Final Report

DOE STTR Phase-II, Topic #: 12-B
Phase-I Grant Award No.: DE-FG02-07ER86293

Recipients:
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Subcontract:
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Project Title:
"Materials Degradation Analysis and Development to Enable Ultra Low Cost, Web-Processed White P-OLED for SSL"

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A. Final Status Comparison to Objectives & Project Goals

The research work conducted under DE-FG02-07ER86293 has been an unqualified success in terms of reaching most of our performance goals as well as stimulating the commercialization of this technology. The progress in printed white OLEDs performance through this project, which has followed the specifications and goals of our scale-up partners has led, in part, to the acquisition of this technology by a strategic partner with the intention to bring it to commercialization. We have also uncovered new example of degradation in doped OLED devices which may further benefit future device development efforts.

Progress over Phase II of DE-FG02-07ER86293 “Materials Degradation Analysis and Development to Enable Ultra Low Cost, Web-Processed White P-OLED for SSL” was initially rapid in terms of device performance improvements. We exceeded our device luminance lifetime goals for printed flexible white OLEDs as laid out in our project proposal. Our Phase II performance target was to demonstrate >1500 hours luminance lifetime at 100 Cd/m2 from a printed flexible device. We now have R&D devices well in excess of 8000 hrs lifetime at 100 Cd/m2, tested in air. We also were able to produce devices which met the voltage target of >1500 hours below 15V operation. After completing the initial performance milestones, we went on to focus on color-related degradation issues which were cited as important to commercialization of the technology by our manufacturing partners. We also put additional focus on cathode work as the active material development that occurred over the STTR time period required an adaptation of the cathode from the original cathode formulations which were developed based on previous generation active layer materials. We were able to improve

compatibility of the cathode with some of the newer generation active layer materials and improve device yield and voltage behavior.

An additional objective of the initial Phase II was to further develop the underlying manufacturing technology and real-life product specifications. This is a key requirement that must be met to ensure eventual commercialization of this DOE-funded technology. The link between commercial investment for full commercialization and R&D efforts in OLED solid State Lighting is often a large one. Add-Vision's lower cost, printed OLED manufacturing approach is an attraction, but close engagement with manufacturing partners and addressing customer specifications is a very important link. Manufacturing technology encompasses development of moisture reduction encapsulation technology, improved cost performance, and reductions in operating voltage through thinner and higher uniformity active device layers. We have now installed a pilot encapsulation system at AVI for controlled, high throughput lamination encapsulation of flexible OLEDs in a novel process. Along with this, we have developed, with our materials supply partners, adhesives, barrier films and other encapsulation materials and we are showing total air product lifetimes in the 2 – 4 years range from a process consistent with our throughput goals of ~ 1M device per month (~30,000 sq. ft. of processed OLEDs). Within the last year of the project, we have been working to introduce the manufacturing improvements made in our LEP deposition and annealing process to our commercial partners. Based on the success of this, a pilot scale-up program was begun. During this process, Add-Vision was acquired by a strategic partner, in no small part, because of the promise of future success of the technology as evidenced by our commercial partners' pilot scale-up plans. Overall, the performance, manufacturing and product work in this project has been successful.

Additional analysis and device work at LBL has also shown a unique adhesion change with device bias stressing which may result from active layer polymer cross-linking during bias stressing of device. It was shown that even small bias stresses, as a fraction of a full device lifetime stress period, result in measurable chemical change in the device. Further work needs to be conducted to fully understand the chemical nature of this interaction. Elucidation of this effect would enable doped OLED formulation to be engineered to suppress this effect and further extend lifetimes and reduce voltage climb.

B. Discussion of Achievements During the Project

Exceeding our performance targets and pushing this technology beyond the 10,000 hrs lifetime mark has been a significant achievement. This progress is directly a result of removing degradation-causing impurities as well as improved device structuring and new, charge-balanced light emitting polymers. . There were three significant degradation and performance limiting factors which we discovered during the last year. The partial resolution of these issues has driven our progress and we believe that we can further reduce the detrimental effects of these to drive performance further. A primary finding was the dramatic impact of residual H2O in our active layer materials, originating from starting materials and handling. Although it was known that environmental moisture leaking through encapsulation during product life was an important factor, the significant impact of starting moisture was somewhat surprising. The impact of residual moisture in the printed OLED process on flexible substrates is increased by the fact that typical moisture reduction steps for glass-based OLEDs may not be used here. Due to the temperature limits of the flexible substrates and the process throughput limits for our low cost manufacturing model, high temperatures (~200C) and long times (tact times > 1 minutes) are not possible or are undesirable from

a cost perspective. Therefore, we have developed moisture reduction approaches consistent with our manufacturing model, but it is likely that further improvements can be made. Also, we made the significant finding that quantum efficiencies in our devices are dominated by hole transport and electron injection limitations. We have adapted the electronic structure of our system to accommodate for this, but it is likely that further optimization may be achieved. Lastly, we performed optical degradation analysis to show that, in the generations of white emitter materials which were first able to meet the project milestones, selective chromophore degradation is not a primary factor and that the chromophore systems are relatively stable throughout device lifetime. The indication is that backbone and charge transport moieties are the sites where device degradation occurs. Photoluminescence and electroluminescence spectra from a white emitting device, at different points during accelerated electroluminescence lifetime testing, is shown in Figure 1.

Later generation white emitting polymers which showed longer lifetime or improved voltage turn-on behavior beyond the initial specification, were less color stable and or had unacceptable color purity. Over the course of the white device development towards product prototypes, this became a major concern for product development partners.

As stated above, the second objective of Phase II was to further develop the underlying manufacturing technology including the development of moisture reduction encapsulation technology, improved cost performance, and reductions in operating voltage through thinner and higher uniformity active device layers. We have now installed a pilot encapsulation system at AVI for controlled, high throughput lamination encapsulation of flexible OLEDs in a novel process. Along with this, a new encapsulation materials set also is in development and we have seen significant progress in barrier films and other materials, consistent with our product goals and manufacturing process. Add-Vision is also developing a complete product specification with end customers to include significant environmental testing as well as basic device performance issues. This is also a key step towards actual commercialization and may highlight areas, due to new environmental barrier or mechanical requirement, where the encapsulation materials need to be further pushed. We have also conducted

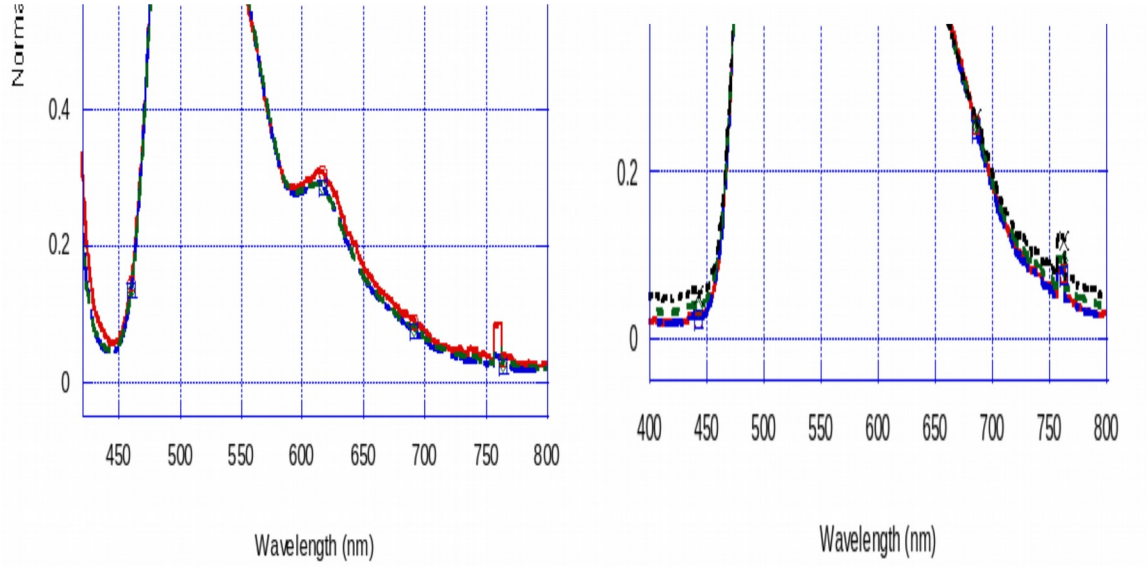

Figure 1. Normalized (Left) Photoluminescence spectra and (Right) Electroluminescence spectra of an actual white emitting device active layer tested at several intervals throughout an accelerated lifetime test (constant current, high luminance/current electroluminescence testing). Note that as the device ages, we do not see large changes in the emission spectrum (there is some slight change in red emission near 620 nm) wile the overall device efficiency drops by a factor of 2X. This indicates that the chromophores themselves are not the primary cause of device degradation. Indications are that degradation of charge transport and backbone functionalities may be the primary degradation pathway.

manufacturability trials with our partners involving >1000 ft2 of processed flexible material. Based on this study and the strong progress in overall device performance, our technical work in the coming period will include large scale printing optimization, particularly with regards to optimizing materials usage efficiency in manufacturing as well as improvements in device uniformity, reduction in device thickness, and improved turn-on characteristics. Materials usage efficiency and device active layer thickness directly impact manufacturing cost as the active layer material, and the inks used to form it, dominate that cost of the finished product. To achieve this, additional work in polymer structure, film morphology and printed film structure will be required. To further assist us with these scaled up materials usage issues, we now have print systems installed at Add-Vision for A4 to >12' x 12" processing which represents a significant scale-up from the R&D sizes that initial device development was based on. This is consistent with the process scale for initial manufacturing and will allow us to directly transfer materials and processes to our manufacturing partners' manufacturing lines.

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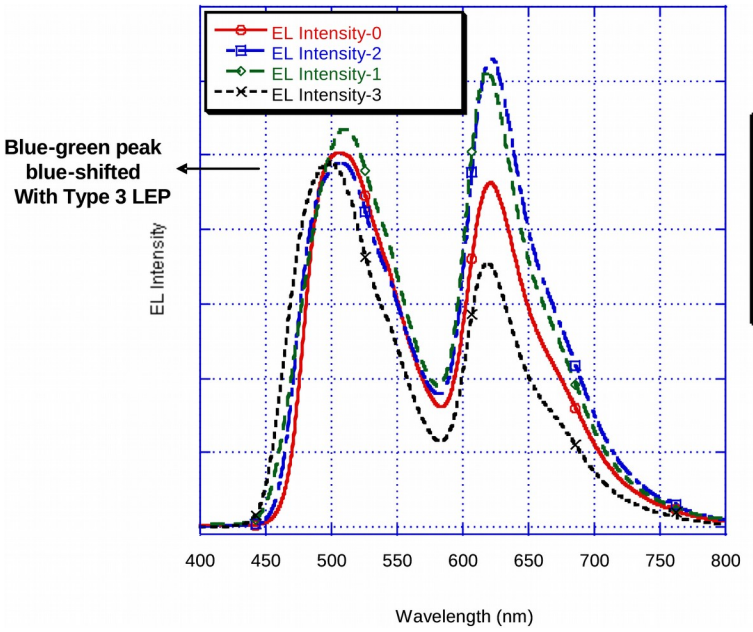

	LEP Type	Initial CIE by radiant camera
-	Type0	0.454, 0.453
-	Type2	0.459, 0.429
-	Type1	0.435, 0.433
-	Type3	0.380, 0.385

Figure 2. EL spectra versus polymer backbone variant and backbone in all-printed white LEP devices. This enabled an improvement in blue spectral content and in improvement in the color purity to within the product specification (EL emission with CIExy <0.4, 0.4.

Additional lifetime bias stress and analysis work at Add-Vision and LBNL showed a new degradation mechanism which was uncovered during the grant extension period. This was exemplified by chemicals changes in the active layer, associated with the p-region of the device, which dramatically affected the adhesion properties of the film even after very short bias periods. This suggested am irreversible, hole-mediated reaction between the light-emitting polymer and the anode interface. Evidence for these changes are is shown in Figure 3., wherein changes in the morphology of anode interface with the LEP, after lift off show changes after only minutes of bias stress. Continued bias stress prevented lift-off separation of the LEP from the anode entirely. In this case, tensile stress failure normal to the plane of the device led to cohesion failure within the LEP layer or at the cathode/LEP interface. Repeated examination of un stressed controls showed clean delamination of the device at the anode LEP interface which would be expected considering the lack of any chemical bonding between the ITO anode and the active layer polymers which, in their unexcited state, would be expected to have unreactive apolar and hydrogen bonding character.

In further pursuit of issues observed during the two year Phase II period, formulation work and microscopic analysis during the extension period has also shown that, with proper cathode formulation and processing, that interfacial stability between the cathode and LEP can be maintained. Figure 4 showed an example of a distinct interface between the printed light emitting polymer layer and the cathode layer in a case where solvent and

process conditions were optimized to prevent significant LEP/cathode interaction. No significant changes in the cathode/LEP interface were noted in cross sectional electron microscopy investigation.

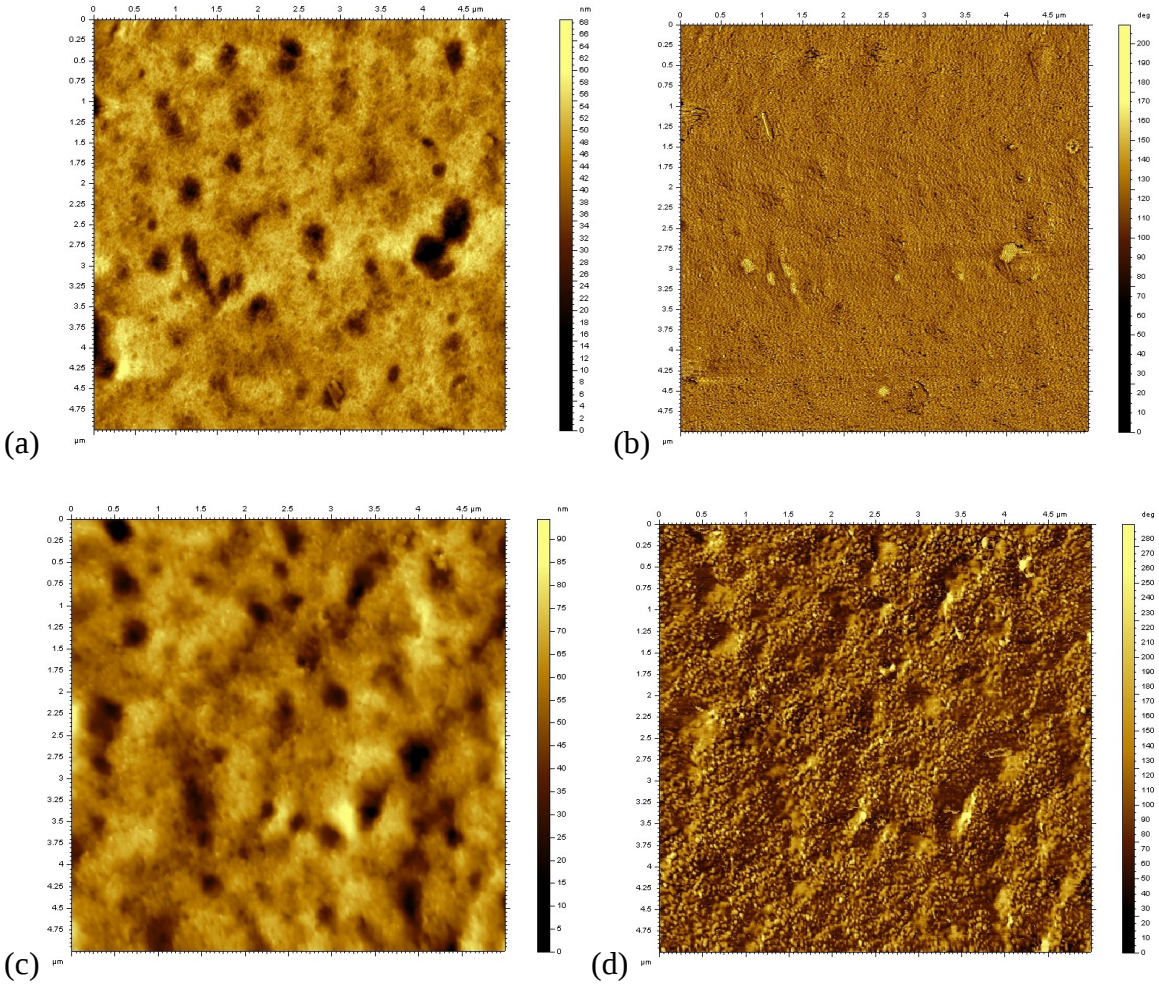

Figure 3. Atomic force microscopy images of the surface of the active layer of the device at the anode interface, taken by Dr. Pete Driscoll at Lawrence Berkeley National Labs. The samples were prepared by an adhesive lift-off process. Image (a) is the topography image of the unstressed interface and (b) is the phase image of the unstressed device. (c) shows the topography of the stressed active layer interface and (d) shows the phase image of the stressed anode layer interface. The topography images are relatively similar, but the phase image indicates a significant difference in the surface properties of the material near the stressed interface. This correlated with the adhesion tests.

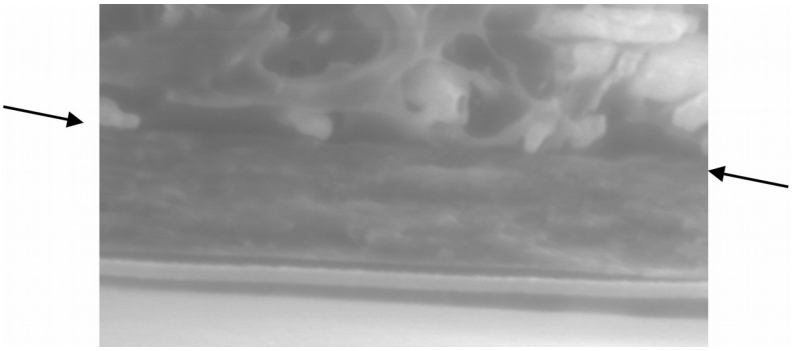

Figure 4. SEM cross-section, prepared by Dr. John Chmiola at Lawrence Berkeley National Labs. The sample was prepared by cryogenic fracture and imaged in a JEOL field emission microscope. The LEP interface can seen clearly and there is little evidence to suggest penetration of the cathode into the LEP.

Future chemical analysis of the interfacial materials in the stressed devices may be employed to uncover the specific reaction related to the observed interfacial changes. The authors feel this would be of significant value to the community as it may indentify a key degradation factor in doped OLED devices. If this factor can then be mitigated, further extensions in device lifetime in low-cost, all-printed OLED devices could be achieved.

C. Changes to Work Plan

A scope change and budget revision was requested and approved in 2010. This scope change was submitted separately and is recounted in the document entitled “DOE STTR DE-FG02-07ER86293 Phase II Scope and Budget Change-Amended Oct 6 2010”.

D. Work Products During this Period.

The most significant product of our ongoing work in this project is the technology transfer to our manufacturing partners. This was expanded to a new partner, Bayer Materials Science in Lever-Keusen Germany. We completed technology training activities at our site and California in April of 2009 and finished the R&D process transfer to their

development site in Germany in the summer of 2009. In 2010 we began development and tool procurement activities towards installing a pilot line for printed doped OLED fabrication at our partner's site. This has led, in part, to the acquisition of AVI's technology in January 2011.

In terms of publications, work related to this project is, in part reflected in two publications which are currently in press:

J. D. MacKenzie, J. J. Breeden, J. P. Chen, P. Hinkle, E. Jones, Y. Nakazawa, J.-H. Shin, V. Vo, M. Wilkinson, Y. Yoshioka, J. Zhang, "Printed, Flexible Doped P-OLED Displays," *SID Symp. Dig. of Tech. Papers, Accepted for Publication 2009.*

A. Arias, D. MacKenzie, I. McCulloch, and A. Salleo, "Materials and Applications for Large Area Electronics," Chem. Rev., *In Press 2009.*

Work under this project has been presented at numerous conferences including an invited talk at the Fall 2008 MRS Meeting, the USDC 2009 Workshop on Flexible Displays and Electronics, the 2009 DOE SSL Workshop in San Francisco and the 2010 Society for Information Display meeting.