

## Direct etch method for microfluidic channel and nanoheight post-fabrication by picoliter droplets

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Photolithography is an expensive and significant step in microfabrication. Approaches that could change lithography would create an impact on semiconductor industry and microelectromechanical systems technologies. We demonstrate a direct etching method by ejecting etchant droplets at desired locations by using microdroplet ejector arrays. This method could be used for easy fabrication of poly(dimethylsiloxane) microfluidic channels and nanometer height postlike structures in microfluidic channels. © 2006 American Institute of Physics.

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Droplet generation methods have become valuable and crucial as numerous applications are posed by today's technology in the fields of semiconductors and biotechnology. For instance, bio-arrays for drug testing could utilize controlled droplet generation techniques, two-dimensional arrays of cells placed on a surface could be tested with droplets of drugs, and DNA arrays could be printed by microdroplet ejectors.<sup>1</sup> Various methods for generating fluid droplets have been reported.<sup>2-7</sup> Here, we utilize an ejection method, whereby acoustic plane waves actuate periodically spaced multiple orifices of a thin rectangular membrane.<sup>8</sup> A droplet ejection method that prints photoresist onto a wafer surface drop by drop has the potential to minimize photoresist waste by the spin-coating method and to eliminate the lithography step for feature sizes as small as 10  $\mu\text{m}$ . Direct printing has become widely used for flat-panel display and light-emitting diode fabrications, where high resolution is not significant, since it is significantly low cost, fast and easy.<sup>3-5</sup>

In this letter, we demonstrate a complementary method to direct photoresist printing that involves solvent ejection instead of photoresist ejection, and photoresist etching instead of deposition. This has several advantages, since solvents are easier to eject than photoresist. Solvent droplets as small as 3  $\mu\text{m}$  in diameter can be ejected through 10  $\mu\text{m}$  diameter orifices.<sup>3</sup> Moreover, there are concerns in photoresist ejection as not to damage photoresist in order to achieve repeatable and uniform deposition. Therefore, inkjet technology cannot be utilized for photoresist ejection, whereas it can be used for solvent or other etchant ejection.<sup>3-6</sup> Furthermore, evaporation of ejection fluid is less of an issue as long as fluid is supplied plentiful to the ejection reservoir. Although direct deposition resolution is not comparable to lithography, it has become influential. There may be conditions under which one cannot print a thin film directly, such as  $\text{Si}_x\text{N}_y$ ,  $\text{SiO}_2$ , or a metal thin film. However, such a thin film could be directly etched by droplets of an etching solution. Direct etching could be a supporting or a replacement tool for those applications wherein direct deposition is appropriate.

Nanotechnology has the potential to revolutionize various fields of research such as biology. For instance, enabling lab-on-a-chip based devices that could detect and sort DNA

molecules by size would have great impact. It could also lead to sequencing at a single-molecule level.<sup>9</sup> Hence, there have been efforts to build nanofluidic channels in the scale of 5 to 200 nm for applications of nano-confinement studies such as confinement of DNA molecules for prestretch and stabilization before going through nanometer-level orifices.<sup>9</sup> The nanofluidic channels are commonly fabricated on fused silica substrates using techniques of nanoimprint lithography and electron beam lithography.<sup>9</sup> These methods are very expensive, labor intensive, complicated, and low throughput. The simple droplet etching method that generates controllable nanometer-high posts could also be used in fabrication of fluidic channels as high as 50 nm and as wide as a few micrometers.

The poly(dimethylsiloxane) (PDMS) fabrication technology has offered the capability of making quick prototypes, especially in microfluidics. Today, not all, but most of the cell biology microfluidic channel applications use microfluidic channel dimensions that are comparable to cell sizes, except for the DNA-RNA nanofluidic channel applications. The cell based biology microfluidics do not need high-resolution lithographical tools. However, researchers rely on expensive lithographical tools in order to define microfluidic channels. A direct etching method would decrease the cost of equipment for a clean room. It could also increase efficiency, since it would be a matter of printing a drawing on a computer screen as a microfluidic channel or a device onto a wafer. Researchers would not need to send out a mask, wait to receive it, run it through an expensive lithographical tool, or complete a final developing step combined with baking steps. The ease offered by a direct developing method could be very significant. Moreover, defining patterns on a surface by using etching as a mechanism has been demonstrated as an enabling tool. Controlling the width of a fluid flow in a microfluidic channel has been used to generate patterns in a microfluidic channel.<sup>10</sup> This part of our craft demonstrates the initial direct developing method results for possible new applications in the semiconductor industry, biology, and nanotechnology.

A diagram of microdroplet ejector array used for the droplet generation is shown in Fig. 1(a). The acoustic waves travel through the fluid reservoir. If there is enough force exerted by acoustic radiation pressure at the orifices to over-

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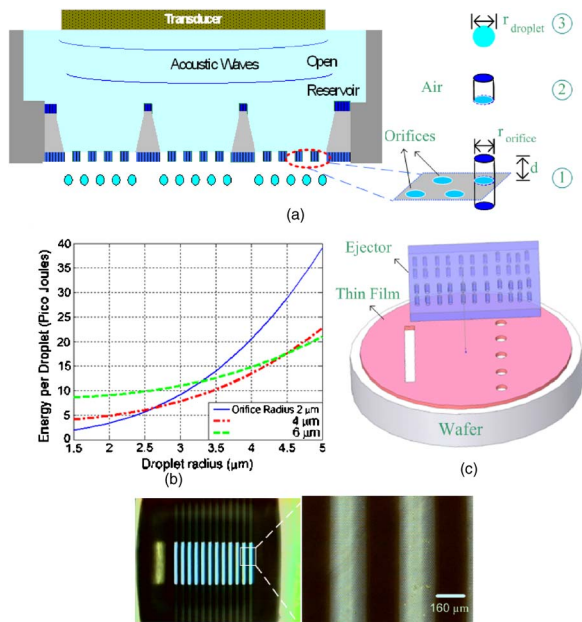


FIG. 1. (Color online) (a) The design and operation of the micromachined droplet generator, and formation of a droplet from an orifice. (b) Energy required for ejection versus droplet radius for three orifice diameters of 2, 4, and 6  $\mu\text{m}$ . (c) The setup for droplet based etching, wherein the ejector is on the top facing downwards, etching patterns on the thin-film coated silicon surface. (d) Micromachined multiple orifice  $\text{Si}_3\text{N}_4$  membrane based two-dimensional ejector arrays, and front view of  $\text{Si}_3\text{N}_4$  membranes with 3- $\mu\text{m}$  orifices with 9  $\mu\text{m}$  periodicity.

come surface tension forces of the fluid, and droplets will then be ejected from periodically spaced multiple orifices of a rectangular membrane array. Chu *et al.* give the Langevin radiation pressure  $\mathcal{N}$  as the mean energy density of an acoustic beam at the surface of air liquid boundary.<sup>11</sup> Hunter *et al.* gives the average intensity of the incident wave  $I_{\text{initial}}$  and the Langevin radiation pressure  $\mathcal{N}$  as  $I_{\text{initial}} = p_{\text{initial}}^2 / 2c\rho_{\text{bulk}}$  and  $\mathcal{N} = 2I_{\text{initial}}/c$ , where  $p_{\text{initial}}$  is pressure amplitude of the incident acoustic wave,  $\rho_{\text{bulk}}$  is bulk density of the liquid, an  $c$  is velocity.<sup>12</sup>

We could develop a basic understanding of the energy required for droplet formation, final velocity, and radius of the droplet by the conservation of energy principle. Energy supplied by an acoustic transducer is spent during drop formation to increase the surface area of the fluid. The steps shown in Fig. 1(a) are approximations to experimental stroboscopic images of droplet formation through an orifice.<sup>2,13</sup> Surfaces created in droplet formation can be calculated as  $\Delta S_{\text{created}} = 2\pi r_{\text{orifice}}d + \pi r_{\text{orifice}}^2$ . The energy consumed during surface creation is given by  $\Delta E_{\text{required}} = \Delta S_{\text{created}}\delta$ , where  $\delta$  is surface tension of the fluid. The last step of the cylindrical droplet geometry changing into a sphere is spontaneous by the minimum energy principle. It does not require energy; on the contrary, it adds energy to the droplet, which is most likely consumed by the internal dynamics of the droplet. Moreover, assuming that there is no evaporation during this transformation process, the radius of a spherical droplet is given by  $r_{\text{sphere}} = [(3/4)dr_{\text{orifice}}^2]^{(1/3)}$ . This is a simple model, actual droplet sizes could be determined by taking into consideration capillary waves and other physical phenomenon taking place at the orifices or by finite element analysis.<sup>2,13</sup>

A droplet ejection would take place if the initial energy  $E_{\text{initial}}$  given to fluid cylinder by the acoustic wave is larger than  $\Delta E_{\text{required}}$ . Thus, an ejection rule can be based on energy

considerations  $E_{\text{initial}} > \Delta E_{\text{required}}$ . A required energy versus droplet radius diagram is shown in Fig. 1(b), where larger droplets need more energy to form. Moreover, the ejection velocity of a droplet is determined by the remaining energy on the droplet cylinder after the energy required is consumed to form the droplet. The mass of a droplet is given by  $m_{\text{droplet}} = 2\pi r_{\text{orifice}}^2 d \rho_{\text{fluid}}$ . The resulting final velocity is derived from the following equation:  $(m_{\text{droplet}} v_{\text{initial}}^2) / 2E_{\text{initial}} - \Delta E_{\text{required}}$ .

The resonant frequencies of a rectangular membrane can be calculated analytically and numerically.<sup>2,3,5,14</sup> Here, resonant frequencies of a rectangular membrane under fluid loading were calculated by finite element simulations (ANSYS 5.7, PA). These membrane resonances do not overlap with transducer actuation frequencies of 500 KHz, 1 MHz, 2.25 MHz, and 3.5 MHz (Panametrics, MA). Outside the resonances membrane displacement is small. Hence, ejection is dominated by acoustic wave radiation pressure enhanced by the fluid reservoir shape and membrane displacement has small effect on droplet generation.<sup>8</sup> A multiple orifice ejector array device is shown in Figs. 1(c) and 1(d). The multiple orifices are 3  $\mu\text{m}$  in diameter and periodically spaced by 9  $\mu\text{m}$  on a 160  $\mu\text{m} \times 2$  mm rectangular membrane array.

The current PDMS process involves first deposition of a SU-8 photoresist followed by masking and developing steps. This step is followed by placing PDMS on a wafer surface and microstructures are formed by the topography of wafer surface generated by photolithography process. The direct etch method could remove the need for a mask and subsequent photolithographic steps at micron scale. A wafer is spin coated with photoresist and droplets of photoresist developer or solvent are then ejected to desired locations. The topography on wafer surface is created by droplet based direct etching on the photoresist coated wafer. A wafer was placed on an XY stage and moved at a certain speed to determine the separation between ejected droplets, as shown in Fig. 1(c).

The droplet ejection was achieved at three transducer resonant frequencies of 500 KHz, 1 MHz, and 3.5 MHz. The ejection frequency and speed of the XY stage can be changed so that there was more or less fluid deposited at a location. At a high wafer translational speed we were able to obtain single droplets on a SU-8 coated silicon wafer surface and the single droplet etch profiles were observed to be uniform, as shown in Figs. 2(a) and 2(c). Small droplets were observed to have an etch depth of 50 nm, whereas larger droplets had an etch depth of 100 nm, as shown in Fig. 2(c). The surface roughness at the plateau of the etched profiles was 15 nm at the worst location. A picture of two droplets overlapping by 20  $\mu\text{m}$  and their etch profile are given in Figs. 2(a) and 2(c). When PDMS is poured on top of the droplet etched topography, nanoheight posts could be formed. One could consider etching a channel by just continuing the ejection of more overlapping droplets on a SU-8 coated wafer surface. We fabricated a 9 cm long, 15.2  $\mu\text{m}$  deep uniform dome-shaped microchannel, as in Fig. 2(b), and its profile is demonstrated in Fig. 2(d). This channel was formed by ejecting droplets at 1 MHz, which corresponds to  $10^6$  droplets per second and at a stage translational speed of 2.1 cm/s. Hence, the separation between two neighboring ejected droplets was 0.021  $\mu\text{m}$ . The experiments were conducted in a dry laboratory environment. A solvent-saturated

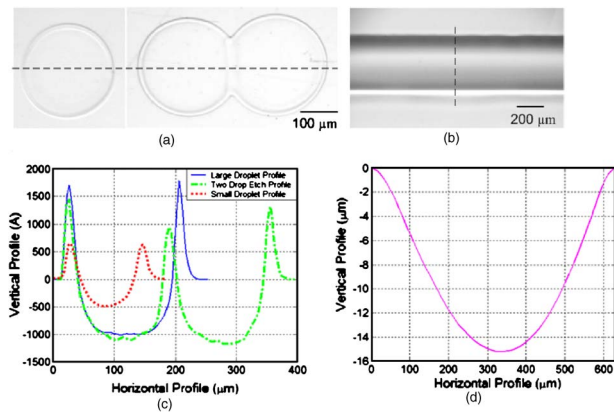


FIG. 2. (Color online) (a) A single acetone droplet and two overlapping droplets placed side by side etching photoresist coated surface of a 4 in. wafer. (b) Multiple overlapping droplets ejected on photoresist etching a 4 in. line. (c) Etch profiles through the profile lines of (a). (d) The profile of the etched line through the profile line of (b).

environment would be better for control of the etching process.

The isotropic wet etch profiles were observed as solvent droplet etches in all directions. The etching was observed to stop when a certain amount of etchant was consumed by the reaction. It was observed that channel depth and width could be varied by changing interrelated parameters, such as stage speed, ejection frequency, droplet size, and overlap separation of ejected droplets on a surface. Microchannel etch depths of  $1.2\ \mu\text{m}$  and  $3.4\ \mu\text{m}$  were experimentally obtained by varying the stage speed. These channels were observed to have uniform profiles along the channel, as shown with the  $15.2\text{-}\mu\text{m}$ -deep microchannels, and could be obtained repeatably. The surface roughness at the plateau of etched profiles was  $15\ \text{\AA}$  through the microchannel. The etched surface profiles were obtained by Dektak (Veeco Ins., Woodbury, NY) profilometer with a  $5\ \text{\AA}$  vertical resolution. The step heights and roughness of photoresist surface were measured by placing a  $12.5\ \mu\text{m}$  radius stylus with a wedge angle of  $10^\circ$  in contact with the wafer surface and then translating it along the surface of the substrate with a speed of  $0.2\ \mu\text{m}/\text{s}$ . The control of droplet sizes, number of droplets per location, and timing of the droplets delivered to a surface can determine the shape of the structure being etched, which could create geometries other than round edges, and with varying channel heights as well.

One concern could be the possible splash of an ejected droplet. The splashing-deposition boundary is given by Ohnesorge number,  $\text{Oh} = \sqrt{\text{We}/\text{Re}}$ , where  $\text{Re} = 2\rho v_D r_D / \eta$  is the Reynolds number,  $\text{We} = 2\rho v_D^2 r_D / \sigma$  is the Weber number,  $v_D$  is the ejected drop velocity, and  $\eta$  is the dynamic viscosity of the liquid.<sup>15</sup> The Ohnesorge number is smaller than the critical limit and the splash of a droplet on surface is not theoretically feasible since it is a small droplet size and surface tension is great enough to hold the droplet together at the droplet landing velocities, which we operate at the range of  $1\ \text{m}/\text{s}$  to  $10\ \text{m}/\text{s}$ , and the droplet size range of  $2$  to  $10\ \mu\text{m}$  diameter.<sup>3-6</sup> However, a droplet spreads out on a surface to a larger area than its initial diameter in air depending on the initial droplet size, velocity, and properties of the surface.<sup>13,15</sup> This spread is further increased during the isotropic etching of droplet on the surface by diffusion.

There were edges in the single-droplet profiles. These were initially thought to be due to the initial velocity that droplet hits the surface, causing a raising of the side edges. Considering the fact that the droplet further etches towards the sides after landing on a surface, the side edges could be due to the distribution of the droplet fluid on the surface during etching. The control of etching of the resist and the final profile depend on volume and concentration of the etching solution and type of reaction. The edges were observed to be smaller for smaller droplets, and the droplet spread area would be smaller at smaller surface impact velocities. The edges were observed to disappear for microchannels since the ejected solution was etching possible side edges. Further research is necessary to investigate droplet surface interactions in the presence of a chemical etching reaction.

We also demonstrate a control of an etching reaction by limiting the volume of one of the reactants down to a droplet size of femtoliter to picoliter range. This could be used to perform and monitor reactions at a microscale level. Ejector arrays capable of drop-on-demand would provide the benefit of better control of etching of surfaces by droplets. The etching reaction could be stopped by flowing an etch stopping solution over a wafer. This method could also be used to etch lines on a metal coated surface or any other organic or non-organic surfaces.

We demonstrated a method of fabricating PDMS microfluidic channels and nanoheight posts by a direct developing method at desired locations by using microdroplet ejector arrays. This method gives us the capability to build microfluidic channels, nanometer-height postlike structures in microfluidic channels, and possible nanoheight fluidic channels by just using a droplet generator. This method does not require expensive electron beam photolithographical tools in order to build fluidic channels of nanometer scale in a single dimension. The smallest feature size is determined by the droplet diameter and the etch reaction. The future of droplet ejectors predicts innovative applications in semiconductor industry, biotechnology, and nanotechnology.

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