AIP Applied Physics Letters

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Utkan Demirci

Citation: Applied Physics Letters **88**, 144104 (2006); doi: 10.1063/1.2191087
View online: http://dx.doi.org/10.1063/1.2191087
View Table of Contents: http://scitation.aip.org/content/aip/journal/apl/88/14?ver=pdfcov
Published by the AIP Publishing

Droplet-based photoresist deposition

Utkan Demirci[a)]
Department of Electrical Engineering, E. L. Ginzton Laboratory, Stanford University, California 94305

(Received 21 March 2005; accepted 7 March 2006; published online 5 April 2006)

Photoresist droplets are ejected onto a wafer surface by an acoustic two-dimensional micromachined ejector array. The spread of single droplets on a silicon wafer surface at varying droplet speeds is studied. Series of photoresist droplets are printed periodically drop on demand on a silicon wafer surface and profiles of a single droplet and two droplets overlapping with varying distances of 25 and 1 μm on a silicon wafer are demonstrated. Moreover, 3.4 μm thick spinless full coverage of a 4 in. wafer with photoresist is demonstrated which indicates a potential for coating wafers in less than a few seconds. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2191087]

A reliable and rapid method of dispensing picoliters of fluids emerged as an attractive technology enabling various microelectromechanical system (MEMS) fabrication methods and bioengineering applications.[1–4] For instance, high throughput arrays for drug testing where arrays of cells placed on a surface could be tested with picoliter droplets of drugs; DNA arrays could be written by drop ejection.[4,5] Current droplet generation techniques such as piezo-jet and bubble-jet are not appropriate for ejection of sensitive fluids such as polymers or biological suspensions. These inkjet technologies either heat or pressurize the fluid reservoir at every cycle of ejection.[6–9] For instance, these ejectors would not be appropriate in the long run for reliable and repeatable direct printing of millions of cells for applications such as three-dimensional tissue printing. Moreover, the poor directionality and droplet size nonuniformity of inkjet combined with the possible clogging of nozzles during ejection of suspensions poses serious problems.[4,9,11] Therefore, the acoustic picoliter droplet generation method demonstrated in this work, which utilizes open-pool nozzleless ejection and acoustics for formation of picoliter droplets of sensitive fluids and cell suspensions, could have interesting applications in biotechnology. Moreover, deposition of organic polymers is the most employed process step in semiconductor fabrication.[6,7] Among various reported organic polymer deposition techniques, the spin coating method dominates current industrial applications.[7,8] However, this method has disadvantages: up to 95% of the expensive chemicals are wasted; the cost of disposing this hazardous waste is high; there is edge bead formation at the wafer edges due to spinning.[8–10] A drop-by-drop polymer deposition method has the potential to minimize hazardous photoresist waste, disposal costs, and remove edge bead formation problem.[11,12]

The basic building block of a two-dimensional (2D) ejector array is an interdigital ring transducer on a piezoelectric substrate, as shown in Fig. 1. These devices launch surface acoustic waves which leak into the medium in contact with the piezoelectric substrate and interfere constructively forming a focus. If the force exerted by radiation pressure at the focal point can overcome surface tension forces of fluid, then a droplet will be ejected.[12]

The droplet diameter can be modeled by fluid cylinder size, as shown in Fig. 1. The diffraction limited acoustic beam expressions are $d=1.02\lambda F$ and $h=7.1\lambda F^2$, where F is the focal number.[12–14] The speed of surface acoustic waves in a substrate v_{piezo} is larger than that of an acoustic wave in water v_{fluid}. The circular acoustic waves propagate into the fluid at an angle of $\Phi=\arcsin\,(v_{\mathrm{fluid}}/v_{\mathrm{piezo}})$. The focal point height can be calculated from this angle and the outer diameter of the device, d_{outer}, as $H=0.5d_{\mathrm{outer}}\tan(\Phi)$. The F number of a lens is calculated by $F=H/d_{\mathrm{outer}}$. The ejected droplet diameter can be calculated by equating the volume of a cylindrical droplet to a volume of a spherical droplet of diameter d_{droplet}, which is calculated as $d_{\mathrm{droplet}}=\sqrt[3]{(3/4)hd^2}=1.77\lambda F^{4/3}$. This simple model predicts the droplet diameter as 26 μm at 34.7 MHz which is close to the experimental 28 μm diameter for droplets. A more accurate method for surface acoustic waves leaking into a fluid medium could give a better F-number prediction. The droplet diameter scales inversely with frequency, as in Fig. 2(a).

The drop spreading on a surface is important in order to develop models for photoresist wafer coverage.[15,16] A simple analytical relation for ejected drop radius in air and on a substrate can be derived by using the conservation of energy and mass principles. The sum of kinetic E_k, surface E_s, and potential E_p energies before a droplet reaches a surface should be equal to the energy sum after deposition, $E_k+E_s+E_p=E_k'+E_p'+E_d'$, where E_d' is the energy dissipated as droplet spreads on a surface.[16] The kinetic and surface energies before droplet lands on a surface is given by $E_k=2\rho v_D^2\pi r_{\mathrm{air}}^3/3$ and $E_s=4\pi\sigma r_{\mathrm{air}}^2$, where v_D is the ejected drop velocity, r_{air} is the drop radius in air, and ρ is the fluid

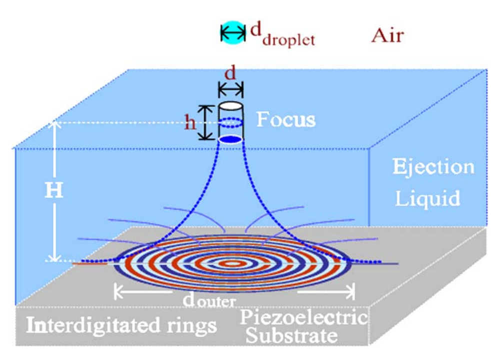

FIG. 1. (Color online) Geometry of a fluid loaded unit cell of a 2D micromachined ejector array.

[a)]Currently at: Harvard Medical School, Massachusetts General Hospital, Center for Engineering in Medicine, Bio-MEMS Resource Center, Charlestown, Massachusetts 02129-4404; electronic mail: utkan@stanfordalumni.org

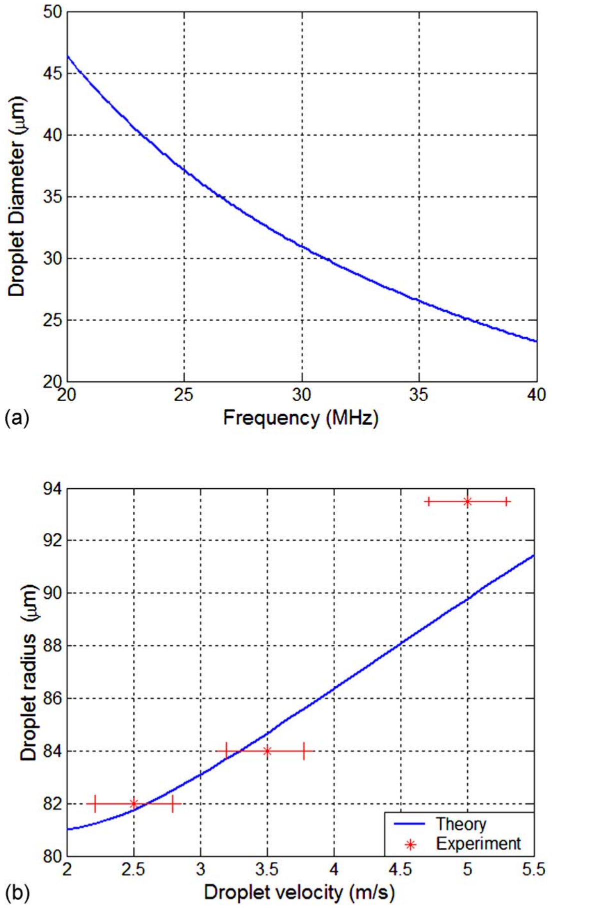

FIG. 2. (Color online) (a) Droplet diameter as a function of frequency. (b) Droplet velocity vs droplet spread on the silicon wafer surface.

density.[16] The initial kinetic energy is spent in deforming the droplet during impact and it becomes zero at the full extension of the droplet. It is hard to determine the dissipated energy during spreading, since the velocity distribution inside the droplet is not known.[16] A simple dissipation model gives $E_d = \mu m v_D^2 / h$, where μ is the viscosity, m is the mass of the droplet, and h is the height of the spread.[16] At maximum spread diameter the surface energy is given by $E_s' = (\pi/4) r_{\text{substrate}}^2 \sigma (1 - \cos\Theta)$, where Θ is the contact angle, σ is the surface tension, and $r_{\text{substrate}}$ is the drop radius on a substrate. Solving for the droplet spread radius gives

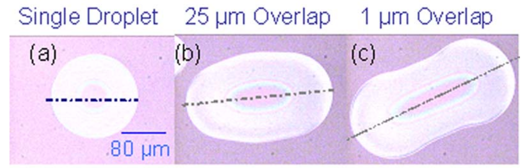

FIG. 4. (Color online) (a) A single photoresist droplet, (b) two droplets overlapping by 25 μm, and (c) two droplets overlapping by 1 μm.

$$r_{\text{substrate}} = r_{\text{air}} \sqrt{\frac{-1 + \cos\Theta + \sqrt{(1 - \cos\Theta)^2 + (6W_e/R_e)[(W_e/3) + 4]}}{3W_e/R_e}}, \quad (1)$$

where R_e is Reynolds number, W_e is the Weber number, and η is the dynamic viscosity of the liquid. We used $r_D = 22\ \mu$m, $\sigma = 30 \times 10^{-3}$ N/m, $\eta = 4$ mPa s, $\rho = 1.01$ g/cm, and $\Theta = 38°$ for calculations.[8] This model does not take into consideration evaporating photoresist solvent and is accurate for only a range of Reynolds numbers.[16] Considering on average 70% of photoresist is solvent, an evaporation correction is required for the conservation of mass and energy of the droplet. The correction factor approach is simple, but the droplet diameter on substrate increase with velocity and trends agree well, as in Fig. 2(b).

An ejector is placed 1 cm high on top of a wafer located on an automated micrometer stage. The ejected single droplets land on the wafer forming profiles, as demonstrated in Fig. 3. The surface tension forces create a new profile after two droplets overlap. Drop-on-demand capability enables overlapping two droplets by 25 and 1 μm, as shown in Fig. 4. The profiles are shown in Fig. 5 and Table I. Printed single droplets are shown in Fig. 6(a). Next, the wafer is moved at a speed of 2 cm/s as ejection is performed at 1 KHz. This corresponds to a droplet every 20 μm generating a 1.8 μm thick photoresist line with $\pm 0.02\ \mu$m thickness uniformity, as in Fig. 6(b). For 4 in. full wafer coverage, the separation between consecutive lines is set to 100 μm. The thickness of the photoresist film is observed to decrease as the number of droplets per location or overlap between two adjacent photoresist droplets or lines are decreased. The 3.4 μm thick photoresist coverage of a wafer is shown in Figs. 6(c) and 6(d). The photoresist thin film thickness uniformity is measured to vary from ± 0.02 to $\pm 0.3\ \mu$m. The surface roughness is measured to vary from 14 to 580 Å over various wafer locations by a Dektak profilometer (Veeco Ins., NY).

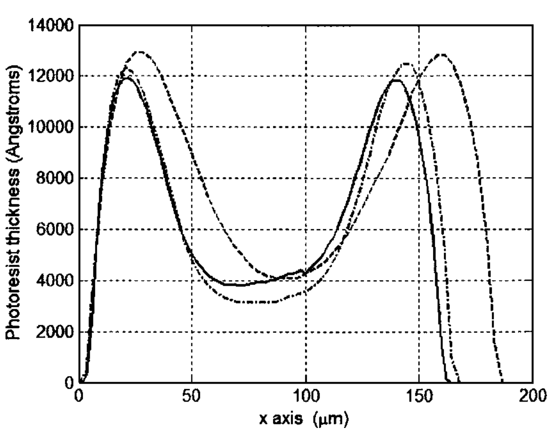

FIG. 3. Three single photoresist droplet profiles on wafer.

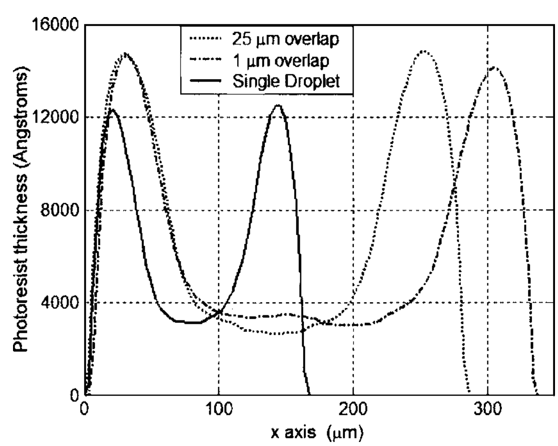

FIG. 5. Profiles of a single droplet and two droplets overlapping with varying distances of 25 and 1 μm on a silicon wafer.

TABLE I. Data for the images shown in Fig. 4 for (a) a single photoresist droplet, (b) two droplets overlapping by 25 μm, and (c) two droplets overlapping by 1 μm.

Droplets on wafer	Surface roughness	Plateau surface roughness (Å)	Area under profile (μm^2)	Area under plateau profile (μm^2)	Average height (Å)	Average plateau height (Å)	Maximum height (Å)
(a)	3286	⋯	108	⋯	6541	⋯	12 597
(b)	4238	35	206	20.2	7117	2834	14 974
(c)	3696	36	215	43	66142	3200	12 597

Experiments are done in a dry laboratory environment without spinning. Thickness uniformity could be improved in a solvent saturated environment. After wafer coating, further spinning is possible. This could lead to thickness uniformities of spin coating with minimal waste. Today's spin coaters waste on average 1–2 ml of photoresist to coat a 4 in. wafer, whereas the proposed method would waste 4.5 nl of photoresist considering that a wafer is first coated with 3.4 μm of resist and thickness is reduced to 1 μm by spinning. Moreover, coating takes approximately a minute in today's tracker systems. Although coating a 4 in. wafer with a single ejector takes about an hour, an array of ejectors could potentially coat a 12 in. wafer in less than 3 s.

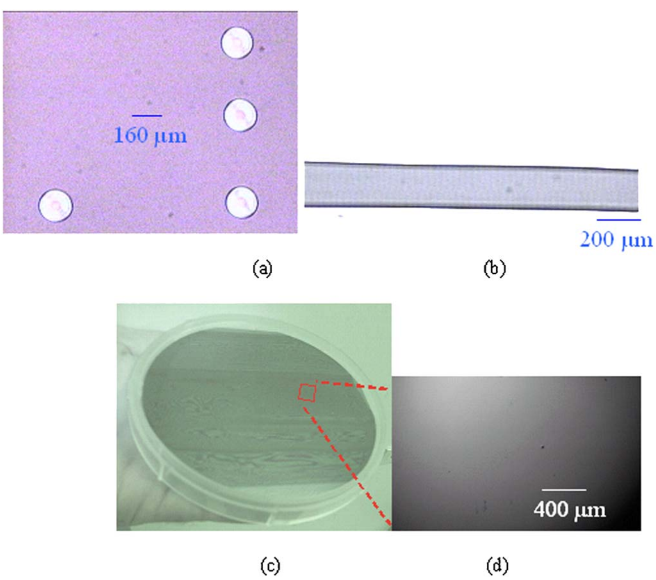

FIG. 6. (Color online) (a) A series of photoresist droplets printed periodically by drop on demand on a silicon wafer surface, (b) a photoresist line directly written on a silicon wafer by ejecting one droplet every 20 μm, (c) full coverage of a 4 in. wafer with photoresist without spinning, and (d) a small area on the coated wafer.

In summary, experimental results obtained with an acoustic 2D micromachined microdroplet ejector array are demonstrated. Photoresist, isopropanol, ethyl alcohol, and acetone are ejected by acoustic ejector arrays in drop-on-demand and continuous modes of operation. Interaction of photoresist droplets on wafer and full photoresist coverage of a 4 in. silicon wafer is demonstrated. Possible applications in semiconductors and biotechnology set a bright future for microdroplet ejectors.

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