

OLED display manufacturing by Organic Vapor Phase Deposition

B. Marheineke

AIXTRON AG, Kackertstr. 15-17, 52072 Aachen, Germany

Phone: +49 241 8909 143, E-mail: b.marheineke@aixtron.com

Abstract

We report on Organic Vapor Phase Deposition (OVPD[®]) an innovative deposition technology for organic light emitting device (OLED) and organic semiconductor manufacturing. The combination of OVPD[®] with Close Coupled Showerhead (CCS) technology results in manufacturing equipment with vast potential for cost effective manufacturing of OLED displays commercially competitive to LCD.

The actual OVPD[®] equipment concept and design is discussed: Computational Fluid Dynamic (CFD) modeling is compared with experimental results proving the excellent controllability of the deposition process. Further other production relevant deposition properties are being reviewed e.g. high deposition rates and high organic material utilization efficiency of the OVPD[®] - Technology. Data from devices made by OVPD[®] show comparable/ superior performance to those fabricated with conventional vacuum thermal evaporation (VTE) techniques. An outlook on further potentials of OVPD[®] with respect to enabling advanced organic device structures is given.

1. Introduction

Organic semiconductor devices typically consist of thin (< 2000 Å) films of either conjugated polymers or aromatic molecules (small molecular (SM) weight organic materials), each requiring different deposition methods. SM-OLEDs today are widely manufactured using Vacuum Thermal Evaporation (VTE), where the organic materials are evaporated or sublimed in high vacuum to form molecular beams towards the substrate.

Organic Vapor Phase Deposition invented by S. Forrest et al. at Princeton University in 1995, provides a novel method for the deposition of organic thin films [1]. OVPD[®] is a technique to deposit small molecular organic thin films utilizing the advantages of gas phase transport. This technology has the potential to overcome the shortcomings of and to substitute VTE in OLED manufacturing.

OVPD[®] is a departure from low pressure CVD; the OVPD[®] process is based on the evaporation or sublimation of small molecular weight organic materials into an inert carrier gas stream at low pressure. The carrier gas transports the molecules to a

cooled substrate within a thermally controlled deposition chamber. There rapid condensation of the organic molecules occurs forming the desired films onto the substrate. By using multiple sources of organic materials, stacks of organic thin films required for a complete OLED or organic semiconductor device can be deposited.

2. OVPD[®] Principle

Figure 1 shows the principle of OVPD[®]. Source materials are placed in containers; as the materials sublime the inert carrier gas (N₂) gets saturated by the organic molecules and transports them towards the substrate. Different materials (e.g. host and dopant) can be homogeneously mixed in the gas phase prior to arriving on the cooled substrate, where they condense to form the desired film.

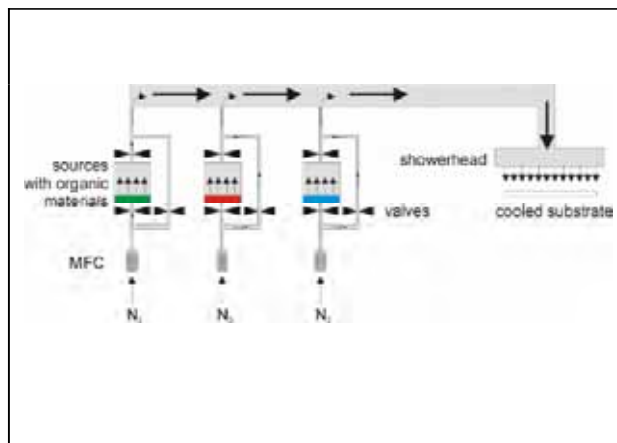


Figure 1. Schematic diagram of the OVPD[®] - Technology

Evaporation or sublimation of materials from a heated source is described by the Clausius-Clapeyron Equation:

$$(1) p_{vap} = p_0 \cdot e^{-\frac{\Delta H_s}{RT}}$$

where p_{vap} is the vapor pressure, p_0 is an empirical material constant, ΔH_s is the enthalpy of evaporation and R and T are the universal gas constant and evaporation temperature, respectively.

Figure 2 displays the vapour pressure as function of evaporation temperature for different material examples. Deposition rate is determined through the molar flow of material onto the deposition area:

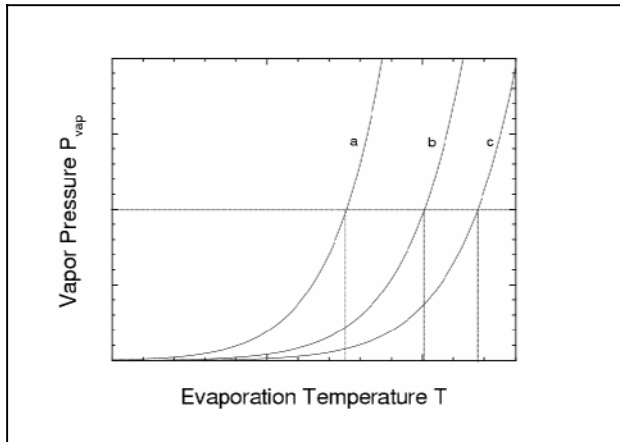


Figure 2. General behavior of vapor pressure vs. evaporation temperature for different materials with different ΔH s ($a > b > c$)

In VTE the molar flow is determined by the vapor pressure as well as the geometry of the evaporation cells and the deposition chamber. Since geometry is generally fixed, the only remaining parameter to adjust the deposition rate is the evaporation temperature. Consequently different materials require different evaporation temperatures for resulting in same deposition rates.

In gas phase transport as used in OVPD[®] the molar flow of materials is to first approximation described by:

$$(2) \quad q_m = \frac{q_s}{V_{mol}} \cdot \frac{P_{vap}}{p_s - p_{vap}}$$

where q_m is the molar flow, q_s is the carrier gas source flow, V_{mol} is the molar gas volume and p_s is the source pressure. The diagram in Figure 3 shows the ideal behavior of deposition rate with carrier gas source flow for different parameters: for one material the molar flow, i.e. the deposition rate, increases linearly with increasing source flow for constant source temperature. With higher temperature, thus growing vapor pressure, the slope of the deposition rate increases. For different materials kept at the same source temperature and same carrier gas source flow the molar flow is different due to the different vapor pressure. However, as can be seen from Figure 3, the same deposition rate can be adjusted for different materials by selecting the appropriate carrier gas source flow.

As discussed with equations (1) and (2) above the deposition rate is a function of source flow, pressure inside the source container and material properties such as the evaporation enthalpy ΔH s and the empirical material constant p_0 .

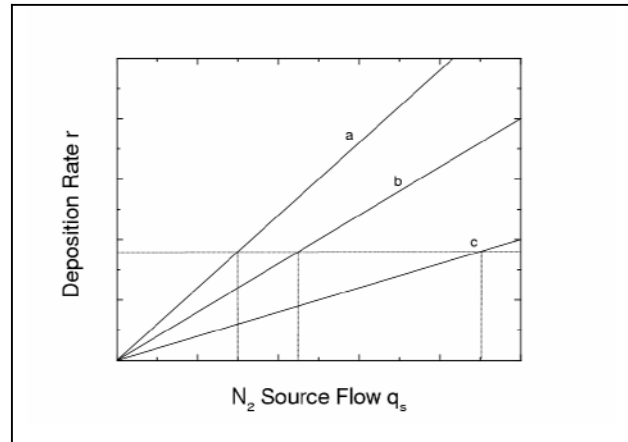


Figure 3. Theoretical deposition rate vs. carrier gas source flow in a gas phase deposition process for different vapor pressures ($a > b > c$)

Experiments have shown slight deviation from the ideal linear behavior as described above. Zhou et al. [2] reported that deposition rate vs. source flow for different materials showed linear behavior up to a certain source flow, and sub linear increase with source flow above this threshold value.

The above discrepancy between theoretical data and experiment has been analyzed in more detail as displayed in Figure 4. Here we compare the ideal behavior of the Alq_3 deposition rate vs. carrier gas flow with experimental data and simulated results on basis of the actual hardware setup. Line A represents the ideal theoretical behavior with the source pressure close to the deposition chamber pressure.

Line B shows the dependency for a constant source pressure of 4 mbar in analogy to equation (2).

The experimental data is shown with line C showing similar behavior as described by Zhou et al.

Last but not least line D represents results from Computational Fluid Dynamic (CFD) modeling of the actual hardware setup. Due to the impedance of the source container and gas lines a pressure build up inside is expected with increasing source flow. For low flow rates this effect shows small impact on the molar flow, i.e. deposition rate is linear with the source flow, whilst at higher source flow the pressure build up becomes more dominant resulting in a sub linear dependency as observed by Zhou et al. It is worth mentioning that despite this effect high deposition rates values exceeding 20 \AA/s are obtained as displayed in Figure 4-C. Comparison of

experimental and simulated data allows deeper understanding of the fluid dynamic conditions within the OVPD[®] source container, which is useful for further optimization of system design yielding even higher deposition rates.

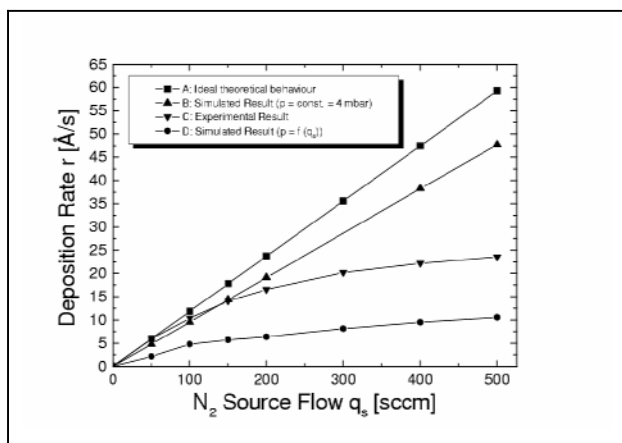


Figure 4. Comparison of theoretical and experimental behavior of the deposition rate as a function of source flow

3. Close Coupled Showerhead Technology

The inherent advantages of OVPD[®] can be exploited on an industrial scale when combined with the Close Coupled Showerhead (CCS) Technology. With CCS the carrier gas and organic materials are injected uniformly through a showerhead injector across the entire deposition area. As the injection is in close proximity to the substrate surface the fluid dynamics enforce a uniform distribution of the species allowing for uniform deposition across the entire area without a need for substrate rotation [3-5] (close coupling effect). In addition to the intrinsic uniformity CCS enables deposition at high material utilisation efficiency.

Figure 5 shows the schematic of AIXTRON's OVPD[®] equipment employing a temperature controlled deposition chamber and the close coupled showerhead design as gas distributor. The organic source materials are heated in physically separated source containers, which are arranged in separate furnaces remote from the deposition chamber, 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 homogeneously mixed in the gas phase prior to being introduced uniformly through the heated showerhead injector across the entire substrate surface where they condense to form the desired film. The integration of a high precision mask

alignment system allows fabrication of full color OLED displays.

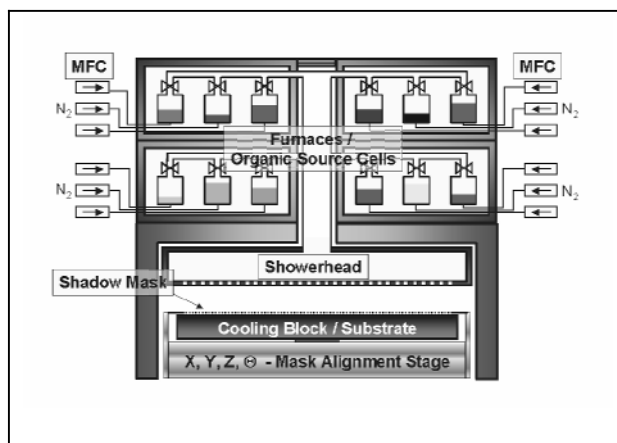


Figure 5. Schematic of the CCS-OVPD[®] production concept. Organic materials are evaporated/sublimed in individual source containers and transported by an inert carrier gas into the showerhead, which injects uniformly across the entire deposition area.

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) and ramping of material flow for graded compositions. 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.

4. OLEDs made by OVPD[®]

Since the introduction of OVPD[®] the fabrication of numerous organic devices was reported [2,5-11], which confirms the feasibility of this technique. In 1997 Baldo et al. [10] reported the first successful fabrication of an OLED deposited by OVPD[®] on both glass and flexible substrates. The simple bi-layer

heterojunction OLEDs already showed performance similar to conventional devices deposited using thermal evaporation in vacuum.

Zhou et al. [4] and Schwampera et al. [5] compared phosphorescent OLEDs (PHOLEDs) made by OVPD[®] with similar devices deposited in VTE. The device structure consisted of a 100 Å-thick copper phthalocyanine (CuPc) hole injection layer, a 300 Å-thick 4,4'-bis[N-(1-naphthyl)-N-phenylamino] biphenyl (a-NPD) hole transport layer, a 300-Å-thick CBP doped with Ir(ppy)₃ emission layer, a 100-Å-thick aluminum(III)bis(2-methyl-8-quinolinato)-phenalphenolate (BALq₂) hole blocking layer, and a 400 Å thick Alq₃ electron transport layer. The Ir(ppy)₃-to-CBP doping ratio was (4.3 ± 0.2) vol %, corresponding to approximately 6 wt %. All organic layers were sequentially deposited by OVPD[®] in a single chamber with the exception of the CuPc layer. Since the OVPD[®] sources at the time were configured for materials with low-to-moderate evaporation temperatures (270-310 °C), CuPc was deposited by VTE as it requires a source temperature in excess of 400 °C. The cathode consisted of 8 to 10 Å-thick LiF, followed by 1000 Å-thick Al, both deposited by VTE in the same chamber used for the CuPc.

As is apparent in Figure 6, the luminous efficiency characteristics of the PHOLED deposited in OVPD[®] at 4.8 Å/s is comparable to devices fabricated by VTE at ~ 1 Å/s; the maximum external quantum efficiency is (7.0 ± 0.1) % at a luminous efficiency of 25 cd/A [4]. Furthermore, the peak efficiencies are obtained at brightness of 1,000 cd/m², which is desirable for passive matrix applications [12].

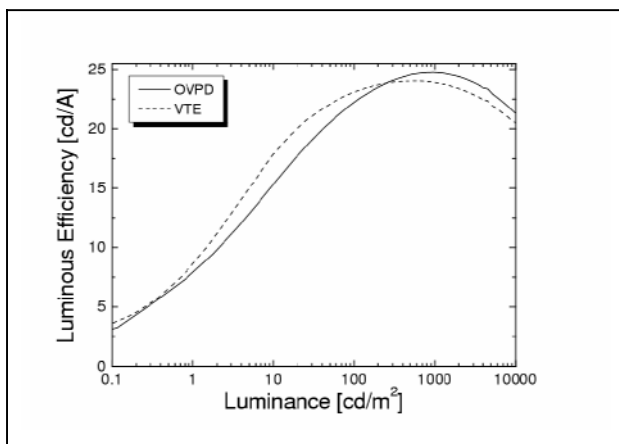


Figure 6. Luminous and efficiencies of PHOLEDs deposited by OVPD[®] and VTE [4,5] (updated)

A critical attribute of OLED performance is operational lifetime. As an initial evaluation, the OVPD[®] PHOLED was tested under accelerated conditions of high dc current injection (40 A/cm^2),

corresponding to an initial luminance $L_0 = 9,000 \text{ cd/m}^2$, and compared with that of a comparable device deposited using VTE.

As shown in Figure 7, the accelerated lifetime of the OVPD[®] PHOLED tracks, or is slightly superior to that of the VTE device, falling to half L_0 after approximately 160 h of continuous operation at room temperature. Figure 7 also shows that the same device tested under typical display luminance conditions of $L_0 = 600 \text{ cd/m}^2$ shows similar lifetime as the VTE device tested under $L_0 = 500 \text{ cd/m}^2$.

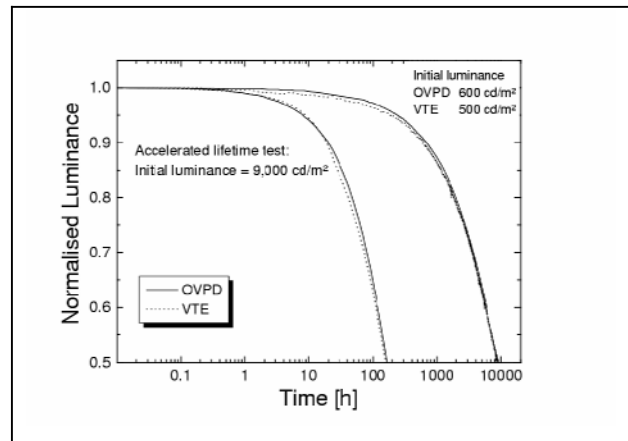


Figure 7. Lifetime data of PHOLEDs deposited by OVPD[®] and VTE [4,5] (updated).

To evaluate the impact of deposition rate on device performance, the rate of the CBP: Ir(ppy)₃ emission layer deposition was varied between 4.8 and 10.3 Å/s, while keeping the deposition rates of all other layers constant [4]. The luminous efficiency characteristics and accelerated lifetime tests prove that the increase of deposition rate does not affect the performance of the OLED.

Further to the initial results on OLEDs made by OVPD[®], other, high performance PHOLED devices were fabricated for further evaluation [13]. The green emitting devices consist of 5 organic layers, which were all deposited by OVPD[®] in a single chamber. The devices were optimized through tuning the dopant to host ratio in the emission layer (4 to 10 %) to achieve maximum luminous efficiency. In Figure 8 the luminance efficiency is plotted versus luminance for devices with different doping ratios. A maximum performance was achieved for a ratio of 8.2 % revealing maximum luminous efficiency of 52.7 cd/A at 100 cd/m²; at a brightness of 1,000 cd/m² the luminous efficiency is still about 50 cd/A. All of these devices showed comparable results to similar devices deposited by VTE further confirming that OVPD[®] is

capable of substituting VTE for OLED manufacturing at higher deposition rates.

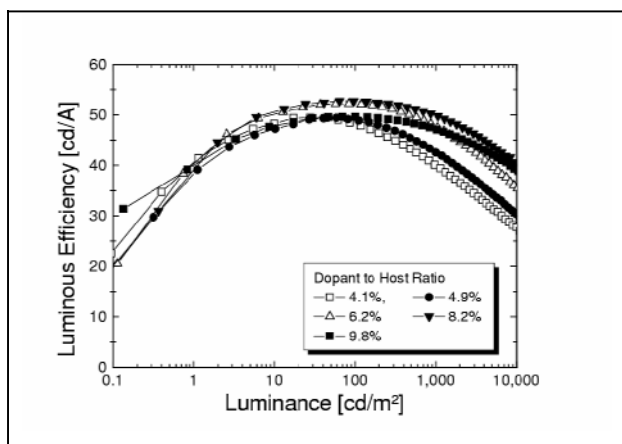


Figure 8. Device optimization of advanced PHOLED in OVPD[®] by adjusting the dopant to host ratio [13]

In addition to higher deposition rates, another advantage of OVPD[®] in comparison to VTE is, besides higher deposition rates, the ease of parameter tuning for optimization. VTE requires adjustment of the deposition rates for dopant and/or host by changing the source temperatures, which is a time consuming and imprecise procedure. OVPD[®] on the other hand allows adjustment of the deposition rate by changing the carrier gas source flow utilizing high precision electronic MFCs as described above. As demonstrated before, this allows fast, highly accurate and reproducible choice of the desired deposition parameters. Consequently dopant to host ratios can be adjusted to the accuracy of a tenth of a percent, which is an order of magnitude better than in VTE.

5. Requirements to OLED Manufacturing

Increasing the productivity for OLED and organic semiconductor devices is necessary to decrease manufacturing cost. This can be achieved either through increasing the size of the mother glass to produce more panels simultaneously or by reducing TACT time to simultaneously handle more than a single substrate in the same time.

In the LCD industry both routes have been followed: whilst the mother glass size was increased from Gen2 in 1993 to Gen8 (mass production expected for 2006) TACT time has been reduced below 1 minute. Currently OLED mass production is typically conducted on Gen2 mother glass size with TACT times in the range of 5 to 15 min.

OVPD[®] offers a joint strategy to increase productivity through both reducing TACT time and increasing mother glass size. To date controllable deposition rates up to 30 Å/s have been achieved [14] offering even higher deposition rates through improved source design and/or multiple source utilisation. Hence, the values currently achieved by OVPD[®] already exceed state-of-the art VTE manufacturing equipment by an order of magnitude, which can lead to significantly reduced TACT times. Consequently OVPD[®] offers potential to realize OLED production lines with TACT times similar to those used in LCD manufacturing.

Scaling of the CCS deposition chamber used for OVPD[®] is a straight forward procedure: the nature of CCS only requires a 2-dimensional resizing of the deposition chamber, i.e. the distance between the showerhead and the deposition area remains constant with unchanged uniformity of the deposited thin films. Just as important as the uniformity is maintaining high deposition rates with increased deposition area. Material utilization efficiency can be increased with larger substrate sizes due to a better area to circumference ratio of the substrate. As described above the deposition rate based on molar flow of organic materials is determined through carrier gas flow at constant source temperature and dependent on chamber geometry. Proper design of the internal of the source containers allows increased flow of organic molecules from the solid or liquid source materials into the gas stream, thus increasing the molar flow towards the deposition area. Further on the molar flow can be increased through utilizing multiple organic sources in parallel without affecting the deposition performance. As a consequence OVPD[®] can be scaled to larger deposition areas without increasing source temperatures, which in turn may be critical to the stability of the organic source materials.

OVPD[®] deposition to date has been performed on mother glasses up to Gen2 sizes, where processes can be easily transferred between different products due to the nature of gas phase transport techniques. Concepts for larger dimensions have already been developed. The development of larger OVPD[®] equipment is following the market demand, which is also driven by the sizes of OLED products.

6. Conclusion

OVPD[®] is a novel technique for the deposition of small molecular organic materials that overcomes many of the limitations of VTE. Its superiority with respect to precise, stable and reproducible control of the deposition processes could, and excellent uniformity across large areas together with high deposition rates and material utilisation efficiency

when combined with Close Coupled Showerhead technology has been demonstrated. OLEDs deposited by OVPD[®] show similar or better performance compared to similar devices made by VTE. Scalability, increased yield and throughput in OVPD[®] are important factors towards making OLED products commercially competitive to LCD. Reduced organic material consumption and reduced maintenance requirements contribute further to the reduction in manufacturing cost, which makes OVPD[®] the technology of choice for the next generation manufacturing of OLED displays and for the manufacturing of next generation organic devices.

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OVPD[®] is a registered trademark. OVPD[®] technology has been exclusively licensed to AIXTRON from Universal Display Corporation (UDC), Ewing, N.J. USA for equipment manufacture. OVPD[®] technology is based on an invention by Professor Stephen R. Forrest et. al. at Princeton University, USA, which was exclusively licensed to UDC. AIXTRON and UDC have jointly developed and qualified OVPD[®] pre-production equipment

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