Supporting Information

Logic Gates Operated by Bipolar Photoelectrochemical Water Splitting

Gabriel Loget,* Gaozeng Li and Bruno Fabre*

Institut des Sciences Chimiques de Rennes, UMR 6226 (MaCSE) CNRS, Université de Rennes 1, Campus de Beaulieu, 35042 Rennes Cedex, France

E-mail: gabriel.loget@univ-rennes1.fr; bruno.fabre@univ-rennes1.fr

Experimental

All solutions were prepared with ultra-pure deionized water (resistivity: 18.2 M Ω cm). The chemicals used for cleaning and etching of silicon wafer pieces were of semiconductor grade: 96-97% H₂SO₄ (from BASF) 30% H₂O₂ and 50% HF (both from Sigma Aldrich). Acetone (MOS electronic grade) and anhydrous ethanol (RSE electronic grade) were purchased from Carlo Erba. The In-Ga eutectic (99.99%) and the Pt wires (99.95%) were purchased from Alfa-Aesar. The p-type silicon (100) wafers (boron doped, 1-5 Ω cm, double side polished) were purchased from Siltronix. 1.5 x 1.2 cm² silicon pieces were cut and degreased by sonication (10 min) in acetone, ethanol and ultra-pure water. The surfaces were then cleaned in 3/1 v/v concentrated $H_2SO_4/30\%$ H_2O_2 at 100 °C for 30 min, followed by copious rinsing with ultrapure water. (*Caution*: The concentrated aqueous H_2SO_4/H_2O_2 (piranha) solution is very dangerous, particularly in contact with organic materials, and should be handled extremely carefully.) The surfaces were etched with ca. 10% ag HF for 2 min in order to remove the oxide layer and generate the hydrogen-terminated surface (p-SiH), and then dried under an argon flow. p-SiH was electrically connected to a copper wire by applying a drop of In-Ga eutectic and silver paste (Electron Microscopy Sciences). After drying of the silver paste, the copper wire and the silver paste were covered with an epoxy-based resin (Loctite 9492, Henkel). The electrolyte was 50 mM H₂SO₄ in water. The electrochemical experiments were performed with an Autolab potentiostat/galvanostat PGSTAT 302N (from Eco Chemie B.V.) in an O-ring cell with a p-SiH or a Pt foil acting as the working electrode (0.79 cm²). The counter electrode was a Pt ring and a KCl saturated calomel electrode (SCE) was used as the reference electrode. The bipolar electrochemical experiments were performed in an open-top 4.7 x 3.5 cm² transparent rectangular cell in which two Pt wires (2 cm long, 1 mm diameter) were positioned at the ends (separated by 4.6 cm). Prior to use, the silicon surface was immersed in 5/1 v/v 50% ultrapure water/HF for 2 min and dried under an Ar flow. The split BE composed of p-SiH and the Pt wire (1.5 cm long, 1 mm diameter) was connected outside the cell to the ammeter (Agilent U1253B), connected to a computer. The light was delivered by a halogen lamp placed 5 cm above the silicon surface (170 mW cm⁻²), and the illumination was manually switched. The current vs time profiles were acquired on the computer using the Keysight Handheld Meter Logger software (Agilent).



Fig. S1. Evolution of the ratio I_{be} light / I_{be} dark as a function of E_{app} for a) 1.9 cm-long and b) 3.2 cm-long BE, when a current flows through the bipolar electrode.



Fig. S2. a-c) Time-dependent profiles of the applied input signals: a) InI (InI = 0 for $E_{app} = 7$ V and InI = 1 for $E_{app} = 10$ V), b) In2 (In2 = 0 in the dark and In2 = 1 under illumination) and the corresponding output signal I_{be} measured for a 3.2 cm-long BE with two Pt wires. The red line indicates the threshold current 1.5 mA.

	AND				
In1	In2	Output	Itot (mA)	Ibe (mA)	Ibe/Itot
0	0	0	37.750 ±0.860	0.004 ±0.003	0.000
0	1	0	38.600 ±0.977	0.113 ±0.035	0.003
1	0	0	60.400 ±1.190	0.140 ±0.024	0.002
1	1	1	61.310 ±0.927	3.345 ±0.284	0.055
	OR				
0	0	0	40.630 ±1.700	0.088 ±0.239	0.002
0	1	1	43.250 ±1.370	3.264 ±0.460	0.075
1	0	1	64.410 ±1.380	5.845 ±0.776	0.091
1	1	1	66.520 ±0.244	14.760 ±0.746	0.222

Table S1. Values of the total delivered current I_{tot} , current flowing through the BE I_{be} and I_{be}/I_{tot} ratio for the AND and OR gates.