Microsieves made with laser interference lithography for micro-filtration applications

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Abstract. A microsieve with a very uniform pore size of 260 nm and a pore to pore spacing of 510 nm has been fabricated using multiple exposure interference lithography and (silicon) micro-machining technology.

The sieve consists of a 0.1 μm thick silicon nitride membrane perforated with sub-micron diameter pores and a macro perforated silicon support. The calculated clean water flux is at least one to two orders higher than that of conventional inorganic membranes.

1. Introduction

Sieving is the main principle of particle retention in the micro-filtration regime (pore size 100 nm–5 μm) [1, 2]. A major micro-filtration application is sterile filtration for the pharmaceutical and food/beverage industry, where pore sizes smaller than 0.5 μm are required to retain bacteria.

Various techniques have been employed to manufacture micro-filtration membranes [3] like stretching, track-etching and phase inversion for polymeric materials, and sintering, sol–gel processing and anodic oxidation for inorganic materials. In many applications inorganic membranes are preferred to polymeric membranes because of their outstanding chemical and thermal resistance. However most inorganic membranes have a strongly diminished clean water flux, because the effective membrane layer is very thick in comparison to the pore size. Also the relatively poor control of the pore size distribution leads to a diminished permeate flux; since the largest pore in the sieve still has to retain particles, the average pore size has to be chosen much smaller than the particle size. Finally, adequate membrane cleaning methods are very problematic and time consuming due to the relatively large inner surface area of the membrane layer and the support.

An ideal micro-filtration system should contain a relatively thin sieving layer with a high and uniform pore density attached to a support with openings as large and numerous as possible in order to maintain the flow rate of the membrane layer and to reduce the interaction of the support with the solution.

In earlier publications we reported the construction of inorganic microsieves with a pore size of 2–5 μm using conventional lithography with hard-contact exposure masks [4]. In order to obtain smaller pore sizes far below 1 μm, electron-beam patterning or wafer stepping techniques with a deep UV-light source may be employed. However both techniques are very time consuming and/or require rather expensive machinery.

A relatively inexpensive technique which makes it possible to pattern large areas of sub-micron periodic structures is interference lithography. Structure sizes below 100 nm have been reported using this technique [5]. Single exposure interference lithography was extensively studied for applications in integrated optic components [6]. In 1993 Saleem and Brueck [7] introduced multiple exposure interference lithography for creating periodic structures in two dimensions. After this the multiple exposure technique was applied to fabricate high density gated field emitter arrays [5, 8] and large arrays of single domain Co dots for high density data storage [9].

Here we report the application of multiple exposure interference lithography for the fabrication of microsieves with uniform pore size less than 500 nm.

2. Device fabrication

Figure 1 shows in cross-section subsequent stages of a process for production of the microsieve consisting of a support and a membrane layer.

The backside of a support (1), a single crystalline 3 in ⟨100⟩-silicon wafer with a thickness of 380 μm, is pre-etched to a thickness of 15 μm using optical lithography and conventional KOH etching (25%, 70 °C). On the front side of the pre-etched support (1) a layer (2) of amorphous silicon nitride with thickness 0.1 μm is deposited by

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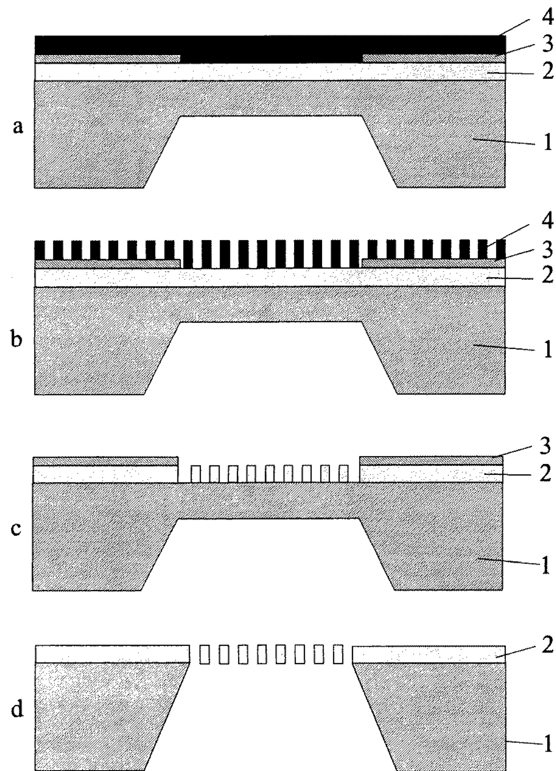

Figure 1. Schematic representation of the fabrication process of a microsieve. The numbers indicate the silicon support (1), the silicon nitride membrane (2), the chromium etch mask (3) and the photo-resist layer (4).

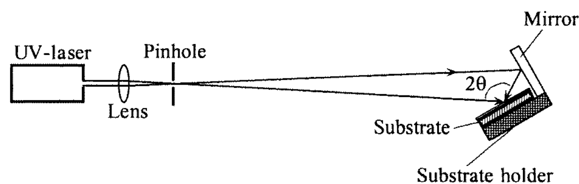

Figure 2. Set-up used for the interference lithography.

means of 'low pressure chemical vapour deposition' by reaction of dichloresilane (SiH_2Cl_2) and ammonia (NH_3) at a temperature of 850 °C. An etch mask layer (3) of sputtered chromium with a thickness of 30 nm is deposited and etched using a photo-resist mask with apertures at the area where the microsieve pattern will be formed, figure 1(a).

On top of this chromium layer (3) a layer (4) of positive resist was spun and patterned using interference lithography. Figure 2 gives a schematic representation of the used exposure set-up, known as 'Lloyd's mirror configuration' [6]. Part of an incoming plane wave will be reflected by the mirror and forms an interference pattern on the substrate surface with the part that reaches the substrate undisturbed. To produce a plane wave, TE polarized light of an Ar^+ ion laser with a wavelength $\lambda = 351.1$ nm was spatially filtered and expanded by focusing it onto a pinhole. Since the beam is only split for a short path length near the substrate, this set-up is very insensitive to mechanical instabilities and no feedback loop [5] is required to stabilize the interference pattern.

The period Λ of the generated interference pattern is

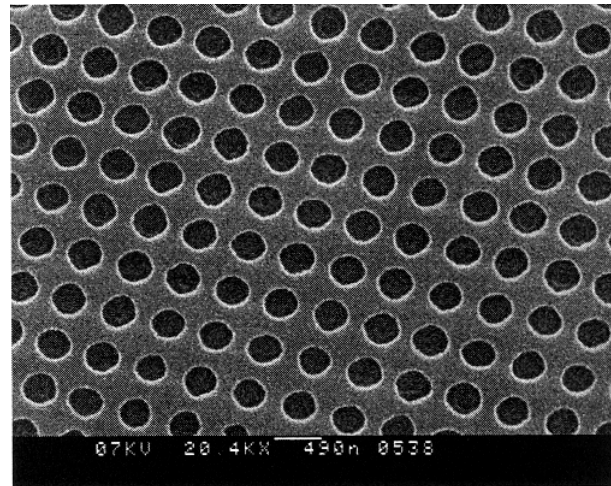

Figure 3. SEM picture of the exposed (2 × 45 s) and developed photo-resist layer.

defined by the relation $\Lambda = \lambda/2\sin\theta$, where the angle 2θ between the interfering beams can be changed by rotating the mirror/substrate configuration. The minimum period that can be fabricated with our configuration is $\Lambda = \lambda/2 = 175$ nm. The corresponding minimum pore size will be approximately $175/2 = 88$ nm.

The thickness of the photosensitive layer needs to be chosen with care to avoid problems with the periodic pattern normal to the substrate surface due to interference between the incoming beam and the one reflected on the substrate surface. Its period is given by $\Lambda_\perp = \lambda/2n\cos\theta_n$ where n is the refractive index of the photo-resist and $2\theta_n$ the angle between the beams inside the resist. We used $\theta = 20°$ and with $n = 1.7$ at $\lambda = 351.1$ nm we find $\Lambda = 510$ nm and $\Lambda_\perp = 105$ nm. Therefore the thickness of the photo-resist layer is chosen smaller than 105 nm.

The area that can be patterned using our mirror of 2.5×2.5 cm^2 equals approximately 9×9 mm^2 for $\Lambda = 510$ nm.

A 100 nm thick layer (4) of positive photo-resist (Shipley S1800-series) was spun, followed by a 5 min prebake at 90 °C to evaporate the solvent. The resist was exposed to the interference line pattern for 45 s. The intensity of the incoming light in the exposed area was measured to be 2 mW cm^{-2} for normal incidence ($\theta = 0°$). After rotating the substrate over 90° the exposure was repeated. The resist was developed for 15 s in a 1:7 mixture of Shipley-Microposit 351 developer and de-ionized water and dried by spinning, figure 1(b). The exposure time was chosen such that only at the crossings of the grid lines (after first and second exposure) the resist receives enough energy to be removed completely after development. Therefore a two dimensional pattern of holes is created in the resist. An SEM picture of the exposed (2 × 45 s) and developed resist is given in figure 3. The diameter of the holes in the photo-resist depends on the duration of exposure, herewith giving a possible tool to vary the pore size at a constant pore to pore distance. However, when the exposure time is chosen too long (2 × 75 s) the holes in the resist pattern may become too large and will overlap, as shown in figure 4.

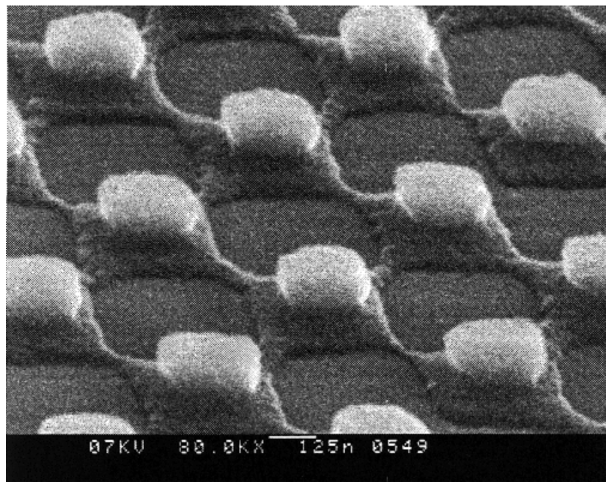

Figure 4. SEM picture of an overexposed (2 × 75 s) and developed photo-resist layer.

Next the interference pattern is transferred into the silicon nitride membrane layer (2) by means of CHF_3/O_2 reactive ion etching at 10 mTorr and 75 W for 2 minutes forming the required perforations, figure 1(c). Subsequently the silicon underneath the membrane layer (2) is anisotropically etched with an SF_6/O_2 plasma at 100 mTorr and 100 W for 10 minutes with an etch rate of 2 μm min^{-1} in order to form the macroscopic openings in the support (1), figure 1(d). An SEM photograph (figure 5) of the resulting perforated membrane layer (2) shows a very regular pore pattern, the pore size being 260 nm with a pore to pore spacing of 510 nm. The pore size was very uniform over the whole 9 × 9 mm^2 area.

3. Device performance

The most important parameters for a microsieve are the clean water flux and the maximum allowed transmembrane pressure. The clean water flux for the microsieve presented here can be calculated [10] to be 1200 ml min^{-1} bar^{-1} cm^{-2}. This value is at least 30 times higher than for many known organic membranes like track etched polycarbonate and stretched PTFE [1] and more than 100 times higher than for inorganic anodic oxidation membranes [11], with a typical rating of 10 ml min^{-1} bar^{-1} cm^{-2} at a pore size of 0.2 μm. The maximum allowed transmembrane pressure can be estimated [10] to be 2 bar. This pressure is sufficient for most micro-filtration applications.

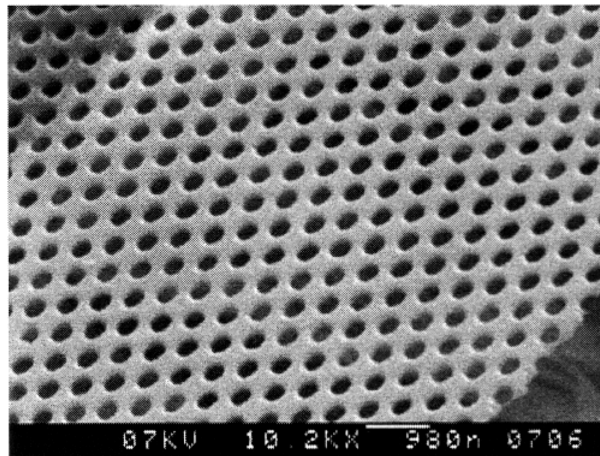

Figure 5. SEM picture of the microsieve membrane showing holes with a diameter of 260 nm in a 100 nm thick silicon nitride layer.

4. Conclusions

Microsieves with sub-micron pore sizes can be made using multiple laser interference lithography. The pore size may practically be chosen in the range between 100 nm and 10.0 μm by adjusting the angle of incidence θ of the incoming laser beams. The exposure method is fast, inexpensive and applicable for large areas.

References

[1] Scott K 1995 *Handbook of Industrial Membranes* (Amsterdam: Elsevier) pp 112, 120

[2] Strathmann H 1992 *Separation and Purification Technology* ed N N Li and J M Calo (New York: Dekker) pp 1–17

[3] Mulder M 1996 *Basic Principles of Membrane Technology* (Dordrecht: Kluwer) p 228

[4] van Rijn C J M and Elwenspoek M 1995 *IEEE Proc. MEMS (Amsterdam, 1995)* p 83

[5] Boltzer C O, Harris C T, Rabe S, Rathman D D, Hollis M A and Smith H I 1994 *J. Vac. Sci. Technol.* B **12** 629

[6] Mai X, Moshrefzadeh R, Gibson U J, Stegeman G I and Seaton C T 1985 *Appl. Opt.* **24** 3155

[7] Saleem H Z and Brueck S R J 1993 *J. Vac. Sci. Technol.* B **11** 658

[8] Spallas J P, Hawryluk A M and Kania D R 1995 *J. Vac. Sci. Technol.* B **13** 1973

[9] Fernandez A, Bedrossian P J, Baker S L, Vernon S P and Kania D R 1996 *IEEE Trans. Magn.* **32** 4472

[10] van Rijn C J M, van der Wekken M, Nijdam W and Elwenspoek M C 1997 *J. MEMS* **6** 48–54

[11] Anopore, alumina membrane filter 1993 *Whatmann Product Guide* catalogue No 9037 9316