

Process Controllability and Stability in Organic Vapor Phase Deposition

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Abstract

High performance green $Ir(ppy)_3$ -based phosphorescent OLEDs (PHOLEDs) have been fabricated by organic vapor phase deposition (OVPDTM). In addition to demonstrating both efficiency and operational device lifetime comparable to devices built by vacuum thermal evaporation, we report on the controllability and stability of the OVPDTM process. Specifically, run-to-run and day-to-day deposition rate reproducibility of better than 2 % for three consecutive days is demonstrated.

1. Introduction

OVPDTM is an innovative technology for the high volume manufacturing of small molecule organic semiconductor devices^{1,2}. The OVPDTM process is based on the sublimation of small molecular weight organic materials into an inert carrier gas stream, which transports the molecules to a cooled substrate where rapid condensation of the organic molecules occurs within a hot walled deposition chamber. A number of organic electronic devices fabricated by OVPDTM have been reported, including OLEDs, organic thin film transistors and organic photovoltaic cells^{2,3}. In this work we report on the progress on the development of the OVPDTM technology to design and build production scalable equipment⁴.

Figure 1 shows the schematic of AIXTRON's OVPDTM equipment employing a hot wall deposition chamber and the close coupled showerhead (CCS) concept as gas distributor capable of depositing highly uniform layers⁵. The organic source materials are heated in physically separated source containers and transported by an inert carrier gas into the hot-walled deposition chamber. Individual valves switch the

source flows to enable rapid on/off control of the respective deposition, which offers high precision control of layer interfaces as well as minimization of material waste. The organic molecules are introduced uniformly across the entire substrate surface through the heated showerhead injector and condense on the substrate to form the desired film. A high precision mask alignment can be integrated to allow fabrication of full color OLED displays.

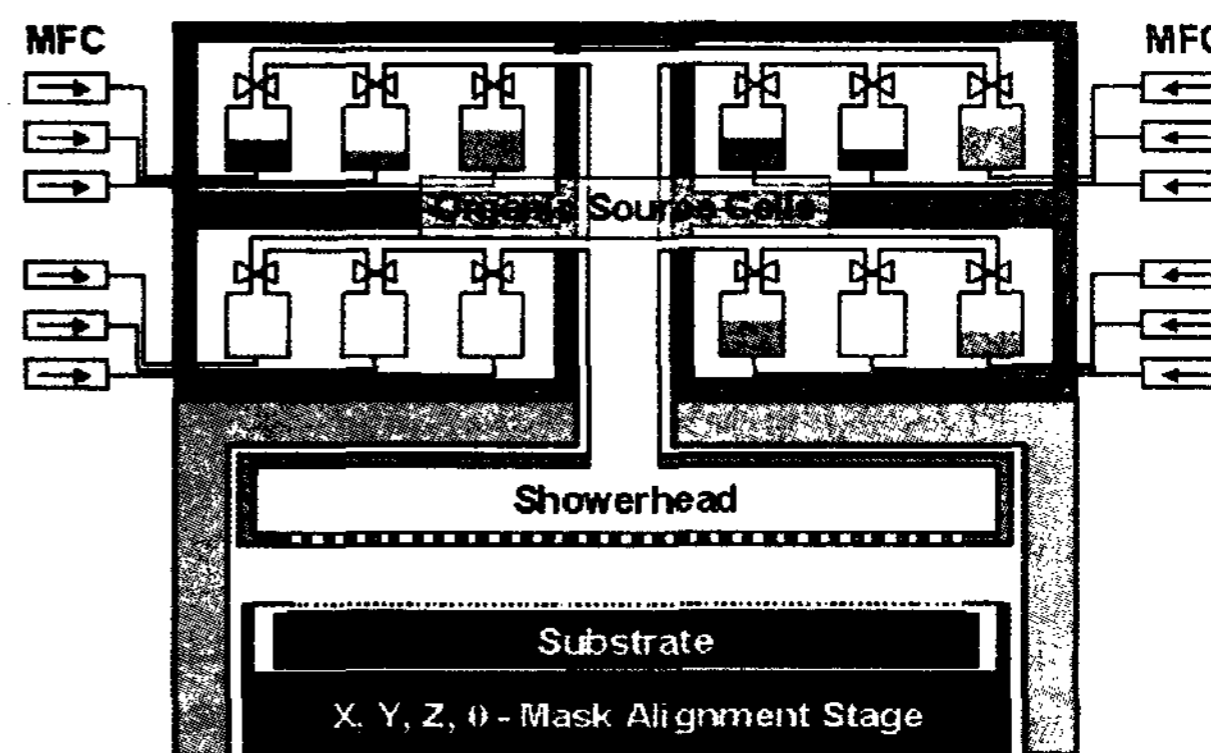


Figure 1: Production Scale OVPDTM Technology

Deposition rates and layer composition such as doping are adjusted by means of mass flow rate of the carrier gas at constant source temperature using individual electronic mass flow controllers (MFC) for each source. This offers a high degree of precision and reproducibility combined with flexibility in multilayer deposition sequences, as well as accurate composition of multi-component layers (co-hosting/co-doping).

Gas phase transport allows the remote placement of multiple organic sources with respect to the deposition chamber, thus preventing cross contamination between source materials. The hot walled deposition

chamber prevents parasitic condensation of the organic material.

Consequently OVPD™ offers potential for low maintenance cycles, high material yield, high reproducibility, well defined doping with multiple dopants and high throughput, which are key factors for industrial mass production at low cost of ownership.

2. Experimental

The experiments were carried out using AIXTRON Gen1 pilot production OVPD™ equipment: the organic molecules are transported in high-purity nitrogen as the carrier gas. The substrate is actively temperature controlled and the source cells are at temperatures in the range 275-310 °C. Thin films were deposited on (150 x 150) mm² indium tin oxide coated glass substrates, or 200 mm diameter silicon wafers. Growth rates and layer thicknesses were characterized *ex-situ* by ellipsometry, or *in-situ* by a quartz crystal monitor. We investigated five organic materials, listed in Table 1, used to fabricate a green phosphorescent OLED (PHOLED) as described by Kwong et al.⁶.

Table 1: Investigated Organic Materials

Alq ₃	<i>Tris-(8-hydroxyquinoline)-aluminum(III)</i>
α-NPD	<i>N,N'-Di-[(1-naphthyl)-N,N'-diphenyl]-(1,1'-biphenyl)-4,4'-diamine</i>
CBP	<i>4,4'-bis(N-carbazolyl)biphenyl</i>
BAlq ₂	<i>Aluminum(III)bis(2-methyl-8-quinolinato)4-phenolphenolate</i>
Ir(ppy) ₃	<i>fac-tris(2-phenylpyridine)iridium</i>

3. Results and discussion

We first evaluated the deposition controllability in an OVPD™ chamber in which we have introduced a quartz crystal monitor to measure the deposition rate *in-situ*. A constant carrier gas flow from an Alq₃ source was adjusted with a target deposition rate of 12.5 Å/s. The gas flow was switched on and off several times. To study the stability of the deposition process, the first deposition was done for 120s. For verification of deposition rate reproducibility, six

layers were then deposited for 20s each, with 15s intervals between the depositions, as shown in Figure 2.

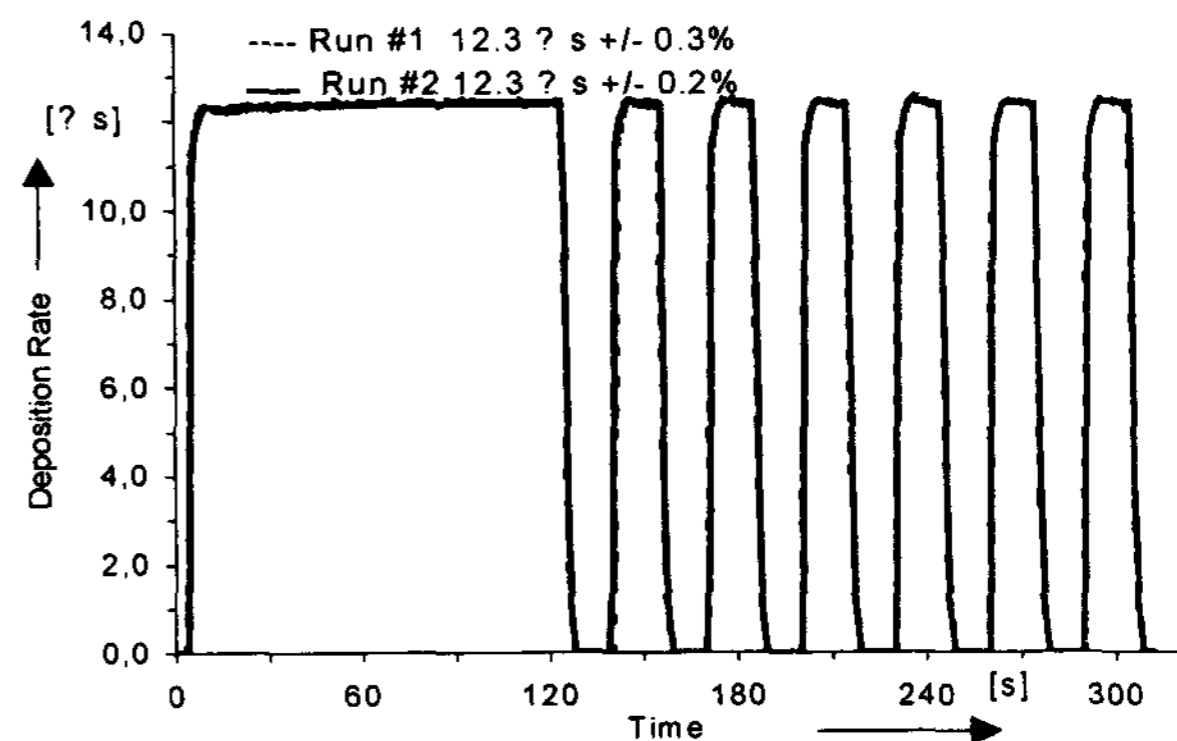


Figure 2: Deposition Rate of Alq₃ vs. Time of two Depositions

The average deposition rate achieved is 12.3 Å/s, corresponding to a deviation of 1.6 % as an offset calibration from the calculated target rate. As a consequence of the stable source temperature and the precise control of the carrier gas the variation of the deposition rate within one run and from run to run is within the measurement accuracy. The two deposition runs recorded in Figure 2 show controlled switching of the source flow: all sequences show steep on/off transitions, as required for realizing sharp interfaces.

The long-term deposition reproducibility was further evaluated on the Gen1 pilot production OVPD™ system in consecutive depositions of the same material on the same day (run-to-run comparison) as well as repetitions of a series of depositions on different days (day-to-day comparison).

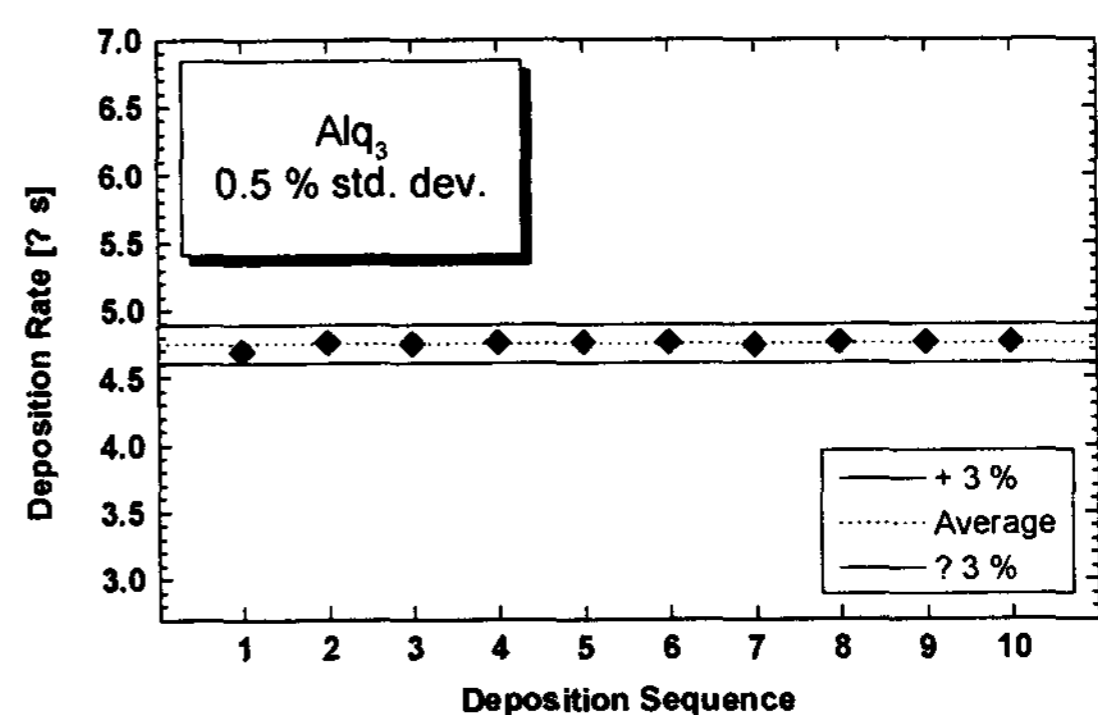


Figure 3: Run-to-Run Thickness Reproducibility of Alq₃

All layer thicknesses were characterized *ex-situ* by ellipsometry. Figure 3 shows the deposition rate versus number of runs for a sequence of ten Alq₃ depositions with identical process parameters. As a reference, the ± 3 % and average deposition rates are

shown. The thickness fluctuation at an average deposition rate of 4.8 Å/s was 0.5 % std. dev. A peak deposition rate of 15.4 Å/s was achieved by using the maximum flow at the source temperature of 300 °C.

The series of ten consecutive depositions were also performed with other materials listed in Table 1. For α-NPD the thickness reproducibility at an average deposition rate of 3.5 Å/s was 0.8 % std. dev, with a peak deposition rate of 9.4 Å/s. For BAQ₂, an average deposition rate of 5.4 Å/s with 1.8 % standard deviation was obtained with a maximum rate of 10.1 Å/s. For CBP with an average deposition rate of 14.1 Å/s, the standard deviation was 0.7 % and the peak deposition rate was 24.3 Å/s. For Ir(ppy)₃, an average deposition rate of 0.99 Å/s at a standard deviation of 0.6 % was achieved, with a peak deposition rates of 2 Å/s; sufficiently high given the peak deposition rate of 24.3 Å/s of the host material and a required 3-20% doping ratio.

The peak deposition rates achieved during these experiments do not represent limits to the OVPD™ technology as such but were limited by the current configuration of the used equipment at the temperatures chosen.

Fig. 4 shows the three-day reproducibility results for the growth of CBP films. During the ten consecutive runs on each day, the run-to-run thickness reproducibility, and the daily average growth rates were both within 1 %.

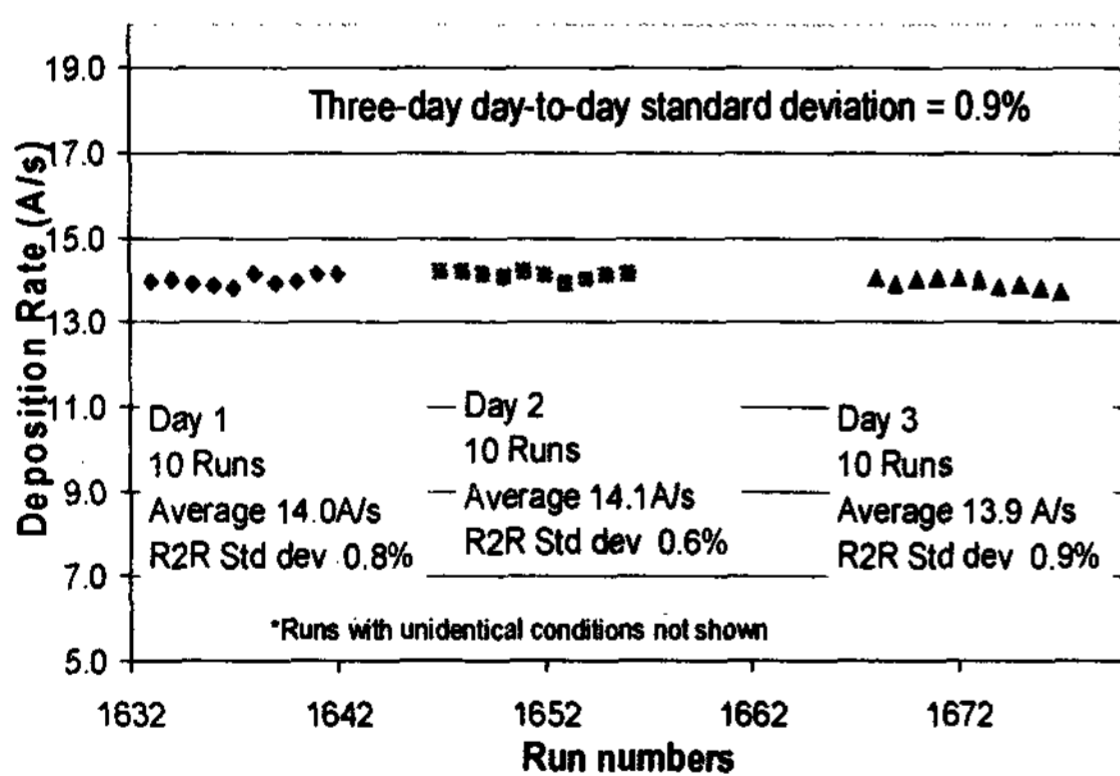


Figure 4: Run-to-Run and Day-to-Day deposition rate reproducibility of CBP

Similarly, Fig. 5 shows reproducible deposition rates for Ir(ppy)₃. The run-to-run fluctuation within a particular day was 0.6 – 2.7 %, whereas the day-to-day variation was ± 2 %. For α-NPD the value is ± 1.45 %, and for BAQ₂ ± 0.9 %.

A day-to-day thickness reproducibility of ± 2.4 %

was achieved for Alq₃ over a period of three days, where no deposition runs were done on the second day. All results of deposition rates and reproducibility are summarized in Table 2.

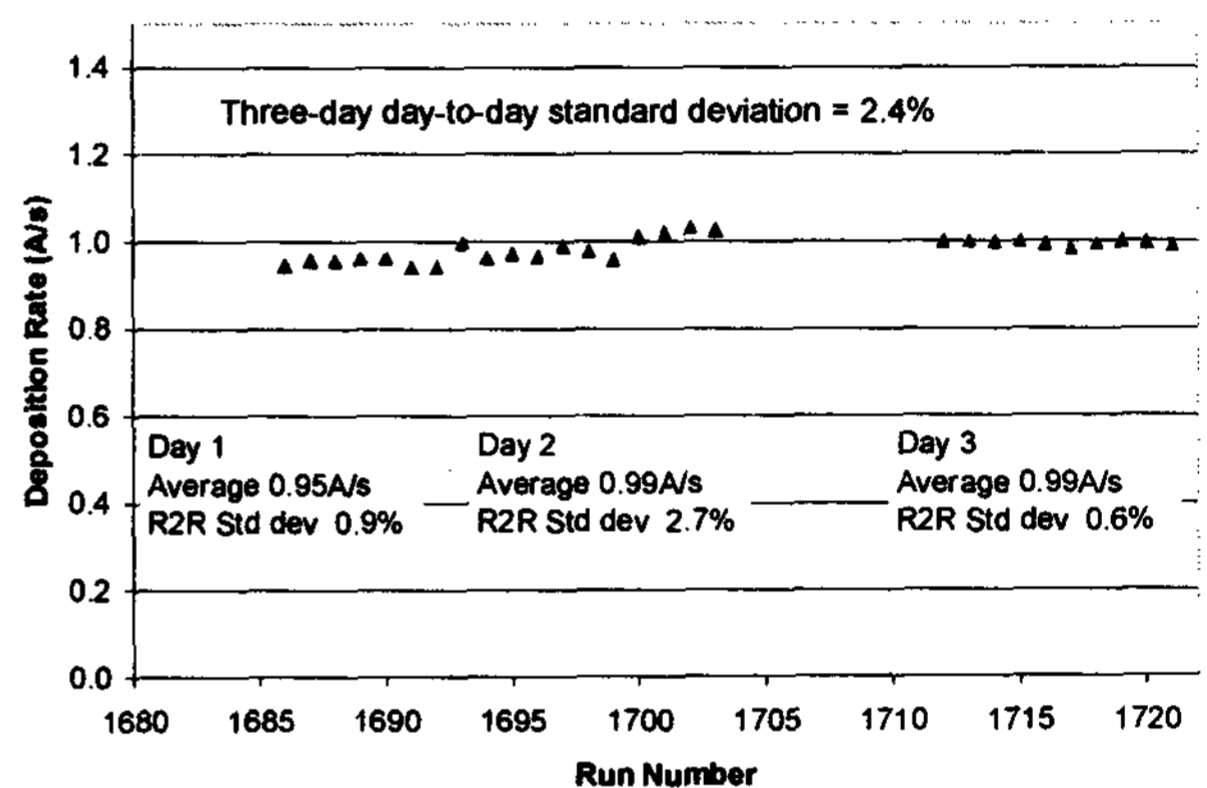


Figure 5: Run-to-Run and Day-to-Day deposition rate reproducibility of Ir(ppy)₃

Table 2: Summary of Achieved Results for all Investigated Organic Materials

Material	Thickness Reproducibility		Typical Deposition rate [Å/s]	Peak Deposition rate [Å/s]
	Run-to-Run Std. Dev. [%]	Day-to-Day Abs. Dev.* [%]		
Alq ₃	0.5	4.8	5	15.4
α-NPD	0.8	2.9	3.5	9.4
CBP	0.7	1.3	14	24.3
BAQ ₂	1.8	1.8	5.5	10.1
Ir(ppy) ₃	0.6	4.0	1	2.0**

* (Max-Min)/Mean **Not limited

The results prove the highly stable and reproducible performance of the OVPD™ technology due to the precise control of carrier gas flow combined with

constant source temperatures. Due to this stability no quartz crystal monitor is necessary for the deposition rate control thus no organic material is wasted for neither *ex-situ* calibration nor *in-situ* monitoring. Furthermore, doping or co-deposition of two or more materials can be easily implemented and controlled by mixing the carrier gas streams for the respective materials at a set ratio.

Utilizing the calibration of deposition versus the carrier gas flow rate we chose appropriate parameters for fabrication of Ir(ppy)₃-based green phosphorescent OLEDs by OVPD™, similar to those grown by vacuum thermal evaporation (VTE)⁶. The device current-voltage-luminescence characteristics were comparable to those fabricated by VTE. As illustrated in Figure 6, the luminous efficiency of the OVPD™ OLED is slightly higher than that obtained by VTE in the range of display brightness. At 1,000 cd/m² the luminous efficiency is 24.4 cd/A, corresponding to an external quantum efficiency of 7 %.

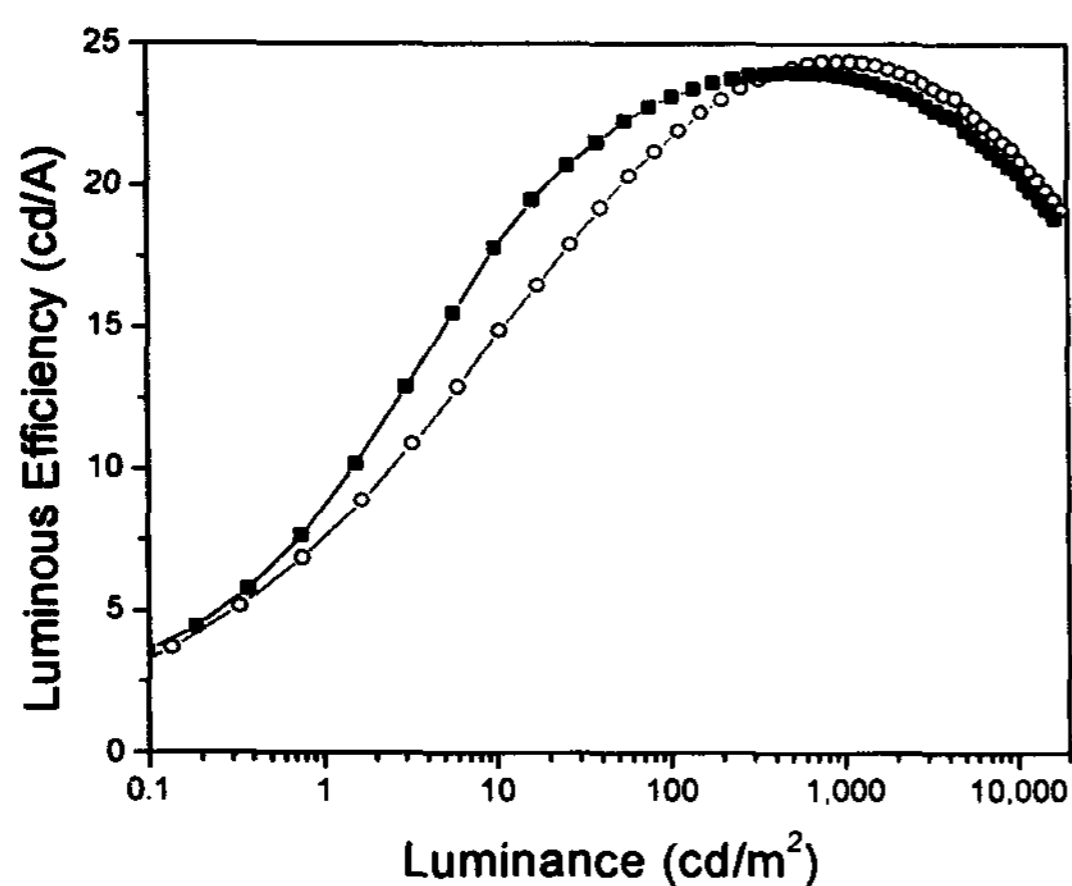


Figure 6: Luminance efficiency of Ir(ppy)₃ based phosphorescent OLED made by OVPD™ (circles) and by VTE (solid).

Another critical attribute of OLED performance is the operational lifetime. As an initial evaluation, the OLED was tested under accelerated conditions of high current injection corresponding to an initial luminance (L_0) of 9,000 cd/m². As shown in Fig. 7 the operation lifetime of the OVPD™ PHOLED matches that of the VTE device.

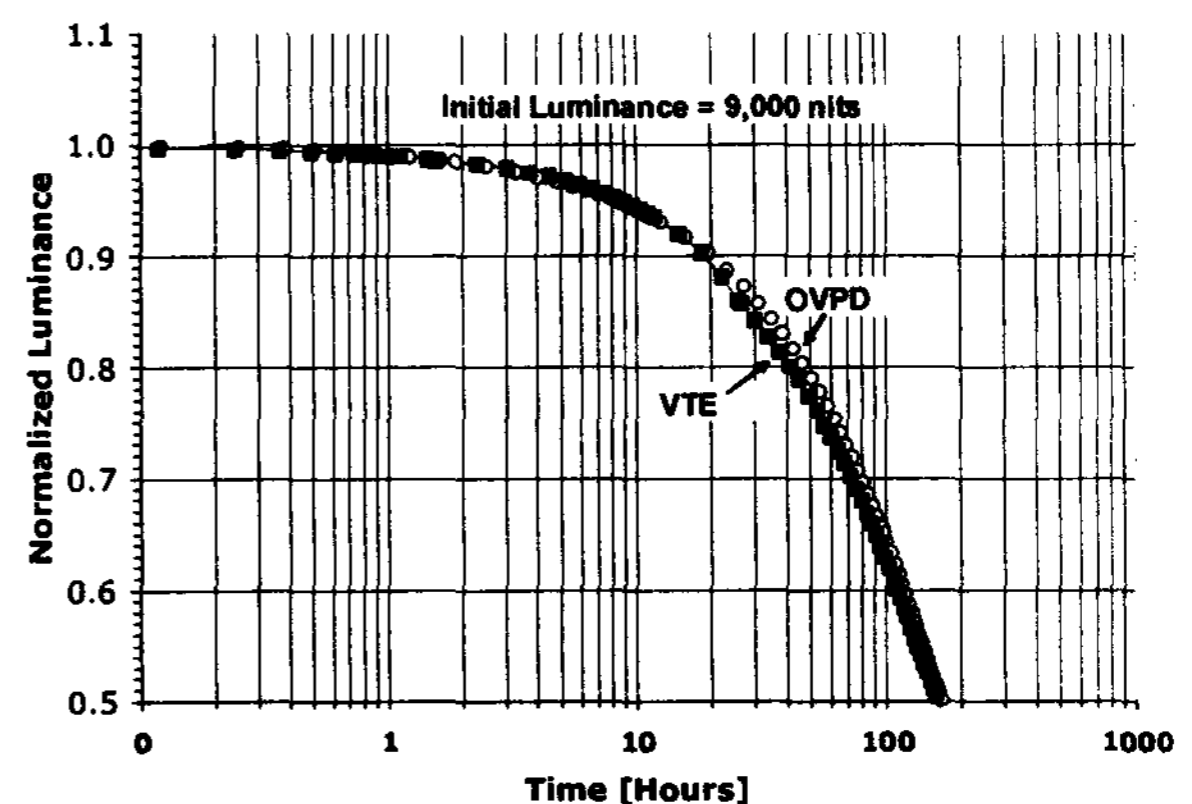


Figure 7: Normalized luminance as a function of time of Ir(ppy)₃ based phosphorescent OLED made by OVPD™ (circles) and by VTE (solid). The lifetime test was performed under accelerated ageing conditions (initial luminance about 9000 cd/m²):

4. Conclusions

Stable and reproducible deposition rates $> 10 \text{ \AA/s}$ were achieved using AIXTRON pre-production (Gen1) OVPD™ equipment for small molecule OLED materials. Phosphorescent OLEDs were fabricated by OVPD™ with precision control of all layers. The devices demonstrated comparable or superior performance to those grown by conventional VTE.

On the basis of these experimental results, this technology shows significant potential for OLED manufacturing with high deposition rates, thus increasing throughput in a manufacturing environment. Accurate control of co-deposition and interface abruptness will further enable the fabrication of increasingly more complex device structures that can enhance OLED performance.

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5. Reference

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