

## A Comparative Study on Fabrication Techniques for On-Chip Microelectrodes

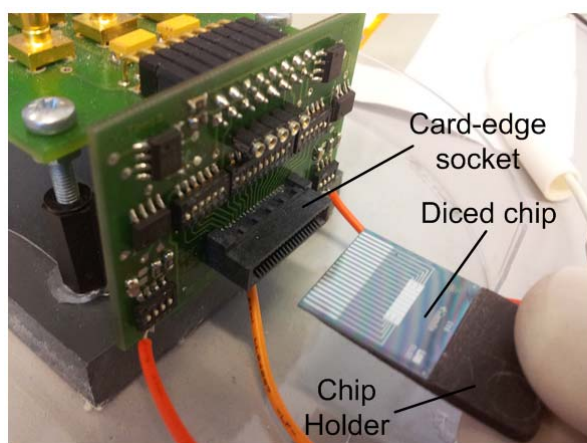
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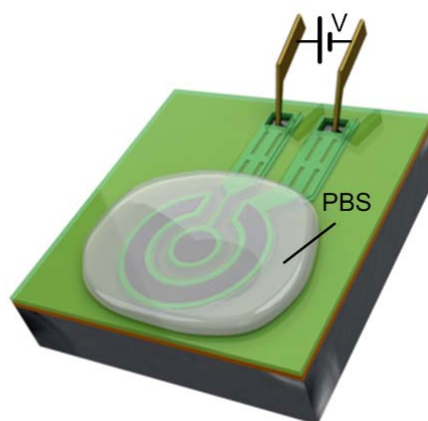
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### SUPPLEMENTARY INFORMATION

#### 1. Hydrolysis Tests

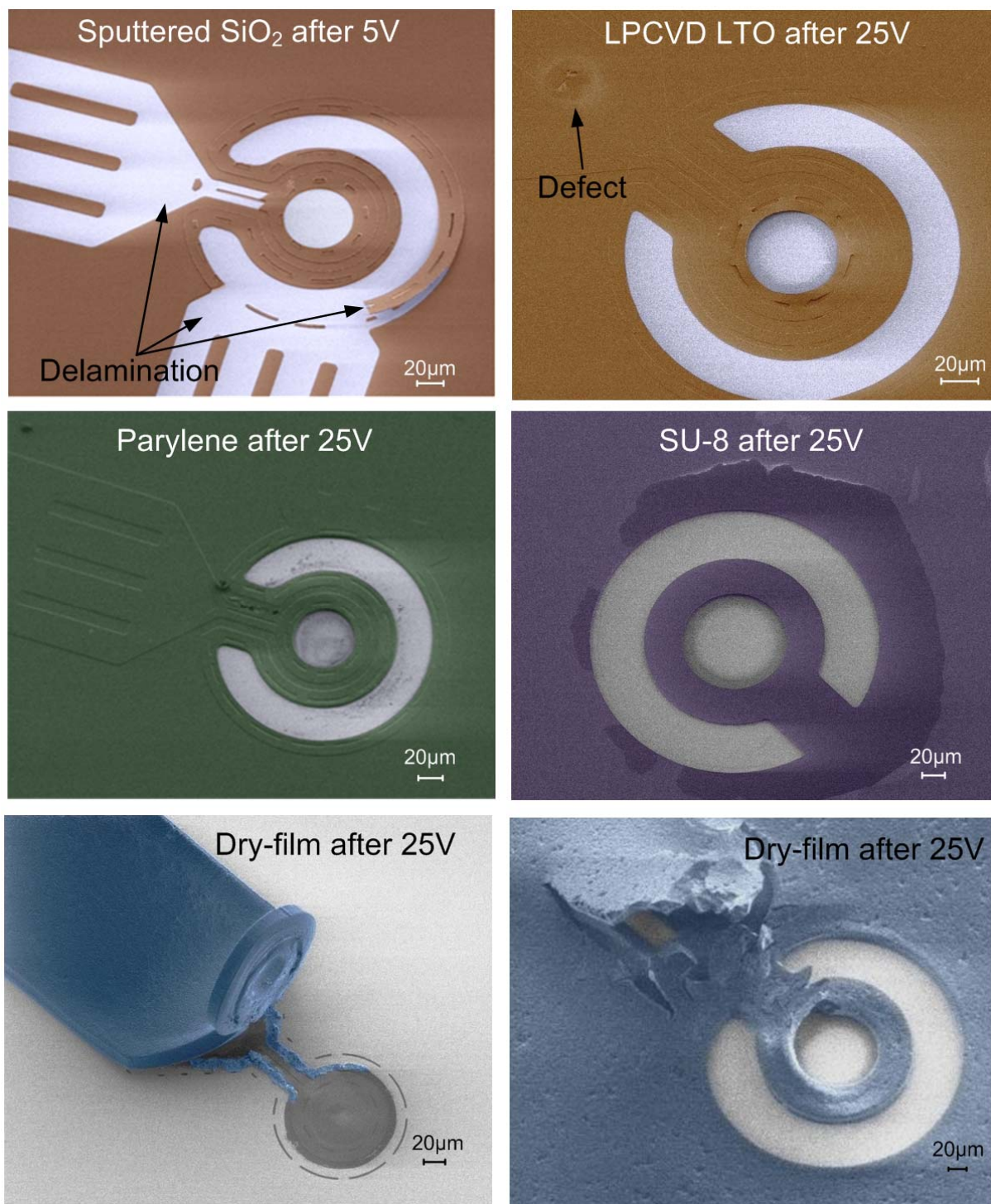


(a)



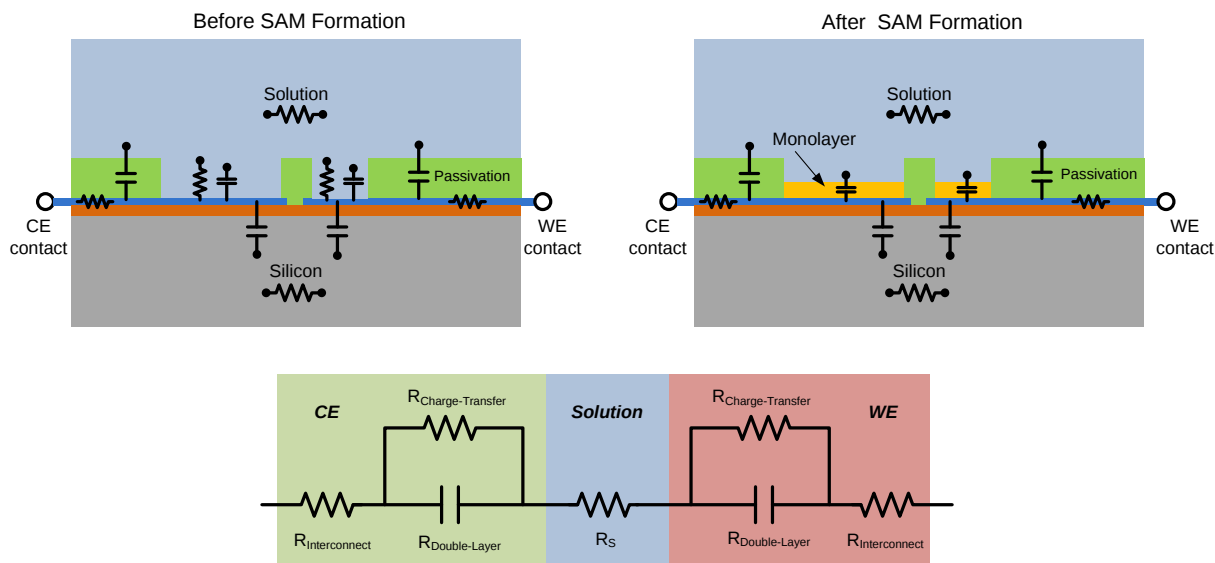
(b)

**Figure S1:** (a) Photo of the test setup comprising a card-edge socket, addressing switches, a potentiostat circuit and a chip holder. (b) Illustration of the two-electrode configuration used in the hydrolysis tests.



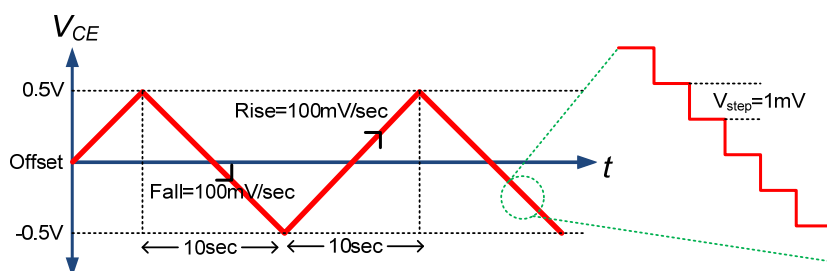
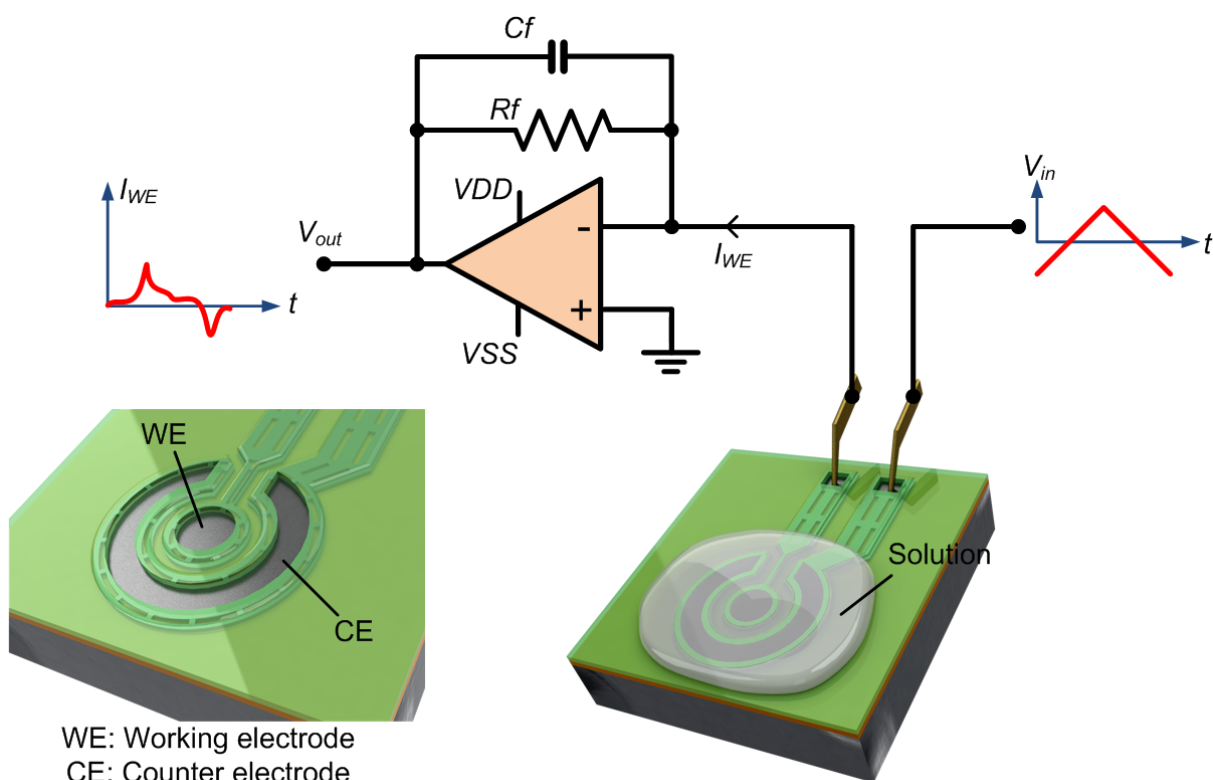
**Figure S2:** SEM images of the electrodes after passivation quality tests. The DC potential between the WE and CE was swept from 1~V to 25~V, as the electrodes were immersed into phosphate buffered saline (PBS) solution.

2. Impedance Measurements



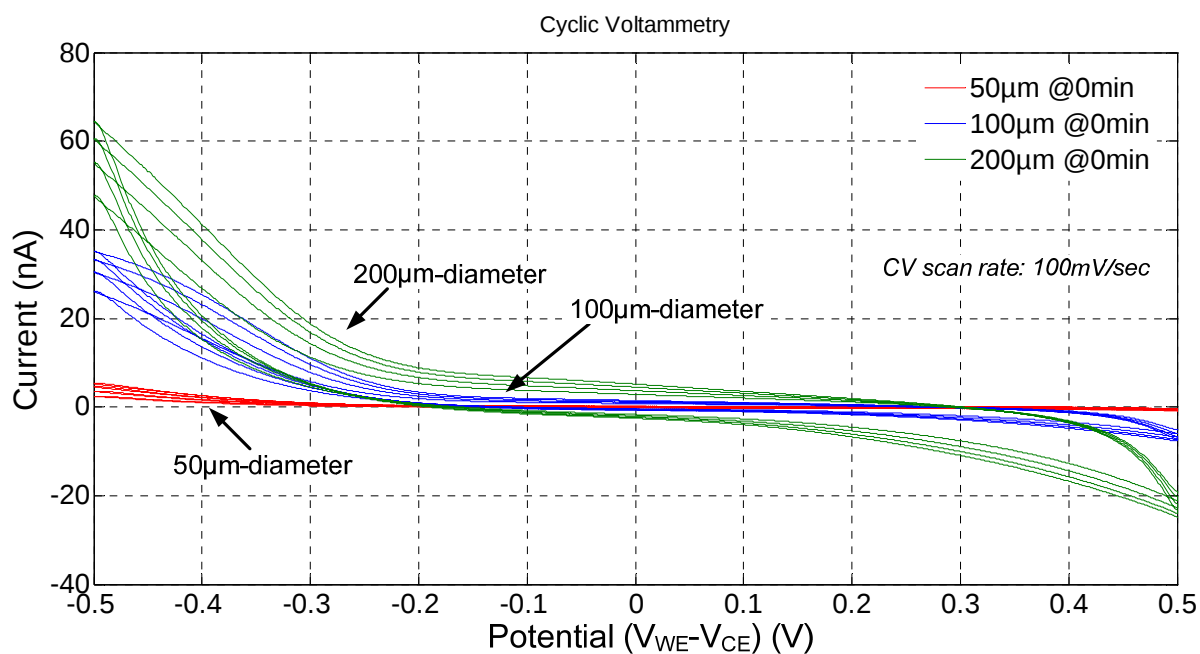
**Figure S3:** Cross-section illustration of the electrodes and the passivation before (left) and after (right) SAM formation, and the simplified equivalent circuit model (bottom).

### 3. Cyclic Voltammetry Measurements

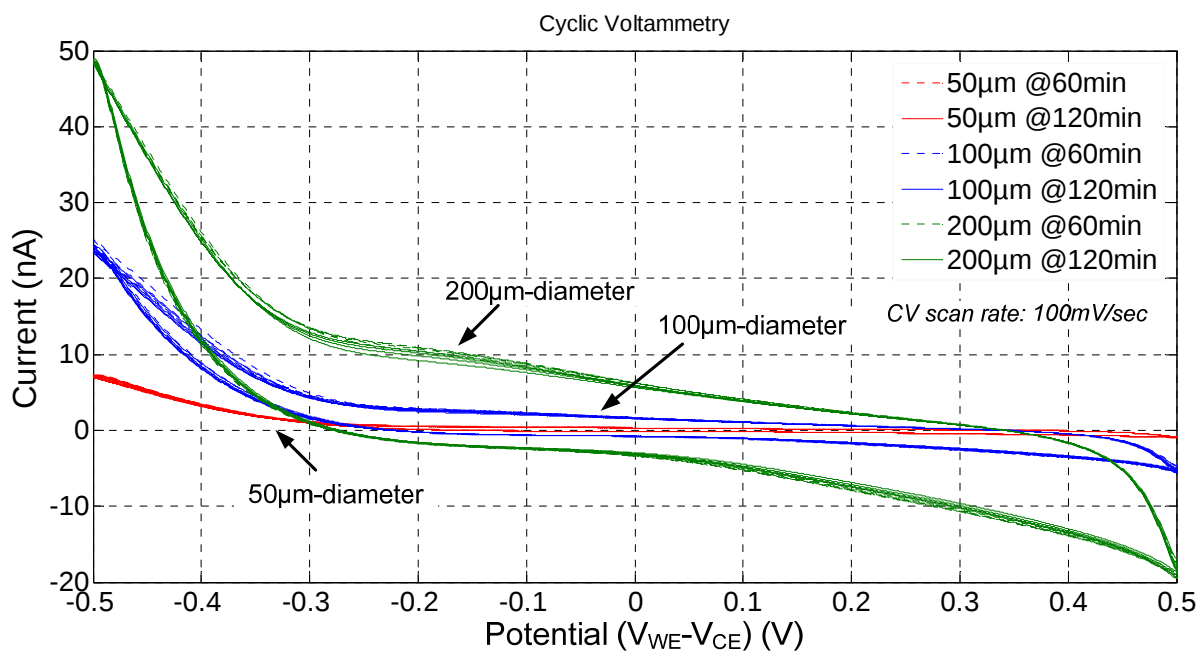


**Figure S4:** Simplified schematic of the two-electrode cell setup. A triangular wave is applied to the CE through the National Instruments data acquisition board controlled by the LabVIEW tool. The WE potential is kept at zero (virtual ground) through the resistive feedback connection of the OPAMP used as the transimpedance amplifier. The resultant current is converted to voltage on the feedback resistor ( $R_f$ ) and output voltage ( $V_{out}$ ) is sampled by the DAQ board.

**a. Chip incubated in 1 mM 1-hexanethiol in ethanol**



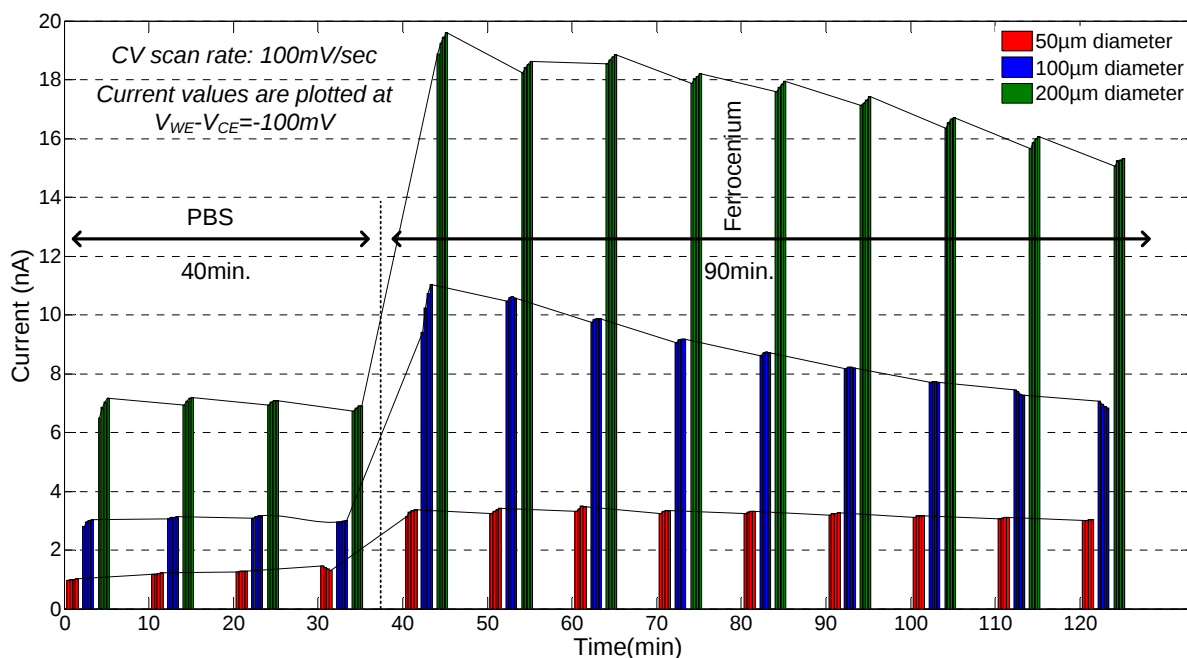
(a) Time=0 minute



(b) Time=60 and 120 min.

**Figure S5:** CV plots of the electrodes after overnight incubation in 1 mM 1-hexanethiol in ethanol; measurements were taken in 100 mM  $\text{HClO}_4$  and 10 mM  $\text{HCl}$ . Every 10 minutes, 4 cycles of CV were recorded with a scan rate of 100 mV/sec. (a) The first CV measurement at time=0 shows a drift for each cycle. (b) The CV plots at time=60 min. and time=120 min show a stabilized profile. (The current values for all measurements are given in Fig. 5 of the paper).

**b. Bare electrode measurements (no functionalization)**



**Figure S6:** Positive peak current values (taken at  $V_{WE} - V_{CE} = -100\text{ mV}$ ) of the CV plot. 50, 100, and 200  $\mu\text{m}$  diameter bare electrodes were measured consecutively every 10 minutes and each bar is composed of 4 consecutive cycles. After 40 minutes of measurement in PBS, the chips were measured in 1 mM ferrocenium hexafluorophosphate in PBS for 90 minutes. Although the electrodes showed fairly constant response in PBS, the ferrocenium peak values decreased gradually. No passivation layer delamination was observed as such delamination would lead to increase in the response instead of a decrease. It is believed that this decay may be related to the modification of the electrode surface or the oxidation of ferrocenium.