Final Scientific / Technical Report

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Solution-Processable Transparent Conductive Hole Injection Electrode for OLED SSL

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DISCLAIMER

Executive Summary

An interconnected network of silver nanowires has been used as transparent anode in OLED devices. This layer was deposited by spin-coating and slot-die coating from an aqueous nanowire suspension. The sheet resistance of the film was 10ohms/sq with a transmission (including the glass substrate) of higher than 85%.

The first phase of the project focused on the implementation of this nanowire layer with a hole-injection-layer (HIL) which has been developed at Plextronics and has been shown to provide good stability and efficiency in conventional OLED devices. We modified the HIL solution such that it coated reasonably well with suitable surface morphology so that actual devices can be manufactured.

During the second phase we investigated the hole-injection and stability of hole-only-devices. We determined that the use of the nanowire network as anode does not introduce an additional degradation mechanism since the observed device characteristics did not differ from those made with ITO anode.

We then proceeded to make actual OLED devices with this nanowire / HIL stack and achieved device characteristics similar state-of-the-art OLED devices with a single junction.

In order to gain traction with potential OLED manufacturers, we decided to contract Novaled to prepare large-area demonstrators for us. For these devices, we used an all-evaporated stack, i.e. we did use Novaled’s HIL material instead of Plextronics’. We successfully fabricated demonstrators with an area of 25cm2 with a double or triple junction stack. Minor stack optimizations were necessary to achieve efficacies and lifetime equivalent with ITO devices made with the same devices stack.

Due to the reduced microcavity effect, the color of the emitted light is significantly more stable with respect to the viewing angle compared to ITO devices. This fact in conjunction with the promise of lower production cost due to the elimination of the ITO sputtering process and the direct patterning of the anode layer are the obvious advantages of this technology.

The project has shown that this nanowire technology is a viable option to achieve OLED devices with good lifetime and efficiency and we are currently working with manufacturers to utilize this technology in a production setting.

Motivation

To date, Indium Tin Oxide (ITO) is still the dominant transparent conductive material used as the anode for fabrication of OLEDs. Replacement of ITO, as highlighted in the MYPP, has been one of the key areas of focus. Although other sputtered transparent conductive oxides (TCO) such as Al:ZnO can have comparable transmission and conductivity, they continue to suffer from similar drawbacks such as brittleness, cost of sputtering, and compatibility with low temperature, flexible substrates. Some such TCOs, in addition, suffer from difficulty in patterning and sensitivity to moisture. Ideally, an ITO replacement could be deposited using wet coating methods to significantly reduce coating and patterning costs (through direct printing), have good flexibility, similar transmission and conductivity to ITO, and without any negative impact on device performance and lifetime. Candidates such as conducting polymers and Carbon nanotubes have been proposed as replacements to ITO, however, despite more than a decade of development, these materials suffer from such fundamental shortcoming as low transmission and high bulk resistance.

Cambrios has created a novel coating material that produces a transparent, electrically conductive electrode targeted for touch screen and liquid crystal display applications. This coating material, called “ClearOhm™”, consists of an aqueous suspension of metallic nanowires. In addition, Cambrios is able to tailor fluid properties such as viscosity and surface tension by including other additives to create formulations suitable for various coating methods. Upon deposition of the coating material on a surface and drying, the metallic nanowires form a highly efficient connected network that has good conductivity and due to the low percolation threshold of the nanowires on the surface, also has high transmission (see Figure 1).

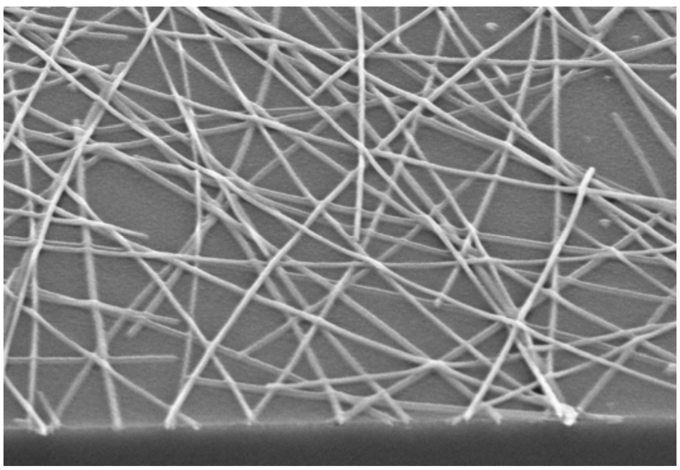

Figure 1: ClearOhm™ transparent conductor consisting of a percolated network

By changing fluid properties and coating parameters, conductivity of the layer can be readily tailored to cover a wide range. Key features of the material are:

- Competitive transmission and conductivity as compared to ITO
- Low process temperature at all sheet resistances enabling compatibility with many types of substrates; particularly at high conductivities required for lighting applications
- Flexibility: due to the layer consisting of highly flexible metallic nanowires, the coated films are extremely flexible and can go through many bending cycles with < 1mm bending radii
- Compatible with many types of existing wet coating equipment and techniques such as slot die, gravure, spin coating etc. This allows rapid deployment of the material onto exiting production lines

The goal of the project was to use Cambrios' ClearOhm™ material as an OLED anode replacing the ITO layer and use the material and process characteristics to optimiz the device performance. In order to ensure that hole injection from the silver nanowires into the emitting layer of the OLED is ensured, we used Plextronics' HIL material which also needed to be optimized to achieve good coating properties on out nanowire film.

In particular, we set out to achieve the following goals:

- Similar transmission and conductivity to ITO coating plus the same HIL layer
- Demonstrate OLED devices with similar or better efficiency as compared to a reference device using ITO
- All process temperatures used to form the electrode will be compatible with using low temperature flexible substrates such as PET

Project Plan

The project was divided into four phases over two years. The main targets for each phase are given below.

PHASE I

- Develop clear understanding of electrode requirements
- Demonstrate planarized two-material electrode film that meets basic film level specification requirements

PHASE II

- Downselect materials systems and demonstrate optimized hole injection into hole transport layer with the down-selected materials combination

PHASE III

- Demonstrate SMOLED and PLED devices using TCHI electrode using commercial emitter stacks

PHASE IV

- Demonstrate OLED device using a state-of-the-art emitter stack in a devices made by a commercial OLED manufacturer

Technical Discussion

We will use the aforementioned phases to guide following technical discussion. In each section we will compare the achieved milestones with the project plan.

PHASE I

We investigated three different nanowire types with different geometries that were synthesized at Cambrios and analyzed their performance with respect to the application as OLED anode (C-AFM, work function). In addition, we also measured surface roughness (coated on glass) which is shown in Table 1. The RMS scales very well with the nanowire dimension and we decided to use the type “G4” for this project because of the low RMS value.

NW ink	RMS [nm]
G1: 180-054	21
G2: 180-053	18
G4: 180-055	15

Table 1: RMS roughness of different NW types

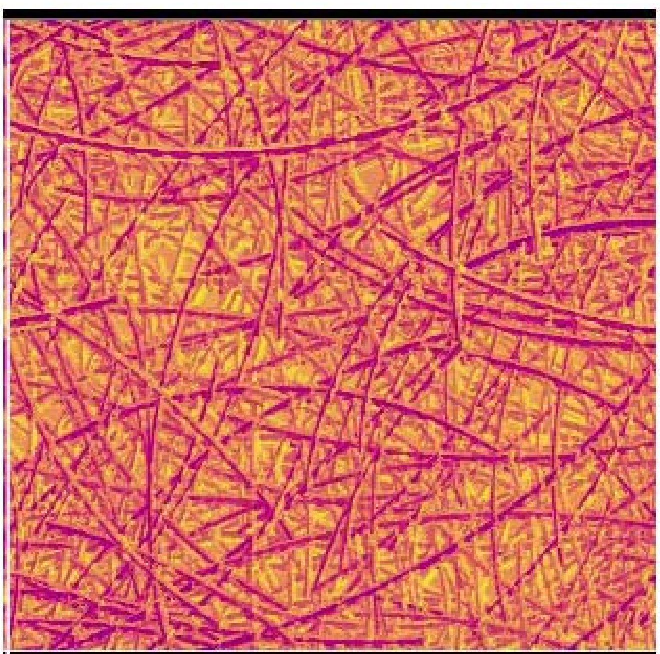

Figure 2: AFM on a glass surface coated with nanowires at 9ohms/sq

Figure 2 shows an AFM image of a glass surface coated with G4 nanowires. The sheet resistance of this film is 9Ω/sq with a transmission of 85.7% and a haze of 4.7%.

In addition to the actual silver nanowires, the nanowire dispersion also contains a polymeric binder and other proprietary components. The binder stabilizes the nanowire dispersion as well as promotes the adhesion of the nanowire on the surface of the substrate. In the AFM image below, the presence of the binder can clearly be observed.

Parallel to the characterization of the nanowire layer, the HIL formulation was optimized for coatability at Plextronics. The resulting improvement is shown in Figure 3. On the left side, microscopic and macroscopic non-uniformities of the HIL coating are clearly visible. These non-uniformities were greatly reduced after the material has been appropriately reformulated.

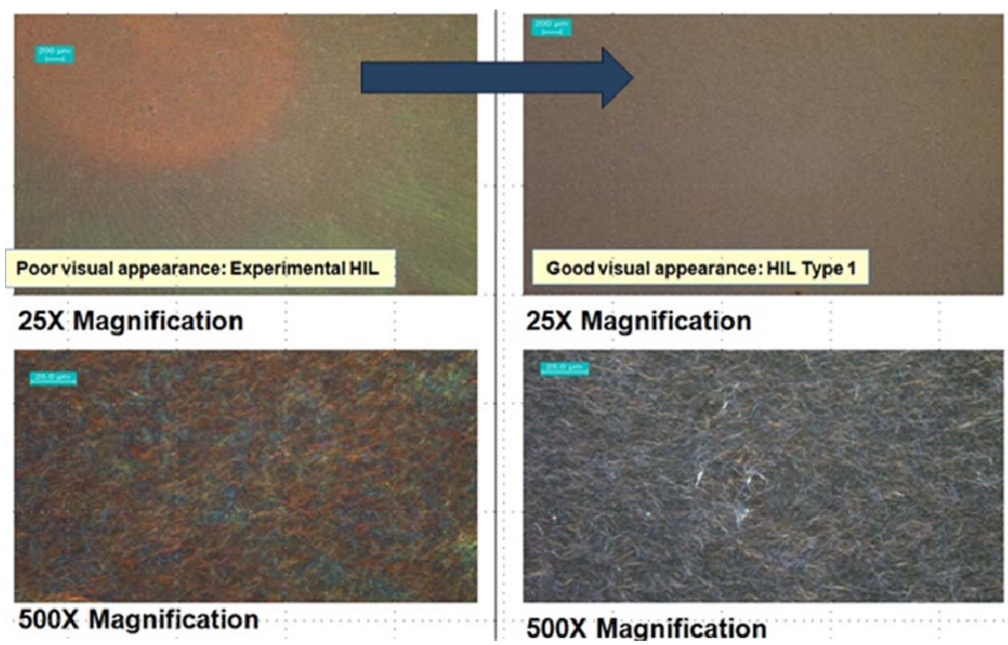

Figure 3: Coatability of HIL on nanowire layer before and after reformulation (DIC microcopy)

With this result, the goal for PHASE I has been achieved.

PHASE II

The next phase focused on fabricating hole-only-devices (HOD) in order to be able to characterize the hole injecting properties of the combined nanowire / HIL film.

To that end, devices with the following structure (see Figure 4) were fabricated at Plextronics.

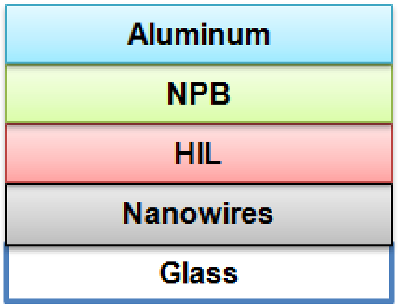

Figure 4: Device stack for hole-only-devices

The manufacturing process was as follows:

- Nanowire dispersion was spun-on and dried in air at 50C for 90sec, followed by 140C for 90sec
- Substrates are cleaned w/ 30s IPA sonication & dried with N2
- HIL is spun in air at 1000 – 6500 RPM depending on desired thickness; annealed in glovebox at 50C for 5min, followed by 120C for 20 min
- Substrates are transferred to vacuum chamber and then deposited with 100nm of NPB
- Al cathode is deposited
- Devices are encapsulated and rest for minimum 4 hours to allow the glue to fully cure
- Devices are IV characteristics are measured and lifetime tested

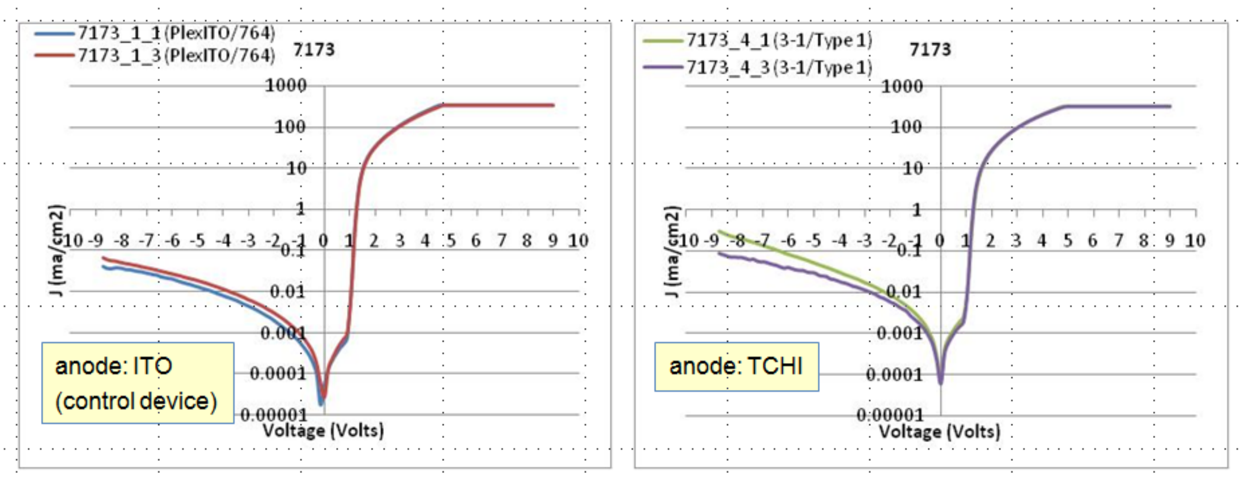

Figure 5: IV characteristics of device made with ITO (left side) and nanowire + HIL (right side)

The IV characteristic of these devices is shown in Figure 5. For comparison, a device with ITO was processed as a control and its IV measurements are shown on the left side. Comparing these two data sets, we observe that there is nearly no change in the IV characteristics of device made with nanowires + HIL coating compared to the ITO device. We therefore expect that we will not face any problems with hole injecting in an emitting device.

We also measured the voltage increase over lifetime. For this, we stressed the device with a very high current density (50 mA/cm2 which corresponds to roughly 25,000nits) and measured the required voltage. The results are shown in Figure 6. The voltage rise is actually smaller for devices made with the nanowire + HIL anode compared to a device with ITO anode. From this we conclude that we did not introduce any additional degradation mechanism by using a nanowire + HIL anode.

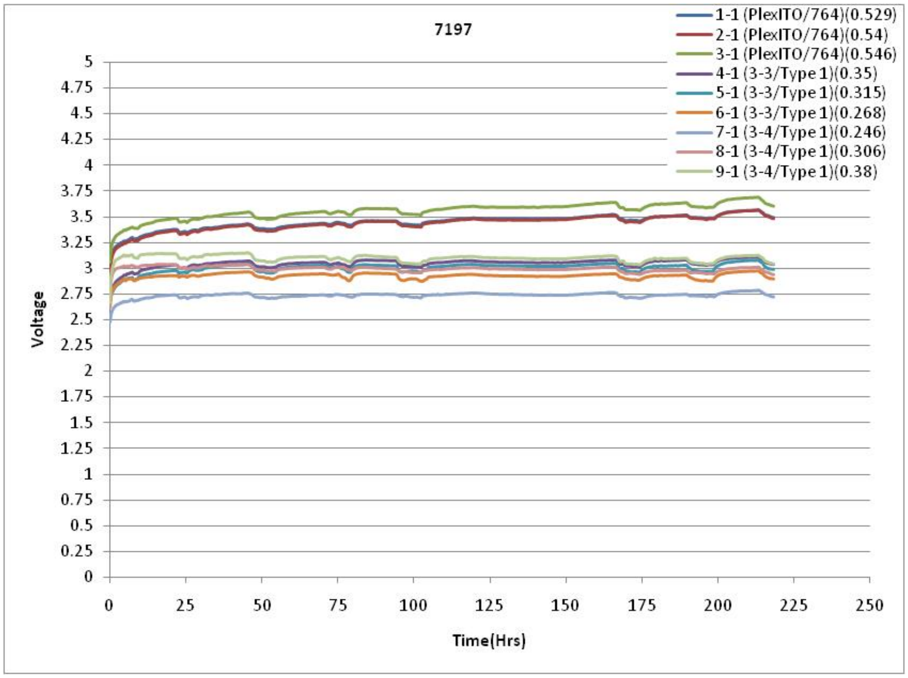

Figure 6: Voltage rise over lifetime of HOD device made with ITO (control) and nanowire + HIL

The results in HOD performance conclude PHASE II.

PHASE III

Actual OLED devices using the nanowire + HIL stack were fabricated in this phase at Plextronics. The stack used for these devices is shown in Figure 7. We then proceeded and measured the IVL characteristics of these devices as well as lifetime.

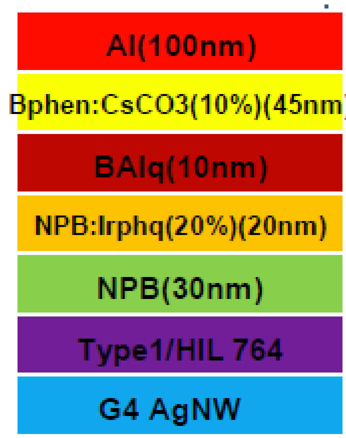

Figure 7: Structure of OLED stack

The IVL data is shown in Figure 8. From this data we infer that the electrical characteristics in forward bias are very similar between the ITO device (control) and the devices made with nanowire + HIL. In particular, we observe a similar turn-on voltage and similar efficiencies. In reverse bias, the leakage current is higher in device with nanowires. This is mainly due to the reformulated HIL since it exhibits a higher conductivity.

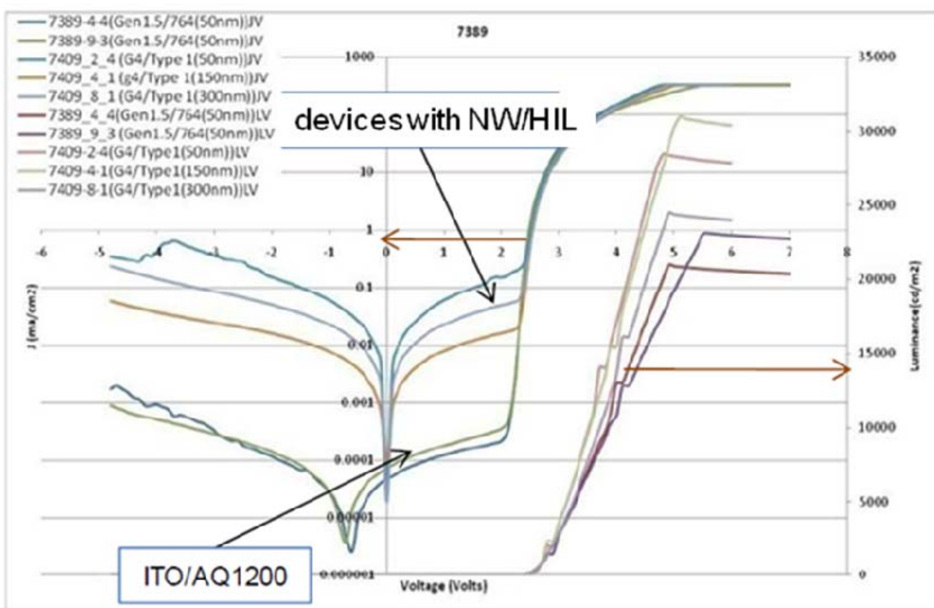

Figure 8: IVL characteristics of devices made with ITO (control) and nanowire + HIL

We also investigated the lifetime of these devices under highly accelerated conditions. The lifetime data is shown in Figure 9.

No additional degradation was observed in devices made with nanowires + HIL anode and also the voltage rise was very similar.

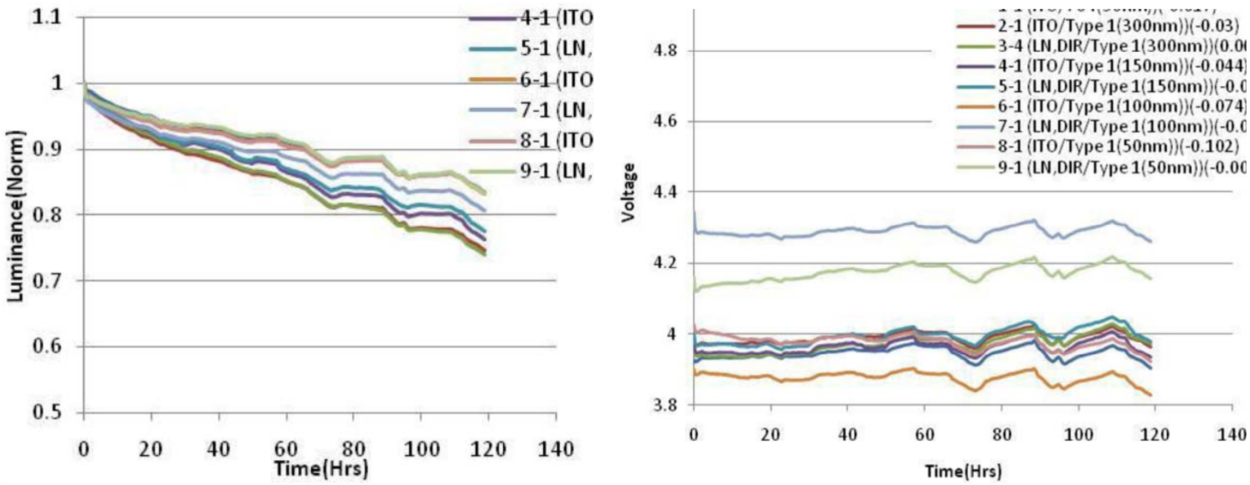

Figure 9: Lifetime data of OLED device with ITO anode (control) and devices made with nanowire + HIL

These results represent the successful accomplishment of milestones for PHASE III and we therefore decided to approach commercial OLED manufacturers with this technology.

PHASE IV

In this phase we approached commercial OLED manufacturers in order to evaluate the commercial viability of this technology. We realized that there is a considerable amount of interest to use the nanowire technology but at the same time a reluctance to switch the HIL material. Given that, we decided (after consulting with the DOE) to ask Novaled (Germany) to use our material as anode combined with their standard OLED stack. Novaled materials are widely used in the OLED market and proving that our material can be used in conjunction with their material would demonstrate the commercial viability of our technology.

We contracted Novaled and sent them our nanowire dispersion. Novaled did the deposition and patterning of this material as well as the deposition of their fully-evaporated OLED stack on top of this material.

The first devices were made with a tandem stack, i.e. to achieve white emission color, a blue and yellow emitting layer were incorporated in the device stack. The emission of such a device is shown in Figure 10 along with a photograph of a plate with OLED devices used to perform some process and stack optimization using a nanowire anode. The processing yield is very good as nearly all devices are functioning as shown in this image.

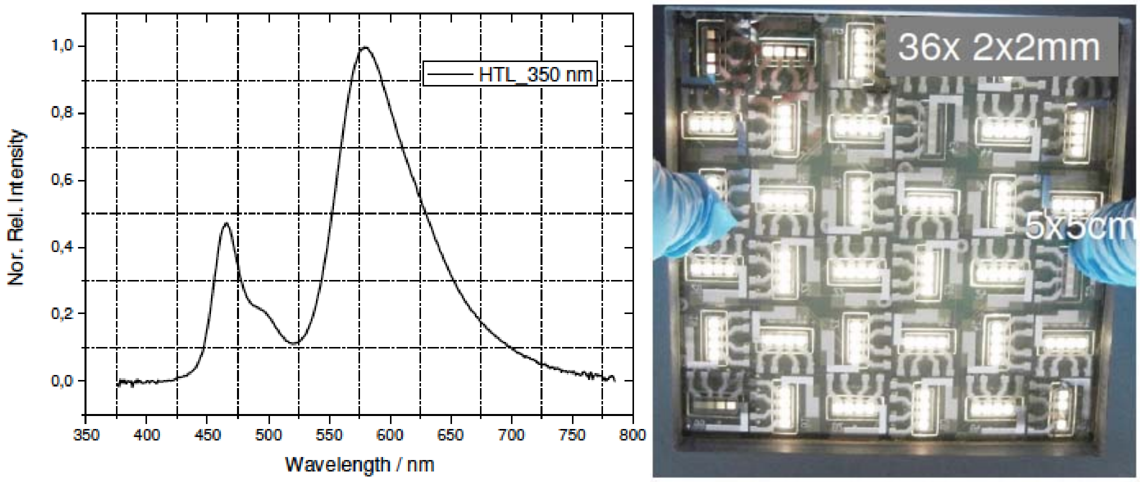

Figure 10: EL emission spectrum of tandem device (left) and plate with OLED devices made with nanowire anode

The goal of the collaboration with Novaled was the fabrication of large-scale demonstrators. To demonstrate the viability of our technology, we needed to prove that large-area devices are possible without shorts and that the performance of these devices is at least similar to ITO reference devices. To this end, we decided to fabricate 5cm x 5cm devices. Some preliminary device optimization was carried out on very small devices (as shown in Figure 10). These device parameters were then verified on devices with an emitting area of 2cm x 2cm. After this final verification, devices on the 5cm x 5cm scale were then fabricated.

Of great concern was the roughness of the nanowire layer. Using an evaporated HIL material on top of the rough nanowire film presented the risk that shorts are being caused because the evaporated material does only provide a conformal coating and will not result in a planarized layer.

Of great importance, therefore, was the choice of the optimal HIL thickness. On one hand, the layer needed to be thick enough to prevent shorts. On the other hand, the layer thickness should be minimized to avoid internal absorption and thus lower device efficiency.

The power and current efficiency of these devices is shown in Figure 11. While the impact on efficiency can be seen (with 330nm thickness resulting in highest efficiencies), the efficiencies are higher than the ITO control. The ITO control in this case is not the optimized stack but rather the same stack as used for the other devices and with an 880nm thick HIL. The efficiency of an ITO device with an optimized stack is slightly higher than the efficiency we obtained for the nanowire device with 330nm thick HIL.

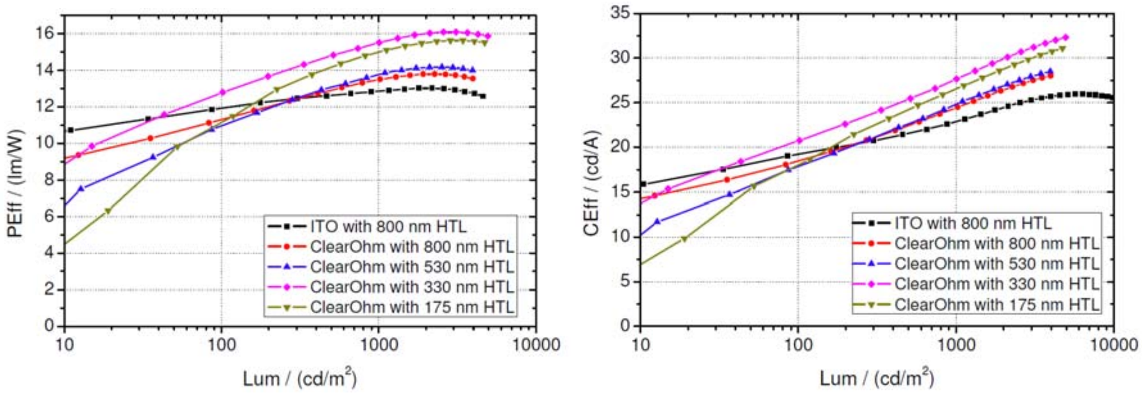

Figure 11: Power efficiency (left) and current efficiency (right) for devices made with ITO anode (control) and nanowire anode with different HIL thickness

The color dependence on the observation angle is an important issue in particular for lighting applications. Due to the microcavity effect in devices using ITO as anode, this color shift is quite severe if it is not addressed by internal or external means.

In devices using the nanowire layer, this microcavity effect is greatly reduced and we expected that this is also reflected in a smaller color shift with observation angle. Indeed, this has been observed as shown in Figure 12. The data shows that the shift in CIE-x and y is greatly reduced in devices made with nanowire anode as to compared to devices with ITO anode.

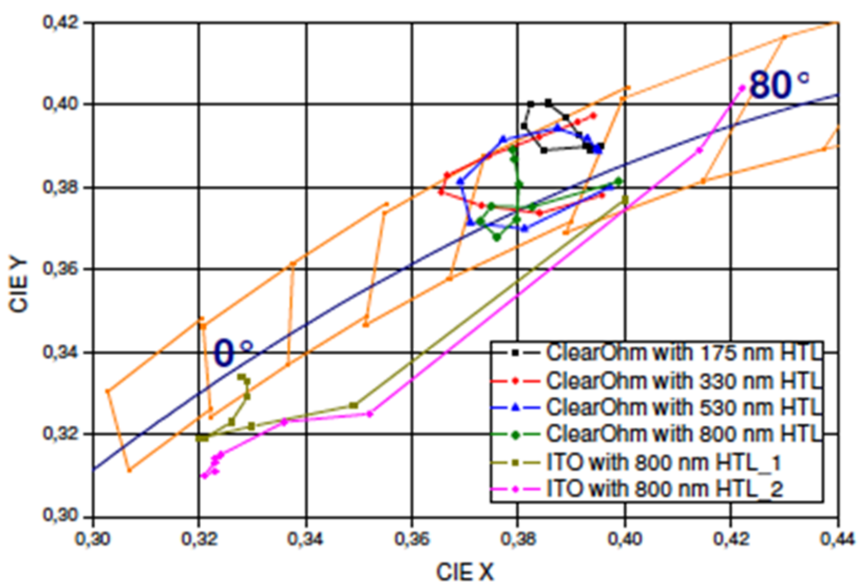

Figure 12: CIE-coordinates as a function of observation angle for devices made with ITO (control) and devices made with nanowire anode

Finally, we also tested the lifetime performance of nanowire devices in comparison to ITO devices. The results are shown Figure 13 for LT50 and LT70. No appreciable difference between ITO devices and devices made with nanowire anode could be detected.

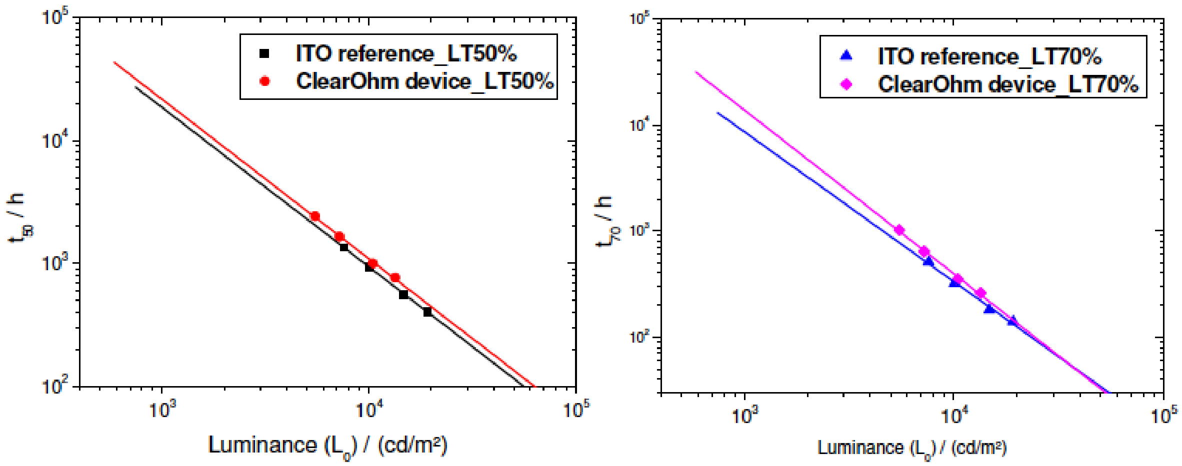

Figure 13: Lifetime data (LT50 and LT70) of devices with ITO anode and devices made with nanowire anode

To compare devices made with nanowires to state-of-the-art devices Novaled fabricated devices with a three-unit stack (where three emitting layers are deposited within the stack of the device) using a nanowire anode.

An image of the two large-area devices (both 5cm x 5cm) is shown in Figure 14. The emission color of the 3-unit was shifted because of unexpectedly low emission from the blue emitter. Further optimization of the layer thickness has since alleviated this effect.

The efficiency for this device is 43.3 lm/W (without light extraction layer) which is similar to device made with ITO anode.

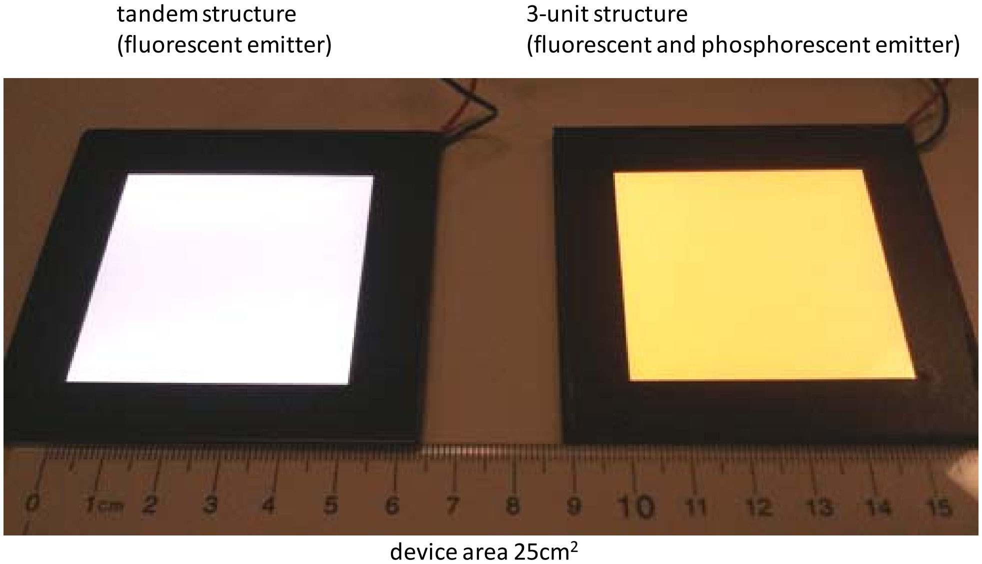

Figure 14: Image of large-area demonstrators made with nanowire anode (left: tandem stack, right: 3-unit stack)

Further optimization of the stack reduced the orange-shift of the device as shown in Figure 15. This graph shows how the CIE coordinates can be shifted towards a warm white by changing some of the layer thicknesses in the device stack. However, we were at this point not able to further blue-shift the color. Even with the optimized stack, the color is slightly outside of the DOE required are for warm white. Further (and probably more radical) stack optimization is needed. This optimization was, however, outside of the scope of this project.

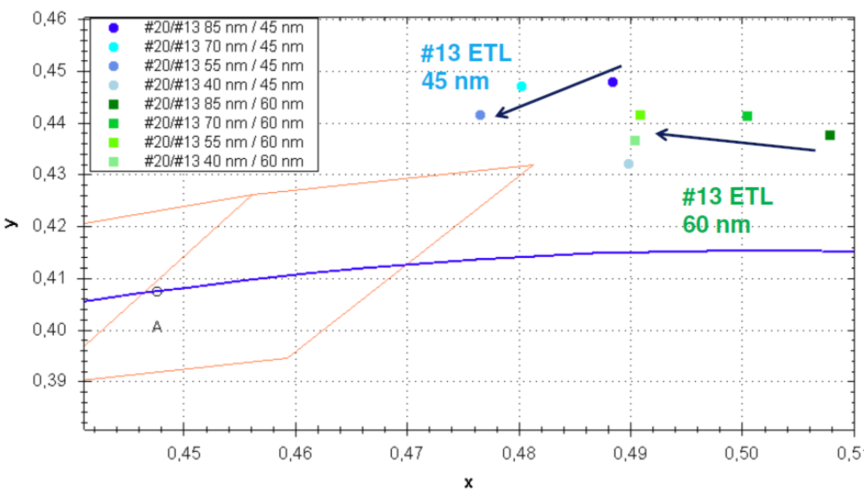

Figure 15: CIE coordinates for optimized 3-unit stack where stack modifications are being used to blue-shift the emission color

Summary

We have achieved the transmission and conductivity of the nanowire layer + HIL as specified in the project plan.

By using either Plextronics’ or Novaled’s HIL, we were in both cases successful in demonstrating OLED devices with similar or better efficiency as compared to a reference device using ITO.

Furthermore, we were able to demonstrate a manufacturing process to form the electrode which is compatible with using low temperature flexible substrates such as PET.

In summary, we have achieved OLED devices using a) a modified HIL provided by Plextronics, and b) a fully evaporated stack fabricated by Novaled. These devices perform comparable to devices made on ITO with respect to current efficiency, power efficiency and lifetime.

In terms of color stability with observation angle, devices based on nanowire anode show a distinct advantage compared to ITO devices.

Conference Papers and Proceedings

IMID Conference (2011, Seoul, Korea)

DOE SSL R&D workshop (2012, Atlanta)