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Fabrication and Experimental Characterization of Nanochannels

Nanofluidics is the science and technology involving a fluid flowing in or around structures with at least one dimension in the nanoscale, which is defined as the range from 1 nm to 100 nm. In this paper, we present the fabrication and characterization of nanochannels in silicon and glass. Since the lateral dimension of the channels is limited by the wavelength of UV light used in photolithography, the channel width can only be fabricated in the micrometer scale. However, the depth of the channel can be controlled precisely by the etching rate of reactive ion etching (RIE). Nanochannels and access holes were etched with deep reactive ion etching (DRIE). Both nanochannels and microchannels were sealed by a Pyrex glass wafer using anodic bonding. The fabricated nanochannels were characterized by capillary filling and evaporation experiments. Due to the small channel height and weak fluorescent signal, fluorescent techniques are not suitable for the characterization of the nanochannels. A long exposure time is needed because of the limited amount of fluorescent molecules inhibit the measurement of transient and dynamic processes. However, as the channel height is shorter than all visible wavelengths, the contrast in refractive indices of air and liquid allows clear visualization of nanochannels filled with liquids. Automatic image processing with MATLAB allows the investigation of ion transport in nanoscale [1].

New and interesting effects emerge. For example, the diffusion dimension of a channel shrinks to less than 100 nm, a number of new and interesting effects emerge. For example, the diffusion process shifts from Fickian regime to Knudsen regime, where the diffusion coefficient depends on the pore size [2–5]. When the channel scales down, the surface tension becomes more significant. The negative pressure caused by this surface tension can even deform the nanochannels [6,7]. The gas–liquid interfacial area increases significantly by corner flow and film flow [8,9]. As the heat and mass transfer phenomena, such as diffusion, strongly depend on the interfacial area, it is expected that there are new phenomena which govern the heat and mass transfer in nanoscale. New theory and more detailed investigations are needed for these new phenomena. Due to the extremely large surface-area-to-volume ratio, the magnitude of the surface charges is on the order of the bulk charges. Thus, ionic transport in nanochannels is determined by the surface charge. In addition to the dominant surface charge, the channel dimension is also on the same order of magnitude of molecules. Thus, the interaction between large molecules such as DNA and the channel wall becomes stronger. The stronger interaction can be used for many applications such as separation and sample concentration. Although many of these effects were known before, as the term “nanofluidics” was mentioned in the literature, only the advance of microtechnology allows the fabrication of nanochannels and a systematic investigation of transport phenomena in nanoscale. For example, with a certain treatment of surface properties, nanochannels show asymmetric diode-like characteristics. Thus, nanofluidic diodes and transistors can be realized [10].

In the past, we have fabricated nanochannels in polymer using silicon mold and hot embossing [11]. Besides hot embossing [11], polymeric nanochannels were also fabricated using surface micromachining [12]. However, for investigations that require structural integrity, silicon and glass are still the favorable choices of material. Furthermore, micromachining of silicon and glass has the advantage of established technologies and facilities. Most of the nanofluidic devices reported in the literature were fabricated in silicon or glass. Nanochannels were fabricated in both bulk- and surface-machining, where the nanoscale channel height was precisely controlled by the deposition rate or the etching rate [13]. Nanochannels with a width of 5 μm and a depth down to 20 nm have been fabricated using silicon-glass anodic bonding, and with a width of 50 μm and down to 25 nm using glass–glass thermal bonding [14].

Since the lateral dimension of the channels is limited by photolithography, the channel width is on the order of micrometers, while the channel height can be controlled for the range from 1 nm to 100 nm. This type of nanochannel with a single dimension in nanoscale is called one-dimensional (1D) nanochannel or planar nanochannel. The channel width can be on the order of micrometers, thus can be patterned using conventional photolithography. The depth or the thickness can be controlled with nanometer precision using the rate of etching or film deposition. Despite the simplicity in fabrication technology, planar nanochannels have a wide range of applications such as preconcentration and separation of DNA or proteins as well as experimental investigation of ion transport in nanoscale [1].

Keywords: nanofluidics, nanochannels, micromachining, RIE, DRIE, capillary filling.
In this paper, we report the fabrication and test of nanochannels fabricated in silicon and glass. Capillary filling and drying experiments were carried out with de-ionized water, isopropanol, and ethanol.

### 2 Fabrication

Figure 1 shows the fabrication process of the planar nanochannels in silicon. The process started with RCA (Radio Corporation of America) cleaning of the wafer (Fig. 1(a)). This cleaning process consists of three steps. The first RCA step removes insoluble organic contaminants with a 5:1:1 H$_2$O:H$_2$O$_2$:NH$_4$OH solution. The second step removes the thin silicon dioxide layer using a diluted 50:1 H$_2$O:HF solution. The third step removes ionic and heavy metal contaminants using a solution of 6:1:1 H$_2$O:H$_2$O$_2$:HCl.

Following the cleaning step, photolithography was used to define the pattern of the nanochannels on a photoresist film (AZ 1512) (Fig. 1(b)). The photoresist was spin-coated in two steps, 500 rpm for 20 s and subsequently 2000 rpm for 10 s. The resist was then soft-baked at 90 °C for 2 min. After the UV exposure, the resist was developed by a mixture of a volume ratio of 2:1 of AZ Developer and DI water for 20 s. The wafer was subsequently rinsed with DI water for 1 min and dried with N2. At the last stage, the resist was hard-baked at 120 °C for 2 min. A resist layer of about 1 μm was confirmed by measurement with an optical profilometer.

Using the patterned photoresist as a mask, nanochannels with a depth of 40 nm–200 nm were etched at a pressure of 4.0 Pa, 30 sccm CF$_4$, 5 sccm O$_2$, an a power of 300 W (Fig. 1(c)). The averaged etching rate with this recipe was 0.564 nm/s. The photoresist was removed by oxygen plasma. Before proceeding to the next stage, the resist was hard-baked at 120 °C for 15 min. The access holes were etched using DRIE for 4 h. The front side of the wafer was covered by a dummy wafer bonded by a thin layer of AZ4420. After the etching step, the photoresist was removed in an acetone bath.

The depth of the nanochannel can be further adjusted by the deposition of a silicon oxide layer (Fig. 1(f)). Finally, both nanochannels and microchannels were sealed by anodic bonding to a Pyrex glass wafer.

After completing the fabrication process, the nanochannels were observed under a microscope. A number of nanochannels were observed to be collapsing. To investigate the reasons of the collapse and to optimize the aspect ratio of the nanochannels, we fabricated nanochannels with various widths, Figs. 3(a). The nanochannels were filled with green fluorescent solution. Due to the weak fluorescent signal, a long exposure time up to 1 min is needed to observe the nanochannels, Figs. 3(a) and 3(b). Since the nanochannels have a height smaller than the visible wavelength, a good channel can be identified as a bright field under microscope. When a channel collapses, its image turns from white to gray and can be observed easily. For channels which originally intact (Fig. 3(c)), the collapse can be initiated by pressing on the channel. Once the top of the channel makes contact to its bottom, the collapse quickly spreads over the entire channel until they are completely cover the entire channel (Fig. 3(d)), except for the narrow region along the edge. The results show that nanochannels made in glass/silicon require a minimum aspect ratio (height to width) of about 4 × 10$^{-2}$, which is consistent with the results reported by Mao and Han [14].

### 3 Characterization

#### 3.1 Capillary Filling

Nanochannels with a height of 45 nm and a width of 10 μm were selected for the capillary filling experiments, as described in Fig. 4(a). Isopropanol and water were used as the working fluid. The liquid was filled into the microchannel manually using a syringe with needle. The images of the nanochannel were observed and recorded with a camera/microscope system. As mentioned above, due to the small channel height relative to the visible wavelength the dry portion of the nanochannel appears bright, while the filled portion is dark. The recorded images were processed by a customized MATLAB program. The program first converted the gray-scale image into a binary image and subsequently measured the length of the dry area. The filling length was calculated from the original length of the dry area. The start of the filling process is detected automatically with program by the change in length of the dry area. Figure 5 shows the measured results of the square of filling length for isopropanol and water at a room temperature of 27 °C. The experimental data are plotted with the relationship from Washburn theory

$$x^2 = \frac{\sigma h \cos \theta}{3\mu} t$$  \hspace{1cm} (1)

where $x$ is the filling length, $t$ is the time, $\mu$ is the dynamic viscosity, $\sigma$ is the interfacial tension, $\theta$ is the contact angle, and $h$ is the channel height. Since the surfaces of silicon and glass are hydrophilic, the contact angle is assumed to be $\theta = 0$. The linear pattern of the experimental data points shows that the filling length follows the Washburn theory. However, for both isopropanol and water, the filling speed in nanochannel is slower than expected with the...
Assuming that this slower filling speed is caused by an apparent viscosity, the value of the apparent viscosity is about 20% and 40% for isopropanol and water, respectively. The phenomenon has been observed consistently by many authors in the past. There are several hypotheses to explain this behavior. Tas et al. [15] argued that the electroviscous effect is one possible cause. However, theoretical analysis from different authors conclude that the electroviscous effect is not sufficient to explain such a high reduction in the filling speed [16,17]. Gruener and Huber [18] and Gruener et al. [19] suggested the reduction in size of the capillary pore due to adsorption of filling liquid molecules on the surface of the solid phase. The thickness of this adsorption layer is about several times of the liquid molecule size, i.e., subnanometer. The adsorption layers, therefore, reduce the speed of capillary filling in structures which is in nanometer size. Especially, the formation of air bubbles was observed consistently in many experiments [17,20,21]. It was showed that there are linkage between the air bubble formation and the reduction in capillary filling speed [21].

3.2 Drying. In the drying experiment, the fluids were first filled in a set of nanochannels with one end closed. The fluid was introduced into one of the reservoirs and started to fill in the microchannel and nanochannels by capillary force. Ethanol was used as filling fluid. To keep ethanol from wetting the outer surface of the chip, a spacer made from poly-dimethyl siloxane is placed above the reservoir. After filling the nanochannels with
ethanol, compressed nitrogen was used to blow the ethanol out of the microchannel. The nitrogen flow drove the evaporated ethanol out of the microchannel. As a result, the partial vapor pressure of ethanol in the microchannel reduced, ethanol vapor in the nanochannels diffused out to the microchannel, causing the drying process in the nanochannels, as shown in Fig. 4(b). The receding speed of the meniscus is determined by the mass transport rate of the ethanol vapor. The partial vapor pressure of ethanol at the meniscus is assumed to be equal to the saturated vapor pressure. In a slit-shaped nanochannel, the channel height is smaller than the mean free path of the vapor. Collisions between the particles and the channel walls then happen more frequently than interparticle collisions. The diffusion phenomenon is then said to be in Knudsen regime, rather than Fickian regime. The Knudsen number (Kn) is used to determine whether the diffusion is in Knudsen regime or Fickian regime. The Knudsen number for slit-shaped nanochannel is defined as

$$Kn = \frac{x_m}{h}$$

Fig. 5 Square of filling length versus time for (a) isopropanol ($\sigma = 20.9$ mN/m; $\mu = 2.00 \times 10^{-3}$ Pa·s at 27°C) and DI water ($\sigma = 72.0$ mN/m; $\mu = 0.89 \times 10^{-3}$ Pas at 27°C)

Fig. 6 Experimental measured drying lengths and theoretical prediction with different values of $p_0$
where \( \lambda_m \) is the mean free path of the particles, with ideal gas approximation.

\[
\lambda_m = \frac{kT}{\sqrt{2\pi d^2 p}}
\]

(3)

where \( d \) is the diameter of the particles, \( p \) is the pressure of the gas, and \( k \) is the Boltzmann’s constant. For the air-vapor mixture in the nanochannel, the concentration of vapor is a function of time and position, therefore, the average diameter of particles is not a constant. However, from Sun and Chen [22], it is possible to estimate the average diameter of particles using the size of an ethanol molecule \( d = 2 \times 1.96 \times 10^{-10} \) m. Substituting \( p = 1 \) bar, \( T = 298 \) K, and \( h = 45 \) nm into Eqs. (2) and (3) gives

\[
Kn = 1.34
\]

(4)

This value of Knudsen number suggests that the Fickian regime is no more applicable. Instead, an intermediate diffusion coefficient must be used. In this paper, the Knudsen diffusion coefficient was used for correlation. In the literature, Knudsen diffusion in parallel pore model has been used to evaluate the mass transport in porous material. The Knudsen diffusion coefficient in straight cylindrical channel is evaluated by balancing the shear stress on the wall of the channel due to partially directional bombardment of particles and the pressure gradient. Using the same approach, the Knudsen diffusion coefficient of gas with molecular mass \( m \) in slit-shaped channel is

\[
D_k = \frac{2}{3} \sqrt{\frac{8kT}{\pi m}}
\]

(5)

The diffusion flux \( \Phi \) (mole per unit area per unit time) is

\[
\Phi = D_k \frac{dc}{dx}
\]

(6)

where \( c \) is the molar concentration of the fluid vapor using ideal gas assumption, \( R \) is the universal gas constant, and \( x \) is the drying length. Because the flux is a constant along the nanochannel, the concentration gradient is

\[
\frac{dc}{dx} = \frac{\Delta c}{x} = \frac{p - p_0}{RTx}
\]

(7)

where \( p \) is vapor pressure at the meniscus and \( p_0 \) is the vapor pressure at the exit of the channel. From Eqs. (6) and (7), the drying speed is determined as

\[
\nu_{dry} = \Phi V_M = D_k V_M \frac{p - p_0}{RTx}
\]

(8)

where \( V_M \) is the molar volume of the liquid. The vapor pressure at the meniscus \( p \) is governed by Kelvin’s equation

\[
RT \ln \frac{p}{p_{sat}} = V_M \sigma \left( \frac{1}{r_1} + \frac{1}{r_2} \right)
\]

(9)

where \( p_{sat} \) is the bulk value of saturation vapor pressure, \( r_1, r_2 \) are two perpendicular radii of curvature. In a totally wetted slit-shape nanochannel, one radius of curvature is equal to half of the channel height \( h \), Eq. (9) becomes

\[
p = p_{sat} \exp \left( -\frac{2V_M \sigma}{RT h} \right)
\]

(10)

and Eq. (8) becomes

\[
\nu_{dry} = \frac{D_k V_M}{RT} \frac{p_{sat} \exp \left( -\frac{2V_M \sigma}{RT h} \right) - p_0}{p_{sat} \exp \left( -\frac{2V_M \sigma}{RT h} \right) - \frac{p_0}{RT}}
\]

(11)

With initial condition \( x = 0 \) at \( t = 0 \), the solution of Eq. (11) is

\[
x = \left[ \frac{2D_k V_M}{p_{sat} \exp \left( -\frac{2V_M \sigma}{RT h} \right) - p_0} \right]^{1/2}
\]

(12)

Equation (12) indicates that the filling speed varies with different values of \( p_0 \). In addition, the scaling effect also influences the filling speed in two ways. First, the channel height affects the diffusivity in Knudsen regime, as in Eq. (5). Second, the channel height determines the radius of curvature of the meniscus, which affects the vapor pressure near the meniscus, through Kelvin’s law. Moreover, the vapor pressure near the meniscus also varies with the surface tension.

The experiments were performed in nanochannels of 10 \( \mu \)m width and 45 nm depth. The silicon chip was observed under the inverted microscope (Zeiss Observer D1) with the reservoirs face up. The images were recorded by the camera (EMCCD AndorIQ) then saved as 16-bit gray-scale multi-images uncompressed TIF file with the size of 1004 pixels \( \times \) 1002 pixels. In the drying experiment, the objective lens magnification of 2.5 \( \times \), camera magnification 1 \( \times \), and exposure time of 10 ms were used. The interval between capturing was 200 ms. The drying length was then measured by a MATLAB program using the recorded images. Figure 6 presents the square of drying length versus drying time. The figure shows a highly linear relationship between those two quantities. The result agrees well with those predicted by Eq. (12) with an effective value of the vapor pressure at the entrance \( p_0 \approx 3 \) kPa. The theoretical results are generated using Eq. (12) with the data are from Refs. [23–26] at the temperature of 25 °C and different values of \( p_0 \). However, it is important to compare the effective value of \( p_0 \) to the real value in future experiments. Such a comparison may reveal the effect of phenomena which have not been considered in this model, such as film flow or corner flow, to the evaporation process in nanochannels. Also, better controlled experiments should be carried out to investigate the relationship between the nitrogen flow and the drying speed.

4 Conclusions

In conclusion, we have successfully fabricated arrays of sealed planar nanochannels in silicon and glass with a depth of 45 nm and low aspect ratios ranging from 0.004 to 0.01. The fabricated device contains both nanochannels and microchannels. The nanochannels were etched with RIE, while the microchannels and the access holes were etched with DRIE. Since the channel height is much shorter than the wave length of visible light, the nanochannels can be characterized using conventional microscope. The dry area of the channel appears bright, while the filled channels are dark. The difference in gray-scale was used to detect the filling length versus time. Filling experiments were carried out for iso-propanol and water. The results show that the filling speed is slower than expected by Washburn theory. The apparent viscosity of the liquid is about 20–40% higher than the bulk values. We are currently working on the cause of this increase in apparent viscosity. Since electroviscous effects can only contribute to 5–10% increase in apparent viscosity, the main cause for the increase in apparent viscosity could be the complex process of evaporation and condensation in front of the advancing meniscus. Trapped and dissolved bubbles could be the cause for slowing down the advancing meniscus of the liquid column. The measured results for drying experiment are highly repeatable with different channels. In the drying experiment, highly linear relationship between the square of drying length and the drying time is observed. This
behavior agrees with theoretical model. However, it is important for further experiment to analyze the agreement between the effective value and the real value of the partial vapor pressure at the entrance. Such an investigation would provide the effective value of the diffusion coefficient in the transition state between Fickian and Knudsen regime. The relationship between the gas flow rate and the drying speed is also an interesting topic for further studies because it reveals the transport phenomenon of gas mixture in micro/nanochannels.

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Nomenclature

- $D_K$ = Knudsen diffusivity
- DRIE = deep reactive ion etching
- $K_n$ = Knudsen number
- $R$ = universal gas constant
- RIE = reactive ion etching
- $T$ = temperature
- $V_M$ = molar volume of liquid
- $c$ = molar concentration of gas
- $d$ = diameter of the pore
- $h$ = channel height
- $k$ = Boltzmann’s constant
- $m$ = molecular mass
- $p$ = partial vapor pressure
- $p_0$ = partial vapor pressure at the entrance
- $p_{sat}$ = bulk value of saturation vapor pressure
- $r_1, r_2$ = two perpendicular radii of curvature
- $t$ = time
- $V_{dry}$ = drying speed
- $x$ = filling length and drying length
- $\Phi$ = diffusion flux
- $\lambda_m$ = mean free path of the gas molecules
- $\mu$ = dynamic viscosity of liquid
- $\theta$ = contact angle between the liquid and the channel wall
- $\sigma$ = surface tension of liquid

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