The influence of fibril composition and dimension on the performance of paper gated oxide transistors

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Supplementary information

1. Paper production

The nomenclature normally used to describe cellulose particles may be somehow misleading due to an inconsistent use of terms in the literature. The current trends in terminology define nine particle types to describe the main cellulose-based particles, which typically differ from each other based on cellulose source, particle size and extraction method. Micron and macrosized scaled particles are defined as wood fiber (WF, plant fiber (PF) and microcrystalline cellulose (MCC). On other hand, those that have at least one dimension in the nanoscale are nanofibrilated cellulose (MFC and NFC), cellulose nanocrystals (CNC), tunicate cellulose nanocrystals (t-CNC), algae cellulose (AC) and bacterial cellulose (BC). In this work the interest is centered on WF and M-NFCs. More details about each kind of cellulose particles can be found in the literature [1]. WFs are the largest of the particle types, and have dominated the paper industry. Purified WFs can be obtained by several methods (bleached Kraft pulp, dissolving pulp, etc.) and have normally tenths of micrometers in diameter and millimeters in length, have high percent cellulose and a relatively low crystallinity index (43–65%). On other hand M-NFCs are small cellulose fibrils obtained from fine refining of WFs or PFs. They have a high aspect ratio, are almost 100% cellulose and contain both amorphous and crystalline regions. The difference between MFC and NFCs is on the fibrillation process that results in finer particle size for the last (4-20 nm wide, 500–2000 nm in length for NFC against tenths of nm wide, 500–>10000 nm in length for NFC) [1].

LPS-A manufacturing

A commercial bleached softwood kraft pulp was steered at low consistency in water until disintegration. This pulp was then refined using a pilot refiner equipped with steel discs to reach a beating index of 47°SR. This figure correspond to the measurement of the pulp freeness and drainability on a Schopper Riegler apparatus according to the standard ISO 5267. Paper was then made from this refined pulp source using a dynamic handsheet former.

The principle of the dynamic handsheet former is the following one: a circular fabric is maintained in rotation at a certain speed in a container (Figure 1). Water is injected into the container and forms a water wall on the container by centrifugal action. The pulp is projected on this water wall by a nozzle. The speed of the jet depends on the flow of the pump and the section of the nozzle. Then the water is evacuated by centrifugal forces and the pulp is distributed uniformly on the fabric. The sheet thus formed is separated and dried manually.
The selected nozzle, referenced as 2504, has a diameter of 1.32 mm. The pump speed was maintained constant at 500 rpm, which correspond to a jet speed of around 675 m/min, and the wire speed kept at 850 m/min. The difference in speed between the jet and the wire gives an preferential orientation to the fibers that tends to align due to extensional forces that exist at the interface. The handsheets were then removed manually placed in between two blotting papers to absorb water and then dried on a drier equipped with a fabric, the wire side being in contact with the drier maintained at a temperature of 100°C during 15 min. The handsheets of paper were then calendered two times in a single nip with a Ramisch calender equipped with a steel roll and polymeric soft roll (91°ShD) under a line load of 1000N/cm at 80°C. Calendering is a papermaking finishing process during which the paper web is compressed between two or more rolls that can be heated. The surface of paper is smoothened by replication of the roll surface while the bulk is reduced by the pressure effect.

**LPS-B and B1 manufacturing**

A commercial paper made from a mix of bleached hardwood kraft pulp was used as the fibre source. This paper was disintegrated into water at low consistency, then refined, submitted to an enzymatic treatment with endoglucanase, refined again before being passed 6 times into a GEA homogenizer (1 pass at 500bar, 1 pass at 1000bar and 4 passes at 1500bar).

The manufacture of M-NFC papers was achieved with a semi-automatic sheet former (Rapid-Khöten). The method was adapted by Guézennec [2] from a protocol first described by Sehaqui et al. [3]. A MFC suspension was first prepared at 0.5% and stirred using a disperser during 30 min. The diluted suspension was then poured into the bottom of a hollow cylinder containing a metallic sieve at its bottom covered with a mixed cellulose ester (nitrocellulose, cellulose acetate) membrane with 0.65 µm pore size (Milipore DAWP29325). After filtration, the gel cake was peeled off from the membrane and stacked between two cover papers and two carrier boards. Films were dried in a sheet dryer at 93°C and under vacuum for 10 min. At last, papers of about 50 g/m2 were separated from the cover papers. The diameter of the films reached 20 cm with this method. No preferential orientation of fibres in x and y direction occurred with this process. No calendering step was achieved after drying the paper.

In case of LPS-B1 the pH was decrease from 7 down to 5.5 using HCl (0.1M) few minutes before the filtering step.

Figure 1- Overview of the dynamic handsheet former (left) and forming part (right). Source Techpap.
Table 1 – Summary of the manufacturing process and characteristics of the lab paper samples used.

<table>
<thead>
<tr>
<th>Paper sample</th>
<th>Source</th>
<th>Pulp</th>
<th>Additives</th>
<th>Thickness average (μm)</th>
<th>Basis weight average (g/m²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Standard tracing paper (STP)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>75 ± 2 μm</td>
<td>38</td>
</tr>
<tr>
<td>Lab paper samples (LPS)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>A</td>
<td>Softwood (spruce)</td>
<td>Bleached Softwood Kraft Pulp (BSKP)</td>
<td>none</td>
<td>63 ± 1.5μm</td>
<td>58 ± 0.50g/m²</td>
</tr>
<tr>
<td>B</td>
<td>Hardwood (mix species)</td>
<td>Bleached hardwood kraft pulp treated with mechanical and enzymatic pretreatment then homogenized with a GEA homogeneizer</td>
<td>none</td>
<td>51 ± 1.4μm</td>
<td>41 ± 2.2g/m²</td>
</tr>
<tr>
<td>B1</td>
<td>HCl</td>
<td></td>
<td></td>
<td>52 ± 0.40μm</td>
<td>41 ± 2.1g/m²</td>
</tr>
</tbody>
</table>

2. Supplementary paper characterization

Thermogravimetric analysis measurements (TGA) were carried out with a Simultaneous Thermal Analyser (TGA-DSC - STA 449 F3 Jupiter). Approximately 3 mg of each sample was loaded into an aluminium pan and heated from 25 °C to 550 °C with a heating rate of 5 °C min⁻¹. All the measurements were performed under air atmosphere.

Figure 2 shows that major weight loss (the onset for cellulose degradation) starts around 270°C for all paper samples and proceed up to around 350°C. However, a minor weight loss detectable for lab paper samples around 100°C that is associated to water desorption. For STP water desorption begins immediately after starting heating the sample confirming the presence of weakly bound water.
The Cole-Cole plot obtained from impedance measurements is presented in figure 3. According some models elaborated to explain the capacitance variation with frequency in EDLs it can be considered the series association of two capacitor-resistor parallel circuits [4]. The first semicircle at high-frequency corresponds to the resistance of bulk of the dielectric in parallel with its geometric capacitance. The resistivity was calculated from the resistance and the values are listed in table 2.

![Figure 3 – High frequency region of the Cole-Cole plot.](image)

<table>
<thead>
<tr>
<th>Capacitance (μF.cm⁻²)</th>
<th>STP</th>
<th>LPS-A</th>
<th>LPS-B</th>
<th>LPS-B1</th>
</tr>
</thead>
<tbody>
<tr>
<td>Resistivity (Ω.cm)</td>
<td>4.9×10⁷</td>
<td>4.3×10⁸</td>
<td>1.4×10⁹</td>
<td>1.3×10⁹</td>
</tr>
</tbody>
</table>
3D profilometry was performed on a AMBIOS profilometer where the surface RMS roughness was inferred by scanning the paper samples surface (0.5 × 0.5 microns area). The different morphology is clearly seen in figure 4. The roughness values are listed in table 3. High magnification SEM micrograph is useful in estimating the average fibrils size for M-NFC.

![3D profilometry scan](image)

Figure 4 – a) 3D profilometry scan of the paper surface, b) high magnification SEM micrograph of samples LPS-B1

<table>
<thead>
<tr>
<th>Fibers’average width/length (μm)</th>
<th>STP</th>
<th>LPS-A</th>
<th>LPS-B</th>
<th>LPS-B1</th>
</tr>
</thead>
<tbody>
<tr>
<td>RMS Roughness(μm)</td>
<td>6.4</td>
<td>5.8</td>
<td>2.6</td>
<td>2.6</td>
</tr>
</tbody>
</table>

3. Supplementary FETs characterization

The $I_{ON}/I_{OFF}$ ratio of the FETs produced on different papers was recorded in function of the switching frequency (from 10 mHz up to 10 kHz) by applying at the gate of the FET a square wave varying the $V_{GS}$ between -20V to 20V (figure 5). This give us an idea of the frequency where is no longer possible to distinguish between two regimes ($I_{ON}/I_{OFF}$ equals 1) and give a sense of magnitude of the maximum operation frequency expected for these devices.

The switching time (the time elapsed from 10 to 90% of the total current variation) of the FETs was determined from the variation of the source to drain current ($I_{DS}$) at 10 mHz (figure 6). At this frequency it was possible to switch the devices between the ON and OFF state. The results obtained are listed in table 4.
Figure 5 - $I_{\text{ON}}/I_{\text{OFF}}$ ratio in function of frequency that allow for a simple determination of the frequency at which is no longer possible distinguish between two states.

Figure 6 – $I_{\text{DS}}$ variation under a square wave of 10 mHz and an amplitude of 40 V (from -20 to 20V). $V_{\text{DS}}$ was fixed at 15 V.
Table 4– Dynamic parameters at 10 mHz extracted for FETs produced on different paper samples.

<table>
<thead>
<tr>
<th></th>
<th>STP</th>
<th>LPS-A</th>
<th>LPS-B</th>
<th>LPS-B1</th>
</tr>
</thead>
<tbody>
<tr>
<td>$I_{ON}/I_{OFF}=1$</td>
<td>Frequency (Hz)</td>
<td>&gt;10</td>
<td>&gt;10</td>
<td>1-10</td>
</tr>
<tr>
<td>Switching time @ 10 mHz (ON) (s)</td>
<td>44</td>
<td>38</td>
<td>39</td>
<td>46</td>
</tr>
<tr>
<td>Switching time @ 10 mHz (OFF) (s)</td>
<td>22</td>
<td>20</td>
<td>42</td>
<td>71</td>
</tr>
</tbody>
</table>

4. References