Supporting Information

Plasmonic Stamps Fabricated by Gold Dewetting on PDMS for Catalyzing Hydrosilylation on Silicon Surfaces

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Figure S1. Transmission spectrum of the band-pass filter used for plasmonic stamping (CW 526 nm, fwhm: 180 nm, Edmund Optics Inc.).

Figure S2. (a) In order to measure the gold film thickness, gold film were sputtered onto a Si wafer cleaned by a standard RCA procedure and then a cotton swab was used to scratch a line in gold film. AFM was used to measure the thickness of the gold. (b) Plot of film thickness vs sputtering time. AFM height images of films with different sputtering times (c) 10 s. (d) 20 s. (e) 30 s. (f) 40 s. (g) 60 s. All the scale bars are 1 µm.
**Figure S3.** Photograph of a customized experimental setup for plasmonic stamping: a silicon wafer was stamped with a plasmonic stamp and sandwiched between a quartz coverslip and a customized reaction holder, which was made of polytetrafluoroethylene (PTFE). Two clips were applied on both sides of the sandwich structure.

**Figure S4.** (a) - (e) AFM images of plasmonic stamps fabricated from dewetted Au films on PDMS with as deposited thicknesses ranging from 5.0 to 13.1 nm. All scale bars are 1 µm.

**Figure S5.** Blank PDMS, heated at 150 °C for 20 h. (a) Optical microscope images (1000× magnification) to show the morphology of the PDMS; scale bar = 10 µm. (b) Corresponding AFM height image. No wrinkles are observed with heating only; scale bar = 500 nm.
Figure S6. As-sputtered 5.0 nm-thick gold on PDMS before heating, (a) Optical microscope images (1000× magnification) to show the morphology of the PDMS; scale bar = 10 µm. (b) Corresponding AFM height image. No wrinkles are observed with gold sputtering only; scale bar = 500 nm.

Figure S7. SEM image of Si(111)-H surface after hydrosilylation with a plasmonic PDMS stamp. No residual gold nanoparticles from the PDMS stamp can be seen. Scale bar = 200 nm.
**Figure S8.** AFM image of the Si(111)-H sample after (i) hydrosilylation using a plasmonic stamp with a sputtered gold film thickness of 9.2 nm, and (ii) galvanic displacement with the aqueous KAuCl₄ and HF solution indicated in Figure S9; scale bar = 200 nm.

**Figure S9.** Method for visualization of hydrosilylation using gold nanoparticle fiduciaries. (a) Schematic outline of gold deposition via galvanic displacement. (b+c) SEM micrograph of two different silicon surfaces: (b) The Si(111)-H surface was functionalized with a monolayer of 1-dodecene by thermal-induced hydrosilylation (150 °C, 24 h),1-3 followed by exposure to an aqueous 1 mM KAuCl₄ and 1% HF mixture solution for 5 min at room temperature in air. The SEM image shows no gold deposited.
onto the Si wafer (image with red border); (c) Immersing a freshly etched sample of Si(111)-H into the same aqueous KAuCl₄ and HF mixture solution directly resulted in gold deposition via galvanic displacement on the silicon surface (image with blue border). (d) XPS spectra of Au(4f) of the Si(111)-H treated wafer upon galvanic displacement confirms the presence of Au(0); SEM scale bar = 200 nm.

Table S1. Summary of static water contact angle measurements. The contact measurement data of Si(111)-H surface after hydrosilylation with 1-dodecene under various conditions are listed. For each condition, at least 10 measurements were collected. The uncertainty given is the standard deviation of these measurements.

| Samples                                      | Illumination condition | Contact angle (°) |
|----------------------------------------------|------------------------|-------------------|
| Si(111)-H                                    | Dark                   | 82.9 ± 1.0        |
| Si(111)-H + 1-dodecene + blank PDMS          | Dark                   | 82.5 ± 1.7        |
| Si(111)-H + 1-dodecene + blank PDMS          | Light                  | 84.0 ± 1.6        |
| Si(111)-H + 1-dodecene + PDMS with 5.0 nm gold film | Dark                   | 82.8 ± 2.0        |
| Si(111)-H + 1-dodecene + PDMS with 5.0 nm gold film | Light                  | 85.8 ± 2.3        |
| Si(111)-H + 1-dodecene + PDMS with 7.0 nm gold film | Light                  | 84.1 ± 3.0        |
| Si(111)-H + 1-dodecene + PDMS with 9.2 nm gold film | Light                  | 82.1 ± 1.8        |
| Si(111)-H + 1-dodecene + PDMS with 11.1 nm gold film | Light                  | 82.5 ± 2.0        |
| Si(111)-H + 1-dodecene + PDMS with 13.1 nm gold film | Light                  | 82.2 ± 1.6        |
| Si(111)-H + 1-dodecene +PDMS with 5.0 nm gold film after dewetting | Light                  | 98.1 ± 1.5        |
| Si(111)-H + 1-dodecene +PDMS with 7.0 nm gold film after dewetting | Light                  | 97.4 ± 1.5        |
| Si(111)-H + 1-dodecene +PDMS with 9.2 nm gold film after dewetting | Light                  | 97.3 ± 1.7        |
| Si(111)-H + 1-dodecene +PDMS with 11.1 nm gold film after dewetting | Light                  | 90.9 ± 2.3        |
| Si(111)-H + 1-dodecene +PDMS with 13.1 nm gold film after dewetting | Light                  | 87.8 ± 2.6        |
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