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Patterning processes for flexible electronics

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1. Introduction

Patterning functional materials is a key enabling technology for flexible electronics. In almost every flexible electronic device, individual materials and layers need to be patterned, and the patterning technologies are nearly as important as the materials properties. Frequently, patterning restrictions are the limiting factors in device performance. Electronic functionality depends upon the ability to construct layers of materials having precisely defined architectures and relationships. These structures require the ability to either deposit (additive) or remove (subtractive) materials in a locally controlled fashion (patterning). A frequent challenge in patterning of multi-layer devices is that the patterning method and patterned material (solvent) for subsequent layers must not adversely impact the shape or material characteristics of previous layers or substrate. Photolithography has been the workhorse patterning technique for the electronics industry and has been used for nearly 50 years on rigid substrates such as silicon and glass. However, photolithography presents many challenges for patterning functional materials on flexible supports. Even on rigid substrates, photolithography can be cost prohibitive for extremely low cost applications such as RFID or smart packaging. Many other techniques have been used to accomplish the patterning of materials on flexible supports. In general, these patterning techniques have either been derived or adapted from conventional electronics processing, from printing processes, or from a hybrid of both. The appropriate choice of patterning technique will depend upon many considerations, including feature size, area of coverage, throughput, registration, environment, position in the overall device structure, and material considerations. Many, if not most, device structures will require the use of multiple different patterning techniques. The purpose of this paper is to review the major patterning techniques that have been used for flexible electronics, and to discuss the unique features, advantages, and disadvantages of each. The focus will be on large-area, high-throughput, additive deposition techniques that can be performed in ambient conditions. Due to space limitations, a number of topics including Registration, Physical processes underlying patterning technologies, and General issues for flexible electronics are covered in the Supplemental Material. Schematic diagrams showing how various printing processes work can also be found in the Supplemental Material.

2. Considerations for patterning processes (including materials)

There are a number of issues to consider for selecting the optimum patterning process. Techniques should be chosen based upon their suitability for patterning the desired materials (volatility, solubility, viscoelastic properties, etc.), as well as by their capability to pattern the necessary feature sizes (lateral resolution, thickness, surface uniformity) required by the device. Economic considerations such as process throughput are also important.

Probably the first specification that comes to mind when evaluating patterning processes is the process (lateral) resolution. In other words, what is the smallest feature that the process is able to pattern? This is certainly one of the most critical requirements for many devices. For example, resolution may limit the switching speed of a transistor or the achievable resolution of a display. This specification, however, may not be as straightforward as it may seem. Like most specifications in flexible electronics, the smallest patternable feature depends on many other process factors as well. In general, the reliability diminishes as the feature size diminishes. For example, it may be possible to pattern a short conductive narrow line reliably, but not a long narrow line. As the line length increases, the probability of breaks and defects affecting (or destroying) the overall conductivity increase. The process capability for patterning lines and spaces can be very different. For example, self-aligned inkjet printing is capable of producing < 100 nm gaps, but the line widths are on the order of 10's of microns.[1] Other factors that can affect the achievable resolution are material properties, process speed, and substrate.

It is also important to consider the process capabilities for the patterned layer thickness. Both extremes of the thickness spectrum are important. For some types of devices (for example, TFT dielectrics), it is very desirable to
be able to pattern very thin uniform films. On the other hand, many types of devices require the patterning of relatively thick layers (for example, battery materials, or RFID antennas). It is unlikely that the same patterning and deposition process will be able to achieve both types of requirements.

Throughput can be an important consideration for flexible electronics, particularly when producing a large number of devices is necessary or a consideration. The process scalability can also be an important factor to consider. Many deposition/patterning processes are done in research settings (for example, filtration) that have no clear path to scale up. Roll-to-roll patterning processes are desirable, as they usually have greater throughput than batch processes. There are usually tradeoffs between throughput and other factors; for example, it is very difficult to achieve both high resolution and high throughput simultaneously (Figure 1). It is important to note that throughput is frequently limited by processes other than patterning itself; for example, drying, curing, or sintering. In general, printing processes have the largest throughput, and photolithography the lowest. Cost is also closely related to throughput. Slow, laborious processes are normally more expensive than high-throughput processes.

Environmental considerations are very important for flexible electronics—in particular, the choice of whether the processing can be conducted in ambient or vacuum environments. Vacuum processes tend to operate in batch mode, which is usually slower than continuous processing. The time it takes to get the materials and devices into and out of the vacuum also needs to be considered. Environmental cleanliness is also an important factor to be considered. How tolerant is the device to dust and foreign materials? Does the process need to be conducted in a clean room, or will a clean zone be sufficient? Vacuum based processes are by their nature very clean, and don’t usually require additional filtration equipment. Rigorous cleanliness can be very difficult to achieve in ambient conditions for high-volume printing equipment.

Although resolution is usually one of, if not the first, specification considered for flexible electronics patterning, it is frequently not the limiting factor. For multilayer devices, registration is equally, if not more, important. Registration refers to how well layers are aligned with respect to each other (usually subsequent to previous layers). This is a complicated specification, which depends to a great extent on the exact process flow. Intermediate (non patterning) processes (for example, thermal treatments) can have a great impact on the registration. For example, TFT devices require a minimum of four layers, and the registration of the last layer to the first layer (gate to source/drain electrodes) is critical. If any part of the channel isn’t covered by the gate, the TFT won’t work at all (See Supplementary Material, Section 1).

Material considerations are also critically important for choosing patterning processes. Vacuum deposition processes typically require volatile materials. Sufficient volatility can be achieved by heating the material. However, many materials decompose when heated before sufficient volatility can be achieved. Printing processes require that the material can be formulated into an ink having the appropriate viscoelastic properties for the particular printing process. Solubility is important, as well as the type of solvent that is used. Not only does the solvent need to dissolve the material, but the solution also needs to have the appropriate viscosity for the process. For example, polymeric organic semiconductors tend to be sparingly soluble in low viscosity organic solvents. These low viscosity solutions are ideal for inkjet printing, but not for printing processes that require higher viscosities. Also, the solvent must not interfere with the substrate, or affect underlying layers. Material loading is important for efficiency. It is usually desirable (particularly for conductors) to have as much active material as possible in the ink. For certain types of printing processes (for example offset lithography), complex rheology is necessary. This usually requires (electrically inactive) additives, which remain after printing. These inactive additives can reduce or destroy the performance of the material. It is also important to consider how efficiently the material to be patterned will be used. Some patterning processes (vacuum evaporation) waste a lot of material, while others (inkjet) are very efficient in ink usage.
The fidelity of the patterned material is very important for flexible electronics. There are many aspects of patterned material fidelity, the importance of which depends upon the exact device structure. It is always desirable to have patterned material be as uniform as possible. Any nonuniformities can cause issues with device performance. Ideally, the patterned material should be smooth and continuous, without gaps, spikes or other discontinuities. Vacuum evaporation processes are very good at producing thin, uniform layers. The edge definition is defined by the photolithography process. Technologies which pattern material as it is deposited usually exhibit some non-idealities which are important to consider, particularly for multilayer devices. Inkjet printing, for example, can give rise to nonuniform patterned features due to the “coffee ring effect” (also known as “coffee stain effect”), whereby jetted materials tend to migrate to the edges of the printed dot. Artifacts due to satellites (droplets of ink splitting off from the main jet and being deposited in unintended locations) are also of concern for inkjet printing. The edges of patterned lines (line edge roughness) can be important factors, the fidelity of which can be greatly impacted by the patterning process. Gravure and screen printing, for example, can exhibit rough edges due to the pattern of the screen or cylinder engraving. These issues can usually be resolved by appropriate optimization of the process conditions, including the rheology of the ink. The uniformity of the patterned material perpendicular to the substrate is also important, particularly for multilayer devices. Spikes, for example, are particularly dangerous, particularly for multilayer devices having thin layers. Flexo printing, for example, frequently gives nonuniform patterned material height, with halation around features caused by ink squeeze from the deformable plate.

3. Types of patterning

There are a number of types of patterning processes that can be used for flexible devices. The physical processes used for patterning technologies are discussed in the Supplementary Material, Section 2, and Substrate related issues are discussed in the Supplementary Material Section 3. This section will review some of the classifications that can be used to compare the various patterning processes. These are compared for the different patterning processes discussed in this article in Table 1.

Additive patterning processes operate by depositing and patterning material at the same time. In other words, the patterned material is only deposited in the desired locations. They are the most material efficient processes, because none of the patterned material needs to be removed.

Subtractive patterning processes, on the other hand, usually start out by depositing material everywhere, and removing the portions of it that are not wanted. In general, the removed material can not be recovered. The most widely used subtractive patterning process is photolithography, which drives the multibillion dollar semiconductor industry. Photolithography is more complex than most additive patterning processes. Many additional steps can be required for photolithography, including making a mask, depositing a photoresist, exposing the photoresist, developing the photoresist, etc. Lasers can also be used to remove material, without requiring all of the photolithography steps. On the other hand, the resolution and registrations that are achievable with subtractive patterning processes far exceed those of most additive patterning processes.

Another important distinction to consider for flexible patterning processes is whether or not the functional material is patterned directly or indirectly. Direct patterning means that the active material itself is patterned, rather than an intermediate layer or material. In most printing processes, the active material is patterned directly, since it is patterned and deposited at the same time. In photolithography and imprint lithography, the active material is patterned indirectly. An intermediate material like a photoresist or mask is patterned first, and the pattern is transferred (indirect) to the active material.

Imprinting processes essentially redistribute predeposited materials. The material to be patterned is usually deposited uniformly, as in photolithography. After deposition, the material to be deposited is softened, usually by
heating beyond the glass transition temperature, and imprinted with a rigid mold. During the molding process, the material is redistributed to conform to the shape of the mold. After the redistribution has occurred, the temperature is hardened, usually by lowering the temperature to below Tg, and the mold is removed, leaving patterned material. This process isn’t strictly subtractive, since very little material is actually removed, but it does resemble subtractive photolithography rather closely. Imprinting requires an initial uniform deposition of material to be deposited, and requires a number of separate steps (deposition, imprinting, removal) to create a patterned layer.

In most patterning processes, there is physical contact between materials other than the material to be patterned and the underlying material or substrate. This contact can cause a number of problems, such as contamination, or perturbation (scratches) of the physical structure of the underlying materials. Contact can also be a problem when depositing material over underlying topology. A few patterning processes (primarily jetting) are able to deposit material without making physical contact of the underlying layers (Table 1).

Another important consideration for patterning processes is their scaleability. In this context, scaleability is the ability of a patterning process to be used over a wide range of different substrate or patterning areas (throughput). Scaleability is desireable for the translation of small scale (research or prototype) processes to manufacturing. Some patterning processes are partially scaleable, meaning that they can be scaled over a narrower range than the fully scaleable processes, usually by adding extra jets or nozzles. This improves the scaleability, but at the expense of complexity. There is usually a limit on how many jets or nozzles can be practically added, hence limiting the scaleability.

As flexible electronics has evolved, it has become clear that no single patterning process fulfills all of the necessary requirements for many purposes. Often, a hybrid of photolithographic and other patterning techniques is employed. Frequently, a complex structured material is patterned by photolithography and transferred to a larger area using other techniques. This transfer process can be done by stamping, or by dispersing the materials in a fluid, which can then be deposited using conventional printing processes. Several papers in this issue describe such hybrid patterning processes.[4-9]

<table>
<thead>
<tr>
<th>Method</th>
<th>Environment</th>
<th>Deposition mode</th>
<th>Patterning type</th>
<th>Contact</th>
<th>Scaleable</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rigid Support</td>
<td>Vacuum</td>
<td>Subtractive</td>
<td>Indirect</td>
<td>Photolithography</td>
<td>No</td>
</tr>
<tr>
<td>Vacuum R2R</td>
<td>Vacuum</td>
<td>Subtractive</td>
<td>Indirect</td>
<td>Photolithography</td>
<td>Yes</td>
</tr>
<tr>
<td>Flexography</td>
<td>Atmospheric</td>
<td>Additive</td>
<td>Direct</td>
<td>Contact</td>
<td>Yes</td>
</tr>
<tr>
<td>Soft Lithography</td>
<td>Atmospheric</td>
<td>Additive</td>
<td>Direct</td>
<td>Contact</td>
<td>Partially</td>
</tr>
<tr>
<td>Gravure</td>
<td>Atmospheric</td>
<td>Additive</td>
<td>Direct</td>
<td>Contact</td>
<td>Yes</td>
</tr>
<tr>
<td>Imprinting</td>
<td>Either</td>
<td>Subtractive</td>
<td>Indirect</td>
<td>Contact</td>
<td>Yes</td>
</tr>
<tr>
<td>Offset Lithography</td>
<td>Atmospheric</td>
<td>Additive</td>
<td>Direct</td>
<td>Contact</td>
<td>Yes</td>
</tr>
<tr>
<td>Flatbed screen</td>
<td>Atmospheric</td>
<td>Additive</td>
<td>Direct</td>
<td>Usually contact</td>
<td>Yes</td>
</tr>
<tr>
<td>Rotary screen</td>
<td>Atmospheric</td>
<td>Additive</td>
<td>Direct</td>
<td>Contact</td>
<td>Yes</td>
</tr>
<tr>
<td>Ink jet</td>
<td>Atmospheric</td>
<td>Additive</td>
<td>Direct</td>
<td>Non contact</td>
<td>Partially</td>
</tr>
<tr>
<td>Aerosol jet</td>
<td>Atmospheric</td>
<td>Additive</td>
<td>Direct</td>
<td>Non contact</td>
<td>Partially</td>
</tr>
<tr>
<td>e-jet</td>
<td>Atmospheric</td>
<td>Additive</td>
<td>Direct</td>
<td>Non contact</td>
<td>No</td>
</tr>
<tr>
<td>Pen/dispensing</td>
<td>Atmospheric</td>
<td>Additive</td>
<td>Direct</td>
<td>Either</td>
<td>No</td>
</tr>
<tr>
<td>Thermal/laser</td>
<td>Atmospheric</td>
<td>Additive</td>
<td>Direct</td>
<td>Contact</td>
<td>Yes</td>
</tr>
<tr>
<td>Electrophotography</td>
<td>Atmospheric</td>
<td>Additive</td>
<td>Direct</td>
<td>Contact</td>
<td>Yes</td>
</tr>
</tbody>
</table>

TABLE 1. FEATURE COMPARISON OF PATTERNING PROCESSES
4. Photolithographic patterning processes (in vacuum)

Photolithographic patterning is well established, and has been used in the semiconductor industry for nearly 50 years. It is the workhorse technology upon which the semiconductor industry depends. The process itself has been extensively reviewed,[10-12] and will not be discussed in detail here. Some of the specific techniques that have been developed to use photolithographic patterning for flexible substrates will be discussed in this section.

4.1. Flexible substrates processed on rigid supports

As discussed in the previous section, there are many issues to consider for patterning processes when using flexible substrates. One strategy that has been employed is to attach a flexible substrate to a rigid support before patterning. This strategy alleviates some of the issues discussed previously for patterning flexible substrates. It also allows the flexible support to behave as if it were a rigid support and to be processed using some of the same equipment that is used for conventional semiconductor processing. A major advantage of this strategy is that it provides a relatively (deceptively?) easy, noncapital-intensive way to produce flexible devices using conventional processes and processing lines. It can not, however, eliminate all of the issues discussed above for flexible substrates. The inherent thermal, chemical, physical, and optical characteristics of the substrate have not been changed by the support, and still need to be considered for subsequent processing steps. Furthermore, some of the disadvantages of conventional semiconductor processing (e.g. throughput) are still retained.

<table>
<thead>
<tr>
<th>Strategy</th>
<th>Bond/debond</th>
<th>EPLaR</th>
<th>SUFTLA</th>
<th>JILO</th>
<th>FlexUP</th>
</tr>
</thead>
<tbody>
<tr>
<td>Support</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Flexible substrate</td>
<td>polymer or metal</td>
<td>PI</td>
<td>PES</td>
<td>Plastic</td>
<td>PI</td>
</tr>
<tr>
<td>Attachment</td>
<td>Adhesive</td>
<td>PI</td>
<td>a-Si/water soluble adhesive</td>
<td>Metal</td>
<td>DBL</td>
</tr>
<tr>
<td>Release process</td>
<td>Triggered</td>
<td>UV Excimer Laser (interfacial melting)</td>
<td>Laser (ablation)</td>
<td>Pulsed electric field</td>
<td>Cutting circumference</td>
</tr>
</tbody>
</table>

TABLE 2 CHARACTERISTICS OF RIGID SUPPORT STRATEGIES FOR FLEXIBLE ELECTRONICS

A number of different types of rigid support strategies for flexible substrates have been developed. Some of the characteristics of these different processes are summarized in Table 2.

4.1.1. Bond/Debond

An approach for the temporary bonding/de-bonding of a flexible substrate to a rigid support has been developed by the Flexible Display Center at Arizona State University, ITRI in Taiwan, and others. The key feature of this approach is the use of a releasable adhesive. The flexible substrate can be released from the support by triggering the adhesive to release by a number of different methods, including mechanical means, solvents, UV light, or thermal release processes (Table 2).[13]

One of the issues encountered with this (and likely other) support approach is the different thermal expansion of the substrate, adhesive, and the support, which is quantified as the coefficient of thermal expansion (CTE). The CTE is the amount that a material expands (or contracts) per degree change in temperature (usually expressed in °C), and is usually expressed in parts per million per degree (ppm/°C). This issue is discussed in section 3 of the Supplementary Material. This CTE mismatch led to bowing of the substrate, which resulted in wafer handling problems in processing equipment, delamination of the flexible substrate from the rigid carrier, and substrate distortion leading to alignment problems.[13] The ASU group came up with a unique solution to the problem by using alumina as the rigid carrier. The CTE of alumina is closer to that of the flexible substrate, and reduced the
thermally induced bowing. The adhesive properties also had a significant effect on the bow of the bonded system.[13-15]

4.1.2. EPLaR

Another popular approach to supporting flexible substrates on rigid substrates is the Electronics on Plastic by Laser Release process developed by IBM and Philips and known as EPLaR. Here, a transparent (glass or quartz) support is used, and polyimide serves as the flexible support and adhesive (Table 2). The polymer is released from the rigid support by UV excimer laser illumination from the backside (through the transparent rigid support). This illumination melts or ablates the polymer at the support/polymer interface.[16-20]

4.1.3. SUFTLA

A temporary support technology called Surface Free Technology by Laser Annealing has been developed by Seiko-Epson, and trademarked as SUFTLA™. In this technique, devices can be transferred from a transparent support (glass or quartz) to flexible supports. The process is similar to the EPLaR process, in that it uses a transparent rigid support (quartz or glass) and excimer laser irradiation through the support to induce detachment. In the SUFTLA process, the TFT substrate is attached to the transparent support using a water-soluble adhesive. The SUFTLA process is unique in that all of the semiconductor processing is done before the flexible support is attached. This reduces the problems of different CTE’s between the device and support, which was noted above. After the device has been fabricated on the rigid support, the flexible support (PES) is glued to the opposite side (top) of the device from the transparent support (bottom) using a non-water-soluble adhesive. Detachment of the device is accomplished by irradiating the device through the transparent support using an excimer laser. Upon irradiation, hydrogen from the exfoliation layer (a-Si) is evolved and causes detachment of the device from the transparent support.[21-23] Alignment accuracy can be maintained at ~1 μm on a Gen 2.5 (370 x 470 mm) substrate.[24]

The SUFTLA process has been used to prepare a thin (0.01 cm), flexible, 6-in. color AMOLED display. This display produced a brightness of up to 150 nits while being bent to a radius < 1 cm, and could be flexed up to 100,000 times without affecting the display.[24] An ultrathin touch panel has also been integrated with the flexible AMOLED display and tested under water in an aquarium for a week.[24]

4.1.4. JILO

Another technique for supporting a flexible substrate on a rigid support was developed by Samsung. They call this process Joule Heating Induced Lift-Off, or JILO.[25] In this technique, a conductive layer is located beneath the flexible plastic substrate. Thermal energy is generated by exposing the conductive layer to a pulsed electric field. The electric field causes the conductive layer to heat up more uniformly than other methods, which is said to allow this process to be used for large area flexible displays. This is used to generate temperatures above the melting point of the flexible plastic, which allows it to be removed. The temperature is controlled by the conductivity of the metal and the electric field conditions. Temperatures as high as 1000 °C could be achieved. Simulation results showed that the maximum temperature achieved was about 600 °C, and the interface temperature between the metal and flexible plastic was >450 °C. Importantly, the authors claim that the heat penetration depth into the flexible plastic substrate is <1 μm, so there is no thermal damage to the device caused by the debonding process.[25]

Samsung has used this process to pattern low temperature polysilicon (LTPS) TFTs for a “large area” AMOLED display, but didn’t state the size of the display area.[25] Details on the performance of the TFT’s were given, but
not the display. It is not clear how general the JILO process is for flexible electronics. For example, if the device contained other conductive layers, they would also be likely to heat up in the presence of the electric field, potentially damaging the device. There has been very little published on the use of JILO for flexible electronic patterning.

4.1.5. FlexUP

Another rigid support strategy for patterning flexible electronics was developed by the display technology center of the Industrial Technology Research Institute (ITRI) in Taiwan. Their process is called flexible universal plane technology (FlexUP). In this process, a weakly adhering debonding layer attaches the flexible polyimide substrate to the rigid glass support. The TFT and OLED remained attached to the rigid glass support during the entire manufacturing process. Debonding occurs simply by cutting the circumference of the polyimide layer such that the cut is within the edges of the debonding layer. The exact composition of the debonding layer was not disclosed, but it appears to be a nanocomposite material which can withstand a processes temperature of 450 °C.[26, 27]

FlexUP has been used to make transparent amorphous oxide semiconductor TFTs and OLEDs. The bias stress reliability of the oxide semiconductor TFTs was improved to over 10 years.[26]

4.2. Unsupported flexible substrates

It is also possible to pattern flexible substrates photolithographically in vacuo without using a temporary rigid support. This technology has been developed by the Center for Advanced Microelectronics Manufacturing (CAMM) at the State University of New York at Binghamton. By removing the constraint of needing a temporary rigid support, roll-to-roll (R2R) patterning of devices on flexible substrates is possible. Although this is a R2R process, it isn’t a continuous R2R process from start to finish. The three separate processes are each R2R individually, but rolls need to be moved from one process to the other manually in a batch process.

One of the primary uses/purposes of this technology is to study the process capabilities and limitations of photolithography in a R2R process.[28, 29] Using this technology, a distortion offset of 1.4 μm in the machine direction (MD), and 0.99 μm in the transverse direction (TD) were found for a relatively low web tension (9.8 N) and small pattern size (200 x 100 mm).[29] These results imply that devices having a feature size of < 10 μm could be produced with acceptable overlay errors (30% of the minimum feature size).[29]

Microelectrodes have been patterned on PET using this R2R photolithography technology. Copper was deposited and patterned in vacuum, followed by etching to create the microelectrodes. Treated gold nanoparticles were deposited on the microarrays to create the chemiresistors. The sensors response to several different gasses including nitrogen, ethanol, hexanes, and acetone were demonstrated.[30-32]

5. Printing processes (Ambient pressure additive deposition)

Some of the most important specifications for the major printing processes used in electronics are shown in Table 3. Figure 1 shows the relationship between two of the most important specifications of patterning processes—lateral resolution (essentially, the size of the smallest feature that can be printed), and areal throughput. Areal throughput is the area printed per unit time. It is computed as the web speed times the width of the web. Web speed is frequently also referred to as (linear) throughput. Semiconductor fabrication processes would be found below and to the left (very low throughput, and very high lateral resolution—small feature size) of the patterning processes shown in this chart. As can be seen in Figure 1, there is a relationship between lateral resolution and throughput. The printing processes with the highest resolution capability are also generally those with the lowest
throughput (and vice versa). The techniques having a throughput > 1 m²/sec are known as “high-volume” printing processes. Since production cost usually decreases as throughput increases, these high-volume printing processes are highly desirable for manufacturing to enable the lowest cost production.

![FIGURE 1 AREAL THROUGHPUT VS. RESOLUTION OF MAJOR PRINTING PROCESSES (© BRUCE KAHN, PRINTED ELECTRONICS CONSULTING, 2014)](image)

### TABLE 3 SPECIFICATIONS OF PRINTING PROCESSES (© BRUCE KAHN, PRINTED ELECTRONICS CONSULTING, 2014)

<table>
<thead>
<tr>
<th>Lat. Res. (μm)</th>
<th>Ink thickness (μm)</th>
<th>Ink viscosity (mPas)</th>
<th>Throughput (m²/sec.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flexography</td>
<td>6</td>
<td>50-500</td>
<td>10</td>
</tr>
<tr>
<td>Soft Lithography</td>
<td>0.03</td>
<td>Monolayer</td>
<td>60</td>
</tr>
<tr>
<td>Gravure</td>
<td>7.5</td>
<td>50-200</td>
<td>0.1</td>
</tr>
<tr>
<td>Pad</td>
<td>20</td>
<td>&lt; 2.5</td>
<td>60</td>
</tr>
<tr>
<td>Offset Lithography</td>
<td>10-50</td>
<td>&lt; 25</td>
<td>0.1</td>
</tr>
<tr>
<td>Screen</td>
<td>30</td>
<td>~ 0.1</td>
<td>60</td>
</tr>
<tr>
<td>Ink-Jet</td>
<td>20-50</td>
<td>&lt; 1</td>
<td>0.1</td>
</tr>
<tr>
<td>Thermal/Ablation</td>
<td>5</td>
<td>N/A</td>
<td>0.01</td>
</tr>
</tbody>
</table>

5.1. Taxonomy

Printing processes can be organized according to the taxonomy shown in Figure 2[2]. The processes that require a physical master (printing plate) are shown on the left, and the ones that don’t require a physical master are shown on the right. Categorization based upon the existence of a physical master is more precise, and is preferred over the often used but antiquated and misleading terms “Analog” and “Digital” printing that have been used to describe processes with and without a physical master, respectively. This taxonomy groups printing processes together that have similar features and characteristics. As shown in Figure 1, the processes with the highest throughput tend to be the processes using a physical master. The printing processes are discussed in this paper essentially in order from the left side to the right side of the taxonomy.
5.2. Techniques using a physical master (Analog)

5.2.1. Flexography

The principles of flexographic printing are shown diagrammatically in Figure 3. In the normal implementation (not shown in Figure 3, also known as “two roll”), ink is transferred from an ink pan via a fountain roll to the anilox roll. A doctor blade is used to scrape off the excess ink from the anilox roll. The implementation shown in Figure 3 employs a chambered doctor blade to transfer ink to the anilox roll. Use of a chambered doctor blade for flexible electronics provides a number of advantages, and is greatly preferred when printing functional materials.[3] The chamber enables the use of smaller amounts of ink than an open pan, and reduces the solvent evaporation tremendously, keeping the ink properties consistent. This method is also environmentally preferred (if not required) for organic solvent-based materials, because the (organic) solvent vapors can be controlled.

The anilox roll is one of the key features of flexographic printing. It controls the amount of ink that is transferred to the printing plate. The anilox roll consists of a number of small cells that are engraved into the surface of the roll. Different anilox rolls are available that contain different size cells and cell volumes. The anilox roll allows the amount of ink deposited to be controlled without changing the printing plate, which is relatively unique among printing processes. Flexographic printing employs a flexible polymer printing plate, much like a rubber stamp. The raised areas of the flexo plate pick up the ink from the anilox roll as shown in Figure 3, and transfer it to the substrate.
There has been much development of flexographic printing technology, and particularly its use for flexible electronics. Although the resolution limit of flexographic printing was once considered to be on the order of 100 µm, feature sizes < 10 µm may now possible. Transparent conductive grids based upon flexographically printed features < 10 µm have been announced, and are now being manufactured and are commercially available.[33-37]

Flexographic printing offers a number of attractive features for printing functional materials. It is a high throughput (volume) process. Printing plates are easily made, can be high resolution (submicron dot size, 400 dots/mm or 10,000 dpi) and relatively inexpensive. Printing plates can have continuous features (lines) without having to rely on printed ink having to flow together (inkjet, gravure, screen). A variety of plate materials exist, from a number of different manufacturers. Plate materials are available that tolerate some organic solvents. The inks used are relatively low viscosity and can be formulated from functional organic materials or particulate suspensions. The printing process is conformal and is tolerant of substrate abnormalities. The thickness of the ink layer can be controlled over a large range.

Flexographic printing has some disadvantages as well for patterning functional materials. One disadvantage of flexographic printing for functional materials is that the height (thickness) morphology of printed features can be nonuniform. This is caused by the squeezing of the ink out from under the edges of the printing plate.[3] This can limit the use of flexographic printing to the later layers of a multilayer. There can be a compatibility issue between the printing plates and organic solvents. Some combinations of plate material and solvents may cause the printing plate material to swell, or change its viscoelastic properties. Since flexographic printing plates are made of relatively soft materials, they can wear and don’t last as long as printing masters made from hard materials (e.g. gravure cylinders).
Recently, there has been great interest in using flexo printing to fabricate flexible transparent conductive grids as an alternative to ITO which is brittle, relatively rigid, and expensive.[38] Krebs has demonstrated the use of flexo printed Ag grids for very large area, entirely R2R-processed flexible photovoltaic cells[39, 40]. These large-area solar cells have been used in many different ways, including a very large 100 m installation shown in Figure 3. [41, 42] One of the key requirements for this installation was that the entire 100 m stretch had to be “without error”. [41] The flexo printing and inline curing of transparent conductive grids has been shown at the extremely high throughput of 100 m$^2$/min.[43] Transparent conductive films are also being produced commercially, based upon flexographic printing.[34-37, 44]

**FIGURE 4. 100 M PRINTED OPV [41](©2014 WILEY PUBLICATIONS, USED WITH PERMISSION)**

In addition to conductors and transparent conductors, flexographic printing has also been used to print a number of other types of materials and flexible devices, including electroluminescent colloidal inks,[45] an electron transporting polymer,[46] antibodies, [47] and fluidic structures in paper.[48]

5.2.2. Soft Lithography (µCP, nCP, nTP, MIMIC, etc.)

Soft lithography is the name for a family of related printing processes, first described by Whitesides in 1993.[49] The common feature of these processes is that a master is made using conventional microelectronic fabrication techniques. Typically, the master is made from either silicon or photoresist. Once the master is created, stamps can be made from it by applying a liquid prepolymer (usually polydimethylsiloxane PDMS, Sylgard 184) and then subsequently curing it. These techniques have been extensively reviewed[50-54] and are discussed elsewhere in this issue,[7, 8] and they will not be discussed in detail here.

The most common soft lithography process is called Micro Contact Printing (µCP). Supplementary Material Figure 2 illustrates how the µCP process is performed. First, a master is created using a microfabrication processes. Second, the liquid prepolymer is applied to the surface of the master. Third, the prepolymer is cured (by heating) and removed from the master. Now, ink needs to be applied to the surface of the stamp. This can be done by either applying the ink directly to the stamp (4) or by using an ink pad (5). Frequently, the inks used are molecules which form self-assembled monolayers (typically thiols) on the surface. Sixth, the stamp is brought into contact with the surface to be patterned. Seventh, upon removal of the stamp, a (self-assembled mono) layer of ink is formed on the substrate surface. Finally, this ink layer can be used as an etch resist to selectively etch the underlying material, as in conventional photolithography.

Similar to flexographic printing, microcontact printing can also be employed using cylindrical stamps.[55] Cylindrical stamps have been demonstrated for patterning gold and silver. The flexible nature of the stamp allows microcontact printing to be used for substrates which are not planar.

Soft lithographic techniques offer extremely high resolution. They provide among the highest resolution of any printing processes. However this high resolution requires access to microelectronics fabrication facilities to produce the high resolution masters. Once the master is produced, however, many stamps can be made from it.
Soft lithography is good for depositing small amounts of materials and thin layers. No rheological additives are necessary in the ink formulations, however materials that form self-assembled monolayers are most common.

Soft lithographic techniques were designed for research (small throughput) applications. Prints are usually made individually by hand. The materials and equipment have not been designed for high volume production, and thus the throughput of soft lithography is limited. Print lengths are usually a few to a few hundred impressions. In order to achieve the highest resolutions and best image fidelity, materials which form self-assembled monolayers are required, which limits the applicability of these techniques. It is usually used for printing thin layers of soluble materials, not particulates or dispersions. Soft lithography is frequently used in combination with etching, much like photolithography, which makes it a subtractive patterning technique for many materials and applications.

5.2.3. Gravure

The gravure printing process is shown schematically in Figure 5. It is one of the highest throughput printing processes for graphic arts, and it is often used commercially to produce high-quality graphic materials, for example, magazines. It is one of the few printing processes that can be used to deposit different amounts of material in different locations. Due to the nature of the engraved cells, the edges of printed features may not be smooth and straight (line edge roughness).

The gravure cylinder is normally made from a metal core that is coated with copper or zinc. The pattern of cells is created in the copper layer by one of three techniques. In mechanical engraving, a stylus is used to carve out the cells as the cylinder is rotated. A number of different cell depths and angles can be created by varying the pressure and movement of the stylus. In indirect engraving, the copper layer is first coated with a photopolymer. The photopolymer is then exposed and developed, so that it can be used as an etch resist. Finally the openings in the cylinder are etched (typically with FeCl₃). The cell depth can be changed by varying the etching conditions (time). Cylinders can also be engraved using direct engraving. This process is similar to indirect engraving except that no photopolymer is used. The cells are etched directly by ablating the metal with a high-intensity laser. Following the engraving, the cylinder is typically chrome coated to improve the wear resistance and polished.

One of the most critical aspects of gravure printing is the doctor blade. Obtaining a good wipe is critical for clean patterning. If the blade doesn’t wipe off the excess ink on the surface of the cylinder properly, a variety of imaging artifacts such as haze or streaks can occur. Importantly, the doctor blade also provides shear to the ink, lowering its viscosity and facilitating cell filling and emptying. There are many blade related settings in gravure printing—the blade material, stiffness, tip angle, blade angle, pressure against the cylinder, etc. All of these need to be optimized in order to get good printing results. The nature of the ink is also important. It can be hard to get good wiping with nanoparticle inks. The nanoparticles are so small that they can easily get under the blade and cause haze or streaking.
Although not nearly as common as in flexographic printing, chambered doctor blades can also be used with gravure printing. A chambered doctor blade system has been recently reported, which allows a commercial press to be used with less than 50 ml of ink[56, 57] Chambered doctor blades for gravure offer many of the same advantages as they do with flexo—low ink volumes, reduced evaporation, and ink mixing.

Since gravure cylinders are hard and not conformable, the smoothness of the substrate is a critical factor for gravure printing, more so than for other printing processes. In order for proper ink transfer to occur, the smooth substrate is pressed against the inked gravure cylinder. Both surfaces need to touch in order for ink to be properly drawn out of the cells. For flexible electronics, the substrates are normally very smooth, so this isn’t a big issue for the first layer. However, gravure printing may not be the best patterning method for printing subsequent layers where there is existing underlying topology, since the cylinder may not be able to touch the area to be patterned, or the pressure required may damage underlying layers.

The cell filling and emptying processes in gravure printing have been studied in detail. Fundamental models of the underlying physical processes have been generated and used to optimize the cylinder engraving and design, as well as process factors.[58-63] This fundamental process understanding will be very helpful for the further development of gravure printing as a patterning technique for flexible electronics.

Gravure printing is attractive for patterning flexible electronics for a number of reasons. It offers high resolution, long life, and good pattern fidelity. Gravure printing has the highest throughput of any commercial printing process (~ 100 m²/sec. at speeds of up to 1 km/min.), and is used where long print length and high quality are desired (magazine and catalog printing). Gravure is one of the few patterning processes that can deposit different amounts of material in an imagewise fashion. Unlike flexo printing, the ink film morphology is uniform, with dome shaped cross sections. Gravure printing also has a number of disadvantages. The fabrication of gravure cylinders is an expensive, laborious process. The use of discreet cells requires proper ink rheology in order to achieve sufficient flow between cells, and may give rise to rough edges. The requirement of smooth surfaces may limit gravure printing to when there is minimal topology (thin layers), or more generally, to the first layer of a multilayer device.
The inks used for gravure printing are similar to those used for flexo printing and are relatively low viscosity (Table 3). Inks can be formulated from soluble materials or (nano) particulate dispersions.

Gravure printing has seen increased use for patterning flexible electronics, particularly for TFTs and circuits. It has also been used to mass print every layer of a TFT, producing > 50,000 transistors.[64] In this work, a special printing layout was also used to avoid registration issues in the print direction. More commonly, gravure printing is used in combination with other patterning processes to print some of the layers of the TFT, and has been used to produce flexible printed circuits.[65, 66]

Other devices have been produced using gravure printing, as well. A rectenna (rectifying antenna) for 13.56 MHz applications was printed using only gravure printing.[67] It has also been used to pattern light-emitting devices including polymer light emitting diodes (PLED),[68, 69] and light emitting electrochemical cells (LEC).[70]

Gravure Offset (Pad)

A derivative of gravure printing is known as gravure offset printing, pad printing or tampography. In this process, the ink is transferred from a plate or cylinder (cliché) to a flexible intermediate surface (offset cylinder or pad) before being transferred to the substrate (hence offset). Pad printing is often used for printing on surfaces that are not flat and is used to transfer a two-dimensional image to a three-dimensional object. It uses relatively small amounts of fairly viscous ink, and can print relatively thick layers. The throughput of pad printing is relatively low, and the equipment isn’t as common as most of the other printing techniques. The plates or cylinders (clichés) are usually made of engraved or etched metal like gravure cylinders, and are similarly expensive.

Gravure offset printing was one of the earliest printing processes used to pattern electronics. It was used as long ago as 1994 for the patterning of (rigid) Si, SiO₂ and Al.[71] The theory of gravure offset printing has been studied,[72-76] as has its optimization for patterning functional materials.[77-80] A modified version of gravure offset printing has been developed which was used to print 10 μm lines and 6 μm spaces; an IGZO TFT was produced using this process to print etch resists.[81] Like flexographic printing, gravure printing has been used to print Ag for the production of transparent conductive films.[82-84] It has also been used for the printing of circuits[85] and displays.[86, 87]

5.2.4. Mechanical Deformation (Imprinting, Indenting, Embossing)

Although most of the atmospheric pressure patterning processes discussed in this section are additive deposition processes that deposit and pattern the desired material directly, some technologies based upon mechanical deformation or imprinting are an exception. There are a number of patterning processes based upon the principle of mechanical deformation (Section 3) that have been used for flexible electronics. Like photolithography, mechanical deformation processes are indirect patterning processes (Section 4). An intermediate material is patterned and used to transfer the pattern to the desired material. In the case of photolithography, a photoresist serves as the intermediate material. For the mechanical deformation processes, a soft (usually polymeric) material is used as the intermediate patterning agent. The hardness of the intermediate material can be modulated either by heat (heating a material to above the Tg to soften it), or by light (curing a polymer by UV exposure to harden it). In both photolithography and imprinting, the functional materials are removed (subtractively) by etching.

Imprinting processes have been well reviewed,[88-90] and won’t be discussed in detail here. In imprinting, a soft material (polymer) is patterned by a hard stamp. As in soft lithography (Section 7.2.1.1.2), the hard stamp is typically fabricated using silicon microfabrication techniques and can have very high resolution (< 100 nm). This hard stamp (or a replica of it) is used to create a pattern in a softer material by pressing the stamp into it. Depending on the exact technique, a heating/cooling cycle or UV exposure can be required. The flatness of the
material to be patterned is also important, and temporary bonding to a flat rigid support may also be necessary (Section 6.1). After imprinting, the intermediate material is essentially just rearranged (from a film of continuous thickness to a relief pattern consisting of high and low spots), but there is usually at least a thin film of the intermediate material everywhere, which needs to be removed (i.e., by reactive ion etching).

A version of imprint lithography which was developed by HP is called Self Aligned Imprint Lithography. In this process, a multilevel stamp is prepared. This stamp has information for every layer encoded in it (each masking layer is encoded in a unique imprint polymer height). All layer masking information is impressed during one imprint step. Since the positions of all of the layers are defined simultaneously, registration errors are virtually eliminated.

The process starts with a uniform coating of every device layer on the substrate. The multilevel mask is then imprinted on the multilayer. Each layer is then carefully etched sequentially. SAIL is a rather complex process, which has not been widely used outside of HP. Although it preserves registration information in a single imprinting event, there are limitations as to what kind of information can be transferred (for example, hidden features behind a layer). Since all of the materials are present at the same time, the etching needs to be carefully controlled, and the materials are essentially limited to robust inorganic materials.

Imprinting is a scalable technology that can produce features < 100 nm at rates of centimeters per second. PDMS stamps can last for thousands of imprints. Imprint lithography can produce some of the smallest feature sizes of any flexible patterning process. As expected from a process with high resolution, the throughput is limited (Figure 1). Imprinting is an indirect patterning process, and like photolithography, usually requires additional material removal steps like etching, lift-off, etc.

5.2.5. Surface energy (Offset Lithography)

Offset lithography is one of the most common printing processes for graphic arts. It is frequently just called offset printing (not to be confused with gravure offset). As described above, it works based on the principle of a difference in surface energy (wetting) of the printing plate (Supplementary Material, Figure 3). The printing plate is typically made of aluminum (hydrophilic), and the image areas are covered by a hydrophobic material. Normally two solutions are applied to the plate simultaneously—a hydrophobic ink solution and an aqueous (hydrophilic) fountain solution. The ink sticks to the image areas of the plate, and the fountain solution wets the non-image areas. Another version of offset lithography uses special silicone printing plates which do not require the fountain solution. This is known as waterless lithography. The term offset comes from the fact that the ink is transferred from the plate to an intermediate and then to the substrate. The intermediate cylinder is known as the blanket or offset cylinder.

Offset lithography offers high throughput, and thin ink layers. The equipment is readily available and inexpensive. The plates are also easy to make and inexpensive. Very high throughput is possible in commercial systems. Offset lithography has been used in flexible electronics primarily for printing silver based conductive features. Some work has also been done using offset lithography for printing organic polymers. Offset lithography has not been used extensively in flexible electronics. The main reason for this is the viscoelastic requirements necessary to formulate offset lithographic inks. They need to start out very viscous (thick and paste-like) at no shear, and reduce viscosity (thin out) considerably when sheared (which is induced by multiple rollers on the printing press). These rheological requirements are rarely found in functional materials, and can usually only be achieved by the incorporation of additives into the ink formulation. These additives are not electrically functional and interfere with the operation of flexible electronic devices. These thick ink deposits give rise to viscous fingering, which interrupts the contact and uniformity of functional materials. Normally, the inks are mixed on the plate with slightly acidic aqueous (fountain) solutions. These fountain solutions are not compatible with many types of functional materials. Also, the
thin ink layers and viscous fingering make it more difficult to achieve electrical conductivity. Frequently, multiple impressions are required to achieve sufficient conductivity.

The use of offset lithographic printing in printed electronics seems to be decreasing, in favor of other printing processes such as flexo and gravure. It has been reported to have been used recently to print electrode patterns, as part of a multiprocess (offset, inkjet, screen, and slot-die coating), sheet-to-sheet production line. TFT backplanes were produced for a variety of different display front planes (electrophoretic, LCD, OLED) and sensors.[95] Another application of offset printing is reported to have produced very fine (1-3 μm) Ag lines over a small area, and 10 μm resolution over an 11-inch diagonal (224x168 mm).[96]

5.2.6. Masking (Screen, vapor)

The screen printing process is shown in Figure 6. Historically, screen printing was called silk-screen printing. Today, silk is not used any more, and the process should be known as screen printing, not silk-screen printing. Screen printing is a version of stencil or mask printing. In screen printing, the mask (emulsion) is supported by a screen (usually made of polyester or stainless steel). The screen support allows the use of areas which are not connected, which would fall through a regular stencil or mask. In screen printing, a wide variety of different screen materials and parameters are available. These related parameters (thread count and thickness, mesh width, stencil and emulsion thickness, screen tension) affect the resolution and thickness that can be achieved. For functional electronic materials, it is important that the ink (solvent) is compatible with the screen and squeegee material. The ink is spread out over the screen (flooding) and forced through it with a squeegee. The squeegee provides a shear that helps transfer the ink through the screen, in a manner similar to that of the doctor blade in gravure printing (see section 5.2.3). Although screen printing is not normally considered a high-volume printing process, the volume can be increased considerably by using rotary screen printing. The rotary screen printing process is shown in Supplementary Material, Figure 4. In rotary screen printing, the screen is wrapped around a cylinder, and the ink is contained inside the cylinder. The cylinder rotates continuously, and the ink is fed through it. In this way, rotary screen printing can operate continuously and increase the throughput considerably over flat bed screen printing, but the throughput still much less than other high-volume printing processes.

![Screen Printing Process Diagram]

FIGURE 6. SCREEN PRINTING PROCESS (SOURCE: © HELMUT KIPPHAN, HANDBOOK OF PRINT MEDIA, SPRINGER, 2001)
Screen printing is widely used in flexible electronics. The equipment is readily available and inexpensive. It is ideal for short runs, and can be automated to produce up to 1000 impressions per hour, as well. It requires relatively little ink, most of which can be recovered, so there is little waste. One of the most useful aspects of screen printing for flexible electronics is that it can be used to deposit relatively thick (10’s of µm’s) layers of materials. This is very useful for printing highly conductive structures, or for printing devices which rely upon material volume like batteries. Screen printing is better suited for printing thick layers than thin layers. On the other hand, like offset lithography, screen printing requires fairly viscous, thixotropic inks, which necessarily include large amounts of inactive ingredients. The throughput is low (for flatbed screen) and the resolution is somewhat limited. Screen printing produces localized ink deposits which need to flow together in order to create continuous features. The height of printed features are frequently non-uniform, and tend to vary following the mesh size.

Screen printing is used extensively for printing sensors. It has been used for printing disposable glucose sensors for about 30 years. Glucose sensors are probably the largest and most well established commercially available application of printed electronics, with a market size of billions of dollars per year and trillions of sensors produced every year. Glucose sensors alone account for about 85% of the world biosensor market. It should come as no surprise then that there is great interest in the use of screen printing for other types of sensors. Recent research has demonstrated the use of screen printed sensors for the detection of Phosphate,[97] PSA,[98] and dopamine.[99] In addition to biosensors, screen printed motion sensors have also been produced recently.[100, 101] Although not usually used for thin layers, screen printing has been used to produce layers < 100 nm thick for optoelectronic devices such as photovoltaics[102] and OLEDs.[103]

5.3. Techniques without a physical master (Digital, NIP)
5.3.1. Inkjet

Some aspects of inkjet printing have been discussed previously (sections 2 and 3) of this review. Inkjet printing operates by generating very small droplets of fluid and depositing them on a substrate. There are three primary techniques for generating inkjet drops. In continuous inkjet, drops are continuously generated and electrostatically deflected either onto the substrate, or into a gutter for recycling. More commonly for flexible electronics, drop-on-demand (DOD) technologies are used, whereby drops are generated as needed. There are two primary DOD mechanisms for ejecting drops from an inkjet nozzle. In thermal inkjet, a small portion of the fluid (ink solvent) is evaporated, forcing ink out of the nozzle. There is concern that the heat generated by thermal inkjet could damage thermally sensitive materials. In piezoelectric inkjet, a voltage is applied to a piezoelectric material which causes it to change its shape (expand), thereby forcing ink out of the nozzle. Piezoelectric inkjet is by far the most common inkjet technology for flexible electronics. A number of manufacturers now produce print heads that are designed specifically for printing functional materials.

Inkjet printing lends itself well to patterning flexible electronics for many reasons, including the ability to print low viscosity materials, the ability to use small amounts of materials, no need for a mask or printing plate, the ease and ability to change the printed pattern, no contact with the substrate, readily available equipment, etc. In recent years, Inkjet printing has been receiving growing interest as a method to deposit and pattern functional materials. Inkjet printing is particularly well suited for the deposition of small amounts of materials that have specific electrical, optical, chemical, biological, or structural functionalities, and pattern them onto well defined locations on a substrate. The materials deposited can be soluble liquids, dispersions of small (or nano) particles, melts or blends. Some types of functional molecules, such as polymers or large biomolecules can not be deposited by the conventional vacuum deposition techniques, and need to be deposited using a solution based technique. One of the most unique and useful capabilities of inkjet printing is its capability of variable printing, that is, the ability to change what is printed at will – without making a new printing plate, etc. This variable data capability has been widely exploited in inkjet printing for printing “sell by” dates, product identification codes, instant awards, etc.
Although not widely employed, the printed image can be adjusted “on the fly” with inkjet printing using a camera and image analysis software to compensate for many of the registration errors that plague other types of printing processes.

Inkjet printing also has a number of disadvantages. Since inkjet printing deposits very small individual droplets, it is a relatively low throughput material deposition technique. This problem can be minimized somewhat by the use of multiple jets. A very high degree of parallelism (1000’s of jets) can be used for graphics printing. However, the throughput of inkjet printing is still substantially lower than the high volume printing processes (Figure 1). Inkjet printing is best suited for the deposition of small amounts of materials, over small areas. Another disadvantage is that inkjet nozzles can be prone to clogging. The material window is somewhat limited since inkjet printing usually requires fluids having viscosities < 20 cP. There can also be a number of issues when using inkjet printing for functional materials. Since individual droplets are produced, it can be difficult to form continuous features. Functional materials may require the use of solvents which may not be compatible with print head components. Inkjet inks can be subject to high mechanical shears in piezoelectric print heads, or high temperatures in thermal inkjet heads. Upon ejection from the print head, droplets of functional materials may clog the print heads, or cause other problems. Fluctuations in droplet volume or trajectory can adversely affect the device performance. Another limitation of inkjet printing is the spreading of the jetted droplets, which limits the feature resolution, and changes the feature size as a function of the distance of the substrate from the print head. Uniformity of the deposited film can be difficult to achieve. A frequent problem observed with inkjet printing is the so called “coffee-ring effect”, whereby jetted materials tend to migrate to the edges of the printed dot. As described before, a technique that has been used to reduce ink spreading (and thereby increase resolution) is to patterning the surface energy of the substrate, thereby constraining the spreading of the jetted droplet.

As described before, a variation on inkjet printing called “Self Aligned Printing” was used to pattern features as small as 60 nm. By modifying the surface energy of a printed droplet (after printing), subsequent droplets rolled off the first one, leaving an extremely small channel (estimated to be ~ 60 nm) between the two droplets. Using this technique, organic transistors were prepared having channel lengths nearly the same as those used in modern computers! These inkjet printed organic transistors were reported to be over two orders of magnitude faster than previous printed organic transistor circuits.

Inkjet printing continues to be a workhorse of printed electronics, has been extensively reviewed,[104-110] and is discussed elsewhere in this issue. It has been used for transparent conductors,[111, 112] organic,[113] metal oxide,[114-117] and CNT[118, 119] TFT’s, sensors,[120-123] displays,[124, 125] and memory.[126]

5.3.2. Aerosol Jet

Another technique for dispensing and patterning materials from liquids onto flexible supports is the Aerosol Jet® system, developed by Optomec, Inc. (Supplementary Material, Figure 5).[127-130] In this system, rather than produce individual droplets of ink, an aerosol is produced (Supplementary Material, Figure 8a, b), focused and directed toward the substrate (Supplementary Material, Figure 8c). Similarly to continuous inkjet, this aerosol stream can be shuttered to interrupt the stream.

Aerosol Jet® printing preserves many advantages of inkjet printing, while reducing some of the limitations. Significantly for flexible electronics, Aerosol Jet® printing offers an extremely wide materials window. Virtually any liquid having a viscosity < 5000 cP can be deposited. Aerosol Jet® printing dispenses a collimated beam of material which does not touch the nozzle. This reduces the likelihood of chemical reactions with the nozzle, and of clogging. This also allows the resolution to be maintained over a wide range of standoff (head to substrate) distances. Larger standoff distances are possible than with inkjet printing. This feature can be important for printing features over
existing topology (as found in many electrical devices and circuits), and enables conformal printing (printing over surfaces that are not flat), which is the application for which Aerosol Jet® technology was originally developed. Since the aerosol is fairly dense, a relatively high amount of material can be deposited for a jetting technique.

Like other jetting techniques, Aerosol Jet® is a relatively low throughput material deposition technique. Also, like other jetting techniques, multiple nozzles can be used, but not nearly the parallelism that has been developed for inkjet printing (10’s of Aerosol Jet® nozzles, as opposed to 1000’s of inkjet nozzles). Starting and stopping deposition requires the use of a mechanical shutter, which slows down the patterning processes.

Like almost every other printing process discussed here, Aerosol Jet® printing has been used recently to prepare organic TFTs from organic semiconductors and CNTs.[131] The characteristics of electrolyte gated TFTs have been studied by the Frisbie group. These TFTs use an ion gel electrolyte as the gate dielectric, and either organic,[132] CNT[133] or metal oxide[134] semiconductors. This high capacitance (~ 1 μF/cm²) dielectric gives a combination of very desirable properties, including very low voltage operation (< 1-2. V) and very high on currents (10⁻⁴ A).[132, 134] Five stage ring oscillators operating at > 20 kHz with stage delays as low as 1.2 μs using a 2V supply have also been produced.[133]

5.3.3. Electrohydrodynamic Printing (e-jet)

The use of electrohydrodynamic or e-jet printing in the graphic arts goes back to at least 1993.[135] Its popularity for patterning flexible electronics came after the work of Rogers in 2007 who showed the ability to use e-jet printing to achieve high-resolution patterning of functional electronic materials on flexible substrates.[136] Several improvements to the process have been subsequently reported.[137-139] Its operation is similar to other jetting processes, however e-jet printing employs a high electric field to induce fluid flow and draw material out of the nozzle. As shown in Supplementary Material Figure 6, a syringe pump or pressure controller delivers fluid to a glass capillary tube, which serves as the nozzle. The capillary tube is coated with gold, which is coated with a hydrophobic perfluorocarbon SAM to prevent clogging. A high (> 100 V) voltage is applied between the nozzle and a conducting support substrate (under the deposition substrate) to create the electric field. The key to obtaining high resolution is to have fine nozzles with sharp tips.

Notably, e-jet printing can be used to make very small features and achieve sub-micron resolutions. A number of different kinds of materials have been printed, including insulating, conducting, and semiconducting polymers, as well as nanoparticles, rods, and nanotubes. As is typical for jetting techniques, the throughput and laydown are low. Although semiconductors and TFT’s have been constructed using e-jet, there is concern over the use of very high voltages (> 100 V), field strengths (> 10⁶ V/m) and the deposition of charged materials.

E-jet printing has been used to make transparent conductors,[140] organic thin film transistors (OTFTs)[141], and metal oxide thin film transistors (MOTFTs).[142-144] It has also been used to print biomaterials.[145, 146]

Recently, e-jet printing was used to simultaneously pattern and align Ag nanowires (NW). In this work, polyethyleneoxide (PEO) was used to increase the viscosity, reduce the surface tension, help the dispersion of the Ag NWs, and reduce whipping instabilities (fast, sometimes violent, lateral bending and stretching of charged jets). However, because of the repulsive forces between high aspect ratio NWs in electric fields, the NWs were disconnected from each other. Although simultaneous patterning and alignment of NWs is very important, the lack of connectivity between the individual NWs will limit the applicability of this process for device fabrication.[147]
In a unique application of e-jet printing for extremely high RF applications, terahertz metamaterials were made using e-jet printing. These metamaterials exhibited a refractive index as high as 18.4 at a frequency of 0.48 THz (480 GHz). [148]

5.3.4. Pen and Extrusion (Pen dispensing, MicroPen, nScript, DPN)

The development of a printing technique that is capable of high-resolution printing in three dimensions with minimal material requirements is extremely important for flexible electronics. Although 3D printing has become extremely popular and excessively hyped by the media, it usually denotes low-throughput, relatively large physical structures, not high-throughput, thin functional flexible electronics. However, pen type dispensing systems have been used for a number of years to deposit functional materials and fabricate devices. These dispensing systems deposit materials under pressure through a fine capillary tip. The capillary tip rides on the bead of material being dispensed but has substantial vertical travel and is tolerant of substrate topology. Features can be written in three dimensions, and can be used for the fabrication of more complicated (three-dimensional) structures than what can be fabricated using conventional (2D) patterning methods.

Several companies produce equipment that can be used for this purpose, including nScrypt and MicroPen (formerly known as OhmCraft). The resolution (achievable dot or line width) of pen dispensing techniques is moderate, on the order of a few 10's of microns, but the positional accuracy is very good (a few microns). These dispensing technologies can be used to pattern a variety of materials, particularly viscous liquids, on a variety of substrates. These techniques offer minimal constraints on the fluid properties and are well suited for use with functional polymeric materials. However, due to their serial writing mode, the scalability and throughput of dispensing technologies are quite limited.

Liquid dispensing has been used to pattern organic features having extremely smooth surfaces (approximately as smooth or even smoother (according to AFM) than the substrate) and very high aspect ratios. Of particular interest are the nearly vertical edges and flat tops of these features.[149, 150] This technique has been used to make features as small as 15 µm and to pattern organic TFTs.[151, 152]

Pen-type dispensing systems have been used to write a number of different types of materials. Several reports have used pen deposition systems to write conductors, for example writing a Pd catalyst and electroless plate Ni.[153] Pen dispensing has been used to write a variety of materials on paper.[154] As in 3D printing, conductive inks can be written in 1, 2, and 3 dimensions.[155] A 2x2 cm TFT array was fabricated by drawing the organic electrodes as well as active layers on a Si wafer using a capillary pen.[156]

Although not strictly an extrusion technique, another type of pen deposition is known as Dip Pen Nanolithography (DPN). DPN is a scanning probe lithography process. In the most common version of this process, an AFM tip acts like a quill pen, and is used to pick up and then write/deposit material on a substrate. This process was developed and commercialized by Chad Mirkin of Northwestern University, but the company that he formed (Nanolnk) went out of business in February 2013. DPN has been used to pattern Ag,[157, 158] PEDOT:PSS,[159] and biomaterial nanoarrays.[160]

5.3.5. Thermal transfer, laser transfer (LDW, LIFT)

There are several printing techniques based upon the principle of thermal transfer. These techniques are sometimes known as dye transfer, dye sublimation, thermal dye transfer, thermal imaging, or laser forward transfer. These techniques work by using a laser to induce the transfer of material from a donor sheet to the substrate of interest. The laser energy melts or vaporizes the surrounding organics, transferring them from the donor layer to the receiver. Unfortunately, this laser energy is sufficient to decompose many organic materials.
Although these are serial printing techniques, and therefore, relatively low throughput ($1000 \text{ cm}^2/\text{min}$), they offer the advantage of a completely dry process, good resolution (\sim 5 \text{ µm}), and good registration (< 200 \text{ µm} registration errors have been reported over areas > 3 \text{ m}^2). [161-164]

Using thermal imaging, Blanchet at Dupont fabricated a flexible, large area (4000 \text{ cm}^2) active matrix backplane array containing several thousand transistors.[162] More recently, both OLEDs and OFETs have been produced on a thin PDMS layer using LIFT.[165]

5.3.6. Electrophotography

Electrophotography, sometimes known as Xerography, can also be used to pattern materials for flexible electronics. This process operates by a number of processes which are run sequentially and repeated for each impression. First the photoconductor drum is charged. Next the photoconductor drum is exposed to an image. The image causes the charge on the photoconductor to change in an imagewise fashion. There is now a “charge image” on the photoconductor. The functional material (toner) is now applied to the photoconductor drum, where it sticks only to the charged area of the drum. This is known as “developing” the image. The functional material is then transferred to the final support and fused (heated) to cause the material to adhere to the support. Following these processes (or before fusing), the photoconductor drum is cleaned and erased, so that it will be ready for the next impression.[166, 167]

Although electrophotography equipment is extremely pervasive (like inkjet printing, almost everyone has one on their desk), it has seen limited use for patterning flexible electronics.[168] The most likely barrier for adoption is the need to form toners from functional materials. In other words, the functional materials have to be made to only stick to the parts of the drum containing the static charge. Electrophotography has been used to print etch resists[169] since this doesn’t require any special toner formulation. Most existing toners can be made to work as resists, and they are easily deposited and patterned. Most of the work using electrophotography for flexible electronics has been done by the Electrox corporation, including the production of active matrix backplanes,[170] RFID antennas,[171, 172] large area placement of discrete components,[173] and the self assembly of nanotubes.[174]

6. Conclusions

Over the last 50 years or so, the conventional microelectronics industry has matured and photolithography has become the dominant technology for patterning materials on rigid substrates. For many reasons which were discussed in this report, photolithography doesn’t work as well for patterning materials on flexible substrates, and alternative patterning techniques have been sought. Initially, flexible electronic devices were patterned using existing conventional and laboratory scale processing equipment that was designed for other purposes. A considerable amount of research has been done using existing photolithography equipment that was designed for rigid substrates. Techniques such as bonding flexible substrates to rigid supports were developed in order to adapt existing equipment to flexible substrates. Much of the early work also employed laboratory scale equipment (for example vacuum evaporators or spin coaters) that was originally designed for other purposes, or not originally intended for multilayer production. Early efforts in flexible electronics were also dominated by research on material properties, with little or no consideration of patterning or scaling. Printing processes have also been envisioned as a path toward flexible electronics for many years. Early attempts to “drop in magic inks” to conventional printing equipment were somewhat but not entirely successful.

The field of flexible electronics is much newer than that of rigid electronics, and there is still a lot of work to be done to develop optimal patterning processes for flexible electronics. As interest in flexible electronics has increased and the field has matured, a number of important lessons have been learned and trends are emerging.
Although an appropriate starting point, it is clear now that conventional equipment that was initially designed for other purposes may have limitations for flexible electronics. There will certainly be some devices (for example, antennas, sensors, etc.) that can be patterned relatively easily using conventional equipment. But there will be limitations as to how far this can be pushed. The field of flexible electronics has matured to such an extent that manufacturers and researchers are now designing equipment specifically addressing the needs of flexible electronics. The decision on whether or not to upgrade equipment will depend upon what types of devices will be made. If the ability to pattern functional electronic devices is seen as important, this should be a consideration for future equipment upgrades.

Moreover, the enormous diversity of materials and substrates that can be used for flexible electronics will require many different patterning processes in order to handle all of the different combinations of properties. The combination and integration of these different patterning processes together will remain a challenge for quite some time. “Finger pointing” between materials and patterning groups is unproductive. It is also important that the rheological characteristics necessary to make materials printable be a consideration in the functional material design and formulation process. The fewer rheological additives required to pattern a material the better.

Printed components will not be able to do everything required, and as well illustrated in this special issue, will need to be integrated with silicon components. As hybrid flexible electronics receive more attention, patterning considerations unique to this type of flexible electronic systems may be necessary.

A number of emerging trends are apparent. An ongoing limitation and challenge for many applications, resolution and registration continue to be extremely important, and need to be improved for almost all patterning technologies in order to achieve more useful electronics performance levels. Vacuum based processes still offer advantages in resolution and registration, however, wherever possible, vacuum based processes are being replaced with processes that operate in atmospheric conditions. Similarly, the trend is to move away from subtractive patterning techniques toward additive patterning techniques. Two of the most significant promises of flexible electronics are the opportunity for large area devices and low manufacturing costs. Realizing these opportunities require a shift from small area to large area capable patterning technologies, as well as a greater emphasis on understanding and enabling the challenges of scaleability.

It is clear that the development of flexible electronics depends critically upon the availability of appropriate patterning technology. A large number of patterning processes have been and are continuing to be developed and used for flexible electronics. These patterning techniques enable the future of flexible electronics.
References


Supplementary Material

For “Patterning Processes for Flexible Electronics”

By Bruce E. Kahn

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1. Registration implications for TFT’s

The ideal situation is shown in Figure S1a, but practical resolution considerations dictate a larger channel (a somewhat less ideal situation is shown in Figure S1b). However, registration errors may give rise to misalignment, as shown in Figure S1c-d. Since a portion of the channel isn’t controlled by the gate, it acts as an insulator (shown as dark region of semiconductor in Figure S1c-d), and renders the device inoperative. To compensate for misregistration, the gate electrode is necessarily made wider than the channel, to ensure that even with overlay errors, it will cover the entire channel (Figure S1e). However, this causes overlap between the gate and the source/drain electrodes (shown as shaded area of electrodes with capacitor symbol Figure S1e). The capacitance generated by this overlap slows down the device.
2. Physical processes which underly patterning technologies

Before considering specific patterning processes themselves, it is useful to consider the physical processes that are employed in patterning. Patterning technologies employ a number of different physical phenomena which include chemical change, relief, surface energy, masking, dispensing, material removal or redistribution, and energy or force-assisted transfer.

Photolithography depends upon the ability to create a chemical change in a material (the photoresist) by locally exposing it to a particular type (e.g. UV light) of energy. The energy induces a chemical change in the material, changing its solubility. In this way, a solubility pattern can be created, and the material that is (made) more soluble can be removed by dissolving it away. The applied energy can be used to either make materials more soluble (positive photoresists), or less soluble (negative photoresists).

Relief is one of the oldest and most common processes used for patterning. Here, ink can be deposited locally depending upon the height of the feature. Depending on the process, either raised areas (flexo, letterpress, pad, µCP, etc.) or lowered areas (gravure, intaglio) can receive ink.

Relief can also be used to cause mechanical deformation in a material. A hard material (stamp) can be used to cause a softer material to rearrange or redistribute. The hardness/softness of the material to be patterned can be induced either by heat (softening a polymeric material by heating it to above its Tg), or by light (hardening a polymeric material by exposing it to ultraviolet light). This principle is used for embossing, cutting, or imprinting.

Another process that is widely used in patterning is the differential control of surface energy. In other words, the wetting properties of specific locations can be made different from each other, and this can control the placement of ink. This phenomenon is used for offset lithography (not to be confused with photolithography). In offset lithography, an oil based ink wets only the hydrophobic portions of the printing plate. Surface energy is also a useful phenomenon to control the location of deposited material in conjunction with other printing processes. For example, surface energy patterning of substrates can be used to constrain the placement of inkjetted material, and thereby enhance the resolution of the inkjet process. [1-3] Surface energy tailoring is also used in conjunction with other printing processes for self alignment. [4, 5]

Masking is used in some patterning processes, to block where material is deposited. In vacuum evaporation-based processing, masks are used above the substrate to block the vapor from positions where it isn’t desired. For printing-based patterning processes, masking is used most commonly in screen printing, where the mask (supported by the screen) controls where ink is allowed to pass through the screen. Although not strictly considered a mask, aerosol jet printing uses a shutter to block the jet from hitting the surface at specific locations.

A number of very popular patterning techniques are based upon material dispensing or direct-write technologies. Here, the material to be patterned is pushed or sprayed through a nozzle, hitting the substrate at a specific location. Examples of dispensing processes are inkjet, aerosol jet, e-jet, and pen dispensing techniques from companies such as MicroPen, nScript, and others. Since material can only be deposited at a single position at a time, these techniques have limited throughput. In some cases (particularly inkjet), parallel dispensing is used to increase the throughput.

Although less material efficient than material deposition processes, material removal or redistribution can also be used for patterning. Most commonly, photolithography is used for removal of material. Other techniques can be used to remove material at specific locations, for example laser ablation. In imprinting processes, material is initially redistributed, and subsequently removed.
Finally, material can be transferred in specific locations by externally applied energy or force. An example of this is electrophotography or laser printing, where electrostatic forces are used to control where materials are deposited. Laser or thermal transfer processes employ a donor sheet of material, which is transferred to the substrate in a specific location by heating the donor or ablating an underlying layer.
3. General issues for flexible substrates

The processes used for patterning materials on rigid substrates are very well developed. The billion dollar semiconductor industry depends critically on these technologies, and has invested large amounts of time and money over the last 50 years or so to bring these processes to their current state of maturity. Not only are the patterning processes themselves well developed, but the semiconductor industry has developed a well-defined technology roadmap for future technology requirements and resolution “node” implementation.[6]

Although the patterning processes are very well developed for rigid substrates, this is not the case for flexible substrates. The patterning process technologies for flexible substrates are much younger and less mature than their rigid semiconductor counterparts. There are many different patterning processes used, and many challenges and opportunities yet to be realized. Substrate flexibility and the related material considerations bring about some unique challenges. The development of flexible electronics technology depends, in large part, on how these challenges are addressed.

Substrate rigidity makes it easier to pattern very small features with high fidelity. By their very nature, flexible supports can deform during handling and patterning. This deformation can distort the fidelity of the patterns, and reduce the achievable resolution and registration. Moreover, the substrate distortion is not necessarily linear or isotropic, and is usually larger in the direction that the substrate is moving (Machine Direction, MD). Pulling the substrate through the patterning equipment tends to stretch the substrate more in the MD. This problem usually increases as more processing is performed, making layer to layer registration a significant challenge for flexible substrates.

Flexible substrates are almost always less thermally stable than their rigid counterparts (Table S1). The semiconductor industry depends on inorganic materials like silicon wafers. The melting point of silicon is 1414 °C, and it can be processed at temperatures of many hundreds °C. Flexible substrates, on the other hand, are usually composed of polymeric materials, which have much lower processing temperatures. The most commonly used substrate for flexible electronics is polyethylene terephthalate (PET), which has a processing limit of about 150 °C (Table S1).[7, 8] Other polymeric materials (for example, polyimide) can be used for flexible electronics which have processing temperatures as high as about 300 °C, but they usually suffer other disadvantages such as cost and optical properties (Table S1). This lack of thermal stability limits the kinds of processing that can be done on flexible substrates. For example, many of the materials that are used in flexible electronics require annealing in order to achieve optimal performance. The limited temperature stability of the substrate limits the annealing temperature that can be used, and therefore, the ultimate device performance. In addition, the dimensional stability of flexible substrates is also temperature dependent. Increasing the temperature reduces the dimensional stability (for example, increases the stretch), which affects the pattern fidelity, registration, and device performance.

Another type of dimensional instability is the inherent expansion and contraction that all materials experience. Most flexible electronic device fabrication processes involve thermal cycling, so this can be a significant issue. This dimensional instability is quantified as the coefficient of thermal expansion (CTE), or the coefficient of linear thermal expansion (CTLE). Mismatches between CTE’s cause adjacent materials to expand and contract at different rates. This can cause cracks in deposited materials and can greatly affect or destroy device performance. Flexible substrate materials typically have larger coefficients of thermal expansion than their rigid counterparts (Table S1). The typical CTE of amorphous polymers (PET and PEN) is ~50 ppm/°C below Tg. Fortunately, these CTE’s can be approximately halved by heat stabilizing the polymer substrate. This is commonly done for PET and PEN (Table
A rule of thumb for tolerable mismatch is $|\Delta \text{CTE} \bullet \Delta T| \leq 0.1-0.3\%$, where $\Delta \text{CTE}$ is the difference in the CTE’s of the substrate and deposited material, and $\Delta T$ is the temperature range of the process.

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Trade names</th>
<th>Tg $^\circ C$</th>
<th>Tm $^\circ C$</th>
<th>CTE ppm</th>
<th>Transparency %T</th>
<th>% H2O abs.</th>
<th>Youngs mod GPa</th>
<th>Tensile strength MPa</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polyethylene terephthalate</td>
<td>PET, Melinex</td>
<td>78</td>
<td>250</td>
<td>15</td>
<td>&gt; 85</td>
<td>0.14</td>
<td>5.3</td>
<td>225</td>
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<tr>
<td>Polyethylene naphthalate</td>
<td>PEN, Teonex</td>
<td>120</td>
<td>260</td>
<td>8-29</td>
<td>85</td>
<td>0.14</td>
<td>6.1</td>
<td>275</td>
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<tr>
<td>Polycarbonate</td>
<td>PC, PURE-ACE, Lexan</td>
<td>150</td>
<td>60-70</td>
<td>&gt; 90</td>
<td>0.40</td>
<td>1.7</td>
<td>70</td>
<td></td>
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<tr>
<td>Polylethersulfone</td>
<td>PES, Sumilite</td>
<td>220</td>
<td>54</td>
<td>90</td>
<td>1.40</td>
<td>2.2</td>
<td>83</td>
<td></td>
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<tr>
<td>Polystyrene</td>
<td>PAR, Arylite</td>
<td>340</td>
<td>53</td>
<td>90</td>
<td>0.40</td>
<td>2.9</td>
<td>100</td>
<td></td>
</tr>
<tr>
<td>Polycycloolefin, Polynorbornene</td>
<td>PCO, Appear</td>
<td>74</td>
<td>91.6</td>
<td>0.04</td>
<td>1.9</td>
<td>1.9</td>
<td>50</td>
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<tr>
<td>Polyimide</td>
<td>PI, Kapton</td>
<td>360</td>
<td>30-60</td>
<td>Yellow</td>
<td>1.80</td>
<td>2.5</td>
<td>231</td>
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<td>Glass</td>
<td></td>
<td>4-9</td>
<td>&gt;90</td>
<td>Low</td>
<td>50-90</td>
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<tr>
<td>Quartz</td>
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<td>&gt;90</td>
<td>Low</td>
<td>76-98</td>
<td>48</td>
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<tr>
<td>Si</td>
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<td>Low</td>
<td>130-185</td>
<td>7000</td>
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<tr>
<td>Stainless Steel</td>
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<td>Alumina</td>
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<td>High</td>
<td>215-413</td>
<td>69-665</td>
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</table>

TABLE S1 PHYSICAL PROPERTIES OF FLEXIBLE SUBSTRATES AND RIGID SUPPORTS (© BRUCE KAHN, PRINTED ELECTRONICS CONSULTING, 2014)

One of the most important substrate requirements for printed electronics is a low surface roughness. Surface imperfections can cause issues with device functionality, particularly for multilayer devices. The thinner the device layers are, the smoother the substrate surface needs to be. Low surface roughness is relatively easily achieved for rigid substrates like silicon wafers and glass, but much more difficult to achieve for flexible substrates. Silicon wafers and glass substrates are prepared in pristine environments from molten solutions, which gives rise to very smooth surfaces. On the other hand, flexible supports are usually extruded, which results in surfaces that are much rougher.
Furthermore, flexible substrates are usually much softer than rigid substrates, and more susceptible to scratches and other defects. Scratches in the surface can also cause problems with device performance. Dirt and foreign material are also serious issues for flexible substrates. There are many opportunities in the production process for flexible substrates that can result in dirt and defects. Extrusion can cause scratches, and various manufacturing processes like slitting and chopping generate particulates, which are problematic by themselves, but can also cause scratches.

Depending on the type of device, the optical properties of the substrate can be important. In the conventional semiconductor world, glass is the transparent substrate of choice. Fortunately, there are many choices of transparent flexible supports. The ones used most commonly for flexible electronics are PET and PEN. Both PET and PEN are transparent throughout the entire visible wavelength range. Other options for transparent supports are PC, PES, PAR, and PCO. Other optical properties like index of refraction can also be important in some cases.

The chemical stability/reactivity of flexible substrate materials can also be an issue for flexible electronics. Polymeric materials are much less chemical resistant than their rigid counterparts like silicon and glass. Polymeric materials can dissolve or swell in organic solvents. Their structural and optical properties can also change. Any type of chemical or physical change that is created by reactivity of the substrate material with materials that are patterned upon it can cause deleterious device performance.

Another substrate issue that is extremely important for certain kinds of devices is the absorption or permeability of the material to vapors and gasses. OLED devices are particularly sensitive to this, requiring H\textsubscript{2}O vapor permeability of \(< 10^{-6}\) g/m\textsuperscript{2}/day and O\textsubscript{2} permeability of \(< 10^{-3} - 10^{-5}\) g/m\textsuperscript{2}/day. Although these permeability rates are relatively easily achieved by rigid substrates such as silicon and glass, this is not the case for flexible polymeric supports. No polymeric material can even come close to the permeability requirements for OLED devices. So when OLED devices are created on flexible polymeric supports, other types of encapsulation are required. These barrier technologies are quite difficult to achieve, and can eliminate many of the very advantages (e.g. cost) that the production of flexible electronic devices were designed to achieve!
4. Diagrams of printing processes

FIGURE S2 MICROCONTACT PRINTING [9] (© 2001 IBM, USED WITH PERMISSION)
FIGURE S3 OFFSET LITHOGRAPHY
FIGURE S4 ROTARY SCREEN PRINTING (SOURCE: © HELMUT KIPPHAN, HANDBOOK OF PRINT MEDIA, SPRINGER, 2001)[10]
FIGURE S5 AEROSOL JET PRINTING (COURTESY OF OPTOMEC, USED WITH PERMISSION)
5. References


