

## Supporting Information

### **A nanogap–array platform for testing the optically modulated conduction of gold–octithiophene–gold junction for molecular optoelectronics.**

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#### **Experimental - Nanogap fabrication**

The preparation of the chip starts from an n-type silicon wafers (B doped) on which are carried out the following steps:

1. Surface oxidation: (in an oxidation oven, Tempress) at 1100 °C for 4 h 30 min to grow 200 nm of SiO<sub>2</sub>.
2. Wafer cleaning: by piranha solution (3:1 H<sub>2</sub>SO<sub>4</sub>, H<sub>2</sub>O<sub>2</sub>) for 10 min than the wafer is rinsed with deionized water and dried with N<sub>2</sub>.
3. Surface activation in plasma of oxygen: to create a surplus of oxygen atoms on the surface of silicon dioxide (applied power of 300 W for 30 s, oxygen flow 300 sccm).
4. Hydroxylation: the wafer is immersed for 10 min in a 1:1 solution of H<sub>2</sub>O<sub>2</sub> and HCl at 85 °C. After this step the wafer surface exposes -OH groups.
5. Mercapto-propyl triethoxy silane (MPTMS) deposition: in a vacuum chamber (p=0.1 Torr) the surface of the wafer is exposed to vapors that create a monolayer of MPTMS on the surface of gold. This molecule was selected due to its binding ability to gold atoms and because it is not conductive. Thus the only layer to be electromigrated is the gold one, and in this way any possible alternative electromigration path is avoided.
6. Au deposition: a layer of 25 nm of gold is evaporated at 300 K and a pressure of 2·10<sup>6</sup> Torr (E-beam Evaporator ULVAC EBX 14-D).
7. Photolithography: deposition of Image Reversal Resist (AZ5214E of Microchemicals) and soft bake. The resist is then exposed to 365 nm by using a UV lamp and using a specifically prepared mask. Afterwards, the wafer is subjected to a reversal bake and a new UV exposure without the mask. The resist is developed using a 4:1 solution of H<sub>2</sub>O and developer basic AZ351B from Microchemicals.
8. Au etching: in a solution of 4g Potassium iodide (KI), 1g Iodine (I<sub>2</sub>), 80 ml water.
9. Resist strip: using acetone and isopropanol and drying of the wafer with nitrogen.
10. Photolithography: deposition of positive resist (HPR 504 from Fujifilm). The resist is subjected to soft bake. UV exposure occurs with a wavelength of 365 nm and using a mask made specifically for aluminum. The resist is using a 1:1 solution of H<sub>2</sub>O and developer basic AZ (of Microchemicals).
11. Ti deposition: a layer of 100 nm of Ti is evaporated at 300 K and a pressure of 2·10<sup>6</sup> Torr by E-beam evaporation..

12. Al deposition: a layer of 700 nm of Al is evaporated at 300 K and a pressure of  $2 \cdot 10^6$  Torr by E-beam evaporation.
13. Al lift-off: it occurs in acetone in ultrasonic bath, followed by rinsing with isopropanol alcohol.

The NanoCube consists of:

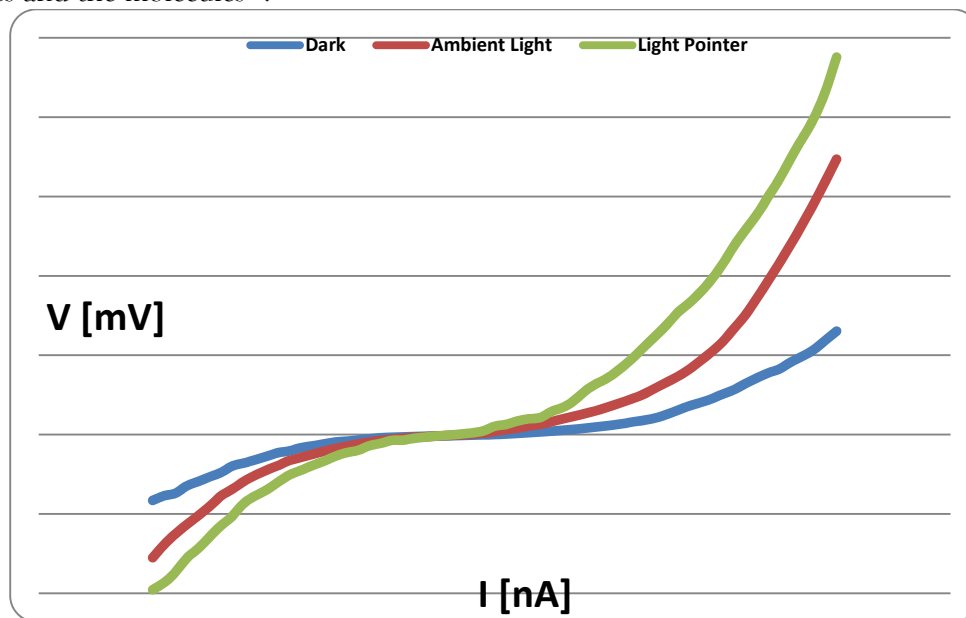
- a driver board that hosts a DAC (Digital to Analog Converter). It produces the input voltage waveform and through an electronic circuit<sup>1</sup> it is possible to electromigrate all 8 gold wires simultaneously;
- a measurement board composed by a transimpedance amplifier with variable feedback, in order to measure a wide range of currents, and an ADC (Analog to Digital Converter);
- a switch board to allow the connection of external instrumentation;
- a digital board that provides electrical power supplies and the bus connection between all boards.

The system is controlled by a Linux Embedded Board that hosts the feedback algorithm. A special board<sup>2</sup> allows us to measure small currents of the order of a few pA. This electronic board was prepared on a layer of polytetrafluoroethylene to minimize the external noise. The noise measurements were compared with those performed with a Sub-Femtoamp Remote SourceMeter (Keithley 6430) to verify the accuracy.

We have developed a wireless connection between the NanoCube and a host computer for experimental data acquisition. This solution allows also the use of the NanoCube in chambers where a wire interconnection could create difficulties, i.e. Raman and fluorescence spectroscopies, dark condition measurements.

## Results and discussion

Figure S-1 shows the I-V curve behavior of the octithiophene-deposited nanogap under dark, and when a white ambient light (285 LUX) and an intense white light (489 LUX) from a torch are applied. The I-V curve asymmetry is usually observed in molecular junction, due to an asymmetric charging effect between the electrodes and the molecules<sup>20</sup>.



**Figure S-1.** Photoresponse I-V characteristics under different illumination conditions (white light, 52 mW) of the tunneling Me-M-Me junction, which can be switched on/off quickly by photoirradiation.

## References

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- 2 C. Ciofi, G. Festa, R. Giannetti, B. Neri, B., presented at IEEE Technology Conference, St. Paul, Minnesota USA, May , 1998.