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Capillary-driven self-assembly of microchips on oleophilic/oleophobic patterned surface using adhesive droplet in ambient air

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This letter describes a capillary-driven self-assembly technique using oleophilic/oleophobic patterned surface and adhesive in ambient air environment. We use a topographical microstructure of porous ormocer functionalized with a fluorinated trichlorosilane for the oleophobic area and gold patterns for the oleophilic area. The resulted oleophilic/oleophobic patterns show significant wettability contrast for adhesive (Delo 18507), with a contact angle of 119° on oleophobic part and 53° on the oleophilic part. Self-alignment of SU-8 microchips on the oleophilic/oleophobic patterns has been demonstrated. The results provide a promising solution for self-alignment of microparts using commercial adhesives in ambient air environment. © 2011 American Institute of Physics. [doi:10.1063/1.3615053]

Capillary-driven self-alignment using droplets [Figs. 1(a)-1(d)], or droplet self-alignment, is a widely used technique in self-assembly[1] and other microassembly technologies,[2] where the surface tension of the liquid aligns microchips to patterns on the substrate. The technique has been demonstrated in air[2–6] and in water medium.[7–11] The medium sets limitations on the type of liquid, substrate, and pad materials that can be used.

Droplet self-alignment has been achieved using solder droplets in air,[12] water droplets in air,[2–4] adhesive droplets in water,[11] and solder droplets in water.[8,13] Adhesives and solder both have the benefit of being able to make a permanent bonding. Adhesives have the added benefit that they can be cured in low temperatures or by using light. However, self-alignment using adhesive droplets in air is very challenging.

The key of droplet self-alignment relies on the contact angle contrast, i.e., the difference in contact angle, between the pattern and the substrate. Most adhesives are oil-like, i.e., they have low surface tension, which typically leads to low contact angle on most surfaces. Consequently, for most adhesives, it is difficult to find pattern and substrate that would lead to large enough contact angle contrast. Earlier work avoided the problem by using vertical solid edges to confine the droplet,[6,14] which are not desired in many applications.

In this letter, we report the development of a patterned oleophilic/oleophobic surface and demonstrate self-alignment of a SU-8 microchip on the pattern using adhesive droplet in ambient air environment. This work is inspired by the recent reports on superoleophobic surfaces, which demonstrate that liquids of very low surface energy, such as oil, decane ($\gamma = 23.8$ mN/m), and octane ($\gamma = 21.6$ mN/m), can have a contact angle larger than 150° on superoleophobic surface.[15–18] The merits of oleophobicity for droplet self-alignment are yet to be explored.

To achieve self-alignment, we need to create not only an oleophobic surface, but also oleophilic patterns on it. There are quite a few solutions[15–18] to create oleophobic surfaces, but many of them are so fragile that further patterning would destroy their oleophobic properties of the substrate. We choose a combination of topographical microstructure of porous ormocer functionalized with a low surface energy fluorinated surfactant for the oleophobic area and gold patterns for the oleophilic area.

Ormocer (trade name ORMOCOMP®, Micro Resist Technology) is a solvent-free polymer resist and has good adhesion to many different substrates, including Si wafer. Porous ormocer can be achieved by exposing cured ormocer to oxygen plasma. Oxygen plasma selectively attacks carbon rich areas, leaving behind porous silicon oxide like matrix.[19] Re-entrant surface curvature in the form of overhang structures is key to enhancement of oleophobicity.[15] The porous ormocer contains lots of such overhangs and is therefore selected for the oleophobic substrate. Furthermore, the ormocer surface is rich in hydroxyl groups, enabling functionalization using silane chemistry. The trichlorosilane is able to bind to the hydroxyl group of the ormocer, but not on gold patterns. Thus, the gold patterns remain oleophilic after treatment with the trichlorosilane. The low surface energy of the fluorinated trichlorosilane, combined with the topography of the ormocer, creates an oleophobic surface.

Fig. 2 shows the fabrication steps of making oleophobic/oleophilic patterned surface. At first, 4 ml ormocer resist is spin coated on a 4 in. silicon wafer and cured with UV exposure. The sample is then processed in reactive ion etcher (RIE) with O2/Ar, 45/5 sccm, power 200W, 1 min, to make porous ormocer. After RIE, the ormocer layer is completely

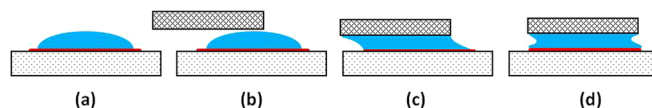FIG. 1. (Color online) Droplet self-alignment: (a) A droplet of a liquid is dispensed on a pattern. (b) A chip is approaching a pattern with a predefined releasing bias. (c) The droplet wets the chip, and a meniscus is formed between the chip and the pattern. (d) The chip is released and the capillary force aligns the chip to the pattern.

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(a) Step 1: Spinning and curing ormocer resist on a silicon wafer

(b) Step 2: Using oxygen plasma to make porous ormocer

(c) Step 3: Spin AZ5214 and use lithography to define pattern shapes on porous ormocer

(d) Step 4: Evaporate gold

(e) Step 5: Lift-off gold by removing resist

(f) Step 6: Functionalize porous ormocer using trichloro(1*H*,1*H*,2*H*,2*H* perfluorooctyl)silane

Si substrate
Ormocer
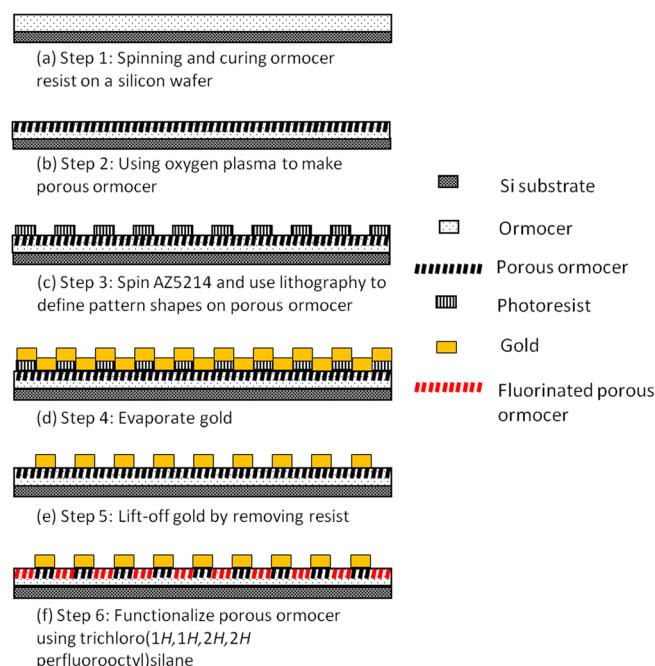Porous ormocer
Photoresist
Gold
Fluorinated porous ormocer

FIG. 2. (Color online) Fabrication process of oleophobic/oleophilic patterned surface. (a) Ormocer resist is spin coated on a silicon wafer; (b) oxygen plasma treatment to make porous ormocer; (c) lithography; (d) gold evaporation; (e) lifting-off gold; (f) functionalization with trichlorosilane.

FIG. 4. (Color online) (a) Gold patterns of 50 nm thickness on the ormocer substrate after functionalization with trichlorosilane; (b) oil-drop-contact angle: 133° on oleophobic substrate; (c) adhesive-drop-contact angle: 53° on oleophilic pattern; (d) adhesive-drop-contact angle: 119° on oleophobic substrate.

nanoporous as shown in Fig. 3. AZ5214E is spin-coated on the porous ormocer and the patterns are defined using image reversal lithography. A gold film of 50 nm is evaporated on the patterned photoresist surface using electron beam evaporation. Finally, the gold is lifted off in acetone bath. The patterned surface is functionalized in a reactor for chemical vapor deposition, where the sample is exposed to trichloro (1*H*,1*H*,2*H*, 2*H*-perfluorooctyl) silane (Sigma-Aldrich) vapor in a nitrogen atmosphere for 24 h at room temperature. Because trichlorosilane is sensitive to water and air humidity, the whole operation has to be carried out in nitrogen environment.

Fig. 4(a) shows the fabricated oleophilic gold patterns on the functionalized ormocer substrate. The wettability of the fabricated surface has been tested with both a normal cooking olive oil and a thermal adhesive (Delo 18507). The contact angle of the olive oil on the oleophobic part of the fabricated
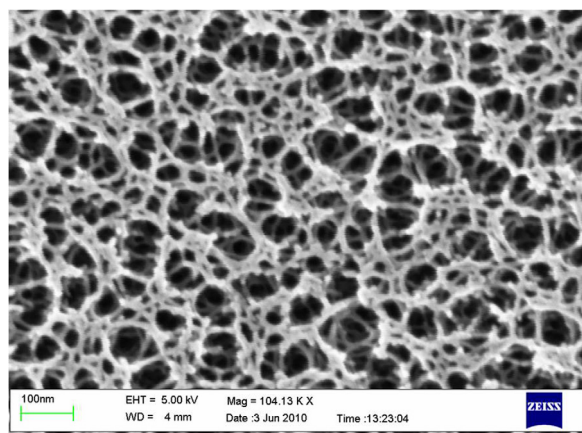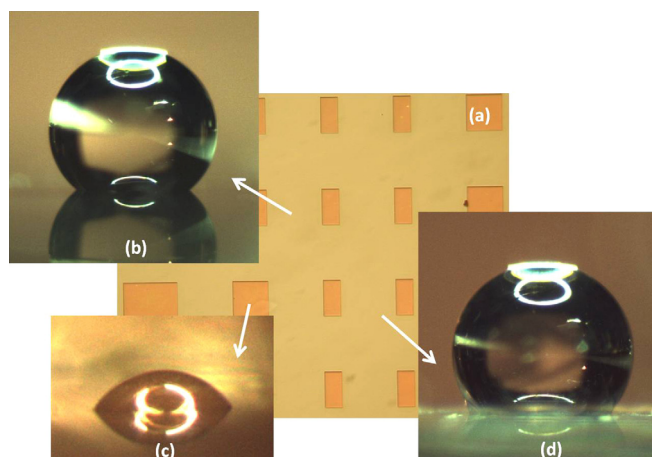
surface is measured as 133° as shown in Fig. 4(b). Contact angles of the adhesive are measured as 53° on the oleophilic gold pattern of the surface as shown in Fig. 4(c) and 119° on the oleophobic part of the fabricated surface as shown in Fig. 4(d). This leads to a contact angle contrast of 66°. Experimental results show that this combination of the contact angles can effectively confine the adhesive drop inside the pattern while providing sufficient wetting on the pattern.

Self-alignment tests have been carried out on several patterns of different sizes using similar sized dummy, cuboid-shaped chips made of SU-8. SU-8 is an epoxy-based negative photoresist suitable to fabricate thick microstructures up to hundreds of micrometers using standard lithography.[20] The fabricated SU-8 chips typically are both hydrophilic and oleophilic, thus we do not need any patterning on the chips. The contact angle on the chip surface was measured as 47° with adhesive (Delo 18507) and 65° with water. The patterns on the ormocer are of size of 100 μm $\times$ 100 μm, 200 μm $\times$ 200 μm, and 200 μm $\times$ 300 μm. The amount of the adhesive is in the range of 0.3 to 2 nl, which is calculated based on the diameter and contact angle measured in the optical images under the assumptions that the droplet is a spherical cap and the gravity can be neglected. The microchips are picked and placed on the patterns using an automatic micro tweezer with an adhesive dispenser (EFD, Inc., Mikros™ dispense pen). The test procedure is illustrated in Figs. 1. The tests were done in ambient room environment.

Fig. 5 shows the frames of the self-alignment processes for an assembly case of a 200 μm $\times$ 200 μm $\times$ 50 μm chip on a 200 μm $\times$ 200 μm pattern. When the chip is moving towards the pattern (a) and then released (b), the capillary force drives the chip, and the chip is then self-aligned according to the pattern (c). The superimposed image (d) of (b) and (c) shows the initial error upon releasing (35 μm, 90 μm and 2°) and the alignment accuracy after self-alignment. The contour of the pattern is highlighted with a dark line to help estimate the final alignment accuracy. The result shows that the initial translational errors and the angle error have been corrected during the self-alignment. It is measured that
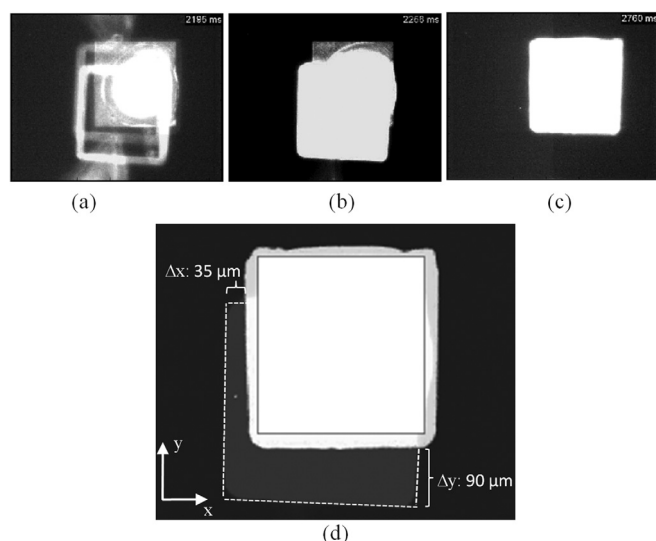

FIG. 3. (Color online) SEM image of the structure of the porous ormocer surface after oxygen plasma treatment.

FIG. 5. Self-alignment frames of a 200 μm $\times$ 200 μm $\times$ 50 μm SU-8 chip on the corresponding gold patterns. (a) The chip is moving towards the pattern. (b) Release the SU-8 chip with a releasing bias of 90 μm and 35 μm in x and y axis individually. (c) Self alignment is realized. (d) The super imposed image of (b) and (c), where the contour of the chip at the releasing position is highlighted with white dashed lines and the contour of the pattern is highlighted with dark lines (enhanced online) [URL: http://dx.doi.org/10.1063/1.3615053.1].

the area of the chip is about 20% larger than the pattern due to the difference of the fabrication processes of the chips and the patterns; nevertheless, the chip aligns well to the center of geometry of the pattern. The final alignment accuracy is inspected using optical microscope by measuring the difference between the geometrical centers of the chip and the pattern. The accuracy is estimated to be less than 1 μm in x axis and 3.5 μm in y axis, where the measurement of this accuracy is limited by the accuracy of the microscopes.

We have repeated the tests with the initial biases around 30 μm and 90 μm in horizontal axes and observed that self-alignment can achieve 100% yield (8 out of 8 tests) when the amount of adhesive is in the range of 0.5–1.5 nl. The amount of the adhesive applied here is in the same range as the volume of the water droplet used for self-alignment test in an earlier work, where high (98%) yield could be achieved.[4] When the amount of adhesive is less than 0.4 nl, all the self-alignments (3 out of 3 tests) failed due to the partial wetting and solid contact between the chip and pattern. On the other hand, when the amount of adhesive is larger than 2 nl, no self-alignment (0 out of 3 tests) can be achieved due to the following situations: (1) the adhesive is overflowed on the pattern; (2) chip is floating on the surface and no self-alignment happens, where adhesive droplet has reached its minimum free surface. The similar phenomena have also been observed and discussed for the self-alignment using water droplets.[3] Furthermore, using water, excess volume of liquid is less harmful to the process, due to that water can evaporate away quickly. With adhesive, the volume is constant during the short period of the experiment because it typically has a very low evaporation rate compared to water in room temperature; therefore, less amount of adhesive should be used for self-alignment than water when other parameters are same. We have also tested the self-alignment of 100 μm $\times$ 100 μm $\times$ 50 μm and

200 μm $\times$ 300 μm $\times$ 50 μm SU-8 chips on the corresponding patterns. Both cases show similar results.

In the successful experiments, the ormocer was oleophobic enough to fully confine the contour of the adhesive inside the patterns. Thus, the surface free energy of the ormocer has no contribution to the driving force of the self-alignment, but the driving force only comes from the surface tension of the adhesive. The benefit of having large contact angle on the substrate and small contact angle on the pattern is that the adhesive can be well confined on the pattern and the chip can be pulled further away (large initial error) before the adhesive starts to wet over the pattern.

The alignment process with adhesive is slower than similar test with water. For 200 μm $\times$ 200 μm chips, it takes about 500 ms estimated from the video frames, in comparison to 50 ms when using water,[2] the reason is that the viscosity increases both the time for wetting a pattern and reduces the restoring force in self-alignment.[21]

In summary, the reported oleophilic/oleophobic patterned surface provides a promising solution for droplet self-alignment using adhesives in ambient air environment. This may lead to potential applications in packaging of semiconductor devices and 3D integration of the micro devices, where adhesives are extensively used.

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