiation dose on the morphology of the resulting PS patterns. AFM measurements of the structures revealed the dependencies of both the electron dose and the structure width on the polymer layer thickness.

The preparation of structured functional polymer brushes, for example, by polymer analogue conversions of grafted polymer chains to introduce polymer-pendant functionalities,[29] can be used for the patterned attachment of, for example, proteins or other biomolecules to create sensor arrays directly onto biocompatible SiC surfaces. Furthermore, the CT-technique allows control of not only the 2D location of the polymer brushes and thus the grafted biomolecules, but also, by varying the locally applied electron dose, the grafting density of functional groups. Currently, work is in progress to investigate further modifications of structured polymer brushes on SiC created by the CT-technique with biomolecules.

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