University of Waterloo
Nanotechnology Engineering

NE 479.1
Prof. Hany Aziz

10 March 2010

[FLEXIBLE OLEDS]

Budd White (20214187) Goran Vlacic (20201180)

REVIEWS

Flexible Organic Light Emitting Diodes

G.B. White[1], G. Vlačić[2]

[1]Nanotechnology Engineering, University of Waterloo, gbwhite@uwaterloo.ca;
[2]Nanotechnology Engineering, University of Waterloo, gvlacic@uwaterloo.ca,

This report gives an overview of Flexible Organic Light Emitting Diode (FOLED) Technology. The technology's brief history is discussed as a precursor to descriptions of basic operation mechanisms, components involved, and fabrication processes. Recent advances in technology are included, such as the advantages of Cyclic Olefin Copolymer (COC) over traditional PET substrates, and the rise of Al/Alq3/Al and CNT electrodes as replacements for ITO and ZnO. The tradeoffs between improvements in flexibility, brightness and lifetime are pointed out to illustrate the possible direction that FOLEDs may go. Finally a market forecast and a commercialization outlook are given to illustrate barriers, competitors, unique competitive advantage, and to help define a future growth strategy.

1. BACKGROUND

1.1 History

Compared with other organic technologies the history of Flexible OLEDs is short lived. It began as a subsidiary of the Organic Electronics field in 1992, when a research group first took their OLED device design and used all flexible layers [1]. The idea may not have come so recently, but the first efficient working devices certainly did. Since then, there has been an explosion of research in the Organic Electronics field, and likewise so in the Flexible Organic Electronics Field. Although the first OLEDs were made using small organic molecules, by the time the idea of flexible layers came around researchers had already started to use large polymer molecules to emit light since it was much less expensive to make large polymers into sheets. The sheets are now more suitable for large-screen displays, rather than using expensive vacuum deposition methods as was done with small molecules.

In the early 1990s, only research groups in academia were interested in the investment, but now it has been quickly taken up by most if not all of the world's major electronics superpowers. Sony released a video of a working device only a few years ago, in 2007, and Kyocera, Phillips, LG, and Samsung have all showcased concept prototypes at electronics shows the world over. These devices have gone from a field in its infancy to a booming world of possibilities over the last 20 years, and have just now begun to find themselves a niche in this enormous market.

1.2 Basic Device Operation

An OLED is a solid-state semiconductor device ranging in thickness from 100 to 500 nanometers thick. Similar thicknesses are seen Flexible OLEDS; which are simply defined as OLEDs that can bend (no set bending radius required for official definition yet). Flexible OLEDS (hereinafter commonly referred to as FOLEDs) may or may not be thicker or thinner than standard OLEDS, depending on the material used in each of the device thin film layers, but on average the device thickness is approximately the same. Figure 1 below shows the device structure and components, which hold true for OLEDs and FOLEDs as well.

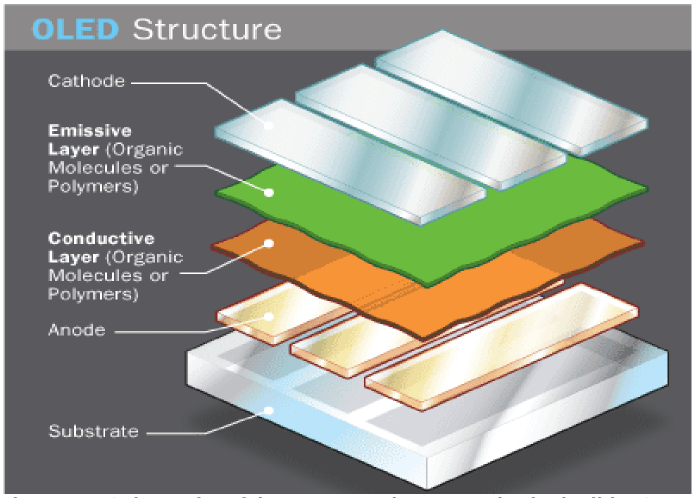

Figure 1: Schematic of layers seen in a standard Flexible OLED device. More recent technology incorporates more organic layers.

1.2.1 Components & Materials

Just like normal OLEDS, Flexible OLEDs can have either two layers of organic material, or three; the latter being the more commonly seen in current devices, since the third layer helps transport electrons from the cathode to the emissive layer.

From bottom to top, the layering is as follows: Substrate, Anode, Conductive Layer, Emissive Layer, Cathode, and then possibly another substrate to close up the device. A sealant may also be placed around the entire device as to avoid leakage, and improve performance by reducing water vapor and oxygen transmission. All of the aforementioned layers need to be flexible. This may seem obvious, but it is harder said than done; especially when it comes to performance optimization.

Looking first at the Organic layers (Emissive and conductive) we see that they are made of organic plastic molecules that are capable of transporting charge carriers through them. The conducting layer transports holes and is commonly made of polyanaline, whereas the emissive layer transports electrons and is usually made of polyfluorene. The substrate in standard OLEDS is usually a clear plastic, glass or foil. However, in Flexible OLEDs the brittleness these materials bring is unacceptable. Such is also the case for the two electrodes (the cathode and the anode) which are usually made of classic electrically conductive materials like aluminum or chromium. These metals are often far too rigid. So, in order to bend, much less brittle alternatives must be found; metal foils, blends of metal / organics [2] [3], nanostructure matrices [4], hybrid polymers [5], and thinner metal oxides and are among some of the top candidates at the time being.

Since the focus of this report is making OLEDs flexible, the layers discussed in greater detail hereinafter will be the three that are brittle in classical OLEDs and thus require alternatives; flexible cathodes, flexible anodes, and flexible substrates. The pure organic layers (emissive and conductive) are flexible by nature and substitutes do not need to be sought for them; regardless of if there are two or three layers of them.

1.2.2 Operation Mechanism

The physics of operation of Flexible OLEDs are nearly identical to that of regular OLEDs. An electrical current flows from the cathode to the anode through the organic layers. The cathode gives electrons to the emissive layer of organic molecules. The anode removes electrons (gives holes) from the conductive layer of organic molecules. At the boundary between the emissive and the conductive layers, electrons recombine with holes and give off photons.

The color of emitted light depends on the type of organic molecule in the emissive layer, and the intensity depends on the current applied (more current creates a brighter emission).

1.2.3 Fabrication

When assembling Flexible OLEDs the substrate is the simplest step, since it can be obtained pre-fabricated, or can be deposited onto almost any surface to later be removed For a while the hardest part of fabricating OLED devices was thought to be applying the organic layers to the substrate. This is classically done with Vacuum deposition, organic vapor phase deposition, inkjet printing, or organic vapor phase printing. Vacuum thermal evaporation, which is traditionally expensive (but works well for mass production) requires high heat which does not bode well with some of the flexible polymer substrates like PET. Organic vapor phase deposition , inkjet printing, and the new organic vapor phase printing, all have a potential future cost advantage and cooperate better with most flexible materials, which often contain heat sensitive organics that must be kept below 300°C [9].

For example, any use of polymers as a substrate, blend, or a suspension matrix for nanostructures, forces closer observation of heating in the fabrication process. The electrodes, which used to be thought of as the easy step, now pose difficulties in synthesis. For example, nanostructure matrices are difficult enough to synthesize accurately on a substrate alone [4], but they now need to be deposited on top of other sensitive organic layers, which introduces new challenges in device synthesis.

2. TECHNOLOGY / APPLICATIONS PERSPECTIVE

This section will cover some of the key requirements of Flexible OLEDs, and their component layers. Then device applications, as well as advantages and disadvantages perspectives will be given.

2.1 Flexibility

It may seem intuitive to say that Flexible OLEDs need to be flexible, but here the exact degree of flexibility in order to deem them useful for technical applications is given as a specific technical requirement. Recent research has shown that panels of FOLEDs can have a bending radius of 3 cm [2]. This means that you can roll up the array into a cylinder with a radius as small as 3 cm, and the device will not break, nor will lines form on your display. OLEDs typically break because the layers that are used to make them cannot withstand the stress and strain that is generated when curving the array. So a bending radius of less than a few inches would be ideal, and current research has already achieved this. Clearly the smaller the bending radius the more flexible and thus better the device, so researchers will work hard to reduce this as much as possible by testing out a variety of different materials for each and every layer. Reducing the thickness of each layer also helps in improving flexibility and dropping the thickness below the 100-500 nm is something researchers are trying to currently achieve.

2.2 Brightness

Another important characteristic from the user's perspective is the brightness of the display. Currently FOLED displays can reach a brightness of 8910 cd/m^2. [6], which falls short of the ~10000 cd/m^2 threshold needed to compete with current display technology. There is no doubt that FOLEDs can eventually meet the brightness requirements of standard displays, but at what price. Brightness and flexibility are often tradeoffs, and the major manufacturers need to decide what consumer segment they will target. They can make them extremely flexible without much concern for brightness (one type of consumer base) or a lot brighter with limtted flexibility (completely different consumer base), possibly even somewhere in between. A proper tradeoff will be looked at later when comparing market trends and commercialization potential.

2.3 Bending Cycles

Although FOLEDs bendabiliy also bestows upon them the very appealing feature of high impact resistance, they do have a mechanism of destruction. After a given number of bending cycles, the performance of the array starts to degrade. A study was done in which a FOLED array was bent then returned to flat 80 times. After 80 cycles, it was found that the brightness of the display decreased from 8910 cd/m^2 to 5760 cd/m^2 [3]. This study was done using 150 nm thick aluminum cathodes and anodes. It was found that the reason for degradation of performance was due to an increased sheet resistance of the electrodes. Similar experiments were also run with different blends of aluminum, some even containing an organic layer between two layers of aluminum, and the observed degradation rate was very much the same [3].

2.4 Efficiency

Another key requirement to look at is the efficiency of the device. FOLEDs are currently at an efficiency of 14.5 cd/A [3]. This is currently well below the performance of OLEDs at 38 cd/A. This may seem very low right now, but just like all the other requirements, efficiency comes at a tradeoff of other parameters. Again, target consumers must be looked at prior to choosing a key requirement balance.

2.5 Materials

Materials used are possibly the most important requirement for FOLEDs and will thus higher significance will be put towards them. All the layers should have a low coefficient of thermal expansion, low moisture absorption, and the substrate should be resistant to chemicals and solvents [9].

2.5.1 Substrate

Some of the materials being used as a substrate in FOLEDs include: plastics and pure polymers, metals, and metal foils. There are a variety of tradeoffs between these three, with plastics and polymers currently holding dominance.

Pure organics, and plastics classically used as a substrate material such as PET are highly flexible, but they let in moisture and oxygen which ruins the other organics (lifetime degradation). To prevent this, different types of sealants can be used that will provide better device encapsulation.

Metals on the other hand don’t allow much moisture and oxygen in, but they have limited to no flexibility.

One recent advance in the field of flexible substrates has been the dawning of a new polymer type Cyclic Olefin Copolymer (COC). COC has only recently begun to replace polypropylene and polyethylene in lenses, vials, medical devices and monitors. COC offers a higher transparency and thus a clearer and crisper FOLED device [9]. One recent study found that the higher visibility was due to smoother surface roughness as measured my AFM. COC is also able to better protect against vapor permeation than classic PET substrates [9].

2.52 Electrodes

The most important requirements of all, due to its elusive hard-to-achieve nature, are flexible electrodes. The traditional approach is to use metal oxides like ITO, but as FOLEDs become more flexible and more robust, new materials start coming in. Some examples include Carbon Nanotube (CNT) Matrices [4], patterned metal oxides [7] [11], and alternative metal/organics [2] [3].

A traditional approach is to use patterned ITO, which with higher and higher thickness lowers the voltage needed to operate the device, which is great, but also causes poor current density, luminescence, and flexibility, and also makes the surface rougher (less clear) [11]. Something that has been shown to improve ITO performance, has been to dope it with ZnO, another common metal oxide used as a transparent and/or flexible electrode material [7]. However, keep in mind that when they are thick enough ITO and ZnO are both very brittle, and when they are thin, they need higher operation voltages; again a tradeoff between performance and flexibility, two key requirements.

More recent work has been done to layer Aluminum with an organic sequentially. For example, one study used a 150 nm Aluminum layer then a 20 nm Alq3 layer (organic) then another Al layer, this time only 50 nm as their electrode material (Al (150 nm)/Alq3 (20 nm)/Al (50 nm))[3]. This proved decrease the rate at which current density decreases compared with thin foil Aluminum electrodes of 150 nm and 200 nm, thereby extending the lifetime to almost twice as much [3].

Finally, recent study shows a drastic increase in FOLED performance with the use of CNT electrodes [4]. The use of this breakthrough material has yielded bend radii of 1.25 cm. However, since CNTs on their own can have scattered undesired vertical alignment, they can cause poor carrier injection and possibly shorts. However, when dispersed into PEDOT:PSS and methanol they tend to flatten out, and we see a lot of these issues go away [4]. Furthermore, CNT electrodes show minimal degradation after over 10000 bend cycles. These statistics suggest that FOLEDs, when paired with CNTs in polymer matrix electrodes, may be able to compete in the display market in the near future.

2.2 Competitor Comparison

Two of the main competitors of the FOLED array are OLEDs and LCD displays. Despite having similar device applications, Electrophoretics will be excluded until later on because of the difference in device structure.

Let's first look at how FOLEDs compare to OLEDs. FOLEDs have many advantages, first of which is their durability. Because the substrate used does not have to be glass, materials with a better impact resistance can be used. This in turn makes the device able to withstand impacts such as being hit by a hammer. Next, an obvious advantage is that FOLEDs are flexible and OLEDs are not. This allows for FOLED displays to be rolled up, making a more compact device for storage or travel. FOLEDs can also be integrated into textiles because of their flexibility. This allows them to be integrated into clothing for fashion or function. Lastly, since FOLEDs are flexible, they can compete in both the rigid display (due to increased durability) and the flexible display markets.

FOLEDs have a few critical disadvantages compared to OLEDs though. First, since the nature of the device is to withstand bending cycles, and the device degrades in brightness with increased cycle time, it cannot currently be used as a sustainable device. Next, since a flexible substrate is used, there is the likelihood of the user to bend the display more than the threshold bend radius and cause permanent damage to the diodes.

Let's now take a look at the advantages of FOLEDs over LCD displays. First, FOLEDs can be made using printable layers at low temperatures. This is a much faster method of fabrication then current silicon techniques. Once the printable layer technique becomes mainstream in the manufacturing community, the print per device will become less than that of silicon devices. Again, this is a function of the number of manufacturers that put time in to optimize this process. FOLEDs also have a higher contrast ratio then LCDs because they do not use a backlight when displaying black. To display black, they can simply turn off the pixel. Another advantage is the viewing angle obtained by FOLEDs. Due to the lack of filters needed in OLEDs, a viewing angle of close to 90 degrees can be obtained. Next, FOLEDs have a much faster refresh rate than LCDs. The refresh rate is as fast that with CRT displays. Finally, FOLEDs are much thinner then LCDs.

FOLEDs also have disadvantages compared to LCD. First, FOLEDs consume much more energy when displaying white. This issue sounds minimal, but a majority of websites and eBooks have a lot of white space. This will quickly drain the battery of any portable device. Next, without a proper seal on the device, contact with water will degrade the organic materials in the device. Finally, there is also an increased risk for an image to burn onto a FOLED screen if it is left for a long period of time.

This competitor comparison goes along with one of this review‘s main conclusions; there are tradeoffs between FOLEDs and existing technology and manufacturers need to identify their target consumer base before trying to optimize all requirements at once.

2.3 Barriers and Limitations

Currently, the biggest barrier for FOLEDs to get to market is their price. Although the process to make devices is much simpler than that of silicon; silicon is still the market norm. Since every electronics company out there has helped to optimize the silicon manufacturing processes and OLEDs are new to market, they currently cannot compete. An example of this comes from Sony recently pulling their XEL-1 OLED digital TV from store shelves because it was too expensive and too small for consumers to justify its added value. This barrier will be broken in the near future as the manufacturing process starts to be optimized by the companies that are buying into the market.

The other major barrier to market that FOLEDs face is its performance degradation after a number of bending cycles. Studies have shown that after a number of bending cycles, the brightness of the device is reduced. This barrier is not as large as the first, as recent research in CNT electrodes has shown itself to potentially mitigate or eliminate this problem.

2.4 Competition & Applications

The technology of a bending array of OLEDs has a bright future as it has many potential applications including clothing, packaged goods, e-readers, large displays, billboards, portable computers, and cell phones to name a few. Since its substrate is flexible, it is impact resistant. This means that it can also be applied to any device that is currently using an electronic display to making the device more flexible and durable.

The main competitors, in both the rigid and flexible display markets, are traditional LCDs, bi-stable LCDs, OLEDs, electrophoretic devices (e-paper), electrochromic devices, and electroluminescent devices. The next section will go beyond this and recommend specific applications in a sea of possibilities and swarm of competition.

3. COMMERCIALIZATION OUTLOOK

OE-A, an Organic Electronics consortium organization does a fantastic job of summarizing the potential commercialization of flexible OLEDs in the short and long run, as seen in the figure below.

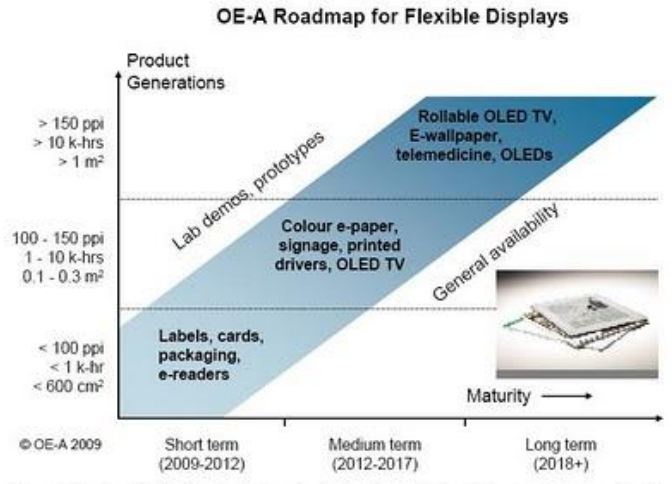

Figure 2: Display Market Analysts believe that Flexible OLEDs are best suited for the labels, cards, packaging, and readers niche, at least for the next 1-5 years, while LCDs still hold market dominance in large flat panel displays.

Due to the creativity of applications for these devices, surprise investors include pharmaceutical and consumer goods packaging companies; they may even be more suited for flexible OLEDs than large display manufacturers, at least in the short run. Major investors in this field include BASF and Bayer, who are both looking to use flexible OLEDs for expiry tags and packaging, possibly even clothing one day.

Large display manufacturers companies interested in the technology include Sony, LG, Kodak, Samsung, and Phillips, which look to use flexible displays in TVs, projectors, and billboards. However, price and manufacturing time are still major barriers to overcome before widespread success within this field, especially given the power of the competing technology mentioned earlier.

Possibly the field of application holding the highest commercialization potential for flexible OLEDs in the near future are durable mobile devices displays, such as those for cell phones, smart phones, and electronic readers. With companies involved including Sony, LG, Samsung, Google, Nokia, Universal Display, Comedo, and Add-Vision to name a few.

Another roadmap from OE-A reiterates the fact that there is enormous competition for the endless potential applications, and that Flexible OLEDs need to find their niche, rather than dream of taking over the entire electronics industry.

Figure 3: Where Flexible OLEDs fit in the bigger picture of Organic Electronics Market Segmentation [8]

Taking a brief look at some market forecast figures tells us that flexible displays have the potential to cash in big time. However, this is to be taken with a grain of salt, considering few market forecasts are accurate this far in advance, especially in such a vibrant and fast-paced industry.

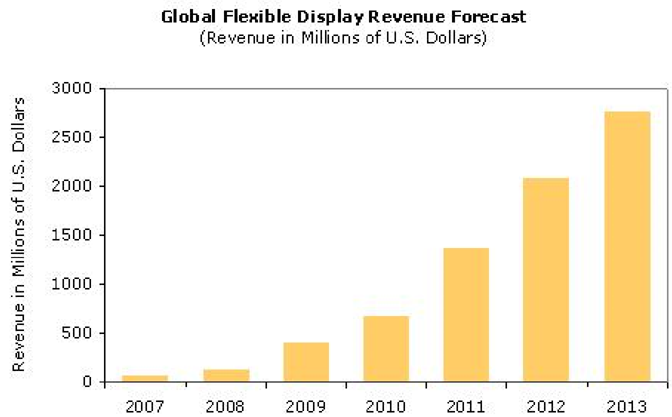

Figure 4: The Global Flexible Display Market, Revenue Forecast as of 2007 [8]

The figure below contrasts the above with a big picture view of the display market, and points out the momentum that certain completion like e-paper has.

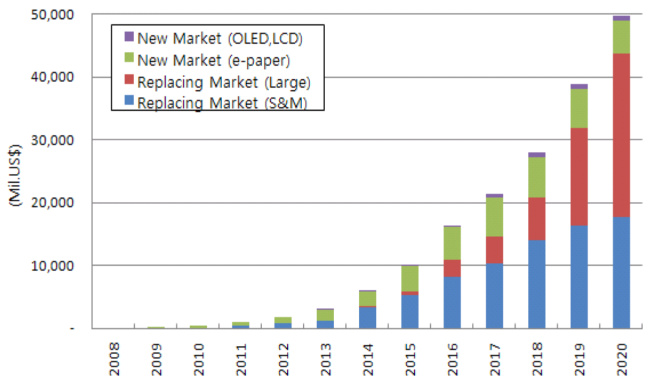

Figure 5: Perhaps the entire OLEDs will fail to gain momentum over some of their competitors, but Flexible OLEDs could differentiate themselves [8]

Competition is fierce and OLEDs (Flexible ones inclusive) are not given much credit by this particular market forecast

4. RECENT ADVANCES

Many of the recent advances in final FOLED products have come thanks to the research effort being put towards flexible electrodes and substrates, as well as other materials as these are currently the key performance limitations. The key technical and research advances have been covered in previous sections and will not be touched upon again. Rather we shall look at some of the big advances in end products that have come as a result of years of work in the past.

Sony Electronics is making one of the largest pushes into the FOLEDs market. After pulling their XEL-1 from production in Japan, they are said to have diverted a portion of its large display OLED research funding to FOLEDs. Two of its devices at the 2009 CES are worth noting: the 4 inch color FOLED display, and their flexible OLED notebook.

Let's first look at Sony's 4 inch display. This bit of technology combines OTFTs and FOLEDs to create a colored, flexible active-matrix display. This device solidifies the notion that FOLEDs will be able to bridge the gap from academia to market. This AM display will start to be integrated into some of Sony's new products in the near future.

Figure 6: Sony's OTFT Flex OLED

Another big player in the Asian display industry, Kyocera, has recently released a concept prototype of a mobile communication device, as seen in Figure 7 below.

Figure 7: Kyocera's new mobile laptop / communications device hybrid

This device further pushes the boundaries of technology as it integrates capacitive sensing into an AM-FOLED display, which results in a foldaway notebook computer that has a keyboard build into the screen. This advancement is sure to make its mark on the display industry in the years to come.

The years ahead for Flexible OLEDs will be challenging, exciting, and possibly ripe with rewards. Only time will tell if manufacturers make the right strategic commercialization decisions.

REFERENCES

1. G. Gustafsson, Y. Cao, G. M. Treacy, F. Klavetter, N. Colaneri & A. J. Heeger, Flexible light-emitting diodes made from soluble conducting polymers, *Nature*, 1992, **357**, 477 - 479
2. Y-H Cheng,, Demonstration of Organic Light Emitting Diodes Fabricated on Flexible Al2O3 – Embedded Poly(dimenthylsiloxane) Substrates, *Japanese J. of Apl. Phys*, 2010, 1-5
3. D. Lian, Improved flexibility of flexible organic light-emitting devices by using a metal/organic multilayer cathode, *J. Phys. D: Apl Phys*, 2009, **42**, 1-4
4. E. Ou, Surface-Modied Nanotube Anodes for High Performance Organic Light- Emitting Diode, *ACS Nano*, 2009, 2-3
5. O. Yilmaz, S. Chaudhary, M. Ozkan, A hybrid organic-inorganic electrode for enhanced charge injection or collection in organic optoelectronic devices, *Nanotechnology*, 2006, **17**, 15, 3662
6. E-J Tung, A High Efficiency Phosphorescent White OLED for LCD Backlight and Display Applications, *Toyota Industries Technical Review*, 2005, **50**, 33-35
7. Z. Y. Xie , Y. Q. Li , F. L. Wong & L. S. Hung,

Fabrication of flexible organic top-emitting devices on steel foil substrates, Mat. Sci. and Eng., 2003, **106**, 3, 219-223

8. Organic Electronics Association, Market Forecast Roadmaps, *OE-A*, 2007, available online: [http://www.vdma.org/wps/portal/Home/en/Branchen/O/OEA/?WCM_GLOBAL_CONTEXT=/vdma/Home/en/Branchen/O/OEA/]

9. H.H. Yu, S-J Hwang, & K-C Hwang, Preparation and characterization of a novel flexible substrate for OLED, *Optics Communications*, 2005, **248**, 1-3, 51-57

10. Y. Cao, OLED Display, University of Notre Dame, available online: [http://www.nd.edu/~gsnider/EE698A/Ying_Cao_OLED.pdf]

11. H-H Yu, S-J Hwang, M-C Tseng, & C-C Tseng, The effect of ITO films thickness on the properties of flexible organic light emitting diode, *Optics Communications*, 2006, **259**, 1, 187-193