

Proposal of a low-cost, mask-less procedure for patterning electrodes of organic devices at nanoscale using electro-discharges

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Abstract

We have recently proposed a novel subtractive technique that enables patterning of conductive thin layers by means of a biased probe with a low continuous (DC) voltage source, taking advantage of the arc-voltaic principles [1]. This technique resembles electro-discharge machining (EDM), commonly used in industry to cut, make holes and conform metal blocks. However, in EDM high voltage (kilovolts) pulses are generated in order to create sparks between a probe and the metal piece. Every spark drives a metal local region to the boiling point, and next the residual metal is removed by an additional gas or liquid flux. In our case, the spark is created by gradually approaching a biased probe at low DC voltage (< 20 V) to the conductive surface, employing a high precision micropositioner. For that purpose we have built a home-made system, consisting of an assembly of three micropositioners (XYZ) with resolution below 100 nm and absolute reproducibility of 1 μm . At a sufficiently short distance (< 1 μm), breakdown of the air electric permittivity between probe and conductor substrate is achieved, and an electric arc is created. A specifically designed electronic circuit provides charge to keep the arc until material is removed and an insulating crater appears below the probe.

The crater size is of the order of the tip diameter, and defines a roughly circular insulating region. When tip rests on this region and next slides on the surface, it approaches the boundary of the circular insulating zone, so a lateral spark will appear which removes a new crown of material, and so on. In such a way, the probe is leaving an insulating path as it travels across the metal surface (Fig. 1). If the probe depicts a closed loop, it is able to electrically insulate the inner region from the outer one, so this opens the chance to pattern tracks and pads for circuits.

By oscilloscope monitoring the voltage between probe and substrate, we observe that sharp voltage drops may be associated with the sparks (Fig. 2). This process takes place in a few μs , what allows a fast motion of the probe during operation (tens mm/s), ensuring scalability to large areas.

In this contribution, correlation between the size of the features and the operating conditions are analyzed (Fig. 3) on different materials and substrates (gold, aluminium, and semiconducting oxides like indium-tin oxide, ITO, or graphene oxide). Preliminary results are obtained with commercial probes with tip diameter > 30 μm . Scalability to nanometer diameters using, for example, atomic force microscope probes is discussed. Comparison between this technique and similar patterning procedures used in organic electronics like ink-jet printing (additive technique) or laser ablation (subtractive technique) is discussed. Whereas the previous techniques are difficultly scaled to nanometer size because physical limitations of liquid drops and laser waist size respectively, arc-erosion appears to be only limited by the tip diameter, as well as its positional control, two technological issues of feasible implementation.

Another interesting feature is that layers like aluminium may be patterned at low voltages (2 - 3 V) whereas transparent conductive oxides such as ITO requires in general higher operating voltages (10-12 V). This procedure allows working on stacked layers as long as the patterning voltage for the top layer is significantly lower than that for the bottom one. This property is useful for certain field effect transistor architectures, as well as the columns-rows arrangement of displays.

As an application, organic light emitting displays have been performed on electrodes patterned with this technique. For this purpose, solution processed active layers have been used to reinforce the concept of low-cost manufacturing. Thus, water-soluble conjugated polyelectrolyte layers have been casted on top and bottom of commercial semiconducting polymers in organic solvents. In particular we have combined a blue-emitting, cationic polyfluorene derivative, poly{9,9-bis[6'-(N,N,N-trimethylammonium)hexyl] fluorene-co-1,4-phenylene} dibromide (**PNMe**), synthesized in our lab, together with a red-emitting, commercial Poly(2-methoxy-5-(3'-7'-dimethyloctyloxy)-1,4-

phenylenevinylene), (**MDMO-PPV**), in the following conventional structure: ITO (100 nm) / PEDOT:PSS (50 nm) / MDMO-PPV (130 nm) / PNMe (70 nm) / Ca / Al (100 nm). Electroluminescence from both materials has been recorded as shown in Fig. 4, revealing interesting physical aspects, for example, that electron-hole recombination zone is wide and extends over both layers. This confirms the robustness of this procedure, which results very promising to face development of micro- and nano-organic devices.

References

[1] J. Jimenez-Trillo, A. L. Alvarez, C. Coya, E. Cespedes, A. Espinosa, *Thin Solid Films* **520** (2011) pp. 1318-1322.

Figures

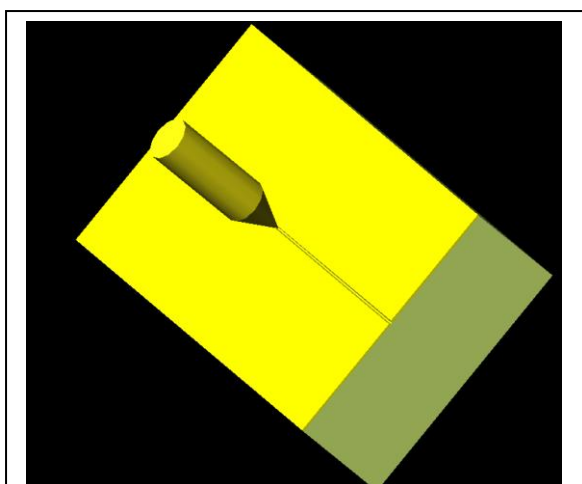


Fig.1. Sketch of a electrically biased tip sliding in contact with a conductive surface, leaving an insulating path of a similar width as the tip diameter.

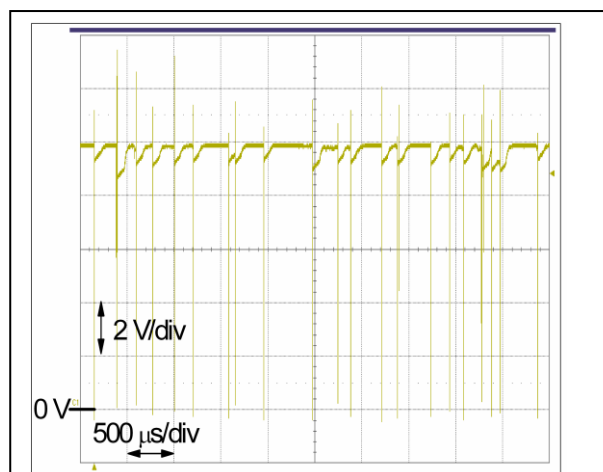


Fig.2. Monitored voltage at the tip during motion. The falls mean discharge processes. Tip speed was 1 mm/s, so a time division is equivalent to a 500 nm path.

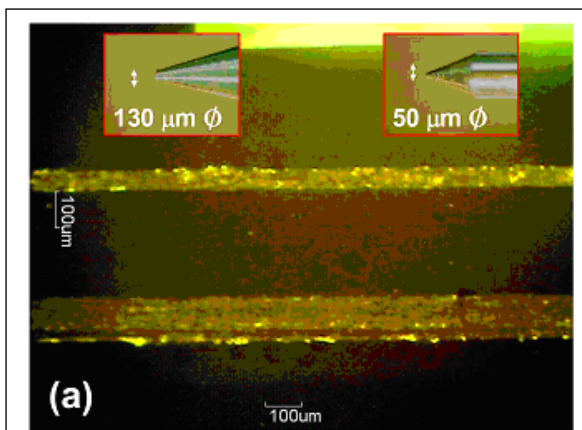


Fig.3. Lines eroded on an ITO surface at 12 V using two different probes with tip diameter of 50 μm (up) and 130 μm (down)

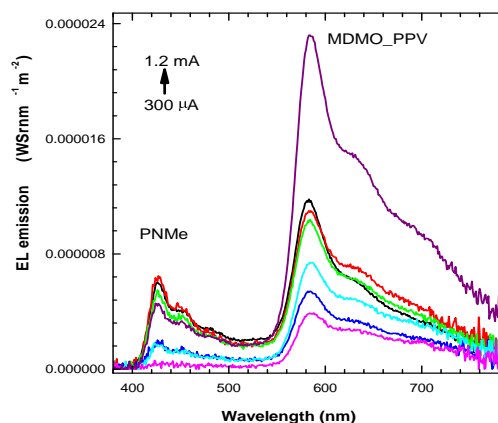


Fig.4. Electroluminescence recorded from a 2 x 2 passive matrix display, with an active bilayer consisting of a blue-emitting cationic polyfluorene derivative, PNMe, and a red-emitting poly(phenylene vinylene) derivative, MDMO-PPV. Spectra at driving currents from 300 μA to 1.2 mA are shown. Luminance ranges from 20 to 140 cd/m², respectively.