Solid State Lighting Program Program Completion Report

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ROLL-TO-ROLL SOLUTION-PROCESSIBLE SMALL-MOLECULE OLEDs

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Roll-to-roll Solution-Processible Small-Molecule OLEDs
Program Completion Report

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1. Executive summary

The objective of this program is to develop key knowledge and make critical connections between technologies needed to enable low-cost manufacturing of OLED lighting products. In particular, the program was intended to demonstrate the feasibility of making high performance Small-Molecule OLEDs (SM-OLED) using a roll-to-roll (R2R) wet-coating technique by addressing the following technical risks

- (1) Whether the wet-coating technique can provide high performance OLEDs,
- (2) Whether SM-OLED can be made in a R2R manner,
- (3) What are the requirements for coating equipment, and
- (4) Whether R2R OLEDs can have the same performance as the lab controls.

The program has been managed and executed according to the Program Management Plan (PMP) that was first developed at the beginning of the program and further revised accordingly as the program progressed.

Significant progress and risk reductions have been accomplished by the end of the program. Specific achievements include

- (1) Demonstrated that wet-coating can provide OLEDs with high LPW and long lifetime;
- (2) Demonstrated R2R OLEDs can be as efficient as batch controls (Figure 1)
- (3) Developed & validated basic designs for key equipment necessary for R2R SM-OLEDs;
- (4) Developed know-hows & specifications on materials & ink formulations critical to wet-coating;
- (5) Developed key R2R processes for each OLED layer
- (6) Identified key materials and components such as flexible barrier substrates necessary for R2R OLEDs

Figure 1 A schematic representation of program achievement

2. Project Background

As a manufacturer and seller of lighting products, GE understands the lighting market potential of a light source that is more efficient than conventional light sources, is thin, light-weighted and flexible, and can be delivered to the customer at reasonable cost. The OLED lighting is an emerging technology that has the potential to deliver in all of these categories. From a customer viewpoint, OLED's unique form-factor such as thinness and flexibility could be a key enabler for early market penetration. GE also understands that because of the cost requirements of the lighting market, the introduction of any new lighting technology is enabled only through considerable focused effort that harmoniously combines the essential elements of a technology with the engineering requirements of mass, low-cost production.

An OLED is made by depositing organic layers onto a transparent electrode (generally the anode) and then applying the counter-electrode (generally a metallic cathode layer). OLEDs are intrinsically large area devices, and have an operating brightness such as 1000 cd/m^2 or $\sim 3000 \text{ lm/m}^2$ and current densities that are several orders of magnitude lower than their inorganic counterparts. Fortunately, the organic semiconductor layers employed in the OLEDs can be deposited at much lower cost per unit area than possible using conventional semiconductor chemical-vapor-deposition processes.

Currently, OLED technology has only been commercialized in volume for display applications. These display devices such as AMOLEDs, which can command a premium price, are manufactured using batch vacuum thermal evaporation (VTE), which is often called as dry-coating, to deposit both the organic active layers and the top electrode onto glass substrates. Directly transitioning these display VTE-processes to make OLED lighting products leads to an estimated cost more than \$1,000 per square meter. Lighting products, unfortunately, have a different cost structure. For instance, US Department of Energy has projected, as shown in its Roadmap for Solid State Lighting Programs, an end cost of $\$100/\text{m}^2$ or less is required before OLEDs become competitive with respect to other lighting technologies.

Achieving such cost-reduction requires developing new-generation processing equipment with larger substrate sizes—an increase from today's Gen 2 ($400 \times 500 \text{ mm}$) to at least Gen 6 ($1500 \times 1800 \text{ mm}$), shorter processing cycle times (reduced from today's four minutes to one minute or less), and higher material utilization rates (an increase from today's 10% to over 50%). However, this approach of batch processing ever-larger OLED substrates requires a massive infrastructure investment which unfortunately leads to a very poor return-on-investment.

The lowest-cost method for coating organic materials is via R2R solution coating, as has been demonstrated by the photo-film industry. Conversely, the lowest-cost method for coating metallic films is via R2R vacuum deposition, as has been demonstrated by the food-packaging industry. GE's approach is to use the best of both processes via a high-speed hybrid R2R

process. GE has adopted a hybrid approach since it can enable large-size (for two-meter-wide web), high-throughput (processing speed capable of tens of meters per minute), and a material utilization rate that is higher than 90%. GE's existing OLED R2R research line combines solution processing of the organic layers with an innovative air-to-vacuum transition stage that allows a metallic cathode to be vapor deposited at potentially high rates of speed onto flexible, plastic substrates. This fully integrated research line was the product of a four-year NIST-sponsored development program (NIST ATP#70NANB3H3003) that ended in 2007 and was designed for printing polymer OLED materials that had been extensively optimized for solution coating. The line uses as an input a roll of eight-inch-wide indium tin oxide (ITO) coated plastic web and outputs a fully functional, large-area OLED device. After that, the GE team has continued to devote significant effort to modifying the equipment and optimizing the R2R process for fluorescent polymer OLEDs. As a result, coating non-uniformity was dramatically reduced from $\pm 50\%$ to $\pm 5\%$ and polymer OLED device yield was improved from 60% to 95%. The integrated hybrid R2R line has proved primary concepts for high-speed polymeric OLED manufacturing (Figure 2).

Figure 2 R2R polymeric OLEDs. (a) 15 feet long green R2R polymeric OLEDs with 96% good panel yield (b) under-cabinet OLED panels made from blue R2R polymeric OLEDs and (c) blue R2R polymeric OLED wrapped around a three-inch-diameter plastic core

In order to enable higher efficacy, GE has switched from polymer materials to solution-processible small-molecule OLED (SM-OLED) materials for its OLED devices. During the process of optimizing the R2R line and R2R processes, GE found that two modules (one for TCO treatment and the other for coating the SM OLED materials) originally optimized for polymeric materials are potentially not compatible with processing SM OLED materials. Thus, these modules will need to be redesigned and replaced. Furthermore, GE found that R2R coated SM-

OLEDs employing existing SM material set and ink formulations originally optimized for spin-coating tend to have poorer quality and performance with respect to their polymeric counterparts. This poses a significant risk when transferring SM materials (necessary for high device performance) to R2R manufacturing (necessary for cost-reduction).

The objective of this program is to close the gap by demonstrating high performance SM-OLEDs using a R2R process. The key to achieving the goal is an extremely close relationship between the manufacturing technology and materials optimization when using wet-coating. Without this close interaction, it is less likely that R2R wet-coating will reach high process yield and high performance at the same time.

3. Project scope and approach

In this program, GE Global Research has collaborated with DuPont Displays, Inc (DDI) to systematically integrate high-performance phosphorescent small-molecule OLED materials, advanced OLED device architectures, flexible barrier films, and an advanced encapsulation scheme with GE's research R2R manufacturing infrastructure.

GE and DDI have extensive, complementary experience with the wet-coated OLED technology that is required to enable wet-coated R2R manufacturing. DDI has been a leader in the development of wet-coatable OLED materials and GE has been a leader in the optimal use of these materials as well as R2R equipment and processes for making large area OLEDs. The team's prior wet-coated OLED experience has demonstrated the need for a tight integration between material optimization and material processing.

The program was built upon GE's state-of-the-art wet-coatable all-phosphorescent SM-OLED architecture. The all-phosphorescent small-molecule material system has a high entitlement for efficiency and lifetime, as has been demonstrated in many VTE-coated devices. The device architecture consists of four wet-coated organic layers: a hole-injection layer (HIL), a hole transparent layer (HTL), an emissive layer (EML), and an electron transport layer (ETL). One of the key enablers for the multilayer structure is a unique set of solvents developed at GE that provides intrinsic differential solubility, without using any additional thermal or chemical treatments, such as cross-linking, that are generally detrimental to device efficiency and/or lifetime.

For wet-coating, unlike its dry-coating counterpart, there are many possible interactions among OLED materials, solvents, device architectures, detailed processing techniques and conditions. In this program, DDI has focused on adapting its material set and developing new materials, particularly emissive materials, to improve performance, film-forming capability, solubility properties etc to enable the use of a broader set of R2R processing conditions. GE has focused on adapting its device design capability, research R2R line and processing know-how to enable a wider diversity of materials and structures to be built.

At the beginning of the program, the team identified five key areas of development based on prior experience, brainstorming and risk analysis:

1. Design, build and validate key equipment modules to enable R2R SM-OLED coating;
2. Optimize and develop SM OLED materials and ink-formulations suitable for R2R;
3. Identify key component materials such as flexible barrier substrate necessary for R2R process;
4. Develop robust R2R processing conditions and specifications for OLED layers, and,
5. Demonstrate high performance all wet-coated OLEDs

Throughout the program, the team has devoted majority of efforts on addressing the areas of development. At the end of the program, the team has acquired valuable knowledge regarding each risk item, developed key processing know-hows and specifications, and validated basic designs for key R2R equipment modules that are critical to the development of low-cost manufacturing of OLED lighting products.

Additional technical details on the areas of development can be found in [Section 8](#).

4. Program Management Plan and Milestones

Figure 3 and Table 1 shows the program flowchart and Gantt chart, respectively, which describe main tasks within this program.

Figure 3 Schematic of program flowchart

Table 1 Program Gantt chart

The final objective is to demonstrate R2R processed small-molecule OLEDs with same performance as achieved with the control lab-scale batch process. To help guide the program execution, we have proposed five milestones for different stages of the program (Table 2).

Table 2 Program milestones (* extrapolated data)

Milestone	Description	Date of completion	
		Target	Actual
1	Complete SM-OLED ink-formulation & process specification	Q4	Q4
2	Demonstrate 20LPW R2R SM-OLED	Q4	Q5
3	Emission uniformity with variation in brightness <20%	Q7	Q5
4	Completion of all wet R2R SM OLED architecture design	Q7	Q7
5	Demonstration of 45LPW R2R SM-OLED	Q8	Q9*

5. Funding Profile

Table 3 shows the funding profile for each budget period.

Table 3 Project Funding Profile

	Start Date	End Date	Government Share	Performer Share	Total
Budget Period 1	04/15/10	03/31/11	\$ 2,078,374	\$ 2,078,374	\$ 4,156,748
Budget Period 2	04/01/11	07/31/12	\$ 1,921,587	\$ 1,921,587	\$ 3,843,174
Total	04/15/10	03/31/12	\$ 3,999,961	\$ 3,999,961	\$ 7,999,922

6. Highlights of technical achievements

- a) Retired major coating-related high risks – significant risk reduction
- b) Demonstrated & validated basic designs for key R2R SM-OLED equipment modules
- c) Developed & validated general specifications for ink formulations and coating processes suitable for R2R
- d) Achieved more than 9X improvement in LPW or EQE for R2R SM-OLEDs through development of ink formulations and optimization of coating conditions
- e) Proven high performance potential of all-wet-coated SM-OLEDs through the demonstration of wet-coated green phosphorescent SM-OLEDs with lifetime (T70) of 170khrs;
- f) Identified & validated a low-cost barrier substrate that meets both OLED performance requirement & desirable moisture barrier properties;
- g) Successfully integrated “Materials” developed in Task 3&4 and “R2R Processes” developed in Task 5, key to achieving the performance target.

7. Future plans and areas of development

Although significant risk reductions have been achieved in the course of the program, additional technology developments are still needed to further mature the R2R SM-OLED. The following summarize key areas of future development:

- 1) High speed R2R cathode deposition module to enable overall high web speed to maximize throughput;
- 2) High speed drying module to minimize line footprint and operation cost;
- 3) R&D on OLED materials, processes and equipment designs to simplify line design to minimize capital expenditure, and
- 4) Identify and grow supply chain for key OLED components.

8. Appendix – Description of major achievements

The program was aimed for addressing three major development needs identified.

1. Performance: the performance of R2R OLEDs was only 1/10 of that can be achieved with batch controls;
2. Coating quality for OLED layers;
3. Process & equipment demonstration: the existing material set & coating modules need to be improved for better R2R compatibility.

8.1 (Task 5A) Identified root-causes for low efficiency for R2R OLEDs

R2R SM-OLEDs made prior to the program had device efficiency only 1/10 of that of laboratory-scale batch controls. Substantial efforts in Q1 were made to understand possible root-cause(s) for the efficiency deterioration. A layer-by-layer approach was taken to qualify each OLED layer sequentially in terms of coating, drying and baking. As one can see in [Figure 4](#), the observed efficiency deterioration is mainly caused by switching small-molecular EML coating technique from spin-coating to R2R printing.

Figure 4 Relative performance of OLEDs with batch-processed layers replaced by R2R processed (All the devices have a common structure ITO anode\HIL\HTL\EML\ETL\ Cathode where HIL, HTL, EML and ETL are wet-coated by either batch-process or R2R process).

The root-cause was then confirmed to be that the small-molecule based emissive layer (SM-EML) coated by the original R2R printing technique using the same ink formulation as optimized for spin-coating is too thin. However, the team experienced tremendous difficulty with measuring the thickness of such thin and soft OLED layers on flexible substrates using standard techniques. In fact, one of the remarkable achievements made in Q1 was a combination of improved skills and techniques that enables measuring thickness of thin organic films on flexible substrates.

8.2 (Task 5B) Demonstrated >6X coating thickness improvement to enable efficiency enhancement

Utilizing quality tools like six sigma and design of experiments, the team brainstormed and screened more than 10 different factors including ink formulations, coating conditions and processing details etc that may affect coating thickness. Three significant factors have been identified to be effective & practical in terms of thickness control.

The first one (also the most straightforward one) is to adjust the solid content of ink formulations because the thickness of a final dry film obtained from a printed wet film with a given wet thickness is proportional to the solid content. Up to 1.5X in thickness can be readily achieved with the same set of materials and solvent. This approach, however, is not the most preferred one because solutions with such high solid contents may have stability issue – solid OLED materials may crash out from solutions over time. Further, the maximum achievable solid content depends on the choice of OLED materials and solvents, which may post undesirable limitations on material design and choices.

The second approach is achieved by developing new ink formulations with better R2R coatability without compromising device performance. Note that, finding an alternative solvent is not a trivial work. One has to first consider intrinsic solvent & ink properties such as solubility, purity and viscosity etc, then orthogonal solubility – whether the solvent of interest affects OLED materials used in other layers, and finally device performance such as efficiency, lifetime and reliability. We identified & screened more than ten solvent candidates and finally down-selected to two solvents that result in more than 2X increases in thickness.

The third approach is through optimization of coating conditions, which alone provides 3X improvement. As shown in **Figure 5**, the combination of latter two approaches results in a total thickness improvement of more than 6X using the same set of EML OLED materials.

Figure 5 Thickness of R2R EML as a function of coating procedure & formulations

The same layer-by-layer test was then repeated using the optimized ink formulations and coating conditions. The results are summarized in **Figure 6** in comparison to the one obtained at the beginning of the program. The optimized process gives more than 9X improvement in EQE, which closes the gap between the R2R SM-OLED and the batch control.

Figure 6 Relative performance of OLEDs with batch-processed layers replaced by R2R processed ("Q1Y1" refers to results obtained in May 2010, at the beginning of the program, and "Q3Y1" results obtained in September 2010 using optimized R2R processes and formulations.

8.3 (Task 5B/C) Improved panel emission appearance

At the beginning of the program, R2R processed SM-OLEDs exhibit unacceptable appearance due to two types of defects: (1) scratches and (2) global dark bands.

The scratches are mainly caused by the coating method. Improved coating quality (uniformity and thickness) significantly reduces the number of scratches (**Figure 7**). The ultimate solution, which was proposed in the Statement of Work and pursued in the program, is to replace the existing coating module with a non-contact coating system.

Figure 7 Images of OLEDs with R2R processed organic layers (Left: using the old control R2R EML process and Right: using the new R2R EML process and coating formulations)

The root-cause for the global dark band is more complex and was not very clear at the beginning of the program. Efforts have been made to understand possible causes and develop corresponding mitigation plans. At least two factors have been identified (1) thin and non-uniform SM-EML coating that causes uneven PL and EL quenching and (2) residual solvents which can degrade cathode, resulting in non-uniform electron injection and emission. Process conditions have been modified to address the concerns. The appearance of R2R OLEDs achieved in Q3 was much better than the one made prior to the program. The R2R SM-OLED panels also show acceptable uniformity with variation in EQE less than $\pm 10\%$, which meets the Milestone 3 (variation less than $\pm 20\%$) (**Figure 8**)

Figure 8 Cross panel (6") uniformity

8.4 Developed & validated R2R coating module

In this program, the team worked with a tool company in designing a R2R wet-coating unit. During the design stage, the team conducted a coating trial using a standard demonstration unit at the vendor site. The trial yielded much valuable information such as basic coating parameters, over-all configuration and tolerance, etc. More importantly, the trial validated the basic design, which retired one of the high risks associated with preliminary designs – the coater was able to handle and print OLED solutions. Trial films coated using the new coating technique showed exceptional uniformity cross 6" inch web width (Figure 9). The trial also revealed one limitation of the standard coater design – a narrow coating thickness range. Some key revisions & modifications to the standard design were made to enable coating stability and quality in a wider thickness range necessary for robust R2R SM-OLED device architecture. Table 4 shows the results of 6"x6" panels obtained using the customized and fully integrated slot-die coater under normal R2R operation.

Figure 9 Cross web uniformity of coating thickness

Table 4: Uniformity and thickness range for 6" R2R OLED panels

Panel #	Variable B	Variable C	Thickness (nm)	STDEV (nm)
1-A	0.62	10	84	2.6
1-B	0.62	10	84	1.7
2-A	0.42	10	62	2.2
2-B	0.42	10	59	1.7
3-A	0.63	5	72	2.6
3-B	0.63	5	73	2.3
4-A	0.21	5	49	1.3
4-B	0.21	5	49	1.7

8.5 (Task 3) Developed materials for better R2R compatibility & performance

The existing GE & DP materials have been screened. The results suggest that the major focus of material development needs to be on HTL and EML. The objective of the task is to develop a complete EML coating formulation that enables R2R wet-coating and high performance. For instance, molecular structures for small molecule OLED materials need to be optimized to achieve right solubility and right morphology in solution and film as well without comprising any opto-electronic properties. One example is shown in [Table 5](#). The control dopant, originally developed for dry-coating, is not well soluble in the solvent systems optimized for R2R process. The dissolution process takes approximately 2 days. By the contrary, the two new dopants provide much better solubility and solution stability while maintaining the device performance.

The material structures, properties, performance and processibility are carefully studied, which provide critical know-hows and correlations of material design, material processing and performance.

Table 5 Comparison of three OLED dopant materials

Dopants	Solubility (mg/ml)	Time needed for dissolution (hrs)
Control_H0	0.1	~40
NEW_H2	10	0.2
New_L3	0.1	0.3

8.6 (Task 4) Proved the entitlement of wet-coated OLEDs

OLEDs produced by R2R wet-coating have the potential of lower cost with respect to dry-coated devices. Meanwhile, performance of wet-coated OLEDs has been improved dramatically in the past several years. For instance, in 2010, GE announced wet-coated white OLEDs with power efficiency of 56LPW. However, there have been some concerns about the stability of wet-coated OLEDs because lifetime for dry-coated devices reported so far is much better than that reported for wet-coated devices. In this work, as part of material evaluation efforts, we have demonstrated all wet-coated green and red OLEDs with record lifetime: a T70 (30% decay from its initial brightness) more than 170 khrs & 55 khrs for green and red OLEDs, respectively. The demonstration clearly suggests that OLEDs with high performance & long life time can be achieved with wet-coating technology.

8.7 Identify low-cost flexible barrier substrate

The availability of flexible substrates is critical to R2R manufacturing. In the past decade, considerable research and development effort has been directed towards developing a mechanical flexible substrate suitable for OLEDs and other organic-based electronic devices. Key requirements for a flexible substrate are optical transparency, mechanical flexibility, chemical resistance, thermal stability, and impermeability to water and oxygen. Among them, impermeability to water and oxygen, which is commonly referred to as the barrier property, represents the most demanding technical requirement for a flexible substrate because active organic materials and electrodes employed in OLEDs are sensitive to water and oxygen, which, if present in the devices, accelerate their degradation. The well-accepted specification for impermeability for OLEDs to achieve a 10-year service time is a diffusion rate for water and oxygen through the substrate of interests of less than 10^{-6} g/m²/day and 10^{-5} cc/m²/day, respectively.

Figure 10 Images of Ca coupon as made and >3000hrs under 60°C/90%RH

Developing new technologies for flexible substrates is outside the scope of this program. The work performed in this area under the program was to evaluate samples from four different vendors. All samples tested so far are compatible with OLED fabrication processes. One particular sample has shown superior barrier performance based on the standard Ca test. Shown in **Figure 10** are images of a Ca film encapsulated with the flexible barrier substrate of interest taken as made and after >3000hrs under 60°C/90%RH.