LAPLACE PRESSURE VALVE UTILIZING NANO-IN-NANO STRUCTURE TOWARD ATTOLITER SCALE LIQUID HANDLING

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ABSTRACT

This paper reports a method of handling attoliter (aL=10^{-18} L) scale liquid in pressure-driven nanofluidic control systems. In order to achieve this, nonmechanical valve was developed that utilized nano-in-nano structure fabricated by two-step etching process using e-beam lithography and dry etching.

KEYWORDS: Nanofluidics, Attoliter scale liquid handling, Contact angle, Laplace pressure

INTRODUCTION

As a result of further downscaling, microfluidic systems are now miniaturized to 10^1-10^2 nm scale, which we call extended nanospace. Though pressure-driven fluidic control has been developed for extended nanospace and applied to wide-use analytical chemical applications [1], aL scale liquid handling has not been well established. For more complicated liquid handling like injection of chromatography, one strategy is integrating a valve into a channel. As for a microchannel, a valve called "Laplace pressure valve" has been reported, which uses a difference of Laplace pressure arising from wettability-patterned surface. However, more precise position control is needed to integrate a Laplace pressure valve into an extended nanochannel. Here, we developed Laplace pressure valve in extended nanospace, taking advantage of a new wettabilty patterning method by combining chemical surface modification with nano-in-nano structure that enhances hydrophobicity.

THEORY

The concept of this study is shown in Fig. 1. The Laplace pressure valve consists of nanopillars fabricated on the bottom of the channel. The whole channel wall is modified into hydrophobic to a certain extent. To handle aL scale liquid, liquid is first introduced from the left side and fills the left and the vertical channels, but stops at the Laplace pressure valve in the middle of the right channel. It is because the nanopillars entrap air in their troughs and make a more hydrophobic composite surface as explained by Cassie's law and make Laplace pressure higher than the pressure applied for introduction of the liquid. Then the liquid is cut and aliquoted by air pressure applied in the vertical channel. The liquid volume is estimated 800 aL in the sizes shown in Fig. 1. This ultra-low volume liquid can be driven by applying higher pressure than the Laplace pressure at the valve.

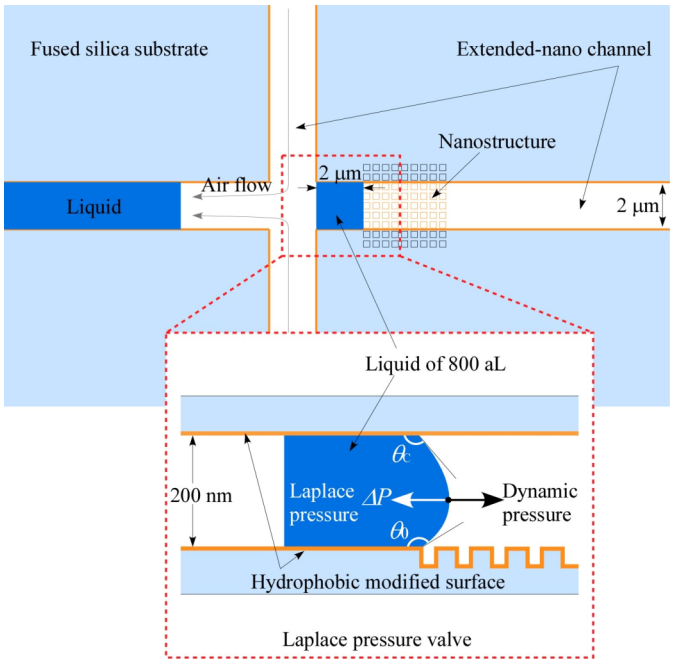

Figure 1: Concept of aL liquid handling

EXPERIMENTAL

Firstly, we verified static contact angles (C.A.) of water drops on nanosturctured surface. Nanopillars (width ~60 nm, pitch 160 nm, height 60 nm) were fabricated on a fused silica substrate by e-beam lithography and dry etching. Then, the whole surface, which had been initially hydrophilic was modified by solution of 10 mM trimethylsilylimidazole (TMS-Im) in toluene. The contact angles of water drops were measured on both flat surface and nanostructured surface.

Next, we integrated nanopillars into an extended nanochannel. A nano-in-nano structure was obtained by a two-step etching process, in which nanopillars (the same size as above) were firstly fabricated, and then extended nanochannels (width 2 μm, depth 220 nm) were overlaid on the pillar area. We observed the channel profile by AFM. After a thermal bonding with a cover plate, the channel wall was modified by octadecyltrichlorosilane (ODS). Water was pushed into the channel under the setup shown in Fig. 2, and a behavior of the water was observed by an optical microscope.

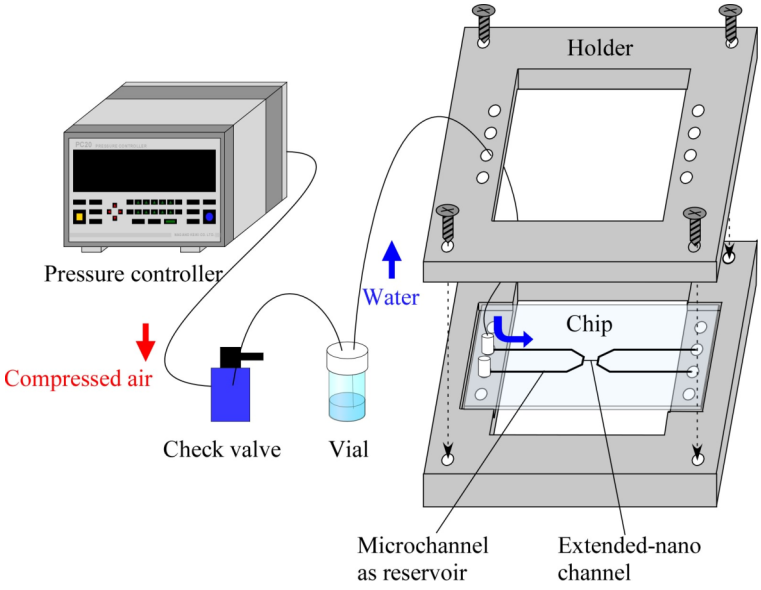

Figure 2: Schematic of the experimental setup

RESULTS AND DISCUSSION

In our condition, after the modification by TMS-Im, the C.A. of the flat surface was 88o, and the C.A. of the nanostructured surface went up to 98^{o} (Fig. 3). These results show that nanostructure fabricated in a top-down process can increase a C.A. beyond 90^{o}, even though the intrinsic C.A. is less than 90^{o}.

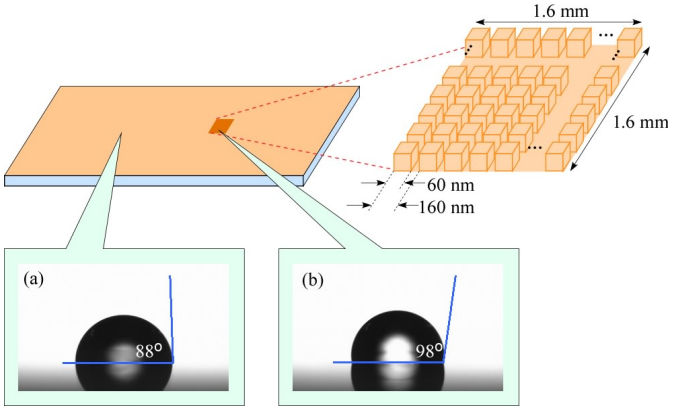

Figure 3: Contact angles on the surface without pillars (a), and with pillars (b)

Fig. 4 shows the channel profile obtained by AFM. The shape of pillars was maintained after the second etching of the channel. In this way, nano-in-nano structure was obtained due to the anisotropicity of the dry etching. Water (surface tension, γ: 72 mN/m) was introduce to the boundary of the pillar area by capillary filling and stopped there when the microchannel on the left side was filled with water. This indicates that the nanochannel was hydrophilic while the pillar area became hydrophobilc. Water did not flow even though applied pressure was increased up to 400 kPa (Fig. 5b). Meanwhile ethanol (γ: 22

mN/m) flowed across the pillar area at 400 kPa (Fig. 5c). The cases of water and ethanol represent the "open" and "close" states in terms of a valve, respectively.

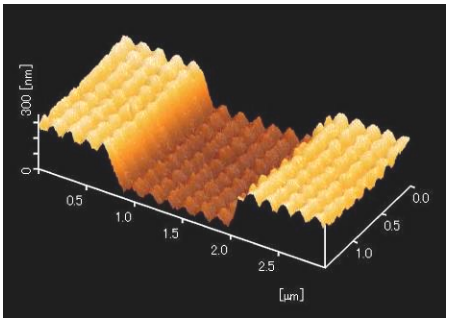

Figure 4: AFM image of nanopillars (height 60 nm) in the channel (width 2 µm, depth 220 nm)

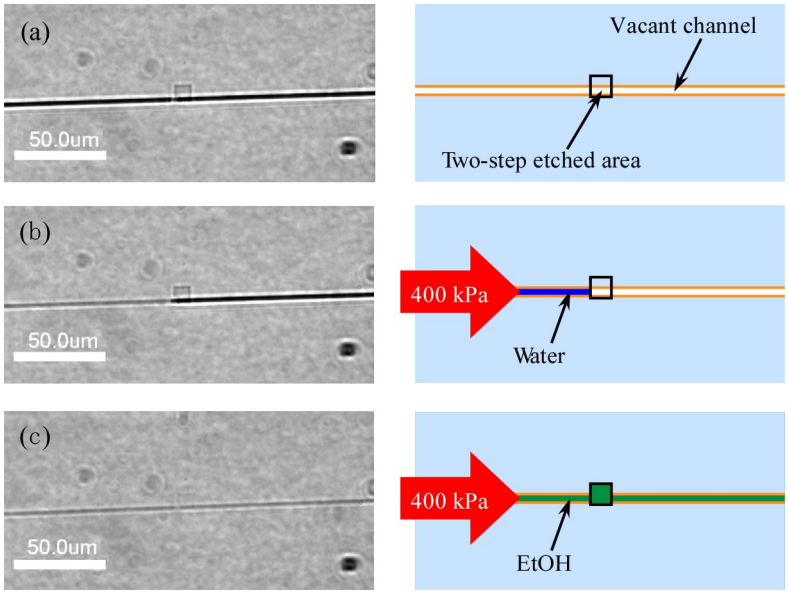

Figure 5: Microscopic observation and schematic of nanochannel. (a) vacant, (b) water, (c) ethanol

CONCLUSION

The Laplace pressure valve in an extended nanochannel was first demonstrated by combining nanostructure and surface modification. In particular, it was found that nanostructure fabricated in a top-down process could change surface from hydrophilic to hydrophobic.

Now, we are integrating this valve into a femto liquid chromatography system [2] to demonstrate the aL scale liquid handling. It is expected to decrease sample volume to aL scale, suppress band broadening and make a theoretical plate number much higher.

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