Supporting Information

Gas/liquid interfacial manipulation by electrostatic inducing for nano-resolution printed circuits

Yifan Li^{ab}, Meng Su^{ab}, Zhandong Huang^{ab}, Shuoran Chen^{ab}, Meng Gao^{ab}, Wenbo Li^{ab}, Dan Su^a, Xingye Zhang^a, Ying Ma^a, Fengyu Li^{*a}, and Yanlin Song^{*a}

^aKey Laboratory of Green Printing, Institute of Chemistry, Chinese Academy of Sciences (ICCAS), Beijing Engineering Research Center of Nanomaterials for Green Printing Technology, Beijing National Laboratory for Molecular Sciences (BNLMS), Beijing 100190, P. R. China

^bUniversity of Chinese Academy of Sciences, Beijing, 100049, P. R. China

*Fengyu Li, E-mail: forrest@iccas.ac.cn

*Yanlin Song, E-mail: ylsong@iccas.ac.cn

Detailed Experimental Methods

Fabrication of pillar templates. Silicon wafers (10 cm diameter, N doped, <100> oriented, 525 μ m thick) were structured by direct laser writing apparatus (DWL200, Heidelberg Instruments Mikrotechnik, Germany) that transferred the computer-predefined design onto the photoresist (Shipley Microposit S1800 series)-coated wafer with about 1 μ m precision. After irradiation and development, the wafers were etched using deep reactive ion etching (DRIE, Alcatel 601E) with fluorine-based reagents, for different times (10 s to 6 min) depending on the desired height of the structures. Spindle-pillar-structured silicon substrates with pillar radius of 5 μ m, gap of 10 and 30 μ m, height of 20 μ m were fabricated. After resist stripping (Shipley Microposit Remover 1165), the substrates were cleaned with ethanol and acetone prior to use.

Reference:

1) Z. Q. Xin, B. Su, J. J. Wang, X. Y. Zhang, Z. L. Zhang, M. M. Deng, Y. L. Song and L. Jiang, Small, 2013, 9, 722-726.

2) B. Su, C. Zhang, S. R. Chen, X. Y. Zhang, L. F. Chen, Y. C. Wu, Y. W. Nie, X. N. Kan, Y. L. Song and L. Jiang, Adv. Mater. 2014, 26, 2501-2507.

Synthesis of silver precursor solution. Silver precursor solution was prepared according to the literature. In a typical synthesis, silver precursor solution was synthesized by vortex mixing 1 g of silver acetate into 2.5 mL aqueous ammonium hydroxide at room temperature for 15 sec. Formic acid (0.2mL) was then titrated into the solution dropwise for 60 sec – vortex mixing after each drop. The solution changed in color from light orange to brown to grayish black indicating the rapid reduction of silver ions to large silver particles. The solution remained undisturbed for 12 h to allow the large particles to settle out yielding a clear supernatant that was decanted and filtered through a 200 nm syringe filter (Whatman Filters, Anotop 25). This clear solution, which contained 22 wt% silver, served as the silver precursor solution.

Detailed electrical measurement. 0.1-mm-thick Au electrodes with different gaps (20,40, $80,160 \mu m$) were deposited on the silver lines basing on the length through a shadow mask by a high vacuum thermal evaporation system (PATOR, ATT010). Two platinum conical probes were placed to contact with the metallic electrodes then applying impressed voltage to detect the corresponding current.



Figure S1. Fabrication of arrayed silver lines with the micropillar templates. a,b) A micropillar template is held horizontally. Then, ionic silver ink is carefully dropped onto the template and covered by a flat substrate, yielding a sandwich-shaped reaction arrangement. c) With the evaporation of solvent, the micropillar arrays serve as wetting defects to control the rupture of ionic silver ink, yielding micrometer-scaled liquid bridges between neighboring micropillars. Such a micrometer-scaled liquid bridge provides a gradually reducing confined space for reaction of the solution and growth of the silver lines; Thus, an array of silver lines can be formed upon the desired substrate. d) After removal of the micropillar templates by physical peeling, precisely positioned silver lines can be generated accordingly.



Figure S2. Large scaled silver lines with precise orientations and positions can be prepared through this simple printing method. a) Top-view scanning electron microscopy (SEM) observation of precisely positioned silver lines. b) Top-view SEM image of an individual silver line, indicating the continuous and uniform structure along one orientation. c) Magnified SEM image of (b) showing that the silver line is compact. d) Histograms of length and e) width of asprepared silver lines. Statistical results are collected from 50 samples in the SEM observation. The average length and width of as-prepared silver lines are 27.0 ± 2.1 µm and 543.5 ± 35.9 nm respectively. f) AFM investigation of the cross-sectional profile of one silver line presenting silver line has a similar triangle shape with gradually reducing size from bottom to top. The concentration of the ionic silver ink is 30mg/mL with fixed SDS concentration 1mg/mL.



Figure S3. Energy-dispersive X-ray spectroscopy (EDS) spectrum of silver lines proves the successfully reduction of silver at mild temperature.



Figure S4. Dependence of silver line width on the concentration of the ionic silver ink. The concentration of SDS is fixed at 1 mg/mL.



Figure S5. Histograms of width of as-prepared silver lines on substrates with different θ_R . Statistical results are collected from 50 samples respectively, the average width of as-prepared silver lines are $13.2 \pm 1.6 \ \mu\text{m}$, $9.9 \pm 1.2 \ \mu\text{m}$, $7.4 \pm 1.1 \ \mu\text{m}$, $4.0 \pm 0.7 \ \mu\text{m}$ to $543.5 \pm 35.9 \ \text{nm}$ with increasing of the θ_R from $1.7^\circ \pm 0.5^\circ$, $14.2^\circ \pm 3.1^\circ$, $51.3^\circ \pm 6.1^\circ$, $72.0^\circ \pm 1.6^\circ$ to $96.6^\circ \pm 0.5^\circ$, respectively. The concentration of the ionic silver ink is $30 \ \text{mg/mL}$ with fixed SDS concentration $1 \ \text{mg/mL}$.



Figure S6. Large-area ultra-long and continuous silver lines are successfully printed onto the nitrile glove. The top-view bright field optical observation of as-prepared architectures, the consecutive silver lines are prepared on common flexible polymer substrate with mild printing and post-processing.



Figure S7. The top-view bright field optical observation of the disordered silver crystals which are fabricated onto nitrile glove due to the absence of micropillar templates as the structural guider.



Figure S8. Digital photograph and the corresponding design graph of an incompletive bilayer circuit printed on PET film.