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Membranes for Micropumps from Macroporous Silicon

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Macroporous silicon is prepared with strongly modulated pore diameter by applying a sawtooth-like illumination profile. Taking into account diffusion limited mass transport, 25 perfectly identical modulations have been achieved, corresponding to a total pore depth of 200 μm. Qualitatively the pore growth may be well characterized by the established model from the literature but for this non-steady-state situation some extensions become necessary. The obtained asymmetric pore profiles make this system an ideal candidate as membranes in particle-size selective micropumps.

Introduction

Brownian motion The motion of small particles with micrometer dimensions is strongly influenced by Brownian motion. Modeling the transport on mesoscopic scales like macromolecules in biological systems, therefore, one always has to include this thermal noise in addition to the applied driving forces. It was shown that under certain conditions like asymmetric potentials, a net particle transport may be obtained for external potentials periodic in time, even for vanishing mean values [1]. As this somehow looks like a rectification of the Brownian motion and may have high relevance in describing transport in mesoscopic systems, this phenomenon was studied in great detail theoretically, for a review, see [2]. Some experiments have shown that these principles may be used to separate particles for different ratchet concepts, but all these techniques suffer somewhat from limited throughput [3, 4].

Macroporous silicon The high perfection of macroporous silicon with billions of identical pores on one wafer would be an ideal system to fabricate particle pumps with high precision at low cost using well-established semiconductor technology. During electrochemical pore growth, the diameter of the pores can be adapted by controlling the light intensity. Some preliminary results with sinusoidal variation of light intensity demonstrated [5] that significant variation is possible, even on short scales. An asymmetric light intensity profile should lead to the desired pore shape. Phenomenological models are able to describe the influence of experimental parameters like light intensity, doping concentration, HF concentration or temperature on the pore formation process. But there is still a lack of quantitative microscopic models that are able to predict all the details of the etching process [6].

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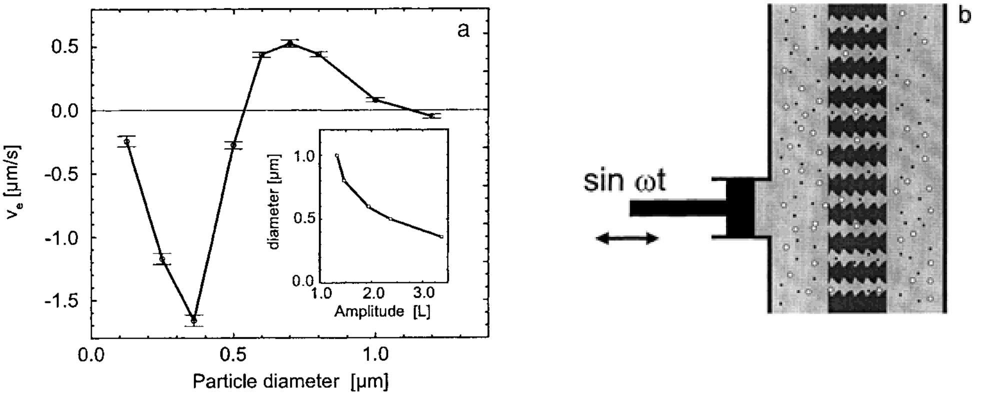

Fig. 1. a) The transport velocity v_e for a realistic model changes sign at 0.6 µm, so particles which are larger or smaller than this value are transported to different sides. As shown in the inset, this crossover can be tuned to a certain extend, leading to a tunable particle separation [7]. b) Schematic cross-section of the pump. The carrier liquid, including the dispersed particles of different size, is pumped periodically through the membrane with the asymmetrically shaped pores

The new concept of a drift ratchet [7] uses the friction between the particles and a carrier liquid as the driving force. The periodic modulation of the pore diameter leads to a modulation of the velocity and therefore of the driving force. Theoretical simulations indicate that for particles in the 1 µm regime strong variations of the net drift velocity can be expected, depending on the particle size. The expected velocities for a realistic model from [7] are depicted in Fig. 1a. Using different amplitudes the pumping behavior may be tuned to some extend. A schematic set-up of the designed pump is shown in Fig. 1b. Two containers are connected through a macroporous membrane with ratchet-shaped pores. The containers and the pores are filled with particles dispersed in a liquid. Pumping the carrier liquid forth and back should lead to a separation of small and large particles into the left and right basin, respectively.

Experimental Macroporous silicon is prepared by electrochemical etching of n-type silicon in hydrofluoric acid under backside illumination [8–11]. The electronics holes generated by the absorbed photons near the back surface diffuse through the wafer and promote the dissolution of silicon mainly at the pore tips. This geometric effect as well as the focusing effect of the space charge region and some crystal orientation dependence lead to pore formation with very high aspect ratios. By additionally starting with prepatterned substrates regular pore arrays have been prepared in the past [11]. According to the established growth model of Lehmann and coworkers [5, 9], the current density at the pore tips is always equal to the critical current density j_{ps}. The porosity p is therefore determined by the ratio of the total current density to the critical current density, or for regular arrangements, where all pores have the same area A_{pore}

$$p = \frac{A_{pore}}{A_{cell}} = \frac{j}{j_{ps}} \,. \tag{1}$$

The total current is controlled by the illumination intensity. Therefore, variations of the pore diameter with depth can be achieved by controlling the light source. This con-

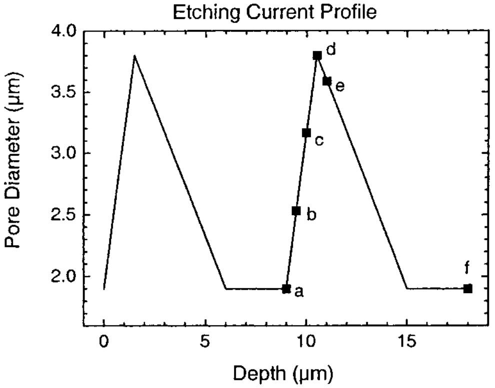

Fig. 2. Two periods of the current profile used for etching. At the marked positions a to f the growth is aborted to investigate the details of pore growth. The corresponding SEM cross-section images are shown in Fig. 5

cept has proven its validity in the past for compensating the variation of other growth parameters like temperature or the dilution of HF with increasing pore depth. For the application of macroporous silicon as two-dimensional photonic crystals, this compensation is well established to get homogeneous pore diameters for several 100 µm deep pores [10, 11].

Results

Depth dependence Our samples were prepared from 5 Ωcm substrates with a photolithographically defined hexagonal pattern of 4.2 µm pitch. A circular area with a diameter of 20 mm was exposed to the 6 wt% HF at 10 °C. The samples reported here were etched using a sawtooth-like current density as depicted in Fig. 2.

The SEM cross-section image in Fig. 3 demonstrates the quality of this etching process. The resulting samples have the expected strong asymmetrically varying pore shapes. There are only slight differences compared to the values from the model in Eq. (1). The sample is laterally homogeneously etched over the whole exposed area without noticeable defects. With increasing pore depth the HF concentration at the pore tips and therefore also the critical current density j_{ps} and the etching speed v are reduced. If the sawtooth-like current density is applied on a linear time scale, this leads to a strong variation of about 20% in the length of a period from top to bottom for a 100 µm deep porous film. Using the reduction of growth speed from the homogeneous

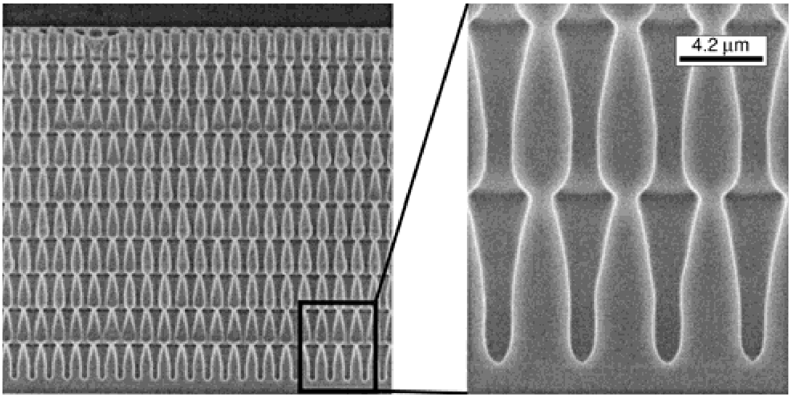

Fig. 3. SEM cross-section image for a sample with ten periods etched according to the profile from Fig. 2

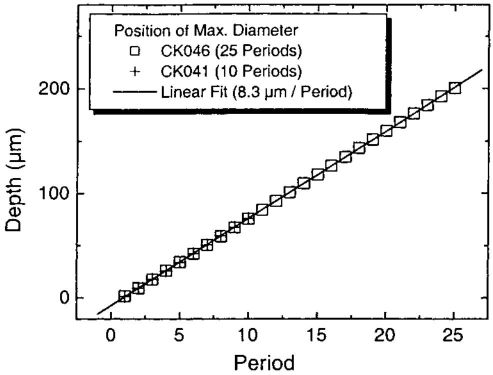

Fig. 4. Using the growth speed from the homogeneous model results in equidistant diameter maxima for up to 200 µm. Just the slope shows about 8% deviation from the forecast

model [9] improves this effect quite remarkably. In Fig. 4 the position of the diameter maxima for each period is plotted together with a linear fit. Up to 25 periods could be etched without noticeable deviation of the linear fit leading to a total thickness of over 200 µm. But there is a well observable deviation between the experimental length of a period, $l_{\mathrm{exp}} = 8.3$ µm, and the forecast, $l_{\mathrm{A}} = 9$ µm, of the established model [9]. This discrepancy will be investigated in the following section.

Pore tips In our experiments the illumination is changed with a sawtooth-like profile as sketched in Fig. 2. One cycle starts, according to the model, with a linear increase of the diameter from 1.9 µm to twice this value on a length of 1.5 µm. Subsequently the diameter is reduced to the original value on a length of 4.5 µm. The cycle then is completed by a 3 µm long part with constant diameter.

The observed periods are noticeable shorter than the predicted values. To investigate in which phase of a cycle this deviation occurs, we stopped the etching process at different positions within a cycle, as marked by the letters a to f in Fig. 2. The SEM cross-sections of these samples are shown in Fig. 5. At the beginning of the cycle, the etching mainly increases

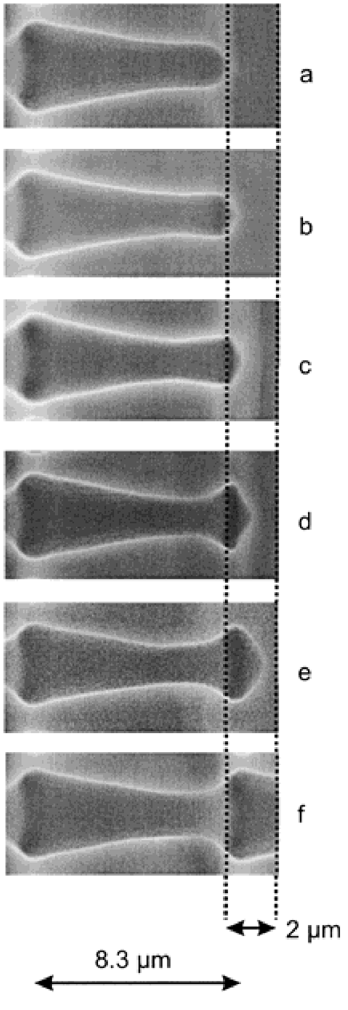

Fig. 5. SEM cross-section image showing pore tips generated by aborting the etching in different phases of a cycle. The letters correspond to the positions marked in Fig. 2

the diameter at the pore tips. The pore tips change their shape from long and spiky to short and flat. The diameter increases whereas there is a strongly reduced etching in growth direction. During this phase more minority carriers arrive at the pore tips than during the phase with constant diameter before. But not only this surplus seems to be consumed by the process of increasing diameter. Only after about 1 μm we come back to a pore growth that is in good accordance with the predictions from the established model [9]. The observed reduction in growth speed has similar reasons as the reduction in growth speed in deep pores. The higher current through the pores leads to increased consumption and production of the etching educts and products, respectively. Because of the diffusion limited transport the composition of the electrolyte at the pore tips is modified, leadings to a reduction of the the critical current density j_{ps} and therefore also to the observed reduction in growth speed and period length.

Shape analysis A crucial parameter for the application in a pumping device is the detailed shape, especially the asymmetry. In Fig. 6 the pore diameter as extracted from SEM images is plotted together with expectations from the model. The depth in the model is scaled by 8.3/9 to account for the small observed discrepancy in growth speed. The extraction of the pore diameters from the SEM images was done for several pores from the same region. The scatter seen in Fig. 6 is due to the difficulty in determining the exact dimensions of the pore, so it represents the measurement error and not the fluctuations from pore to pore. The solid line is a smooth curve through the mean values at each position. The agreement with the model, which is shown as a dotted line, is quite good, although it can be noticed, that the lower diameter is measurable below the predictions from the established model.

As it is very difficult to understand why the diameter of the pores should get even smaller than the values expected from etching with constant diameter, we etched samples with constant diameters and otherwise the same parameters. Whereas for the large diameters (3.8 μm, i.e. porosity $p = 74\%$) the obtained pore diameter is exactly as designed, the lower diameters (e.g. 1.9 μm, $p = 18.5\%$) also show a clearly measurable deviation to smaller diameters. If we take this dependence into account by just changing the lower diameter, we get the dashed line in Fig. 6. For this set of parameters, this modified model gives a very good description. Further investigations are necessary to get a more detailed picture of changes in the microscopic processes.

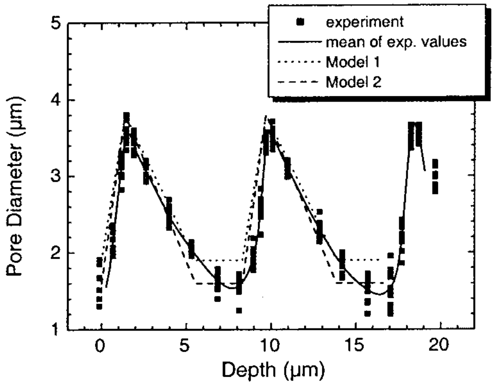

Fig. 6. Comparison of the experimentally obtained pore shape, the values from the established growth model 1 and the modified model 2

Conclusions Large arrays of ratched-shaped macropores were fabricated by modulated photoelectrochemical etching of n-type silicon. By adapting the modulation of the etching current to the diffusion limited transport in the pores, we were able to produce 25 identically spaced repetitions of the ratchets. A comparison of the pore design based on the established model, and the obtained pores show reasonable agreement, except for low porosity and some deviations due to the non steady-state conditions. the achieved asymmetric profiles make these films ideal candidates for membranes in micropumps based on drift ratchets.

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References

[1] R. BARTUSSEK and P. HÄNGGI, Phys. Blätter **51**, 506 (1995).
[2] P. HÄNGGI and R. BARTUSSEK, in: Lecture Notes in Physics, Springer Series, Vol. 476, Eds. J. PARISI et al., Springer-Verlag, Berlin 1996.
R. D. ASTUMIAN, Science **276**, 917 (1997).
F. JÜLICHER, A. AJDARI, and J. PROST, Rev. Mod. Phys. **69**, 1269 (1997).
[3] L. GORRE-TALINI, S. JEANJEAN, and P. SILBERZAN, Phys. Rev. E **56**, 2025 (1997).
[4] D. ERTAS, Phys. Rev. Lett. **80**, 1548 (1998).
[5] V. LEHMANN and U. GRÜNING, Thin Solid Films **297**, 13 (1997).
[6] M. HEJJO, AL RIFAI, M. CHRISTOPHERSON, S. OTTOW, J. CARSTENSEN, and H. FÖLL, J. Electrochem. Soc. **144**, 627 (2000).
[7] CH. KETTNER, P. REIMANN, P. HÄNGGI, and F. MÜLLER, Phys. Rev. E **61**, 312 (2000).
[8] V. LEHMANN and H. FÖLL, J. Electrochem. Soc. **137**, 653 (1990).
[9] V. LEHMANN, J. Electrochem. Soc. **140**, 2836 (1993).
[10] A. BIRNER, U. GRÜNING, S. OTTOW, A. SCHNEIDER, F. MÜLLER, V. LEHMANN, H. FÖLL, and U. GÖSELE, phys. stat. sol. (a) **165**, 111 (1998).
[11] F. MÜLLER, A. BIRNER, U. GÖSELE, V. LEHMANN, S. OTTOW, and H. FÖLL, J. Porous Mater. **7**, 201 (2000).