Silicon Array of Elongated Through-Holes for Monodisperse Emulsion Droplets

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Monodisperse emulsions are of great significance in both scientific and industrial fields, since they have advantages such as their better stability and simplified physical properties. A novel micromachined emulsification device has been developed for monodisperse emulsion droplets. It has uniformly sized through-holes, called straight-through microchannel (MC), on a silicon microchip. An oblong straightthrough MC successfully yielded monodisperse oil-in-water (O/W) emulsion droplets with an average droplet diameter of 32.5 μm and a coefficient of variation below 2% by forcing the dispersed phase into the continuous phase through the straightthrough MC. On the other hand, a circular straightthrough MC yielded polydisperse emulsion droplets. Straightthrough MC emulsification revealed that an elongated cross-sectional shape in the oblong straightthrough MC contributes significantly to the spontaneous formation of monodisperse emulsion droplets without any turbulent mixing.

Introduction

Emulsions are dispersed systems in which one of the two (or more) immiscible liquids dispersed as small spherical droplets in the other. The emulsion droplets usually range from 0.1 to 100 μm in diameter (McClements, 1999). Precisely size-controlled emulsion droplets with a narrow size distribution lead to better emulsion stability and facilitate control of their properties. In addition, monodisperse emulsions are suitable for fundamental studies, because the interpretation of experimental measurements is much simpler than when using polydisperse emulsions (McClements, 1999). While emulsions are generally prepared by the mechanical disruption of the interface between two immiscible liquids, the resulting emulsions show a considerable polydispersity over a wide range (McClements, 1999; Karbstein and Schubert, 1995). Some studies have also been carried out to develop a phenomenological model for forming emulsion droplets from a circular capillary or nozzle (Peng and Williams, 1998; Scheele and Meister, 1968).

The remarkable development of micromachining technology over the last decade led to the fabrication of miniature embedded systems involving many micromachined components and structures, termed microelectromechanical systems (MEMS) (Maluf, 2000). Potential microfludic devices fabricated by this technology have attracted interest in various areas, such as DNA amplification and analysis on a chip (Kopp et al., 1998; Burns et al., 1998), capillary electrophoresis (Harrison et al., 1993), and chemical and biochemical microreactors (Haswell and Skelton, 2000). These microdevices are precisely replicated by the combinations of photolithography, etching, and molding (Maluf, 2000; McCreedy, 2000). Better analytical and reactive performance of these microdevices can be achieved by hydrodynamics on a micron scale, which involves the significant effects of interfacial tension, viscosity, and laminar flow.

Kawakatsu et al. (1997, 1999) proposed a microchannel (MC) emulsification technique to form monodisperse emul-

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sion droplets using MC arrays precisely fabricated on a single-crystal silicon microchip. Monodisperse oil-in-water (O/W) (Kobayashi et al. 1999, 2001; Tong et al., 2000) and W/O (Kawakatsu et al., 2000; Sugiura et al., 2001a) emulsion droplets with coefficients of variation below 5% were formed by forcing the dispersed phase into the continuous phase through the MC with a uniform size. The MC emulsification process does not require any turbulent mixing, since a grooved MC with an elongated section can spontaneously form monodisperse emulsion droplets (Sugiura et al., 2001b). In contrast, small number of channels per silicon chip, which is attributable to their limited layout, leads to low throughput of emulsion droplets.

In the present article, we report simple and ingenious emulsification phenomena in which oblong through-holes microfabricated on a silicon microchip spontaneously form monodisperse emulsion droplets. These uniformly sized through-holes are referred to as a straightthrough microchannel (MC). Deep reactive ion etching (RIE) in MEMS fabrication techniques realized precise microfabrication of straight-through MCs with a high aspect ratio. A highly integrated layout of this MC, realized by deep RIE, can achieve higher throughput of emulsion droplets. We also describe droplet formation from a circular straightthrough MC in order to verify why elongation of a straightthrough MC is necessary. A microscope video system (Kikuchi et al., 1992) enables real-time visual observation of the straightthrough MC emulsification, which helps us analyze the emulsification behavior.

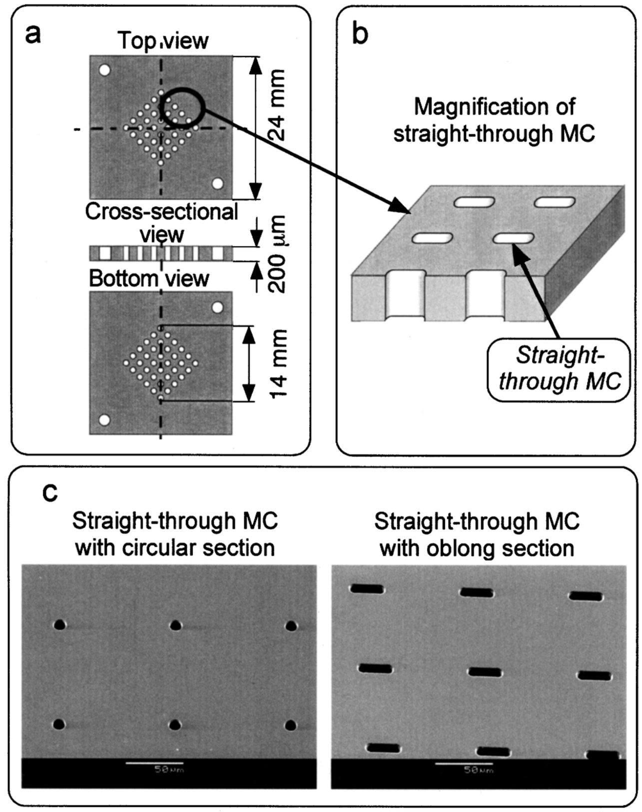

Figure 2. Straightthrough MC plate and SEM images of straightthrough MCs.

(a) The top view, cross-sectional view, and bottom view of the straightthrough MC plate. (b) Magnification of an oblong straightthrough MC. (c) SEM images of straightthrough MCs.

Straightthrough Silicon Microchannel

Device fabrication

Figure 1 depicts the fabrication process of a straight-through silicon MC plate. The microfabrication of a straight-through silicon MC plate started from a 4-inch silicon wafer that was 200 μm thick. A 0.2-μm-thick aluminum layer was vapor-deposited on the silicon wafer as a protective layer against deep RIE (Figure 1b). A positive photoresist was spun on the substrate, and the designed channel patterns were transferred to the substrate via a mask with UV light as a radiation source (Figures 1c and 1d). The aluminum etching and photoresist removal were carried out after this substrate was developed (Figure 1e). The photolithography processing and chemical etching give an aluminum mask against deep RIE on the substrate. Deep silicon etching was then performed by a deep RIE [inductive coupled plasma (ICP)-RIE; Plasma Thermo Inc.] until deep microholes completely penetrated the substrate (Figure 1f). This process plays a critical role in fabricating uniformly sized straightthrough MCs. Thermal oxidation was used to grow a hydrophilic silicon oxide layer to prevent wetting by the dispersed-oil phase on the substrate, and then the silicon substrate was cut into individual chips.

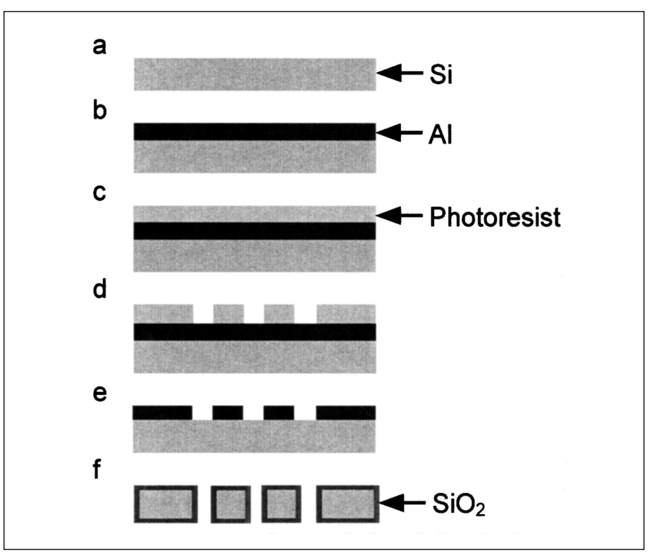

Figure 1. Fabrication process of a straightthrough silicon MC plate.

(a) standard silicon wafer (4-in.); (b) aluminum vapor deposition; (c) spin-coating of positive photoresist; (d) photolithography and development; (e) aluminum etching and photoresist removal; (f) deep silicon etching with ICP-RIE and thermal oxidation of the substrate.

Device design

A model of the straightthrough silicon MC plate is presented in Figure 2. The micromachined straightthrough MC plate measures 24 mm$\times$24 mm$\times$0.2 mm, with two 1-mm-diameter feed holes for a dispersed phase fabricated at the corners of the plate (Figure 2a). A total of five thousand channels is placed around the center of this plate (Figure 2b). The measured effective channel area was 1.0×10^{-4} m^2. Figure 2c shows scanning electron microscopy (SEM) images of the micromachined straightthrough MCs. In order to prevent droplets growing at adjacent channel tops from contacting each other, each channel is positioned at a 100-μm interval for both cross-sectional shapes of the straightthrough MCs. The circular and oblong straightthrough MCs had equivalent diameters of 10.0 and 17.3 μm, respectively. The equivalent diameter of one channel is defined as four times the cross-sectional area divided by the wetted perimeter of the channel. These MCs had coefficients of variation below 1%, exhibiting the high uniformity required as emulsification devices for monodisperse emulsion droplets. Hence, we succeeded in fabricating straightthrough MC plates for forming emulsion droplets.

Materials and Methods

Materials

We used soybean oil (Wako Pure Chemical Industries, Japan) as the dispersed phase of the emulsification system, and 0.3 wt % sodium dodecyl sulfate (SDS; hydrophilic lipophilic balance (HLB), 40) (Wako Pure Chemical Industries, Japan) aqueous solution as the continuous phase.

Straightthrough MC emulsification system and procedures

The straightthrough MC emulsification system (Figure 3a) consisted of the straightthrough MC module, the straightthrough MC plate, a reservoir to feed the dispersed phase, a syringe pump (Model 11, Harvard Apparatus Inc., USA) to feed the continuous phase, and a microscope video system (Kikuchi et al., 1992). The straightthrough MC plate was tightly held between two rubber spacers in the module. The droplet formation behavior was directly observed on a TV monitor (PVM-20M4J, Sony Co., Japan) through an inverted metallographic microscope (MS-511B, Seiwa Kougaku Seisakusho Ltd., Japan), a CCD camera (KP-C550, Hitachi, Japan) with total magnifications of 500 to 2,000.

The reservoir for the dispersed phase and the syringe pump for the continuous phase were connected to the inlets of the MC module, which was initially filled with the continuous phase. The dispersed phase, pressurized slowly, was fed into the module, contacting the back of the straightthrough MC plate via the flow path for the dispersed phase. When the applied pressure exceeded the breakthrough pressure, the dispersed phase broke through the straightthrough MC, initiating droplet formation as illustrated in Figure 3b. The oil droplets formed were recovered by the continuous-phase flow. The applied pressure of the dispersed phase and the continuous-phase flow velocity are regulated by real-time direct observations during the droplet-formation process.

Measurement and analytical method

Video images taken during the experimental runs were analyzed to understand the droplet formation from the straightthrough MCs. An image-processing software (WinRoof, Mitani Co., Japan) was used to measure the droplet size of over 200 droplets from pictures taken with the microscope video system. The average droplet size and size distribution were then calculated from the measured droplet sizes. The coefficient of variation, which presents the width of the size distribution, was determined by the following equation:

$$CV = (\sigma / D_{av}) \times 100, \qquad (1)$$

where CV is the coefficient of variation (%), σ is the standard deviation (μm), and D_{av} is the average MS diameter (μm).

Results and Discussion

Droplet formation from circular straightthrough MC

We first investigated droplet formation from a circular straightthrough MC with a 10.0-μm equivalent diameter

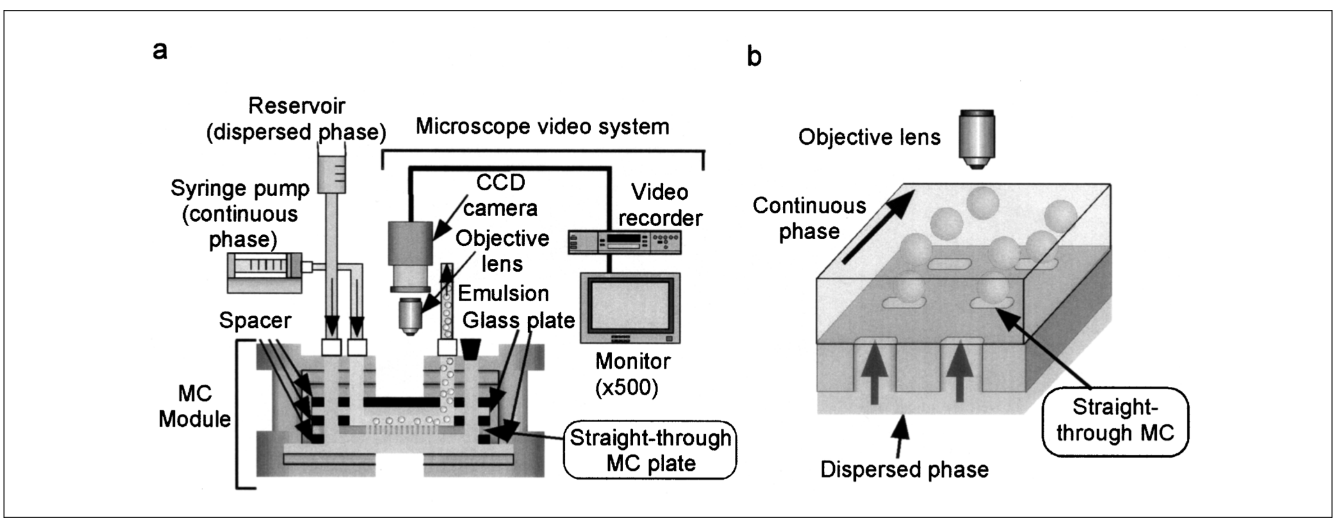

Figure 3. Experimental setup for straightthrough MC emulsification.

(a) The system for straightthrough MC emulsification. (b) Flow through straightthrough MC in the module.

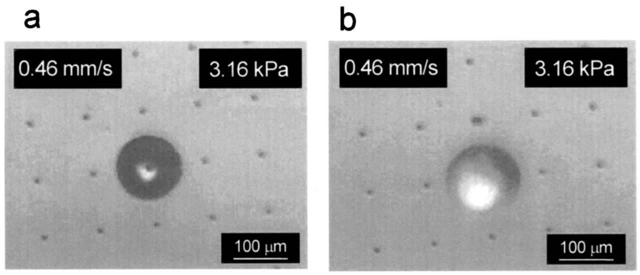

Figure 4. Microscopic images of droplet formation from the circular straightthrough MC.

(a) Breaking through the channels and droplet formation using a circular straightthrough MC. (b) Image of an oil droplet formed using a circular straightthrough MC.

(Figure 4). Droplet formation started with a hemispherically shaped droplet after breaking through the channels at a breakthrough pressure of 3.16 kPa. However, the droplets continued growing up to about 100 μm, which is nearly ten times the equivalent MC diameter, before detaching from the channel tip, as shown in Figure 4a. An image of the oil droplet formed is provided in Figure 4b. The droplets appeared to be difficult to detach from the circular channel tip. Furthermore, the size of the droplets formed in the circular straightthrough MC tended to decrease with an increase in the continuous-phase flow velocity and to increase with the applied pressure of the dispersed phase. The size of the droplets formed was thus significantly influenced by the operating conditions, indicating that a circular straightthrough MC has difficulty forming monodisperse emulsion droplets.

Droplet formation from oblong straightthrough MC

Figure 5 depicts microscopic images of the emulsification process using an oblong straightthrough MC with a 17.3-μm equivalent diameter. When the applied pressure reached 1.80 kPa, the dispersed phase broke through the channels and droplet formation started (Figure 5a). The oil-in-water (O/W) emulsion droplets formed had an average diameter of 32.5 μm and a coefficient of variation of 1.5%, verifying their excellent monodispersity. The size of the resulting droplets was less than one-third those obtained from the circular straightthrough MC. The monodispersity of the formed droplets can also be confirmed by the image in Figure 5b. This demonstrates that the oblong straightthrough MC made the formation of monodisperse emulsion droplets possible.

We also investigated the effect of the continuous-phase flow velocity on the droplet size and size distribution for the oblong straightthrough MC. The continuous-phase flow velocity was regulated between 0 and 9.2 mm/s. The Reynolds number (Landau and Lifshitz, 1987) *Re* ( ) is used to characterize the tendency of a flowing liquid phase to develop turbulence. The calculated Reynolds numbers in this study were below 0.2, indicating a laminar continuous-phase flow. The average droplet diameter and the coefficient of variation of the droplets formed were independent of the continuous-phase flow velocity in the range examined (Table 1). We also revealed that the oblong straightthrough MC yielded monodisperse emulsion droplets, even without the continuous-phase flow (Figure 5c). These results suggest that droplets were spontaneously detached from the channel tip without the shear force necessary for droplet formation from a circular capillary (Peng and Williams, 1998). Therefore, it was found that an oblong straightthrough MC was available for forming stably monodisperse emulsion droplets in a gentle continuous-phase flow.

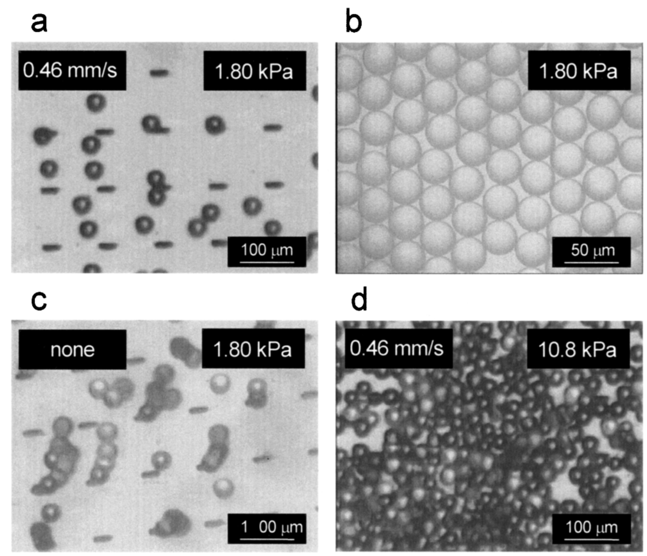

Figure 5. Microscopic images of droplet formation from the oblong straightthrough MC.

(a) Breaking through the channels and droplet formation using an oblong straightthrough MC. (b) Image of monodispersed O/W emulsion droplets formed using an oblong straightthrough MC. (c) Monodisperse emulsion droplet formation without continuous-phase flow. (d) Droplet formation from most of the channels.

In addition, we investigated the effect of the applied pressure of the dispersed phase on the droplet size and size distribution for an oblong straightthrough MC. Less than 10% of the channels worked at around the breakthrough pressure. The ratio of the channels that formed droplets increased as the applied pressure increased over the breakthrough pressure, and more than 95% of the channels formed droplets at 10.8 kPa, as shown in Figure 5d. The average droplet diameter and the coefficient of variation of the droplets formed

Table 1. Effect of Continuous-Phase Flow Velocity and Applied Pressure of the Dispersed Phase on the Average Droplet Size and Coefficient of Variation for Oblong Straightthrough MC

Cont. Phase Flow Vel. (mm/s)	Appl. Press. of Disp. Phase (kPa)	Avg. Droplet Size (D_{av}, μm)	Coeff. of Variation (CV, %)
0	1.80	32.7	1.4
2.3	1.80	32.9	1.7
4.6	1.80	32.4	1.8
9.2	1.80	32.6	2.1
0.46	1.80	32.5	1.5
0.46	3.60	33.0	1.6
0.46	7.21	32.9	1.7
0.46	10.8	32.8	1.6

changed little over the examined applied pressures (Table 1). This result indicates that this elongated cross-sectional shape of a straightthrough MC enables stable formation of monodisperse emulsion droplets over a wide range of applied pressures above the breakthrough pressure. The dispersed-phase flux increased with the applied pressure, and reached 65 L/(m^2 h), which corresponded to the droplet formation volume rate of 6.5 mL/h per MC plate. We observed that channels stably formed uniformly sized droplets at rates between 3 and 11 droplets per second.

The preceding results demonstrate that the cross-sectional shape of the straightthrough MC critically influences droplet formation, and that an oblong straightthrough MC is capable of excellent performance in forming monodisperse emulsion droplets.

Effect of cross-sectional shape of straightthrough MC

The effect of the cross-sectional shape of the straightthrough MC is discussed next, based on the types and balance of the forces acting on a single droplet from a channel.

A circular straightthrough MC has a droplet formation behavior similar to that in a circular capillary (Peng and Williams, 1998). A droplet growing at the channel tip with a circular section is mainly subjected to external forces, consisting of the drag force from the continuous-phase flow, the interfacial-tension force, the buoyancy force, and the inertial force from the dispersed phase (Peng and Williams, 1998). The interfacial-tension force acts against droplet detachment, while the other forces induce the droplet detachment. A droplet growing at the channel tip in this straightthrough MC swung along the continuous-phase flow due to the drag force. When the droplet size reached a critical volume, the swing caused by the drag force made the droplet detach from the channel tip. This droplet formation demonstrates that the drag force works as the driving force to detach the droplet. However, the drag force from the continuous-phase flow on a micron scale fluctuates, resulting in the formation of polydisperse droplets from this straightthrough MC. Additionally, smaller droplets tend to be forced to detach by the stronger drag force from a faster continuous-phase flow velocity (Peng and Williams, 1998), since the droplet detachment from the circular straightthrough MC is determined by the balance between the interfacial-tension force and the drag force from the continuous phase. This is the reason the resultant droplet size depends on the continuous-phase flow velocity. The circular straightthrough MC therefore had difficulty stably forming size-controlled monodisperse emulsion droplets.

The oblong straightthrough MC exhibited the monodisperse emulsion droplet formation with and without a continuous-phase flow. Monodisperse emulsion droplets would be obtained in this straightthrough MC because of a driving force different from that for droplet formation using a circular straightthrough MC. The effect of the continuous-phase flow in this case is negligible, since the oblong straightthrough MC yielded monodispersed droplets without the continuous-phase flow. The interface near the channel tip was forced to elongate during the droplet growth from the oblong straightthrough MC. In general, such an elongated interface tends to be unstable. The growing droplet also had a spherical shape for its upper portion. At the point where the droplet size attained a critical value, the droplet was sheared and detached from the channel tip without any turbulent flow. It is thought that instability from the elongated interface may play an important role in forming the monodisperse emulsion droplets. Sugiura et al. (2001b) have proposed the spontaneous droplet formation mechanism from a grooved MC with an elongated section caused by interfacial tension. This droplet formation mechanism may be applicable to the droplet formation from the oblong straightthrough MC as well. That is, the force to restore the interfacial-tension force gradient of the elongated interface at the channel tip may shear the droplet from the channel tip. Further study of the droplet formation mechanism from the oblong straightthrough MC is in progress.

Conclusions

Rapidly developing MEMS technology helped create the microfabrication of an ingenious emulsification device, called the straightthrough MC plate with uniform through-holes. We found that the micromachined oblong straightthrough MC performs better in forming monodisperse emulsion droplets by forcing the dispersed phase through the simply elongated cross-sectional shape of the straightthrough MC. The elongated cross-sectional shape of the straightthrough MC allowed spontaneous formation of monodisperse emulsion droplets, even without any turbulent mixing. This provides a new insight into applicable nozzle-based dispersing systems. This micromachined emulsification device has the potential for preparing functional microspheres and microcapsules that require monodispersity. It can also be used as size-controlled membrane filters.

Acknowledgment

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