Unconventional Nanostructuring Approaches

A. Neubauer[1], P. Hudek[2], G. Stangl[3], K. Riedling[3], D. Pum[1], W. Fallmann[3], U.B. Sleytr[1], H. Löschner[4], I. Kostic[2], F. Rüdenauer[5]

This paper describes two rather unconventional approaches towards nanostructuring: The first approach uses a novel type of material — two-dimensional crystalline protein layers, the so-called S-layers — in lieu of a photoresist. These layers not only promise an exceedingly high intrinsic lateral resolution due to their structure and nanometer-range thickness, they may also play a key role as geometrically and physicochemically precisely defined immobilization matrices in the binding of functional molecules (e.g. enzymes or antibodies) in bioanalytical sensors, as supporting layers for functional lipid membranes (for example, in ion sensitive field effect transistors), or as intermediate layers for binding ligands in the design of resists for nanostructure lithography.

The second approach presented here is unconventional not due to the technology used but with regard to the devices that are to be created: An array of silicon columns, which are prepared by electron beam lithography and anisotropic plasma etching, is to serve in a space experiment as a "brush" for cosmic particles, which are to be trapped between the columns and subsequently analyzed with an atomic force microscope. This contribution describes the preparation of large uniform arrays of photoresist columns with a high aspect ratio, which constitutes the first step for the preparation of the silicon or quartz structures proper.

1. Patterning of Monolayers of Crystalline S-layer Proteins on a Silicon Surface by Deep Ultraviolet Radiation

1.1. Introduction

Surface layers referred to as *S-layers* are two-dimensional crystalline protein layers with the unique capability to recrystallize with perfect uniformity at liquid surfaces or on solid supports such as silicon wafers, even if the surface exhibits a demanding three-dimensional topography. They are ideal patterning structures for supramolecular engineering due to their high molecular order, high binding capacity, and perfect uniformity. In particular, the recrystallization of S-layer subunits on substrates suitable for micro- and nanofabrication, such as silicon, gallium arsenide, or gold, allows the application of S-layers as patterning structures for molecular manufacturing.

S-layer proteins form the outermost cell envelope component in many archaeo- and eubacterial strains [1]. The center-to-center spacing of the morphological units is in the range of 3 to 30 nm, the thickness of the S-layer is in the 10 nm range. Basic research

[1] Center for Ultrastructure Research and Ludwig Boltzmann-Institute for Molecular Nanotechnology, University of Agriculture, A-1180 Vienna
[2] Academy of Science, Bratislava, Slovakia
[3] Institut für Allgemeine Elektrotechnik und Elektronik, TU Wien, A-1040 Vienna
[4] IMS — Ionen Mikrofabrikations Systeme GmbH, A-1020 Vienna
[5] Österreichisches Forschungszentrum Seibersdorf, A-2444 Seibersdorf

on the structure, chemistry, and morphology of S-layers has shown that the inner face is often net negatively charged and more corrugated in comparison to the outer face, which shows a neutral charge characteristic and a smooth topography. We have used the S-layer of *Bacillus sphaericus* CCM 2177 in the DUV patterning experiments described in this work [2]. This S-layer exhibits a square lattice symmetry with a lattice spacing of 12.8 nm (Figs. 1 and 2).

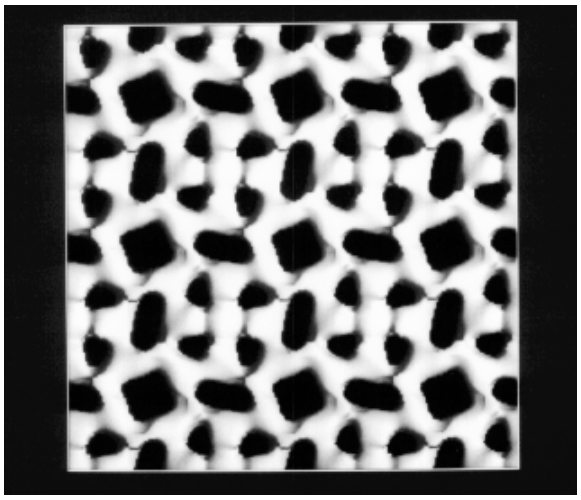

Fig. 1: A computer image reconstruction of an S-layer (square lattice 12 nm, thickness 8 nm).

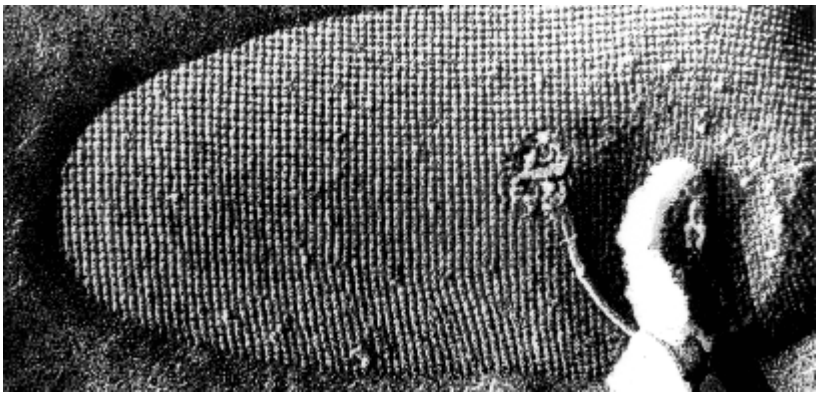

Fig. 2: TEM image of cell surface proteins from Bacillus Sphaericus CCM 2177.

1.2. Experimental

Polished silicon wafers with a native oxide layer (orientation (100)) and hydrophobic characteristics were used as substrates for the recrystallization experiments. The preparation of the S-layers has been described in detail in Ref. [2].

Line and square patterns were transferred onto the S-layer by exposing the protein monolayer to deep ultraviolet ArF and KrF excimer laser radiation (193 and 248 nm, respectively) through an e-beam structured quartz mask with etched antireflective chromium. The S-layer lattice was completely removed by one pulse of ArF radiation with a

dose of 70 mJ/cm^2. The step height between exposed and unexposed areas was approximately 8 nm, which is in perfect agreement with the thickness of the S-layer as determined by scanning force microscopy. In contrast, the S-layer was only carbonized but not ablated even at a dose of ten KrF laser pulses (with 110 mJ/cm^2 per pulse). These results show that the protein adsorbs at least ten times less at the KrF wavelength, compared to the ArF line. Thus we conclude that the energy of the photons at 248 nm is not sufficient to crack the chemical structure of the S-layer. Interference patterns in the S-layer created by the exposure to ArF radiation indicated a gap of 50 – 80 nm between the mask and the S-layer due to a thin intermediate water film.

In our latest results, we succeeded in using the S-layer as the top layer in a two layer resist system. As bottom-layer resist, a spin coated novolak AZ 1350 SF (Kalle Hoechst) was used. This resist film was prepared with a thickness of about 600 nm on a polished silicon wafer after vapor phase HMDS adhesion promotion. It is well known that this resist material may be patterned by KrF excimer laser radiation (248 nm).

The pattern transfer process comprised two steps: First, the S-layer on top of this sandwich system was structured as described above with an excimer laser DUV ablation technique with only one shot at 193 nm (ArF) radiation (with 70 mJ/cm^2). Subsequently, the wavelength was changed to 248 nm (KrF), and the novolak resist at the bottom was ablated with 5 shots at 80 mJ/cm^2 by blank exposure, where the patterned top resist served as a mask material. This is possible because the energy of the photons at 248 nm is not high enough to ablate the top protein resist. The technique presented here yielded very steep sidewalls in the resist material as shown in Fig. 3. The width of the lines is 600 nm, and the width of the gaps, 250 nm.

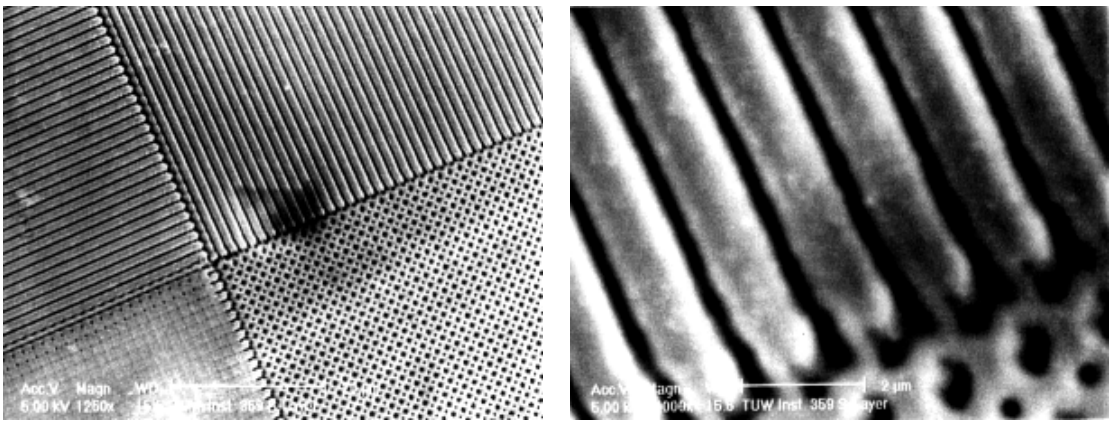

Fig. 3: Scanning electron micrographs of a patterned S-layer/novolak resist assay.

1.3. Conclusion

Many scientific and practical applications of S-layers require a specific patterning with structures down to the sub-micrometer range. DUV radiation proves to be a particularly feasible approach for the pattern transfer because it does not deteriorate the unique properties of S-layer lattices as immobilization matrices for functional macromolecules. A further application of structured S-layers could be the selective growth of embryonic neuronal cell tissue, which could establish a biocompatible interface between microelectronics circuitry and organic cells.

This work has shown that S-layers might be introduced as a novel resist material in microelectronics technology. Practical applications will require some form of reinforcement of the S-layers in order to enhance their resistance against the usual plasma etch processes (Fig. 4). This may be done by coupling additional ligands to the S-layers, or by depositing compounds of heavy metals [4 – 6].

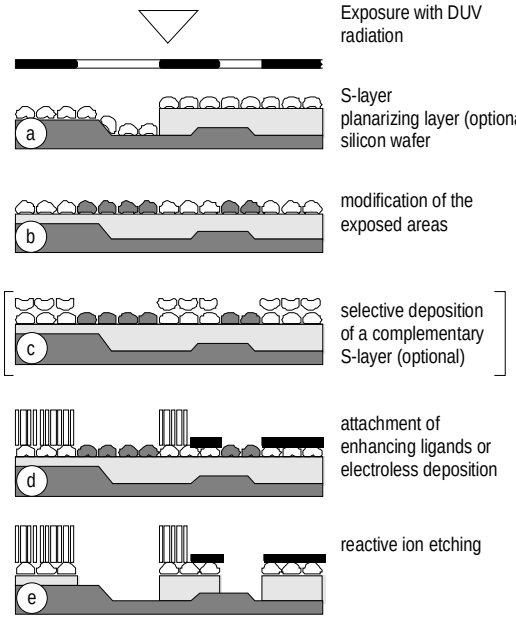

Fig. 4: Schematic illustration of patterning an S-layer recrystallized on a silicon wafer.

2. Micro-Technology of Densely Spaced Non-Conventional Patterns

Regular arrays of sub-0.5 µm tips are of increasing interest, for example, as field emitters, calibration structures, or, in our particular case, as collector surfaces for sub-µm dust particles in a space experiment. This contribution describes the preparation of 1 x 1 cm^2 arrays of columns with a high aspect ratio and a diameter in the sub-micrometer range using a chemically amplified polymer resist (CAR) and electron beam lithography (Fig. 5).

One of the prerequisites for an optimized transfer of the structures by plasma etching from the resist layer into an inorganic substrate (for example, silicon or SiO_2) is a uniformly structured, relatively thick resist layer with close to perpendicular sidewalls, as shown in Fig. 5. This requires a careful optimization of the deposition, exposure, and pre- and post-exposure resist processing. In the experiments reported here, a single film of a three-component negative-toned Novolak CAR (Kalle Hoechst AZ PN 114) has been used. Although the high sensitivity of this resist type makes it very attractive, particularly for electron beam exposure, it causes problems with the control and the uniformity of the critical dimensions. It also requires a careful compensation of proximity effects during electron beam exposure if the pattern dimensions decrease below 0.5 µm, and an optimized resist processing. The most critical factor in resist processing turned out to be the post-exposure delay, which must be less than a few minutes.

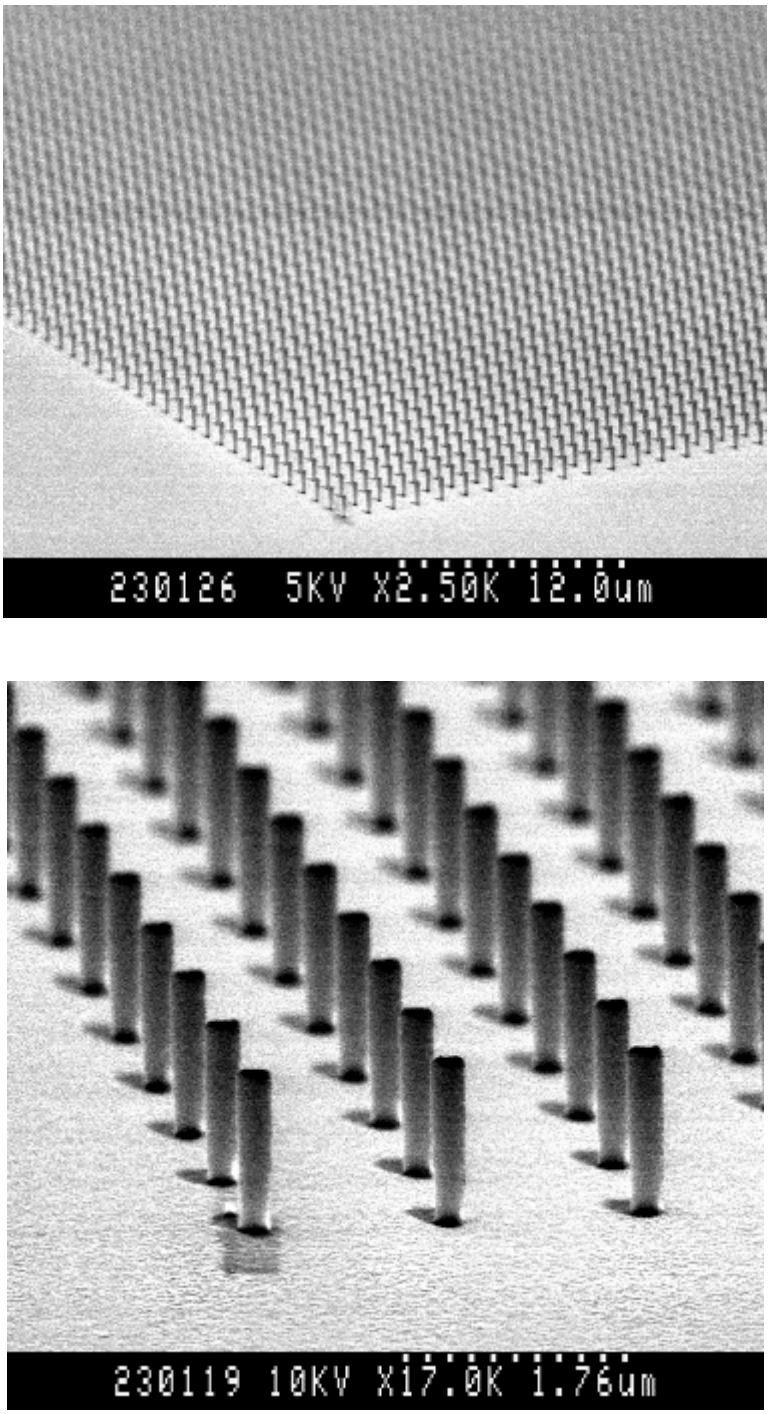

Fig. 5: An array of 1.5 µm high and 150 nm diameter resist pillars (aspect ratio 10:1). The period is 1.0µm.

Although a simulation of the exposure process is indispensable for controlling the proximity effects, the optimization of the entire process heavily depended on experimental work. This is true because the complexity of the three-component resist system and the lack of an exact model of the resist response prohibit a comprehensive simulation.

Acknowledgment

The work on S-layers was supported by the Society for Microelectronics, the Erwin-Schrödinger Gesellschaft, the Austrian Science Foundation, grants S 7204 and S 7205, and the Austrian Federal Ministry of Science, Transport and the Arts.

The preparation of the pillar structures was supported by the Society for Microelectronics, the Erwin-Schrödinger Gesellschaft and Ost-West-Fonds project OWP 92.

References

[1] D. Pum, U.B. Sleytr, P. Messner, M. Sàra (Eds.): “Crystalline bacterial cell surface proteins”, Academic Press, San Diego, 1996.

[2] D. Pum and U.B. Sleytr, Thin Solid Films 244 (1994), p. 882.

[3] D. Pum and U.B. Sleytr, Supramolecular Science 2 (1995), p. 193.

[4] J.M. Calvert, M.S. Chen, C.S. Dulcey, J.H. Georger, M.C. Peckerar, J.M. Schnur, P.E. Schoen, J.Vac.Sci.Technol. B, 9 (1991), p. 3447.

[5] J.M. Calvert, J.Vac.Sci.Technol. B, 11 (1993), p. 2155.

[6] G.N. Taylor, R.S. Hutton, S.M. Stein, H.E. Katz, M.L. Schilling, and T.M. Putvinski, Microelectr. Engineering 23 (1994), p. 259.