NANO LAPLACE VALVE FOR FEMTOLITTER LIQUID GENERATION AND HANDLING REALIZED BY NANOPILLAR-IN-NANOCHANNEL FABRICATION AND SURFACE MODIFICATION

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ABSTRACT
Femtolitter scale liquid (droplet in air) generation and handling methods by pressure-driven flow are essential for next analytical and bio technologies (e.g. pL scale single cell analysis). However, it was difficult to integrate valve function in nanofluidic systems due to the extremely small volume. Here, we report the integration of a chemical valve, Laplace valve, by developing nanoscale superhydrophobic patterning method. As a proof of concept, 1.7 fL water droplets were successfully generated and driven by air pressure.

KEYWORDS
Nanofluidics, extended nanospace, Laplace valve, femtolitter liquid

INTRODUCTION
Recently, micro chemical systems on a chip are miniaturized to 10^1-10^2 nm scale, which we call "extended nanospace." In extended nanospaces, unique liquid properties such as higher viscosity, lower dielectric constant, and higher proton mobility are reported and taking advantage of these unique liquid properties, new chemical devices (e.g. single cell analysis systems, highly efficient chromatography systems and etc.) have been developed [1]. In general, for realizing the devices, fluidic control is essential, and especially in extended nanospaces, attolitter (10^{-18} L) to femtoliter (10^{-15} L) scale liquid handling is quite important because volumes of $(100\ nm)^3$ and $(1000\ nm)^3$, which are extended nanoscale, become aL and fL, respectively.

In order to handle such small amount of liquid, one strategy is integrating a valve into an extended nanospace channel. However, conventional mechanical valves cannot be integrated even into microspace, though a number of miniaturized mechanical valves were fabricated by using MEMS (micro electric mechanical systems) technology. Non-mechanical valves were also realized in microspace. Among the non-mechanical valves, a valve using wettability called "Laplace valve" is a good candidate for valves in extended nanospace. However, in the extended nanospace, wettability patterning with < 1μm precision is required due to the small space.

In this study, we propose a new wettability patterning method by a combination of nanostructure and surface modification. It is well known as lotus effects that microstructure of surface changes the wettability, and particularly, hydrophobicity or water-repellency is enhanced to so-called superhydrophobic ($\theta > 150^o$). So far, surface wettability was tuned by using microstructure for the purposes of water-repellency, self-cleaning, and etc. Here, we have conceived that nanostructure, which is smaller than extended nanospace channels, can be used to enhance hydrophobicity locally (< 1μm scale) in an extended nanochannel. That is, if nanopillars are fabricated on the bottom of an extended nanochannel in advance followed by hydrophobic surface modification of whole channel, wettability patterning will be formed that consists of hydrophobic region of the flat surface and more hydrophobic region with the nanopillars. The advantage is that the fabrication precision determines the patterning size, which is quite important to generate aL to fL liquid inside nanochannels.

EXPERIMENT
The principle of nano Laplace valve is briefly explained in Figure 1. Nanopillars enhance hydrophobicity after uniform surface modification. The boundary of the nanopillars serves as a wettability boundary and works as a passive valve. Because the boundary of the wettability can be regulated by nanofabrication, precise wettability patterning with nanometer scale precision can be realized.

Nano-in-nano structure was obtained by a two-step etching process, in which nanopillars were firstly fabricated, and extended nanochannels were overlaid on them. As the fabrication procedures were essentially the same as those described in our previous papers [1], the outline and additions of the two-step etching process are given here. A fused silica substrate with 0.7 mm thickness and 30 mm × 70 mm sides was spin-coated with electron beam resist and conductive polymer. A pattern of nanopillars and markers for the alignment was drawn by using electron beam lithography system and developed in o-xylene and rinsed in 2-propanol. The exposed pattern was etched by a mixture of SF_6 and CHF_3 gasses in a plasma etching system. After removal of the residue of the resist by a mixture of

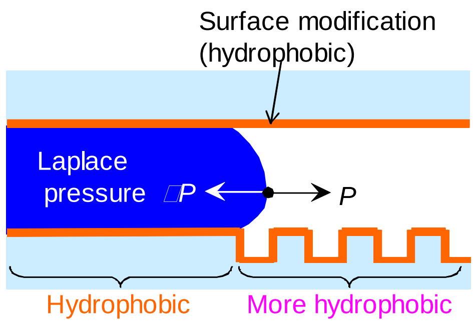

Figure 1. Concept of nano Laplace valve by nanopillar-in-nanochannel and surface modification

o-xylene and dimethylsulfoxide (v:v = 1:2), the positions of the nanopillars and the markers were obtained by scanning electron microscope (SEM). Then, electron beam resist and conductive polymer were spin-coated again, and a pattern of extended nanochannels was overlaid on the nanopillars by referring the positions of the markers. After the pattern was developed and etched, a profile of the nanopillars was remained due to the anisotropicity of dry etching process. Widths of the extended nanochannels were measured by SEM, and depths of the channels and the profile of the nano-in-nano structure were measured by atomic force microscopy (AFM) as shown in Figure 2. U-shaped microchannels (width: 0.1 mm, depth: 6 um) as reservoirs were also fabricated by photolithography and dry etching technique. The substrate with the channels was thermally bonded with another substrate.

Figure 3 shows a schematic of a setup for fL scale liquid handling. An inverted microscope (IX71, Olympus) equipped with a CCD camera (ImagEM, Hamamatsu photonics) was used under the bright field illumination to observe behavior of fluids in extended nanochannels. The chip was set in an aluminum chip holder and put onto a stage of the microscope. The inlets of microchannels were connected with Teflon tubes through o-rings and Teflon screws. The Teflon tubes led to vials connected with PEEK tubes, pressure controllers and compressor. Compressed air generated in the compressor, of which pressure was controlled by the pressure controller, pushed water or air in the vials to the extended nanochannels through the Teflon tubes and microchannels.

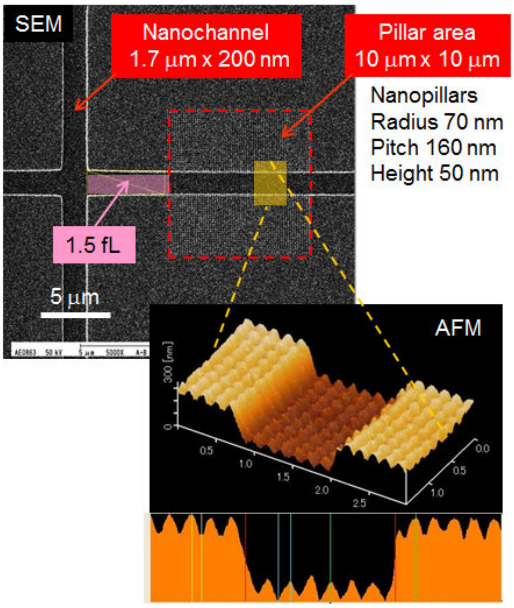

Figure 2. AFM image of fabricated nanopillar-in-nanochannels

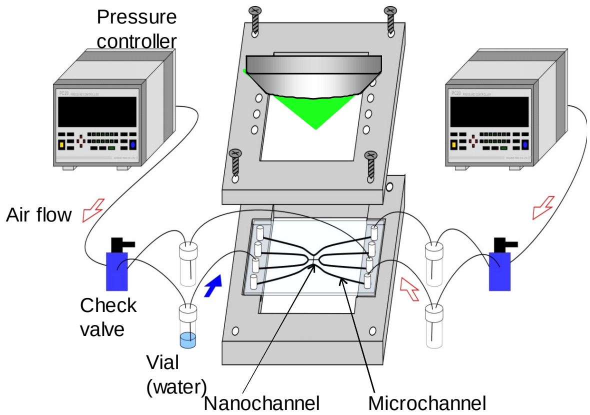

Figure 3. Pressure-driven liquid handling system and microchip

RESULTS AND DISCUSSION

For verifying the working principle of the Laplace valve, a chip with a single extended nanochannel 2.2 μm wide, 220 nm deep and 2 mm long was prepared and nanopillars were fabricated on the bottom of the nanochannel. Water was pushed into the extended nanochannel through the microchannel at a certain pressure, and the pressure was gradually increased. At first, water stopped at the boundary of the nanopillar area. When the pressure was increased to 226 kPa, water flowed across the boundary. The stop and flow at the boundary correspond to “close” and “open” state of the Laplace valve, respectively. From this result, the principle of the Laplace valve in the extended nanospace was verified, and its pressure barrier was successfully measured. Next, we evaluated the measured Laplace pressure barrier (226 kPa) by comparing with a theoretical value. The theoretical value cannot be calculated by normal equation assuming uniform wettability around channel wall, because wettability of flat top/side walls and bottom wall with the nanopillars are different. Therefore, we calculate ΔP by the following equation:

$$\Delta P = \gamma\left(\frac{\cos\theta + \cos\theta^*}{b} + \frac{2\cos\theta}{a}\right) \qquad (1)$$

where a and b are the width and height of the channel and θ and θ^* are contact angle of flat wall and nanopillar, respectively . In the condition of that a = 2.2 [um], b = 220 [nm], γ = 72 [mN] (water at 298 K), θ = 100° and θ^* = 118 °, ΔP is calculated to be 222 kPa. Compared with the experimental value of 226 kPa, good agreement is verified with the theoretical value.

For droplet generation and handling, a chip with two orthogonal extended nanochannels with 1.7 μm wide and 200 nm deep was prepared, and nanopillars were fabricated on the bottom of the horizontal nanochannel (Figure 4). The volume of the chamber between the intersection and the Laplace valve was 1.7 fL. The pressure barrier at the

Laplace valve were measured to be 230 kPa and the pneumatic pressure necessary to drive water in the vertical channel was also measured to be more than 500 kPa. On the bases of these values, fL scale liquid handling was demonstrated as follows. Firstly, water was introduced from the left side to the Laplace valve under 230 kPa. At that time, the vertical channel was also filled with the water. Then, pneumatic pressure was applied from the both sides of the vertical channel at 600 kPa and from the right side of the horizontal channel at 400 kPa in order that the pressure at the Laplace valve would not exceed the pressure barrier of 230 kPa. Due to the pneumatic pressure, the water split at the intersection and remained at the chamber. The volume of the water that remained at the chamber was estimated at 1.5 fL by pixel counting. After that, the left side of the horizontal channel was turned open to the atmosphere. Immediately, the Laplace valve opened and the 1.5 fL water was driven to the left side (Figure 5).

Liquid handling by a combination of pneumatic control and a valve utilizing wettability has been reported. However, the channel sizes were micrometer scale, so that the volume of the liquid was not below several hundred pL. In this study, liquid handling was successfully achieved in an extended nanospace and its volume was 5 orders smaller.

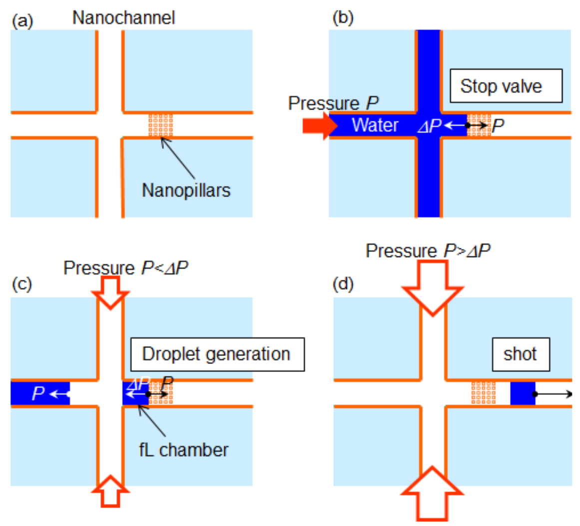

Figure 4. Procedures for fL liquid generation in air and shot.

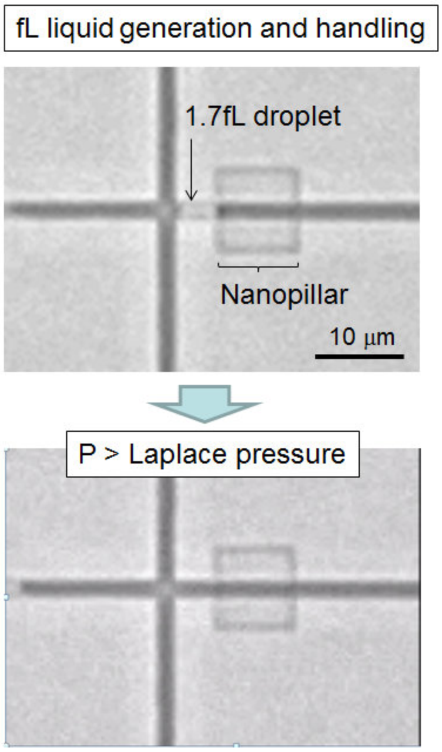

Figure 5. 1.7fL droplet generated in air (upper) and shot of the droplet by applying higher pressure than Laplace pressure

CONCLUSION

Nanoscale wettability patterning was achieved by combination of top-down fabrication and surface chemical modification. Due to the high precision of the wettability patterning, 1.7fL droplet was successfully generated and handled. This device will contribute to ultra-small volume analytical technologies such as single cell analysis utilizing nanofluidic channels.

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