

Patterning of Thin Poly(*N*-vinyl pyrrolidone) Films on Silicon Substrates by Electron Beam Lithography

Sina Burkert,¹ Thomas Schmidt,² Uwe Gohs,¹ Ingolf Mönch,³ Karl-Friedrich Arndt²

¹Leibniz Institute of Polymer Research Dresden, 01069 Dresden, Germany

²Physical Chemistry of Polymers, Technische Universität Dresden, 01062 Dresden, Germany

³Leibniz Institute for Solid State and Materials Research Dresden e.V., 01069 Dresden, Germany (IFW Dresden)

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ABSTRACT: Poly(*N*-vinyl pyrrolidone) (PVP) is a widely used biocompatible polymer. PVP can be crosslinked by electron beam irradiation even in dry state. In contact with water it forms hydrogels. In a previous work we analyzed the crosslinking behavior of PVP bulk gels and thin PVP films on silicon wafers under electron beam irradiation. In this work, we applied the electron beam lithography on dry PVP films. Different patterns with a width of less than 100 nm were written into the film with the e-beam of a

scanning electron microscope. The topography of the patterned film is investigated by atomic force microscopy. For further applications, we tried to create a gradient of crosslinking density within the film using a combination of e-beam irradiation and e-beam lithography. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 106: 534–539, 2007

Key words: electron beam irradiation; lithography; hydrogels; thin films; swelling

INTRODUCTION

The crosslinking of polymer chains can occur both in solvent^{1,2} and in the absence of solvent,³ as a direct effect of high-energy radiation on the polymer materials. The homolytic bond cleavage and the intermolecular coupling of the resulting radicals lead to network formation. Charlesby and Alexander first reported on crosslinking of poly(*N*-vinyl pyrrolidone)⁴ and various other polymers,⁵ under irradiation of their aqueous solutions. Later, the hydrogel formation in irradiated solutions of PVP was investigated by other groups. Hydrogels, especially hydrogels based on PVP, are extensively used in medicine and pharmacy.^{6–8}

Irradiation of aqueous solutions provokes a radiolysis of water. Reactive H•, and especially OH•, radicals were formed. In dry state more energy is needed to create comparable reactive radicals during the breakage of the C—C or the C—H bond. The absence of solvent makes it possible to crosslink polymers as a coated film, which we could show in a previous work.⁹ We synthesized PVP bulk gels, as well as PVP films fixed on a silicon surface. As seen

for various other polymers, the network density rises with the increase of the dose. The properties (degree of swelling) of the resulting bulky hydrogel or layer depended on the applied dose.¹⁰

Based on previous investigations,¹¹ we show in this article that one could apply e-beam lithography on patterning of PVP films. An advantage of e-beam lithography is the simple synthesis of hydrogel structures with small lateral sizes down to nanometer resolution. The height of the structures could be controlled as well. The influence of radiation dose on the pattern was analyzed by atomic force microscopy (AFM).

It is known that a higher crosslinking density resulted in a smaller degree of swelling.¹² Therefore, we were also interested in forming a gradient of crosslinking density directly in the film. For creating regions with different swelling behavior, we combined the electron irradiation of the whole PVP film with electron beam lithography. Its swelling in water is observed. Generally, the patterning of polymers and patterns with different degree of swelling showed high application potential, e.g., for lab-on-the-chip¹³ and protein adsorption.^{14–16}

EXPERIMENTAL

Materials

Poly(*N*-vinyl pyrrolidone) was obtained from Sigma-Aldrich (Germany). Its molecular weight was determined by static light scattering in methanol to $M_w = 479,000$ g/mol. The polydispersity was determined

Correspondence to: K.-F. Arndt (karl-friedrich.arndt@chemie.tu-dresden.de).

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by SEC (Knauer, Germany) in chloroform to $M_w/M_n = 3.2$. Si wafers (2", Silchem GmbH, Freiberg, Germany) exhibiting a native oxide layer of thickness $t = 2.0$ nm (determined by spectroscopic ellipsometry) were used as substrate. The spin-coated PVP films had an overall thickness of 200 nm after drying in vacuum for several hours.

Synthesis of PVP films

The films were prepared by spin-coating of PVP dissolved in pure ethane acid onto Si wafers using a Spin Coater P6700 (Speedline Technology, Franklin, USA). Standard conditions for the film preparation were: 3 wt % PVP and 3000 rpm. The solutions were filtered through 0.45 μm nylon filter before coating. The prepared films were dried (at 60°C) in vacuum for several hours to remove the remaining solvent and to avoid the uptake of atmospheric water.

Patterning of PVP films by electron beam lithography

To obtain structures in the PVP film with a resolution lower than 1 μm , the focused electron beam (~ 10 nm in diameter) of a S-4500 (Hitachi, Japan) with electron energy of 20 keV was used. The coated Si substrates were irradiated in a high vacuum (10^{-5} Pa). The position of the e-beam and dwell time at each pixel position was controlled by an ELPHY data acquisition and control computer system (Raith GmbH, Dortmund, Germany). Different patterns could be created by using the scripting capabilities of the ELPHY software.

Exposure areas were generated by digitally scanning the e-beam across the polymer surface. An average dose, D , for such an exposure was calculated

(simplified) according to

$$D = \frac{It}{A}$$

with

$$A = na^2$$

where I is the beam current, t is the dwell time per pixel, n the number of pixels per writing area, and a the size of a single quadratic pixel without an overlap to the next one. Typically experimental conditions, using a beam voltage of 20 keV and a writing field of $100 \times 100 \mu\text{m}^2$ were: $I = 23$ pA, $t = 1.6 \mu\text{s}$, interpixel distance ~ 6 nm. The beam current was determined by a measurement system, consisting of a Faraday-cup as part of the sample holder and a picoampere meter (Kethley 6485). The irradiated samples were developed after irradiation in pure water and ethanol.

The samples for the synthesis of the crosslinking gradient were first spin-coated and then crosslinked by e-beam irradiation ($E = 120$ keV, electron accelerator ANDREA 1, FEP Dresden, Germany) under inert atmosphere (N_2). The applied radiation doses were adjusted at different dose rates by changing the beam current ($I = 2\text{--}20$ mA) and the exposure time (speed of the conveyor belt: 1–18 m/min). The radiation dose D absorbed by the PVP films was calibrated using an alanine film dosimeter^{17,18} of 10 μm thickness and an overall uncertainty of $<3\%$. After irradiation the samples were extracted with ethanol and dried under vacuum.

Regions with higher crosslinking densities were formed by a further irradiation with the focused e-beam (for scheme of experimental procedure, see Figure 1).

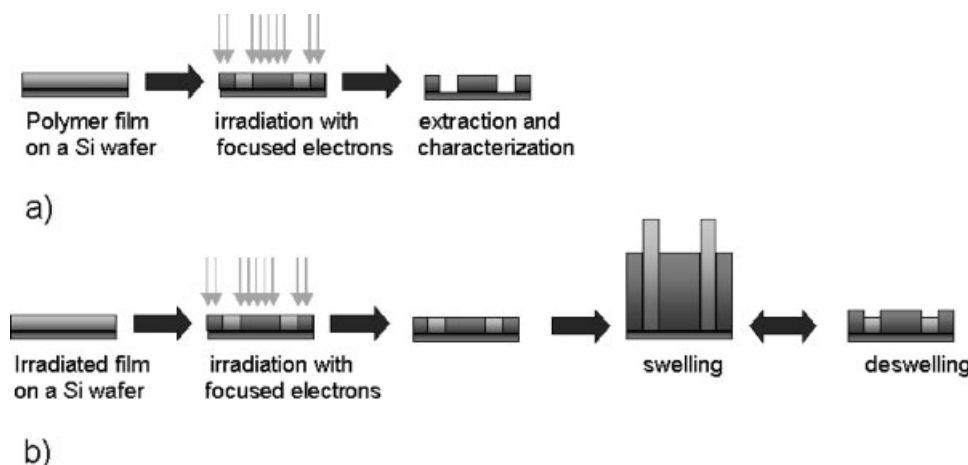


Figure 1 Scheme of irradiation experiments. (a) Patterning by electron beam lithography: the irradiated regions stayed on the wafer. (b) Creating of a gradient of crosslinking density: combination of e-beam irradiation and e-beam lithography.

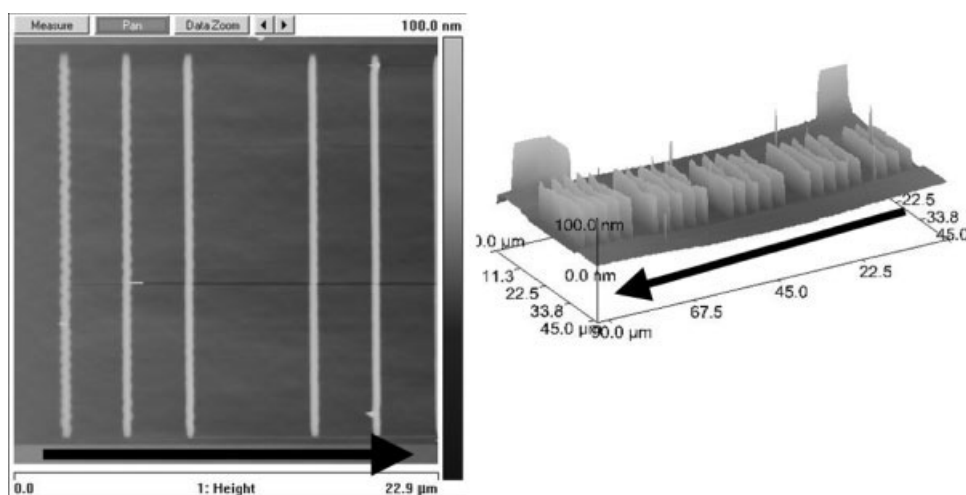


Figure 2 Crosslinked PVP stripes at dry state on Si wafer. Left: AFM image, dose rises along the arrow from 70 to 110 $\mu\text{C}/\text{cm}^2$. Right: 3D visualization of the stripes, dose rises along the arrow from 70 to 290 $\mu\text{C}/\text{cm}^2$, which corresponds to a rise in the height of the stripes.

Reflectometric interference spectroscopy

The thickness of the dry PVP films (t_0) and of the irradiated and extracted PVP films (t) were determined by reflectometric interference spectroscopy (ETA-CSS-BID Version 4.1, ETA Optik GmbH, Germany). The reflection of the incident light from a halogen lamp source (angle = 60°) was detected with a 2-diode array spectrometer operating in the wavelength range 400–900 nm, to determine the film thickness.

Atomic force microscopy

A 3-dimensional image of the synthesized patterns could be made by atomic force microscopy (AFM

Dimension 3100, Digital Instruments, Nanoscope IV-Controller, software version: 6.13r1). The tapping mode was used to map the irradiated structures at ambient conditions. AFM tips of “Veeco MPP-11,100” with a resonance frequency of 300 kHz and a spring constant of 20–70 N/m were used at ambient and liquid conditions. Home-made liquid-cell equipment was used to visualize the swollen structures.

RESULTS AND DISCUSSION

Patterning of PVP films using e-beam lithography

Different pattern (stripes, squares, dots, logo of “Technische Universität Dresden” (TUD)) were writ-

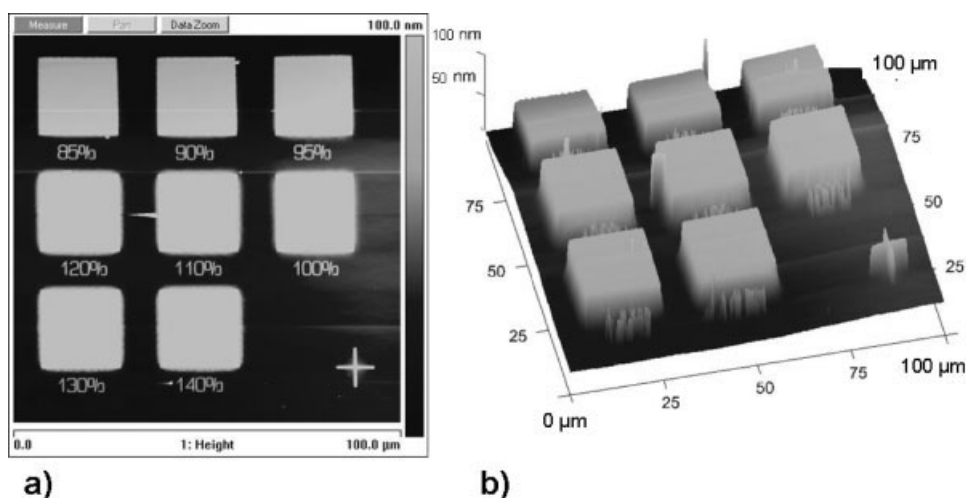


Figure 3 AFM image of irradiated PVP squares on a Si substrate at the dry state (a) and their 3D visualization (b). Percentage correlates to percentage of irradiated dose (100% equals 100 $\mu\text{C}/\text{cm}^2$). Increasing brightness shows increasing height (from 50 to 100 nm).

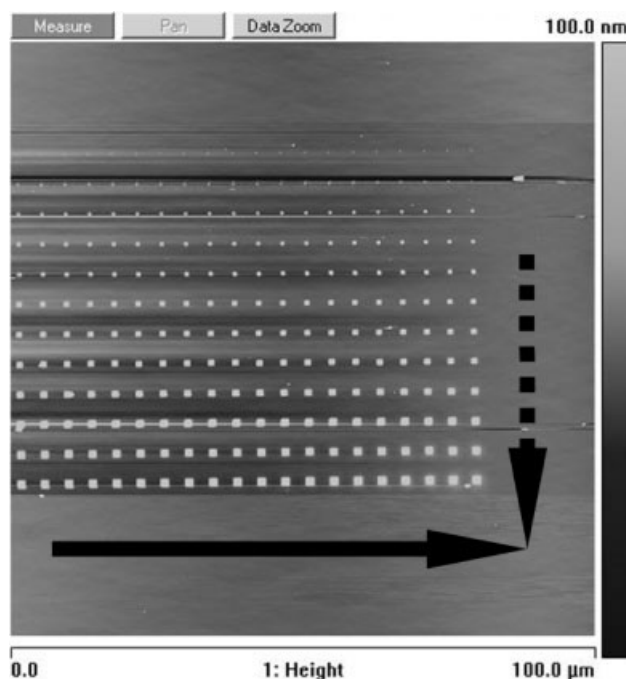


Figure 4 AFM image of irradiated PVP dots on a Si substrate at the dry state. The dose rises along the dark arrow from 100 to 300 $\mu\text{C}/\text{cm}^2$. The width of the irradiated square rises along the dotted arrow from 100 to 1200 nm.

ten with the e-beam of a modified SEM. The remaining non treated polymer and the sol-content in the irradiated areas were washed away during extraction. Even though the wafers were investigated in dry state, the structures remained stable over a long period of time. As expected, the irradiation dose influences the properties of the pattern. We were

able to control the applied dose and as a result, we obtained different heights of the patterns (see Figs. 2–4). The stronger the applied radiation dose, the higher was the pattern, which did not depend on the irradiated image. Figure 2 shows crosslinked stripes of PVP with a length of 25 μm and a width of 500 nm. The wavelike structure diminished to form stable lines with increasing crosslinking density. The right picture shows a 3D-AFM image of the irradiated lines. It is clearly seen, that the height rises along the arrow.

Especially, as seen in Figure 3(b), sharp contours could be achieved by electron beam lithography. We irradiated squares in the PVP film with a width of 20 μm . Also in this case, their height depended on the radiation dose and increased linearly from 50 nm to 100 nm. The percentages [Fig. 3(a)] could give an idea how strong the zones were irradiated. At 85% the structure appeared very sharp, whereas at 140% the structures became diffuse. Here one could observe the proximity effect,^{19,20} which revealed to the irradiation of adjacent polymers due to the scattering and reflection of the e-beam on the silicon wafer.

The AFM image in Figure 4 shows that it was possible to minimize the structures to a lateral width of 100 nm with a dose of 100 $\mu\text{C}/\text{cm}^2$. This was the smallest square which could be visualized by the AFM. These small dots remained very stable on the surface after the extraction.

The proximity effect, mentioned before, could be visualized more clearly in Figure 5, where the logo of the “Technische Universität Dresden” was created by electron beam lithography. The AFM image rep-

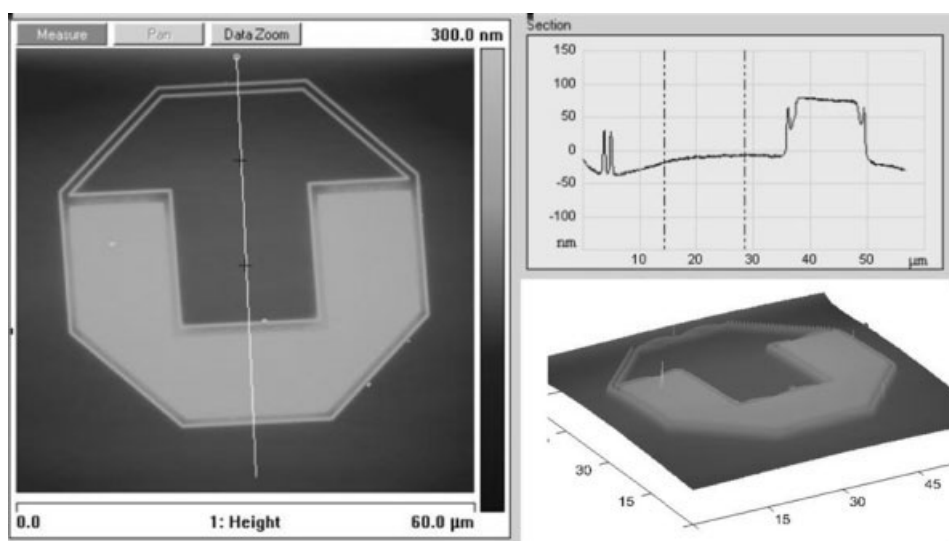


Figure 5 Visualization of the logo of the “Technische Universität Dresden.” Left: AFM image of irradiated PVP ($D = 100 \mu\text{C}/\text{cm}^2$) on a Si substrate at the dry state. Proximity effect is seen between the lines and the irradiated area. Right: Height profile along the axes (small line in left figure) and 3D image of the logo. Differences in height (lines = 50 nm, area = 80 nm) are due to the proximity effect.

resents the height profile and a 3-dimensional view of the structure. Additional side crosslinking due to backscattered electrons induced an indistinct structure and increasing height, which could be seen in the section profile.

Generation of a gradient in crosslinking density by e-beam lithography

To create a gradient in crosslinking density we took an irradiated PVP film (dose = 350 kGy), which was already extracted and dried under vacuum. The film with an initial thickness of 150 nm was irradiated a second time by a focused e-beam of modified SEM [see Fig. 1(b)]. By this method we could induce a local gradient of crosslinking density in the film.

From the Flory-Rehner equation,²¹ it follows that the degree of swelling is indirectly proportional to the crosslinking density. On the other hand, the crosslinking density increases with the dose, with other words, the higher the dose, the lower the degree of swelling. Hence, the double irradiated zones swelled less. We expected no or only small changes in thickness of the dry film and differences in the thickness of different irradiated zones in the swollen state. Using atomic force microscopy we could investigate the different states of swelling in the film.

The logo of the “Technische Universität Dresden” (see Fig. 5) was written with the focused e-beam on the irradiated PVP film. Figure 6(a) indicates an

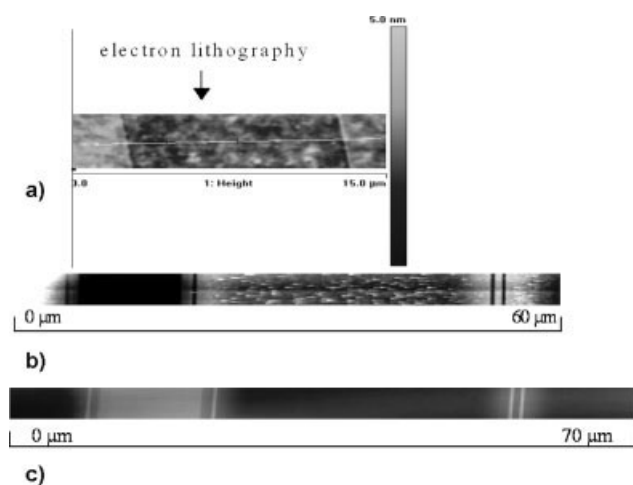


Figure 6 The logo of the “Technische Universität Dresden” (see Fig. 5) was written on an irradiated PVP film ($D = 350$ kGy) by e-beam lithography with a dose of $100 \mu\text{C}/\text{cm}^2$. The thickness of the gel was measured along the axes shown in Figure 5. (a) AFM image at dry state; extra irradiated zone lies 2 nm lower than the surrounding area. (b) PVP film as in (a) after swelling in water for 30 min; surrounding area swelled with a factor 10, double irradiated area with a factor 6 (brightness corresponds to the height). (c) AFM image of an irradiated PVP film on a Si wafer at dry state (same region as in (b)) after deswelling.

AFM image of a part of logo in the dry state. It shows that the region irradiated by the focused electrons laid ~ 2 nm (1.5% of the initial height) lower than the surrounding area. One could speak of “shrinkage” of the irradiated area, which was due to an increase of crosslinking density. This volume contraction was observed in literature before.²² During swelling in water, the surrounding area swelled with a factor of 10, whereas the doubled irradiated regions swelled with a factor of 6 [see Fig. 6(b)]. This AFM image was directly taken after a swelling time of 30 min. After that time the film (film thickness $< 1 \mu\text{m}$) has reached its equilibrium degree of swelling. Now we go back to the initial state like in Figure 6(a). To remove the water, the sample was dried in a vacuum oven ($T = 60^\circ\text{C}$) for several hours and measured again. Contrary to our expectations, the twice-irradiated regions lay 15 nm higher than the surrounding area, which corresponds to 110% to the initial height [see Fig. 6(c)]. To exclude an effect of remaining water, the sample was dried for more than 1 week under vacuum. Surprisingly, the AFM image remained the same and could not be compared to Figure 6(a).

Our explanations for this finding are the following: Poly(*N*-vinyl pyrrolidone) is a very hydrophilic polymer, which augmented the attractive forces on water. It is well known from literature that with higher irradiation dose at ambient conditions, polymers become more and more hydrophilic. Excited oxygen from ambient air could be incorporated in the polymer film and therefore form hydrophilic groups, which are mainly at the surface. However, with decreasing film thickness, the effect becomes global.^{23–26}

The high hydrophilicity of crosslinked PVP complicated the elimination of water. We assume that water, which could not be removed during the drying process, remained in the highly crosslinked regions and provoked a remaining swelling.

CONCLUSIONS AND OUTLOOK

In this work we concentrated our research on electron lithography of poly(*N*-vinyl pyrrolidone). Dry spin-coated PVP films of a defined thickness in 10^2 nm range were crosslinked by electron beam irradiation directly and irreversible as a film on a Si wafer. Different pattern could be created with the e-beam of a modified scanning electron microscope. The position of the e-beam was controlled by specific software. Non treated polymer could easily be washed away. The crosslinked patterns are stable fixed on the wafer without any adhesion promoter. The atomic force microscopy helped a lot to investigate the stability and the swelling behavior of the structures.

With AFM we were able to show that electron beam lithography creates very sharp and fine structures in nanometer scale in a PVP film. Even after a longer period of time those structures remained stable.

Electron beam lithography could as well induce a crosslinking density gradient in a crosslinked film. Swelling measurements showed that with increasing crosslinking density the swelling degree decreased. This gradient could as well be visualized with AFM.

After drying the higher crosslinked regions protruded out of the surface, which could be explained with remaining solvent in the network, which could not be removed and induced a swelling.

Because of the biocompatibility of PVP a wide range of application will be possible for those small structures. Uses in biotechnology, sensor technique, protein adsorption and bio-medicine in nanoscale and microscale could be expected.

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