Supporting Information

One-step facile fabrication of controllable microcone and micromolar silicon arrays with tunable wettability by liquid-assisted femtosecond laser irradiation

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Keywords: (Femtosecond laser microfabrication; microcone and micromolar silicon arrays; controllable wettability; liquid manipulation)

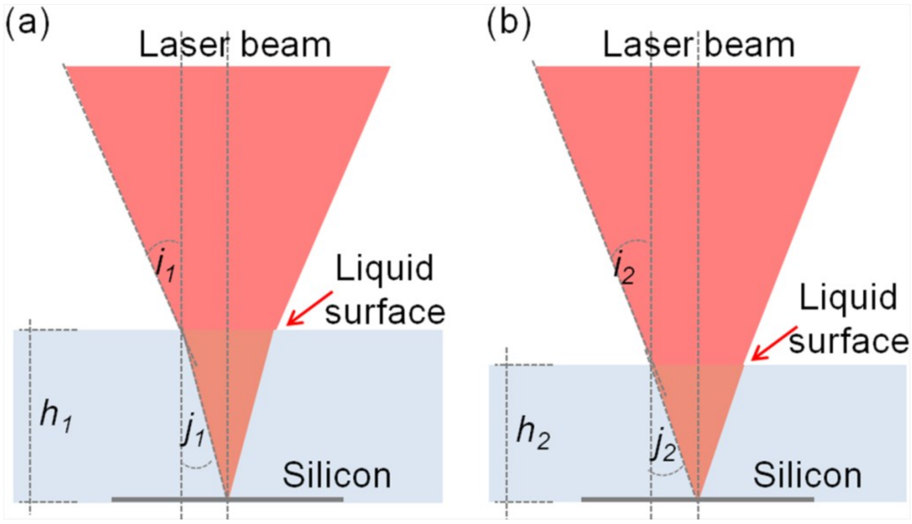

Figure S1. The focus conditions for the laser beam in liquid with different height. (a) the height of h_1, (b) the height of h_2.

For liquid experiments, the silicon sheet was stuck to the bottom of a 20 ml glass container. When the glass container was filled up with ethanol or sucrose, the height of the liquid layer above the sample surface was about 12 mm.

Within the experimental setup of pulsed laser ablation in liquid, the laser beam has to penetrate the liquid layer before reaching the material surface. During this process, the focal length of the focusing lens will change due to refraction by the liquid layer. Considering the refraction of a focused linear beam, the focal length will increase[1,2] for

$$\Delta f = l\left(1 - \frac{f}{\sqrt{n^2 f^2 + (n^2 - 1)r^2}}\right) \qquad (1)$$

where f is the focal length of the focusing lens in air, l is the liquid thickness, n is the refractive index of the liquid, and r is the radius of unfocused laser beam. For $r \ll f$, the formula can be simplified to

$$\Delta f = l\left(1 - \frac{1}{n}\right) \qquad (2)$$

Hence, the amount of energy deposited on the surface will vary for the varying focused position. From Formula (2), it can be calculated that the focal length will increase 3.176 and 3.304 for ethanol (n=1.36) and sucrose (n=1.38), respectively. In order to obtain the same focusing condition, we move the sample surface away at length of $\triangle f$ to achieve optimum focusing. Monitoring of the adjustment was accomplished by a CCD camera with a video monitor. It was indicated that the position of focal point was on the silicon surface, with the error ±1 μm.

The focusing in different height of liquid layer can also be illustrated in Fig. 1. With the liquid height of h_1 (Fig. 1(a)) and h_2 (Fig. 1(b)), the refractive index can be expressed as

$$n_1 = \frac{\sin i_1}{\sin j_1} \qquad (3)$$

$$n_2 = \frac{\sin i_2}{\sin j_2} \qquad (4)$$

For a certain liquid, the value of n_1 is equal to that of n_2 and the laser beam incident angle i_1 is equal to i_2, hence the refraction angle is equal, namely $j_1 = j_2$. Combing the focal length of the lens of 63 mm and the diameter of the unfocused laser beam of mm, j_1 and j_2 can be calculated, and the value is 5.5°. Based on this discussion, the diameter of the focusing point is consistent at different height of liquid layer.

Additionally, the focus is completed by a flat field lens with the focal length of d=63 mm. The diameter of the unfocused laser beam is about r=4 mm. Hence, the numerical aperture of the lens is

$$NA = n \sin \alpha \qquad (5)$$

n is the refractive index, and n=1.516. α is the half aperture angle, and

$$\sin\alpha = \frac{r}{\sqrt{d^2 + r^2}} \qquad (6)$$

The diameter of the laser beam d_o can be expressed as

$$d_o = k\lambda / NA \qquad (7)$$

here, k is a constant and the value is 1.22. λ is the laser wavelength and the value is 800 nm. Combing equations (1) - (3), it can be calculated that d_o=13.5 μm.

The focus point is so small that the microstructures cannot be induced if the silicon is not at the focal plane.

References:

1. H. Liu, F. Chen, X. Wang, Q. Yang, H. Bian, J. Si, X. Hou, *Thin Solid Films*, **2010**, *518*, 5188-5194.

2. Z. Yan, D. B. Chrisey, *J. Photoch. Photobio. C* **2012**, *13*, 204-223.

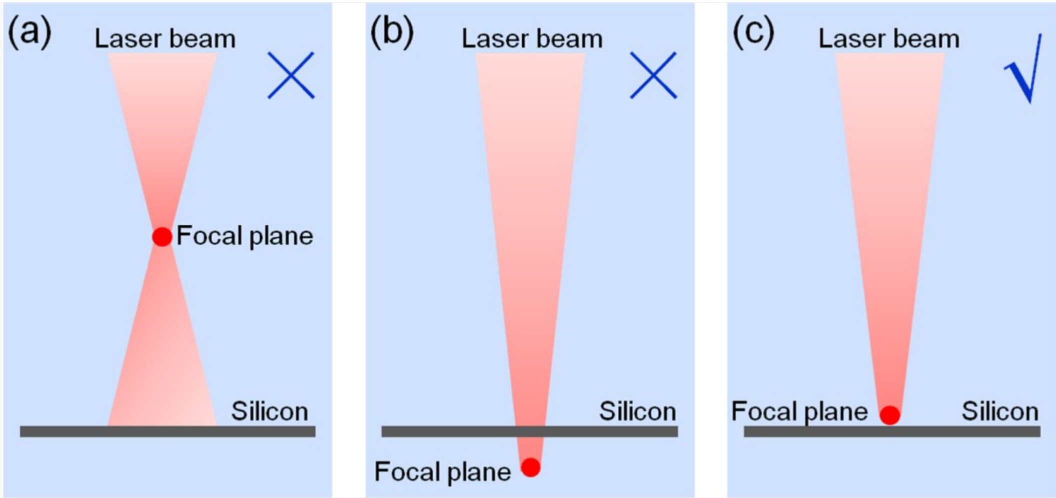

Figure S2. The relationship of the focal plane and the sample surface. (a) and (b) show the focal plane are over or under the silicon surface, respectively. In this case, the processing is multi-filament ablation. However, in our experiments, the laser beam is focused on the silicon surface (c).

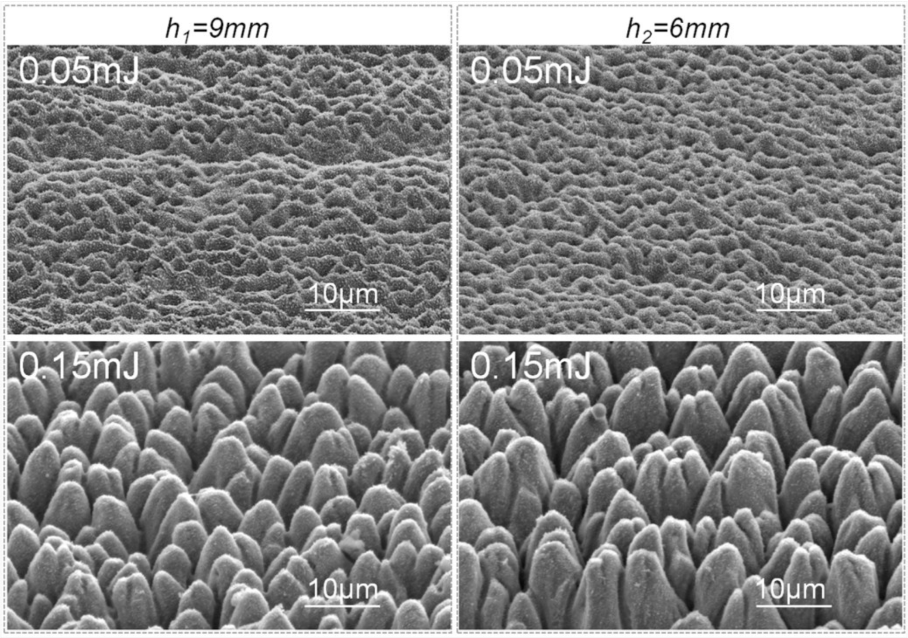

Figure S3. The SEM images of the microstructures fabricated by femtosecond laser in ethanol with height of h_1=9 mm and h_2= 6 mm at pulse energy of 0.05 and 0.15 mJ. It can be seen that the formed microstructures are not affected by the height of the liquid used in our experiments. This is because the focusing point is always kept on the silicon surface no matter what the liquid height is to obtain the same amount of energy depositing.

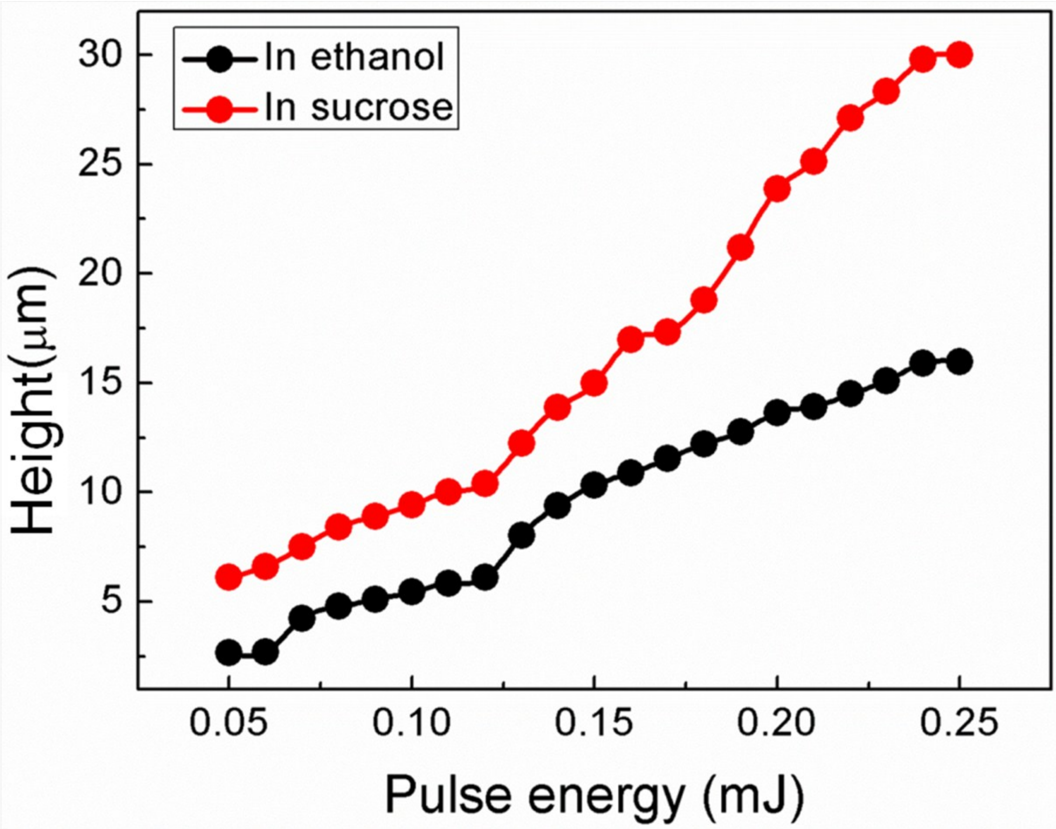

Figure S4. The height of the microstructures as functions of pulse energy. With the pulse energy increased from 0.05 to 0.25 mJ, the height can be increased from 3.3 to 17.6 μm for microcones (black line) and 5.9 to 33.7 μm for micromolars (red line), respectively. This results show that the height of the microstructures are tuned by simply changing the solution and adjusting the pulse energy.

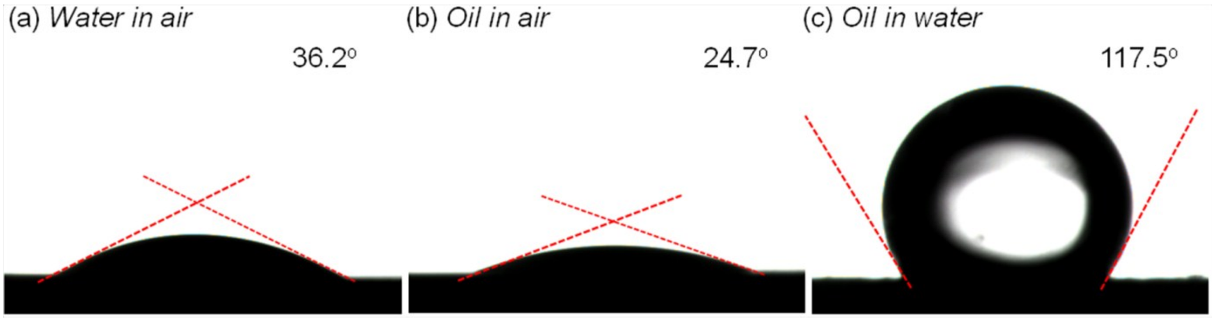

Figure S5. (a) the water contact state in air on flat silicon surface. The contact angle is 36.2°, declaring hydrophilic. (b) the oil contact state in air on flat silocon surface. Due to the low surface tension, the oil possesses contact angle of 24.7°, lower than that of water. (c) the oil contact model underwater on flat silicon surface. It is indicated that the hydrophilic flat nickel surface is tuned to oleophobic one when it is immersed in water, and the contact angle is 117.5°.

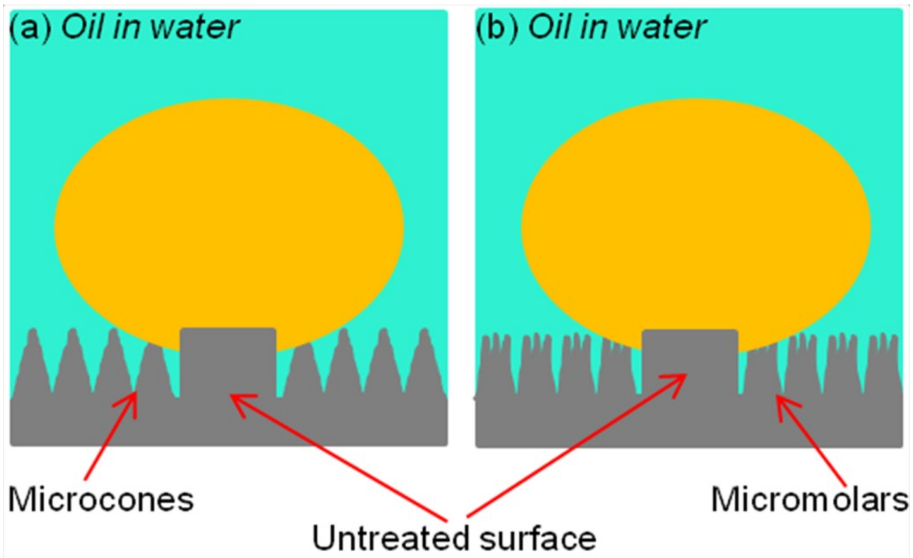

Figure S6. Schematic diagram of underwater oil along the set path. The untreated silicon is oleophobic, while the treated areas (a) microcones and (b) micromolars are superoleophobic. By taking advantage of this property, we have designed a path composed of untreated fine line and treated thick lines on both sides. In this way, the fine line can grasp the oil droplet and control it to move along the setting path, and the ultralow adhesion force of the processed lines on both sides ensure the oil droplet to move without loss.

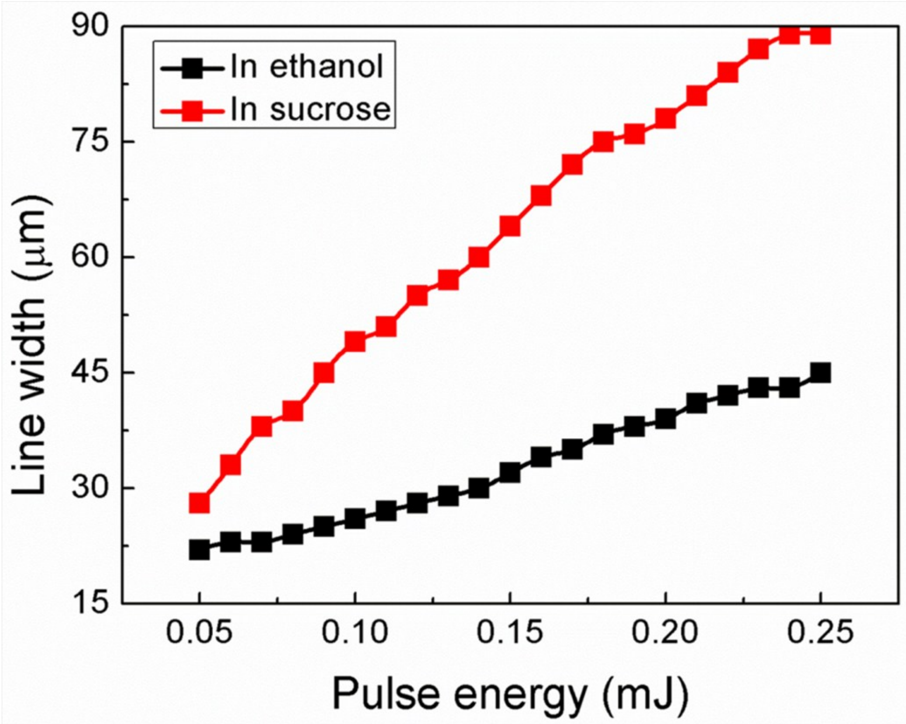

Figure S7. The line width of the scanning lines as functions of the pulse energy. Under the ethanol assisted femtosecond laser irradiation, the line width is increased from 23 to 42 μm with the increasing pulse energy. On the contrary, the line width produced under the ethanol assisted femtosecond laser irradiation is ranged from 28 to 89 μm.

Supporting video. The transfer of a 5 μl oil droplet from the low adhesive A surface to the high adhesive C surface by using medium adhesive B surface as a "mechanical hand" in less than 37 s.