

FINAL PROJECT REPORT

Project Title: Application of Developed APCVD Transparent Conducting Oxides and Undercoat Technologies for Economical OLED Lighting

Award Number: DE-FC26-08NT01576

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Technology Focus: Product Technology

Relevant Subtask Priority Area:

Solid State Lighting Product Development IV, Program Area of Interest 5 (Low cost substrates and encapsulation for OLEDs (MYPP subtasks 4.1.1. and 4.3.1))

Acknowledgment: "This material is based upon work supported by the Department of Energy under Award Number(s) DE-FC26-08NT01576."

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Executive Summary:

Economics is a key factor for application of organic light emitting diodes (OLED) in general lighting relative to OLED flat panel displays that can handle high cost materials such as indium tin oxide (ITO) or Indium zinc oxide (IZO) as the transparent conducting oxide (TCO) on display glass. However, for OLED lighting to penetrate into general illumination, economics and sustainable materials are critical. The issues with ITO have been documented at the DOE SSL R&D and Manufacturing workshops for the last 5 years and the issue is being exasperated by export controls from China (one of the major sources of elemental indium). Therefore, ITO is not sustainable because of the fluctuating costs and the United States (US) dependency on other nations such as China. Numerous alternatives to ITO/IZO are being evaluated such as Ag nanoparticles/nanowires, carbon nanotubes, graphene, and other metal oxides. Of these other metal oxides, doped zinc oxide has attracted a lot of attention over the last 10 years. The volume of zinc mined is a factor of 80,000 greater than indium and the US has significant volumes of zinc mined domestically, resulting in the ability for the US to be self-sufficient for this element that can be used in optoelectronic applications. The costs of elemental zinc is over 2 orders of magnitude less than indium, reflecting the relative abundance and availability of the elements. Arkema Inc. and an international primary glass manufacturing company, which is located in the United States, have developed doped zinc oxide technology for solar control windows. The genesis of this DOE SSL project was to determine if doped zinc oxide technology can be taken from the commodity based window market and translate the technology to OLED lighting. Thus, Arkema Inc. sought out experts, Philips Lighting, Pacific Northwest National Laboratories (PNNL) and National Renewable Research Laboratories (NREL), in OLED devices and brought them into the project.

This project had a clear focus on economics and the work plan focused both on doped ZnO process and OLED device structure that would be consistent with the new TCO. The team successfully made 6 inch OLEDs with a serial construction. More process development is required to optimize commercial OLED structures. Feasibility was demonstrated on two different light extraction technologies: $\frac{1}{4}$ lambda refractive index matching and high-low-high band pass filter. Process development was also completed on the key precursors for the TCO, which are ready for pilot-plant scale-up. Subsequently, Arkema has developed a cost of ownership model that is consistent with DOE SSL R&D Manufacturing targets as outlined in the DOE SSL R&D Manufacturing 2010 report.

The overall outcome of this project was the demonstration that doped zinc oxide can be used for OLED devices without a drop-off in performance while gaining the economic and sustainable benefits of a more readily available TCO. The broad impact of this project, is the facilitation of OLED lighting market penetration into general illumination, resulting in significant energy savings, decreased greenhouse emissions, with no environmental impact issues such as mercury found in Fluorescent technology.

1. Project Objective:

As extensively discussed, concluded and documented at the February 2007 DOE SSL workshop, as well as more recent workshops, the reliance on indium tin oxide (ITO) or indium zinc oxide (IZO), as an anode material for use in organic light emitting diode devices (OLEDs), is one of the largest product-development barriers to the successful commercialization of OLED white-lighting devices. The primary reason is economics, but there are other issues. There are issues with manufacturing and activation disparity caused by inconsistent stoichiometry in ITO. Additionally, there is a blue adsorption band that limits ITO film thickness to less than 120 nm resulting in a limitation of approximately 15 ohms/sq at greater than 85% transmission. Ion migration of Indium does lead to “clouding” in the OLED device, and the long-term stability of ITO in air is relatively poor and requires reactivation in a UV/ozone chamber.

A suitable alternative TCO material for glass substrates, doped ZnO, has already been developed and demonstrated by Arkema Inc. with a major Flat Glass producer for application in the fenestration market. To date, however, this technology has not been applied to OLED devices in a commercially successful manner. What remains to be developed is a cost-effective manufacturing process for depositing these materials in a form that can be integrated into OLED devices that, heretofore, were developed for use with ITO. This was identified as a high priority, Product Development R&D, subject at the workshop and is consistent with the Solid State Lighting Product Development IV, Program Area of Interest 5, Low cost substrates and encapsulation for OLEDs (MYPP subtasks 4.1.1. and 4.3.1).

The primary objective of this project was to develop a commercially viable process for “Substrates” (Substrate/ undercoat/ TCO topcoat) to be used in production of OLED devices (lamps/luminaries/modules). This project focused on using Arkema’s recently developed doped ZnO technology for the Fenestration industry and applying the technology to the OLED lighting industry.

The secondary objective was the use of undercoat technology to improve light extraction from the OLED device. In optical fields and window applications, technology has been developed to mitigate reflection losses by selecting appropriate thicknesses and refractive indices of coatings applied either below or above the functional layer of interest. This technology has been proven and implemented in the fenestration industry for more than 15 years.

Successful completion of this project would provide doped ZnO coated on inexpensive soda lime glass resulting in a significantly lower cost relative to the current ITO coated Flat Panel Display Glass substrates. Additional benefits will be a more consistent TCO that does not need an activation step with better optical performance. Clearly, this will serve to enhance penetration of OLED technologies into the lighting market.

2. Technical Approach, Work Plan, Results Versus Milestones and Discussion:

The combination of the doped ZnO developed technology (Arkema) and Philip’s OLED technology is the foundation of this project. Thus, the three key phases in the technical approach are: 1) off-line TCO application development, 2) application of undercoat technology to OLEDs, and 3) demonstration of OLED prototype. Work was done both in parallel and iterative mode to meet the proposed milestones in the timeline. Further alliances were made during the project with two national laboratories (National Renewable Energy Laboratory (NREL) and Pacific Northwest National laboratory (PNNL)), which helped bring better understanding to the project that will be discussed in the specific milestone below.

The main challenges for this project was to obtain homogeneous substrates on a 6” scale that met the optoelectronic properties are: lower deposition temperatures, heat management, coater head design, minimize capital and operating costs projected for an off-line coater, and to open a route to roll to roll processing on flexible substrates. Doped ZnO has excellent optoelectronic properties, but must have the

proper process conditions , i.e. substoichiometric ZnO is difficult to dope and excess O₂ leads to loss of electrical properties at high temperature, presumably due to O₂ trapping.

The challenges for optical modeling for refractive index matching are difficult to address before the project, especially since there was not a good model for the doped ZnO, i.e. the Drude equation does not fit well in the blue region. Refractive index matching works well for films that are 150-600 nm in thickness. At 150nm or less there is less of an overall effect in refractive index matching due to other prevailing effects and at greater than 600nm there are so many reflections that it is difficult to model and experimentally make refractive index match the emitter transmission versus the “Substrate” transmission. This technology could improve the light transmission in the proposed range, enabling films with lower sheet resistance. Additionally, doped ZnO has lower absorption in the blue region than ITO. Overall, the combination of the ZnO material properties and the knowledge of layered constructions could lead to more conductive films with higher transmission. Clearly one of the major challenges was merging Arkema’s and Philips’ optical experimental and modeling knowledge.

The project summary will follow the initial milestones, Table 1, where the initial hypothesis and approach will be enumerated along with comparison to objects set in the work plan as well as, issues and changes made during the project to reach the overall project objectives.

Table 1 Project Timeline

Milestone	Description	Completion	Deliverable
1	Define deposition process temperature	Q1	Report
2	Define undercoat structure <ul style="list-style-type: none"> ▪ Model undercoat/TCO film stacks ▪ Model full OLED construction 	Q2	Report
3	Define precursors for deposition process <ul style="list-style-type: none"> ▪ Zn precursor locked-in ▪ Dopant(s) and dopant precursor locked-in 	Q3	Report
4	Demonstrate anode properties (1-inch sample) <ul style="list-style-type: none"> ▪ Undercoat/TCO film stack 	Q3	Report
5	Demonstrate cleaning and patterning efficiency <ul style="list-style-type: none"> ▪ APCVD TCO equivalent to ITO standard 	Q3	Report
6	Demonstrate OLED with target properties (1-inch sample)	Q4	Report
7	Demonstrate anode properties (6-inch sample)	Q5	Report
8	Demonstrate white OLED on 6-inch TCO anode	Q6	Device

	<ul style="list-style-type: none"> ▪ 25 lumens/watt ▪ Homogeneity > 80% 		
9	Demonstrate blue OLED on 6-inch TCO anode <ul style="list-style-type: none"> ▪ 80% higher external efficiency than similar device without undercoat 	Q7	Device
10	Demonstrate commercially feasible synthetic process for APCVD precursor chemistry on need for 6" line	Q8	Report
11	Design pre-Engineering coating process <ul style="list-style-type: none"> ▪ Coating throughput consistent with Philips Gen-4 line ▪ Gate 3 operational cost estimate 	Q8	Report
12	Demonstrate 12-inch square OLED lighting fixture <ul style="list-style-type: none"> ▪ 4 - 6-inch square panels 	Q8	Device

I. **Milestone 1:** Define Process Temperature

(End of Q1)

- a. **Initial Plan:** This is not an exhaustive study and was limited to one quarter of work. Using Arkema’s library of precursors, we evaluated lower deposition temperatures to facilitate engineering and design of an off-line coater that would fit into a Pilot OLED production facility. Indications are that selection or creation of an appropriate precursor can improve or resolve these property tradeoffs by balancing the stability/reactivity of the precursor and the ability to incorporate a dopant into the ZnO for high conductivity. The target properties would be what we could produce at higher temperature and if the below criteria cannot be met we will continue the project at a temperature where acceptable TCOs can already be made. The analytical tools used for these responses are profilometry, 4-point probe, AFM, and UV/Visible spectrophotometer. The criteria are: 1) deposition rate > 15nm/sec, at 140 nm film thickness 2) sheet resistance < 20 ohms/sq 3) surface roughness < 4nm rms 4) Z_{max} < 30 nm 5) visible transmission of > 85%.
- b. **Project Results and Discussion:** Significant effort was put into meeting the first milestone of the project that focuses on lowering the processing temperature while maintaining optoelectronic properties. Two approaches were evaluated. *Approach 1* evaluated Arkema’s current precursors, used at higher temperatures (500-700°C), and drives the temperature as low as possible. *Approach 2* was to use the current Zn precursors with slightly modified dopants, i.e. previous work indicated the dopants were too stable.

We determined that *Approach 1*, using our known precursors, we could lower the deposition temperature to 375-425°C to meet the Q1 milestones with the key parameter of resistivity to be equal or lower than 2.5×10^{-4} ohm cm. Thus, we reported in the second monthly report that we met the Q1 Milestone one month early. Other Phase 1 criteria are in Table 2. However, it is clear a further decrease in temperature is not feasible for this set of precursors.

Table 2 Phase 1 Target and Results

	Target for Phase 1	Approach 1
T %	> 85	>90
SR Ω/\square @ 140 nm thickness	< 20	17-20
Surface roughness rms (Z_{max}) in nm	< 4 (30)	3-6 (30-60)
Deposition rate (nm/sec)	> 15	15-100

For *Approach 2* the challenges are to have precursors that are stable at vaporization temperatures yet react/decompose onto the substrate at the desired deposition temperature. Where the precursors react is also critical, i.e. too early and powders will form above the substrate surface or if it decomposes too late then there will be poor incorporation of dopant. Thus, we used molecular modeling (DFT) to help us in designing and subsequently making a library over 80 dopants with a broad diversity of bridging ligands, Figure 1.

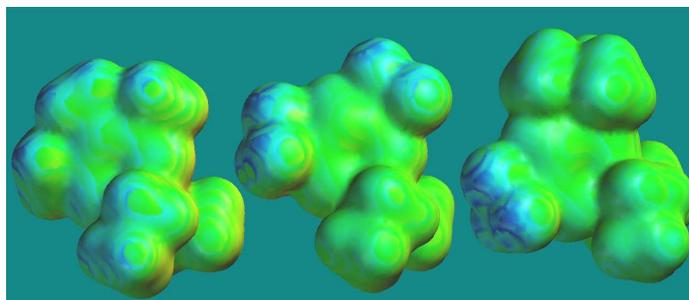
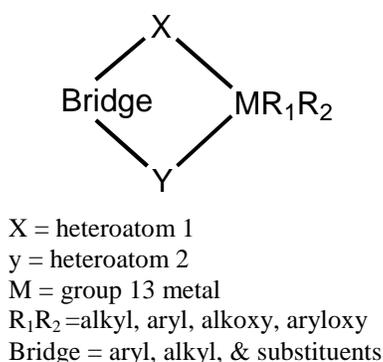


Figure 1. DFT space filling electron density models with blue being higher density a) symmetrical bridge, consistent with observed experimental of fragmentation of R first b) symmetrical bridge with electron withdrawing groups c) unsymmetrical bridge

The key strategy for this evaluation was destabilizing the bridging ligand to form a highly reactive $[MR_2]^{-1}$. The dopants fall within 3 classes for the bidentate ligand: 1) x, y=heteroatom 1 ; 2) x, y=heteroatom 2 and 3) x=heteroatom 1, y=heteroatom 2. The primary screen of these dopants were carried out using thermal analyses (DTA, TGA, DSC and pyrolysis GCMS). Interestingly, the hits were from Classes 1 and 2 where the heteroatoms were equivalent, but the bridge had substituents making it electronically unsymmetrical, i.e. a more subtle effect. These hits had residuals of 1-10 wt% (measured by TGA) and vaporization temperature range from 50-70°C. Ideally, the residual is 0 wt% and the vaporization temperature is in the stated range with only one weight loss event. However, in practice dopant residuals, up to 15 wt% are acceptable due to the low usage, i.e. does not significantly affect the cost or periodic cleaning of the vaporizer. Subsequently, we scaled up the top 10 dopants from 150 mg to approximately 10 g for our high throughput APCVD coater evaluation. Three of these dopants are of interest based on resistivity; however, none of these three dopants surpass Arkema's standard Al or Ga dopants, but does identify a potential B dopant. Subsequently, a PCT application, WO2010/151430 A1, was submitted after running the course of a provisional US patent application. While further work is warranted to reach lower processing temperatures for polymer substrates it was deemed outside the scope of this project. Thus, the project work continued based on Approach 1 results.

II. Milestone 2: Define undercoat Structure

(End of Q2)

- a. **Initial Plan:** This task is focused on developing optical models that combine Arkema's expertise on undercoat and TCOs with Philips Lighting expertise on OLED modeling. The objective is to develop an undercoat construction that would improve transmission of the OLED device. This modeling would generate targets for thickness and refractive index for the undercoat layer. Thus, helping to speed up the feasibility stage of this project. The key deliverable was having construction geometry targets for undercoat and TCO for the subsequent tasks.
- b. **Project Results and Discussion:** The second milestone is based on Optical modeling at Arkema and Philips Lighting. At Arkema we have found that there is not a good optical model for doped ZnO that accurately describes the conductivity and insulating properties of the doped ZnO. Building our program, we used a double oscillator with an oscillator to suit each of the previously mentioned properties. The results indicate a 95% fit level that was significantly better than just using the Drude model, Figure 2. Not only is this of immediate help for this Milestone 2, it will also be used for the 6" ellipsometer mapping tool that will be discussed in Milestone 7.

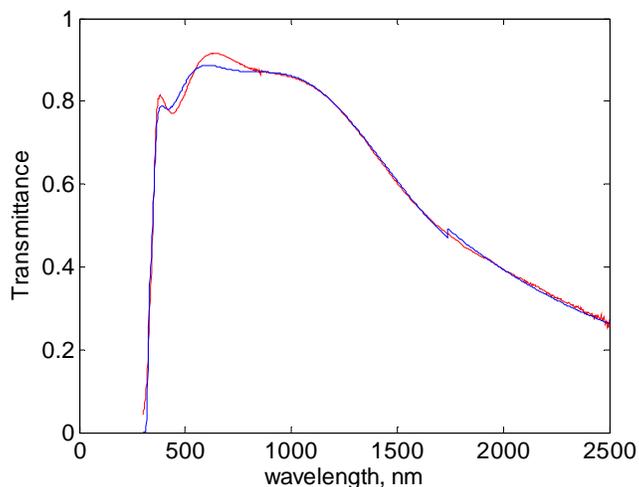


Figure 2. Transmission over large spectral region based on dual oscillator model (blue), actual data (red).

Modeling a $\frac{1}{4}$ lambda undercoat effect at Philips indicates that this approach will only improve outcoupling by 3-7%. Because of the calculated low outcoupling improvement a high-low-high (HLH) band pass filter (also referred to as the double cavity) approach was also calculated that predicts a light outcoupling enhancement by 70%. Unfortunately, the initial high-low-high band pass filter is over 400nm thick and the costs may outweigh the benefits not to mention the process difficulties. However, generating a structure with different materials resulted in reducing the thickness by 50% with similar outcoupling results, Figure 3. While this approach is outside the scope of the original project we decided to move forward with a feasibility study. Thus, to generate the HLH we used Philips PVD group for the HLH band pass filter and Arkema deposited doped ZnO on top. We continued with the first approach to confirm the modeling and quantify the benefit of $\frac{1}{4}$ lambda undercoat. Both of these will be discussed in Milestone 9.

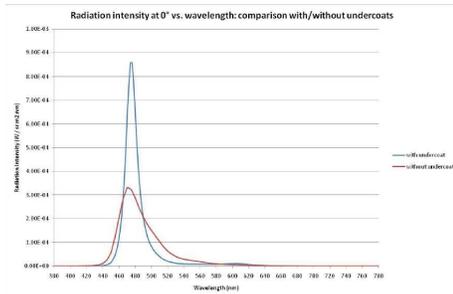


Figure 3. Modeling of radiation intensity versus wavelength, (Blue = HLH structure)

III. Milestone 3: Define Precursors for Deposition Process (End of Q3)

- a. **Initial Plan:** This is a key milestone and marks an end to screening experiments and once completed the project moves to focus on developmental issues. Both the Ga and Al dopant precursors have been defined in Milestone 1; however, there are two potential Zn precursors. The advantage of the first Zn precursor is optoelectronic properties and the advantages of the second Zn precursor are: faster deposition rate, clean vaporization, better deposition efficiency, which all improve the economics of the second Zn precursor. The analytical tools used for these values are profilometry, 4-point probe, AFM, and UV/Visible spectrophotometer. To demonstrate OLED device feasibility the criteria are: 1) Deposition rate of greater than 15nm/sec, 2) sheet resistance at 140 nm film thickness < 20 ohms/sq, 3) surface roughness less than 4nm rms, and 4) Z_{max} less than 30 nm, and 5) visible transmission of greater than 85%.
- b. **Project Results and Discussion:** While there are over 16 parameters to optimize, we found a surprising result for the second Zn precursor that was significantly different than the first zinc precursor. For the second Zn precursor water concentration was significantly higher. This resulted in equivalent or better optoelectronic properties and elimination of an absorption peak in the NIR. Very exciting results were obtained at this point where the resistivity obtained were lower than commercial ITO and challenged some of the ITO lab records (typically demonstrated on < 5x5 mm²), but on a 6” substrate! The resistivity at 300 nm thickness = $1.76 \times 10^{-4} \Omega\text{cm}$ and at 1,200 nm = $1.43 \times 10^{-4} \Omega\text{cm}$. Note that this is a troubling result since resistivity should be constant as thickness is taken into account. The implication is the film is not homogenous across the depth of the film. Further characterization by FIB TEM indicates that it is not homogeneous which is consistent with the resistivity changes with thickness variation. Figure 4.

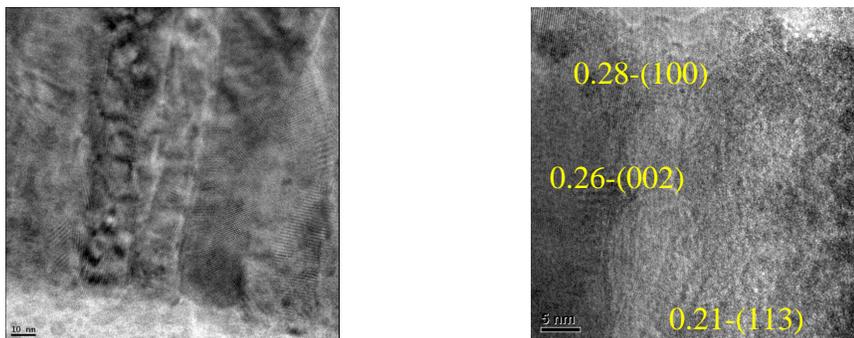


Figure 4. FIB TEM data a) glass substrate (white) showing trapezoidal growth of doped ZnO b) expansion of a) showing reflections from different growth orientations over the depth of the film

Using the proper undercoat should (used for Milestones 2 & 9) eliminate this issue by accelerating nucleation. Thus, all precursors are locked in so process work can begin.

While most of the results were encouraging, we also found an issue that would take a long time to resolve for Milestones 4 & 7. Non-homogeneity of the samples was noted, which is directly related to the deposition equipment. It appears on the surface map that the edges are significantly different than the center with multiple minima and maxima, Figure 5.

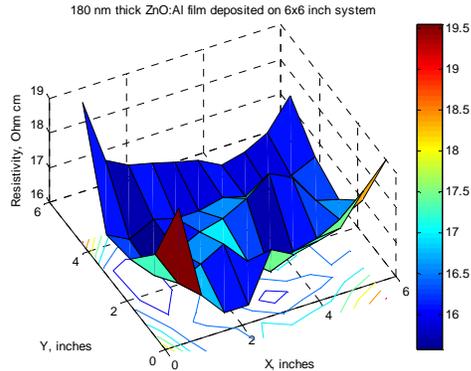


Figure 5. Sheet resistance map for a 6” substrate.

- IV Milestone 4:** Demonstrate Anode Properties, (End of Q3)

 - a. Initial Plan:** The criteria and measurements are the same as *Define Precursors for Deposition*, but on a 1”x1” substrate.
 - b. Project Results and Discussion:** As depicted in Figure 5, the homogeneity coming from our modified 4” line was not good, but was sufficient for the first few Milestones. In parallel, we had been modeling gas flows to optimize a 6” coater design and the design was sent out for fabrication. Unfortunately, there were some issues with some of the detailed fabrication and getting it correctly done took longer than expected pushing the project behind by a quarter. Subsequently, at the mid-term review this milestone was merged into Milestone 7, 6” x6” anode demonstration to catch up with the delay. Other reasons for skipping the 1” substrate was due to tooling to make OLED’s was for 6” substrates and additionally the team could focus on the 6” homogeneity issues. At the time we believe this risk was reasonable since the 1”x1” center of the coated 6” substrate (Figure 5) had relatively good homogeneity with less than 10% variation in sheet resistance and transmission. Looking back with hindsight this was the right decision and potentially we should of made this decision sooner. Especially since resolving homogeneity of the 6” substrate turned out to be one of the key issues of the project to solve and will be discussed in more detail in Milestone 7.
- V. Milestone 5:** Demonstrate Cleaning and Patterning Efficiency (End of Q3)

 - a. Initial Plan:** This was to insure the current process of cleaning and patterning OLED devices would work with minor modifications. The new TCO needed to pass Philip’s processing steps equivalent to or better than the ITO standard substrate. Thue, no deterioration in the coating while maintaining the following properties at 140nm thickness: 1) sheet resistance < 20 ohms/sq, 2) surface roughness less than 4nm rms, 3) Z_{max} less than 30 nm, and 4) visible transmission of greater than 85%.

b. **Project Results and Discussion:** The fifth milestone has been demonstrated on samples generated from our modified 4" coater on which most of the feasibility work at Philips has been carried out. This is important to be able to process the doped ZnO to work with Philips current processing technology. The first test was a 60 %rh: 80°C test for a period of 2 months, Figure 6. Since there was some concern of Na⁺ migration, we also evaluated the doped ZnO with several undercoats including: TiO₂, SiO₂, SnO₂ and compared them to APCVD doped ZnO, PVD AZO, and ITO. The results indicate that ITO and APCVD doped ZnO have the best results indicating the glass:TCO and TCO:air interfaces are stable to these conditions. The two surprising results are how much the sputtered doped ZnO deteriorates and how much a TiO₂ undercoat adversely affects the stability of the doped ZnO.

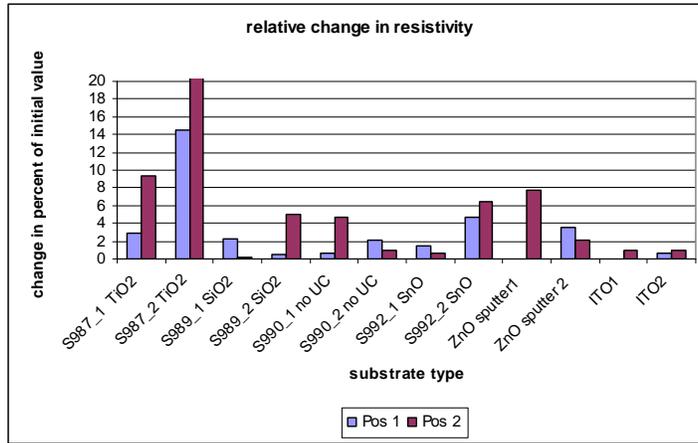


Figure 6. Stability test of TCOs in 60:80 test.

After passing the 60:80 stability test the next series of tests were carried out to demonstrate that doped ZnO is stable to prototypical cleaning conditions. Thus, the TCO substrates were exposed to solvents, cleaning solutions, and mechanical cleaning, where the surface roughness (rms) actually decreased. There was no observed etching, but removal of fine surface particles was observed, Figure 7. Thus, we have shown that the Substrate is stable through a standard OLED cleaning process.

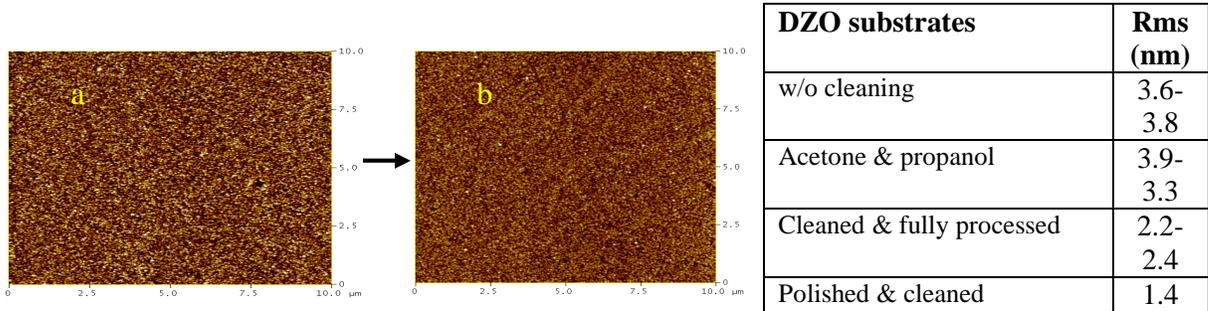


Figure 7. AFM a) without cleaning b) cleaned and fully processed

VI. Milestone 6: Demonstrate OLED with Target Properties (1 inch² sample) (End of Q4)

a. **Initial Plan:** This milestone focused on operational stability of the OLED device and the criteria were to the pass 60:80 corrosion test @ 504 hours as measured by: 1) transmission decrease < 2%, 2) sheet resistance increase of < 0.5 ohm/sq, 3) OLED onset voltage increase of < 0.2V, 4)

contact resistance increase in TCO to metal of < 0.1 ohm/sq, 5) turn on voltage similar to ITO, and 6) shorting level comparable to ITO using Weibull statistics (60 large area samples)

- b. **Project Results and Discussion:** OLED device work started after the cleaning and stability work. One of the first efforts was on planarizing (more in Milestone 7) and finding compatible hole injection layer (HIL) materials for ZnO, i.e. ZnO is sensitive to acid. Over 6 HILs were tested, devices were made, subsequently driving them hard to failure. This test identified several candidates that were used at an optimum thickness of ~ 100 nm to minimize shorting to levels equivalent or better than ITO.

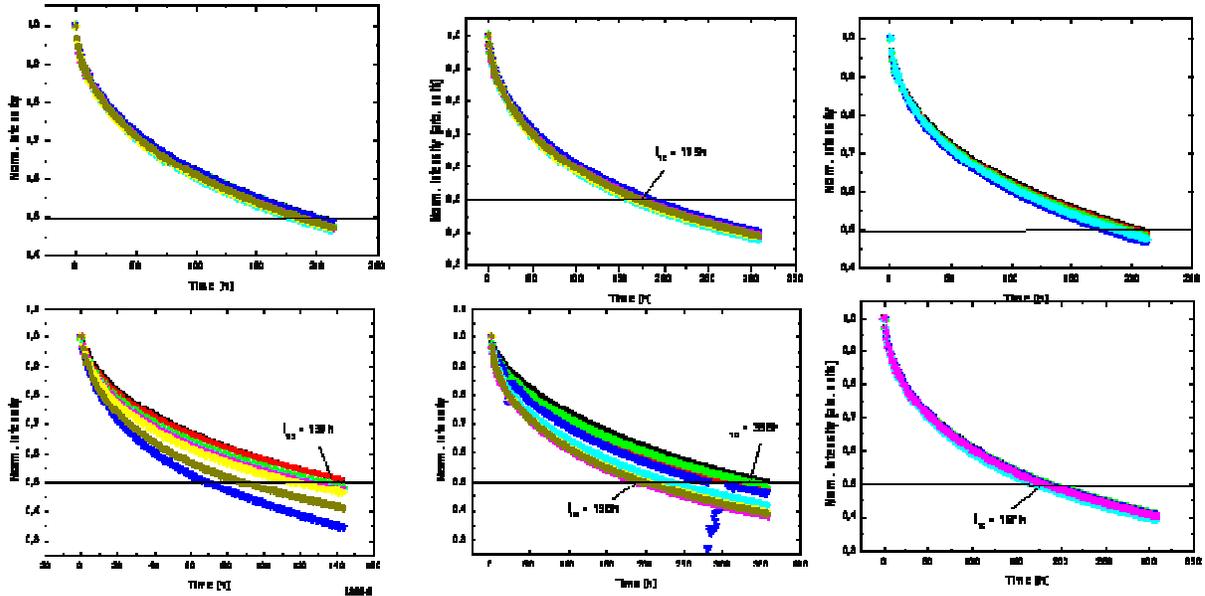


Figure 8. Identifying appropriate HILs. Each plot is a different HIL and the different color curves are thickness of the specific HIL. ITO reference for $\frac{1}{2}$ life (black horizontal line) is ~ 150 hours.

The 5×5 mm² results are also very encouraging. Current Voltage (IV) plots are similar to reference ITO devices using standard Philips OLED stacks, Figure 9. Both efficacy and efficiency are similar relative to an ITO standard for sample 3419-2. Note that the 3420-2 is a different OLED stack using doped ZnO with a cooler color temperature as noted in Figure 9.

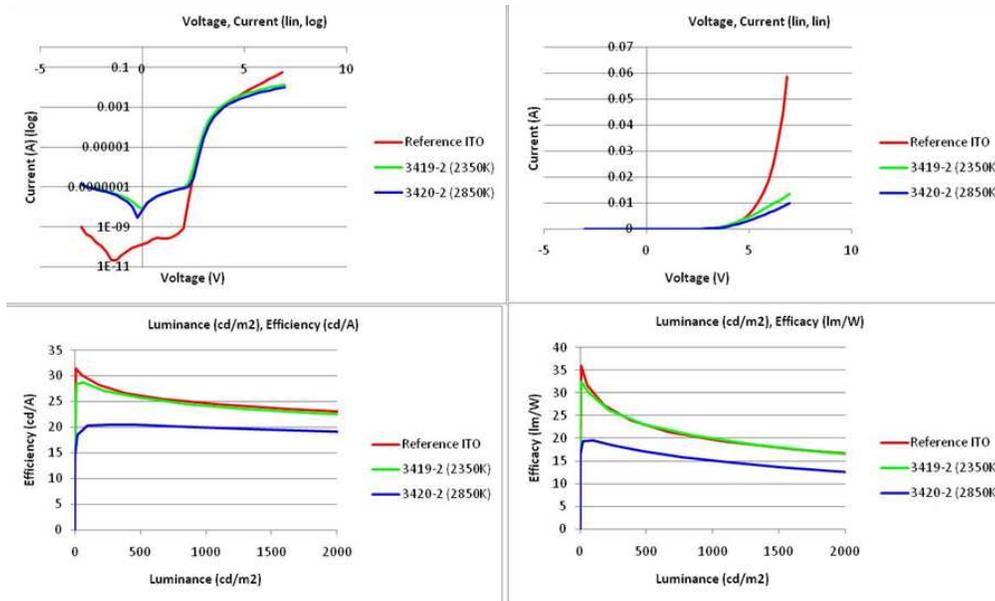


Figure 9. 5mmx5mm OLED devices made using doped ZnO and compared to a standard ITO containing OLED device

Due to the delay in the 6” APCVD coater this milestone was also affected and at the mid-term review we folded this into Milestone 8 to catch up with the project timeline so the emphasis would be switched to > 1”x1” devices. However, the team felt confident with the positive results with the 5mm x 5mm OLED devices to make this jump. Thus, enabling the team to focus on scale-up issues.

VII. Milestone 7: Demonstrate anode properties (6-inch sample) (End of Q5)

- a. Initial Plan:** Concerns about the TCOs for OLED devices centered on: surface roughness, stability, and homogeneity. Going into the project we understood that the modified 4” coater would not be sufficient due to non-homogeneity. Thus, the design, fabrication, installation, and commissioning of the new 6” coater was critical to the project. The target properties were the same as the precursors with the added qualifier of homogeneity with less than 10% of the value across the substrate.
- b. Project Results and Discussion:** OLED devices have been prepared using substrates from the previously modified 4” Arkema coater. However, the homogeneity (sheet resistance) varied up to 10-15% that could lead to minor benefits or deficiencies being hidden in the noise. The new 6” coater was initially planned to be up and running at the end of Q4, but due to fabrication and issues it was not complete until the end of Q6. Note that this work has led to very homogeneous substrates, especially on the center 5”x5” section with less than 3% variation for sheet resistance, transmission, thickness, electron concentration, mobility, and surface roughness.

Considerable effort and thought was put into the design of this coater to make it more modular and cost effective. This involved flow dynamic modeling and engineering support to try out new concepts. Flow modeling does not model chemical behavior so coater development typically involves experimental work in combination with the flow modeling. There were many obstacles we needed to overcome in this development work such as analyses of the 6”x6” substrate, coater head alignment, vaporization, precursor stability, and heat management.

Analyses of a 6"x6" substrate requires specific equipment, which is why we incorporated an ellipsometer with a 6" stage that would scan from ~ 300 to 2200 nm in the capital budget. We also found it useful to build an automated 4-point probe instrument for sheet resistance, i.e. it would take a long time to measure 196 points, plus the potential for transcription errors. Both of these pieces of equipment required 100s of samples to calibrate and correlate the values to single point measurements. The ellipsometer allows us to get macro surface roughness, film thickness, electron concentration and mobility (via measurement of plasma wavelength). The earlier optical modeling in Milestone 2 of ZnO facilitated in the calibration of the ellipsometer. This work is very important since an automated 1-hour scan can replace weeks of profilometry work for film thickness and 2 weeks of AFM work. While the accuracy may not be as good as the traditional method, it is sufficient for process screening and the benefit really lies in effective surface mapping in a short period of time, Figure 10.

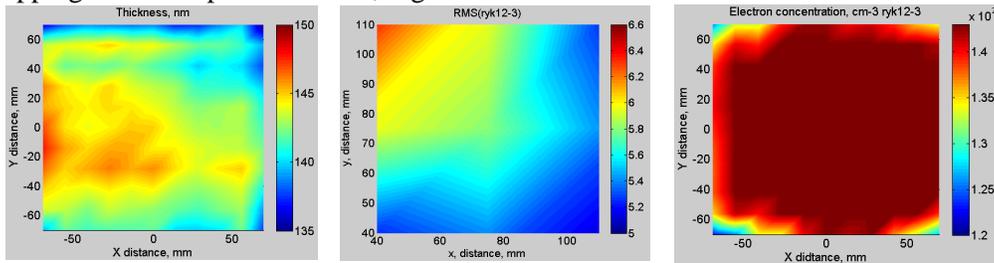


Figure 10. Examples of 196-point surface mapping of 6" substrates using ellipsometer a) film thickness b) surface roughness RMS in nm c) electron concentration.

The other analytical tool was not planned on, but as we started mapping sheet resistance it became clear that for 196 points the process needed to be automated. This required both fabrication and software skills as we developed this method and correlated the house built automated 4-point probe to our standard 4-point probe, Figure 11. One can see a lot more details comparing a sixteen-point plot sheet resistance map in Figure 5 to the automated 196-point plots in Figure 11. Note that there was not a sacrifice in accuracy with this high throughput tool, but significant man-power was saved and was redistributed on other parts of the project.

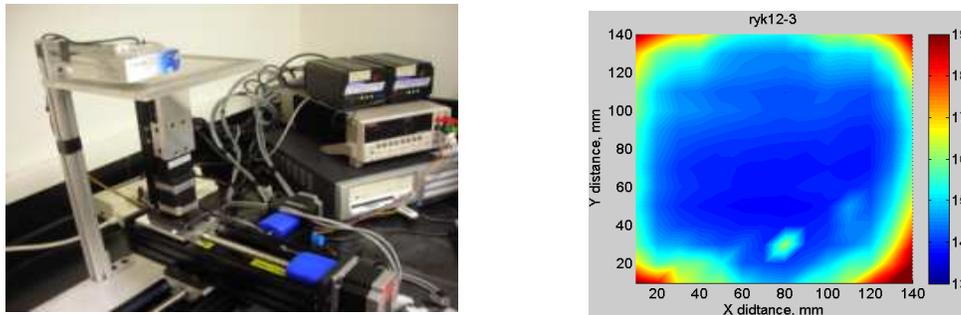


Figure 11. a) automated 4-point probe using x, y, and z stages b) a typical sheet resistance map from same sample as in Figure 10.

In parallel to the analytical work, we were working on getting the flow and exhaust for the new coater into an operable regime. Initially, for corrosion consideration we went with stainless steel construction that required outside fabricators, but as baffles and distribution plates needed redesign we converted to Al so we could carry out the modifications in house. The static depositions depicted in Figure 12 shows some of the issues such as over-exhausting, poor distribution and burrs on the coater head, even a small glass wool thread that got caught on the

assembly resulted in the issues with the deposition next to last one on the far right and finally an operable deposition on the far right.

Moving to dynamic mode, we initially observed two issues: banding that runs perpendicular to the coating direction, and streaking that runs parallel to the coating direction, Figure 13. We eventually determined that banding was due to precursor pulsing and streaking was due to coater imperfections. This was particularly important for the dopant since it was used in such small quantities. The initial set-up had a syringe pump into a heated vaporizer, but what we were observing was the falling of a drop. This could be partially rectified by making sure the needle was touching the packing, but we switched to a bubbler that resolved this issue. However, this was short lived as we found out that both precursors were not stable to prolonged heat cycling (~ 1 month of lab cycling). Subsequently, we successfully changed to a commercial vaporizer that exposes the precursor to a short heat history and relies on atomization of the liquid precursor before vaporizing the precursor to get a homogeneous distribution.

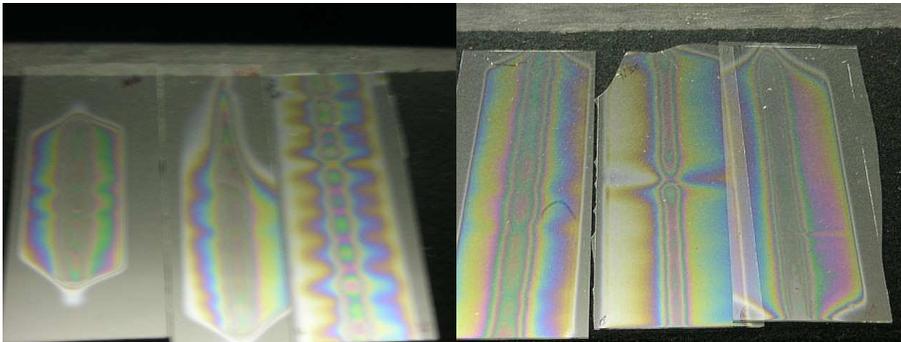


Figure 12. Static depositions on a 6" width glass strips with a variety of issues. The one on the far right is getting into the operable range.

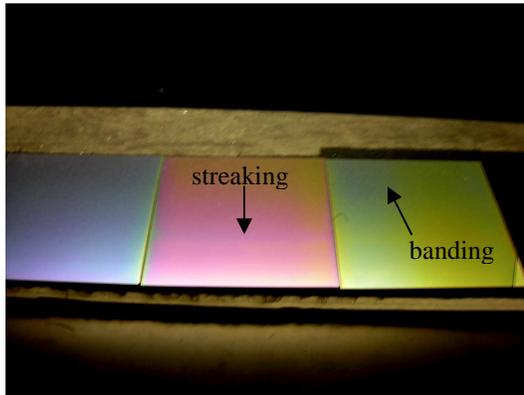


Figure 13. Dynamic mode coatings on 6" substrates a) homogenous coating b) an example of streaking and c) an example of banding

Heat management is another issue that we had to address. For our lab coaters we use Ni blocks to heat substrates to temperature and maintain the temperature during the coating process and with 3.2 mm soda lime glass this has not been an issue due to the mass of the substrate. However, dropping down to 0.7mm thick soda lime glass, the glass mass is significantly lower yielding a significant delta in temperature between the bottom and top surfaces of the glass. This results in significant curling of the glass and even breakage. This does not put stress into the glass since we are operating well below the substrate's T_g so when it cools it will be flat, but this does mean one

cannot coat evenly over the surface due to the curvature. We did have some success using IR heaters above the surface that decreased the deflection and at least allowed us to coat the glass substrate, but the substrate coating could not be made with good homogeneity. The solution to this issue would be to have an even heat (more oven like), but the cost would be too high and outside the scope of this project. However, in production the likely thickness for the least expensive flat glass will be between 1.5-3.2 mm that would minimize this issue. Thus, the team decided to move forward with 0.7mm borosilicate glass due to the lower thermal expansion coefficient and the fit with the OLED tooling at Philips, i.e. another solution could be to go to 3.2 mm soda lime glass.

Thus, in March 2010 we were able to start making substrates with good homogeneity and began shipping 6"x6" substrates in increments of 10-30 substrates to Philips for OLED device work. Thus the development work shifted to surface roughness and how to decrease or minimize the effect. While we are able to generate 3-5 nm rms with a 30 nm Z_{max} the hope is process improvements could move surface roughness to < 2 nm rms and 20 nm Z_{max} to minimize costs of a thicker layer or polishing, etc. Three approaches were initially conceived to address this issue: 1) thicker HIL layer (discussed in Milestone 6), 2) polish TCO surface, and 3) APCVD process development. However, we added two other approaches for feasibility since it would expand the scope too much for a detailed evaluation and these were 4) inorganic topcoat, and 5) thicker HTL with additives (will be discussed in Milestone 8). The thicker HIL layer strategy to minimize shorts has been used in production of displays (Eastman Kodak) and does work as we discussed in Milestone 6. Polishing the TCO also works very well, but adds cost to the device by removing the top 50 nm plus the processing to remove the layer. So the remainder of this section will focus on process development (3) and inorganic topcoat (4) approaches.

We initially started at 12-18 nm rms and with selected parameter optimization we were able to reach 3-5 nm rms. The question is can we reach below 2 nm rms that would facilitate OLED fabrication. We determined that surface preparation is critical to get reproducible results and KOH wash was a critical component. This is important to remove defects and particles from the glass substrate. We also found that the AFM tip needs to be changed frequently when mapping a surface otherwise there is 25% variability. Currently we do not know if this is due to particles or plowing into the surface. We did find that impingement velocity has an effect on grain size. This means that a higher vertical component will lead to smaller grain size with an expected decrease in surface roughness. This is on-going work that is still being carried out after the close of the DOE project.

Using a metal oxide topcoat can reduce surface roughness if one can induce nucleation. Thus, planarization will be very dependent on metal oxide, precursors and deposition conditions. Since this was outside the scope of this work we only carried out initial feasibility experiments. Subsequently, we evaluated a TCO with a thick (500nm) and very rough surface rms = 23-24 nm and Z_{max} 179-279 nm. Coating this substrate with a 10-20 nm thick metal oxide resulted in decreasing the surface roughness by a factor of ~ 4 at 5-8 nm rms and Z_{max} 55-65 nm, Figure 14. This is a significant jump and demonstrates the feasibility of a metal oxide planarization of the TCO. Other benefits that were observed are: improved acid resistance and air/heat stability. Other benefits that were not evaluated are charge injection and through conductivity improvement that would be out of the scope of the project.

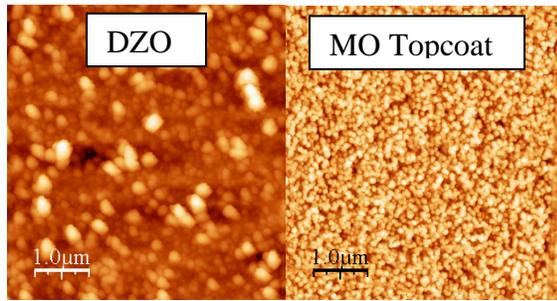


Figure 14. AFM at same magnification, of a) DZO b) DZO coated with 20 nm of topcoat

VIII. Milestone 8: Demonstrate white OLED on 6-inch TCO anode (End of Q6)

- a. **Initial Plan:** This milestone focuses on scaling up the OLED device to 6” with two major criteria: meeting ITO in efficacy (25 lm/W), and homogeneity of > 80% on the OLED device.
- b. **Project Results and Discussion:** The work in this area was complicated by the desire to move to the most current manufacturing technique that offers cost savings by better raw material usage, faster throughput, or simplification of the OLED device design. Our partner’s development line was modified to bring in-house these new and developing techniques and the process took longer than expected, essentially shutting down operation for 3 months, which is one of the reasons we requested and were granted a time extension on the project for an additional quarter.

Scale up to 3x4 cm² (over an order of magnitude scale up) required process optimization, especially as new techniques that were worked out for ITO were brought into the 6” line. Planarization of the doped ZnO was done using a thicker HTL with additives. Patterning the TCO could be done either by laser ablation or photolithography and the former was the method of choice. Some of the issues that were overcome were: maskants and processing choices, compatibility with acid sensitive materials, ink jet printing and wetting requirements for doped ZnO. Clearly, the optimization for a TCO with a different surface energy was time consuming, but very good results were achieved within a few months, Figure 15. These larger devices yielded similar results where ITO and doped ZnO had similar IV characteristics, Figure 16.



Figure 15. Pictures of 3x4cm² OLEDs with various processing issues that needed to be resolved

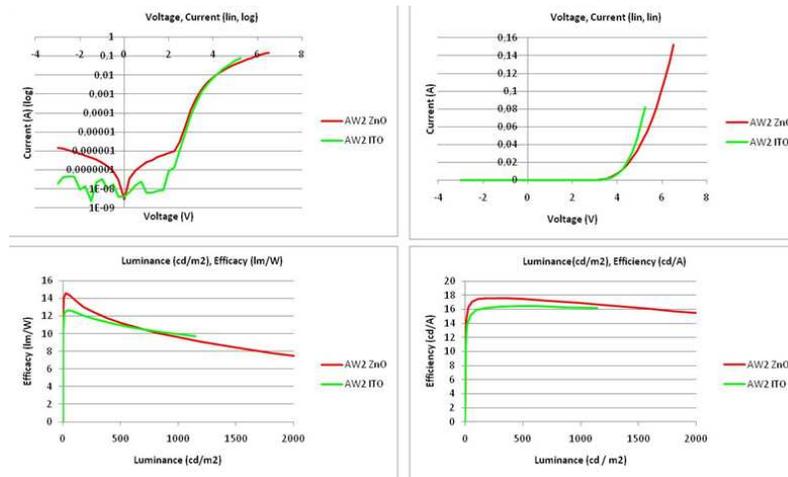


Figure 16. IV plots of doped ZnO versus ITO on the same OLED stack. The OLED stack is different than the previous stack so lm/w is lower, but the comparison doped ZnO to ITO is the key point.

The scale-up to 6” devices was limited by timing, because of the unforeseen, significant development work on the new processing equipment. However, a considerable amount of knowledge was obtained. Initially, a grid approach was used to minimize ohmic drop over the substrate, but simplification of the process led to a serial structure for the devices at the end of the project that was successful. Some of the issues for the Grid approach were color point, adhesion of silver grid, processing, and shorting. While a lot of these issues were resolved for the serial structure there is more stability testing and process optimization that will occur past the project stopping point. Thus the final milestone 12 will not be reached, as the strategy was to use four of the 6” devices to make the 1ft² prototype. However, this will be constructed outside of the project.

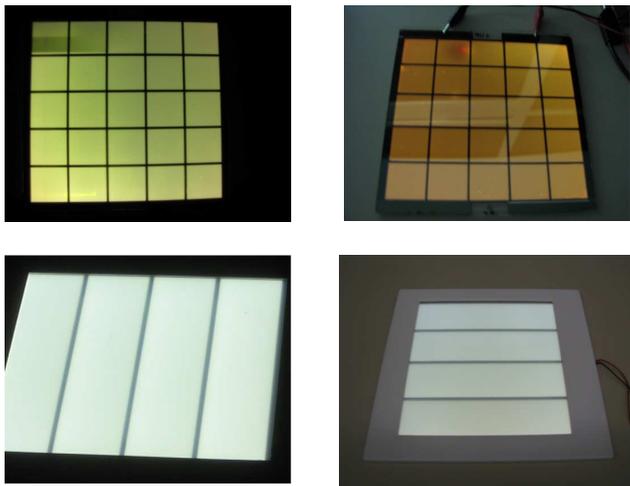


Figure 17. 6” OLED devices a) grid design with color point shifted, partial maskant on top left corner b) grid design showing shorts c) serial device d) serial device.

IX. Milestone 9: Demonstrate blue OLED on 6-inch TCO anode (End of Q7)

- a. **Initial Plan:** Use $\frac{1}{4}$ lambda refractive index matching to achieve higher external efficiency, but after milestone 2 we also added a high-low-high band pass filter for feasibility with the objective of approaching 80% higher external efficiency relative to a device without the undercoat.
- b. **Project Results and Discussion:** Modeling results from Milestone 2 were used to help set compositional targets. Even though the modeling for light extraction results indicated that the $\frac{1}{4}$ lambda index matching would only have a 2-5% effect we pursued this to confirm the modeling since this structure is consistent with current low emissivity on-line process. Visually one can see the reflected color is reduced and quantitative transmission measurements indicates that there is up to a 7% improvement at 475 nm, Figure 18.

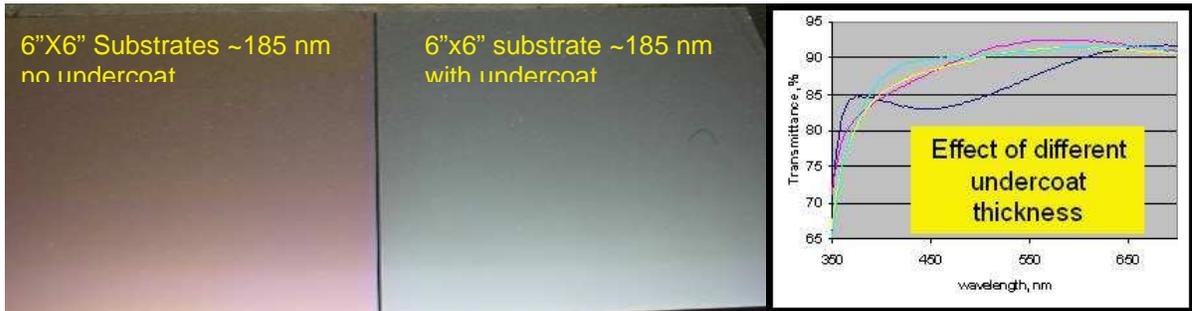


Figure 18. a) 6” substrate with no undercoat b) 6” substrate with antiiridescent undercoat, photo taken on black felt in light box c) Transmission spectra, blue = no undercoat, all other colors have undercoat with varying thickness

Due to timing engaged PNNL (Dan Gaspar and Asanga Padmaperuma) in the evaluation of our undercoat samples. They used 2 different HILs and found that indeed the EQE increases by approximately 10%, Table 3. While this is an improvement in itself it is not sufficient to reach the DOE SSL long-term targets.

Table 3. Tabulated results from Blue OLED devices made at PNNL

Sample	HIL (thickness, nm)	Volts (V)	EQE (%)	Increase %
DZO	HIL 1 (30)	3.8	12.0	---
DZO + Undercoat	HIL 1 (30)	3.8	13.4	11.6
ITO	HIL 1 (30)	3.9	14.8	---
ITO	HIL 2 (35)	4.4	15.2	---
DZO	HIL 2 (35)	4.0	12.1	---
DZO + Undercoat	HIL 2 (35)	4.0	13.2	9.1

The 10% EQE improvement is consistent with the optical modeling (3-7%). However, as mentioned in Milestone 3, the undercoat used for light extraction accelerates nucleation resulting in a more homogeneous doped ZnO. A PCT application, WO 2011/005639 A1 was filed on the optical extraction as well as the accelerated nucleation leading to a more homogeneous TCO.

The second approach of making the HLH structure and subsequently coating doped ZnO was also consistent with modeling results where the actual results yielded a 2.15x improvement versus the

modeling of 2.6x, Figure 19. The difference is likely due to the homogeneity of the 6"x6" sample, which also limited us to 5x5 mm² OLED device. Since this approach was not planned for in the project scope, no work was carried out to optimize or scale up the OLED devices. However this does demonstrate the effectiveness of using a HLH band pass filter. Interestingly, it also results in a significantly deeper color shift for blue that has applications in other areas.

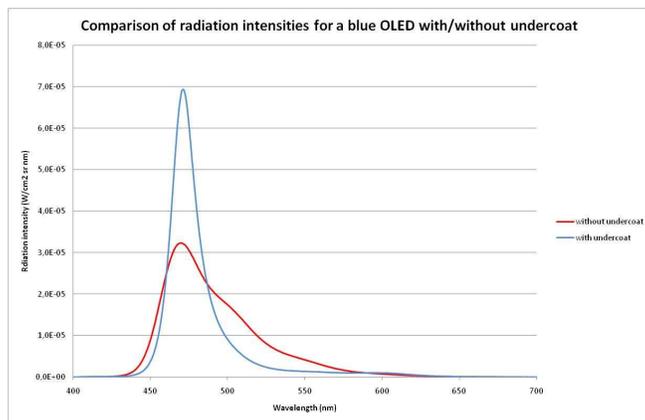


Figure 19. Actual data comparing band pass filter (blue trace) versus no undercoat (red trace)

- X. **Milestone 10:** Demonstrate commercially feasible synthetic process for APCVD precursor chemistry on need for 6" line (End of Q8)
- a. **Initial Plan:** Evaluate multiple synthetic routes for both selected Zn and dopant precursors with an emphasis on the Zn precursor due to the molar use being at least 25x more than the dopant.
 - b. **Project Results and Discussion:** Multiple routes were evaluated for the Zn precursor that were broken into Short-Term and Long-Term processes. The short-term is based on direct reaction to the precursor and is dependent on pricing and availability from key raw material suppliers, while the long-term process is back integrated to commodity chemicals and clearly requires significantly more process work and capital.

For the Zn short-term process we demonstrated near quantitative yield at 100% volume efficiency (no solvent), short cycle time, with no waste stream. Potential raw material suppliers have been identified and qualified with volume specific pricing. We have scaled this process up to 0.5 Kg in the laboratory. For the Zn long-term process we have developed a process based on elemental Zn or ZnX₂, with high salt formation and acceptable yield with the back integration improving the cost significantly. The trigger to incorporate the long-term process is approximately 100 MT that translates to approximately 10M m² of coated substrate. R&D MSDS sheets have been generated and we have taken the next steps to determine pyrophoric/flammability classifications for both toxicity testing and DOT purposes, thus toxicology testing will likely be done on the water-quenched product.

For the dopants we also developed a process with quantitative conversion and high isolated yield. However this process does require solvent due to an autocatalytic decomposition reaction when done with little or no solvent. The process has been safely scaled to 5 Kg. Again R&D MSDS sheets have been generated and we have taken the next steps to determine pyrophoric/flammability classifications for both toxicity testing and DOT purposes, thus toxicology testing will likely be done on the water-quenched product.

Therefore, chemical processes are ready for Pilot Plant scale-up and toxicity testing is defined, which will be required for commercialization, resulting in milestone 10 completion per plan by the end of the project.

XI. Milestone 11: Design pre-Engineering coating process (End of Q8)

- a. Initial Plan:** Coating throughput consistent with Philips Gen-4 line Gate 3 operational cost estimate.
- b. Project Results and Discussion:** We expanded the scope to a gate 3 (pre-Pilot work) Cost of Ownership model to help us understand what needs further definition and what are the sensitivities of specific parameters. A lot of assumptions had to be made to put the model together such as volume, yield, run-time, maintenance, operational costs, capital costs and precursor costs. At 50,000 m²/yr, this crude model indicates that the COO is consistent with the DOE SSL target of \$14/m². Clearly scale-up is needed to resolve potential issues and eliminate assumptions that went into the model. Not surprisingly, the main drivers are capital and operation due to the low volume of product to disperse these costs. Scale up to full production (greater than 5M m²) amplifies the uncertainty in the calculation, but our approach is consistent with the DOE SSL Manufacturing 2010 Multiyear price target, representing a pathway to achieve the desired economic target.

XII. Milestone 12: Demonstrate 12-inch square OLED lighting fixture (End of Q8)

- a. Initial Plan:** Is to take four of the 6” devices and merge them into a single device that has equivalent performance to a similar device made from ITO.
- b. Project Results and Discussion:** Due to the incomplete Milestone 8, Milestone 12 could not be carried out in the allotted time. However, both Philips and Arkema are committed to moving forward since the project did demonstrate equivalent performance of doped ZnO that not only would have a major economic impact, it also has a supply and control impact. Especially, since China, which has the largest reserves of indium, has recently instituted an export control on indium. Note that the US has sufficient quantities of Zn so it could be self-reliant for doped ZnO in optoelectronic applications such as OLED lighting.