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Suppression of the sidewall effect in pillar array columns with radially elongated pillars

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ABSTRACT

An important bottleneck of pillar array columns designed for liquid chromatography is that small deviations of the target 'magical distance' at the sidewall region leads to detrimental sidewall effects, due to local differences of linear velocities at the sidewall region versus other locations in the pillar bed. In the present study, we demonstrate that a lateral elongation of the pillar significantly increases the tolerance for offsets of the magical distance. By shifting the sidewall distance 600 nm for 2 pillar aspect ratio (AR) designs (AR = 3 and 9), only minor sidewall effects on the measured plate heights could be observed for the AR = 9 columns, while the plate height was roughly doubled when using the wrong versus the correct sidewall distance for the AR = 3 columns. Technologically, this constitutes a huge advantage because small deviations (order of 100 nm) between the set and the finally achieved value for the inter-pillar distance are very common using mid-UV lithography based etching processes.

1. Introduction

Pillar array columns (PACs) have been studied rather intensively during the last decade as a new support in liquid chromatography [1–10]. The main advantage of PACs is that they offer a dramatic reduction of the eddy-dispersion because the photo-lithographic etching techniques with which they are fabricated, enables to produce beds consisting of perfectly repeated and uniform unit cells. Their potential has been demonstrated by computational fluid dynamics simulations as well as by experimental characterization. However, an important limitation of PACs is the occurrence of the so-called sidewall effect. [4,11,12]. While the structural order of PACs is a crucial element of their improved performance, the fact that they need to be enclosed by a containing wall however also inevitably distorts the shape of the PACs at the pillar layer most close to the sidewall of the array. Due to the perfect order, this distortion persists all along the length of the bed. This inevitably leads to a persisting difference in flow resistance between these two outer layers and the rest of the bed. As a consequence, the bands either persistently lag or lead near the sidewall. Because of the ongoing radial dispersion, it gradually affects the entire column cross-section, eventually consuming most of the available separation efficiency [4].

The theoretically best way to overcome this sidewall problem is by changing the width of the through-pore immediately adjacent to the sidewall such that the flow resistance near the sidewall is the same as in the through-pores in the rest of the bed. Theoretical calculations have shown that, for the case of a bed of cylindrical pillars, the flow resistances can be completely equalized when the distance between the (straight) sidewall and the nearest pillars (5 μm diameter, 40% porosity) is 750 nm [11]. However, the same calculations also revealed that a small deviation from this rule can lead to a dramatic increase of the dispersion again (5% deviation, corresponding to a 250 nm error can lead to an increase of the plate height with 0.7 reduced plate height uses). This extreme sensitivity raises a severe challenge for the fabrication of PACs, because the dimensions of the etched pillars inevitably undergo a deviation of a few 10 nm to several 100 nm during the transformation of the mask design to the actual microfabricated device. Unfortunately, this deviation usually has the biggest effect on the pillar spacing at the sidewall, as this is usually the smallest dimension in the column. Having only access to mid-UV lithography, as most universities and research institutes, [13,14], this sidewall effect is in fact the main reason why most of the recent work of our group focused mainly on columns with

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a relatively large inter-pillar spacing (mostly 2.5 μm), because the replication of the mask is always better for larger features (applying a given wavelength during lithography).

Very recently, our group has also proposed the use of radially elongated pillars (REP's) as a means to reduce B term dispersion and the footprint of the channel [15]. Defining a pillar aspect ratio AR as the ratio of the radial over the axial pillar width (see Fig. 1), it was demonstrated that a fivefold reduction of the minimal plate height could be obtained by moving from a bed with radially elongated pillars with an AR close to unity (AR = 1.2) to a bed with AR = 15, while keeping the same inter-pillar distance. During that study, it was noticed that the bands remained very straight, also close to the sidewall, despite the fact that no efforts had been made to optimize the sidewall region. In the present contribution, this effect is studied in detail, by comparing PACs with two different sidewall distances (SWD = 2.0 μm and SWD = 2.6 μm) and with two degrees of radial pillar elongation (resp. aspect ratio AR = 3 and 9), giving in total 4 combinations to be tested (see Figs. 1a–d).

2. Experimental

2.1. Sample and coating

The dyes Coumarin C440 (Cas no. 26093-31-2, Sigma–Aldrich, Belgium), and C480 (Cas no. 41267-76-9) were dissolved in HPLC-grade methanol at a final concentration of 1×10^{-3} M, after which they were filtered. When only one coumarine was being tested, C440 was used at 0.2 mM concentration. In all other cases, the concentration was reduced by blending it with the proper water methanol mixture to a concentration of 0.40 mM, 0.20 mM for C480 and C440 respectively to obtain more or less the same intensities at the detector. A C8 hydrophobic coating was applied on the porous silica layer by means of a liquid-phase coating procedure consisting of the following steps. First, the microchannels were flushed with methanol for 1 d and anhydrous toluene for 1 d. A solution of 5% octyldimethylchlorosilane (C8) in anhydrous toluene was pumped through the channel for 72 h at room temperature. Afterwards, the channels were flushed with anhydrous toluene for 1 d and with methanol for 1 d.

2.2. Microfabrication and channel design

The pillar array columns were patterned using mid-UV photolithography (photoresist, Olin 907-12), followed by a Bosch-type deep-reactive-ion etching step (Adixen AMS100SE) up to a depth of 8 μm. Next, the through-holes were defined by mid-UV lithography from the back side (photoresist, Olin 907-35), again followed by a Bosch etching step to produce the through-holes. After this, the resist was removed by oxygen plasma and nitric acid. The microfluidic channels were subsequently sealed with a Pyrex wafer (thickness 0.5 mm), anodically bonded to the silicon using an EVG EV-501 wafer bonder (EV Group Inc., Schaerding, Austria). Next, the chip was diced. A holder was made in-house to provide the interfacing with HPLC connection pieces. The channels were 1 mm wide and 12 mm long, and were preceded by an injection box as shown at the top of Fig. 3. In each PAC, the spacing between the REP features in the bed was 3.0 μm. The axial distance between the pillars was in each case equal to 3 μm. Fig. 2 shows SEM images of two of the finally produced PACs, one with aspect ratio AR = 3 and one with AR = 9.

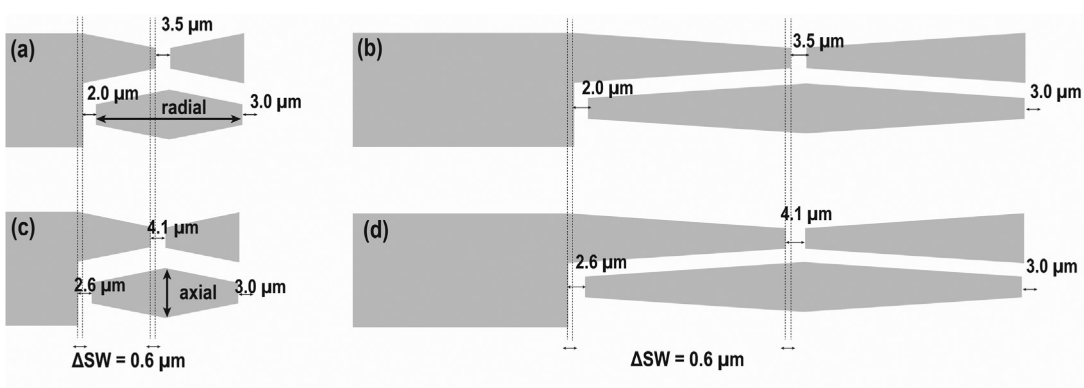

Fig. 1. Sidewall details of the masks designed the different PACs tested in the present study: (a) AR = 3 and SW-distance = 2.0 μm; (b) AR = 3 and SW-distance = 2.6 μm; (c) AR = 9 and SW-distance = 2.0 μm; (d) AR = 9 and SW-distance = 2.6 μm.

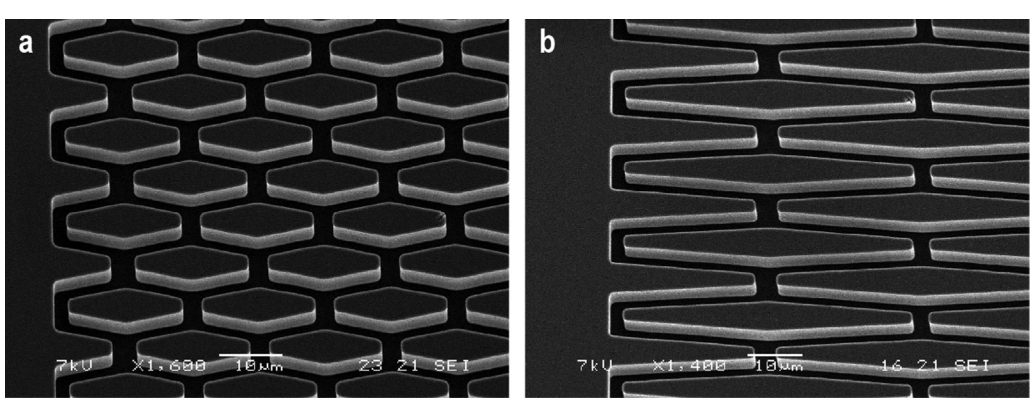

Fig. 2. SEM image of a PAC with (a) AR = 3 and (b) AR = 9. In both cases, the characteristic SW-distance was equal to 2.0 μm.