

OLED Fundamentals

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**Materials, Devices, and Processing
of Organic Light-Emitting Diodes**

Edited by
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Cover Image. A flexible transparent organic small molecule light emitting panels (see Chapter 6, "Small Molecule Fundamentals" by Xin Xu, Michael S. Weaver). Courtesy of Universal Display Corporation.

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*To my family and to all of the members of the Pacific Northwest
National Laboratory OLED team, past and present.*

Daniel J. Gaspar

To my parents Tatyana and Vladimir.

Evgueni Polikarpov

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14.1 Introduction

Since the early days of organic light-emitting diode (OLED) development by Tang and VanSlyke at Kodak, vacuum thermal evaporation (VTE) has been the most commonly used deposition process (Tang and Van Slyke 1987). Vacuum thermal deposition is conceptually a very simple process, where pure versions of the desired materials are evaporated from crucibles using thermal energy. Adjusting the temperature of the crucible can control the rate of evaporation, and therefore the rate of deposition. For OLED materials, the evaporation temperature is typically low (<300°C) and the crucibles are resistively heated and controlled using a thermocouple and PID control system. The resulting vapor then

propagates along a line of sight path to the substrate where it condenses to form a film. This line of sight propagation also enables simple patterning through the use of shadow masking, currently the dominant technique for both lighting and displays.

While the promise of a low-cost printable display technology has been a key driver for interest in OLEDs, vacuum evaporation remains the method currently used for almost all small molecule displays and lighting in production as of 2014.

14.2 Thermal Evaporation Advantages

VTE has several advantages that have led to the dominance of this technology. The first advantage of VTE is the ability to deposit complex, multilayer device structures with almost unlimited combinations of different materials. Vacuum deposition is well suited to forming these complex structures because each layer can be deposited as a pure material without solvents, with precise control of thickness and (with the use of masks) lateral distribution, and with virtually no interactions with the other layers in the structure. Other deposition methods, particularly solution-based methods, typically use solvents to enable printing or coating of the organic materials. While these approaches are typically low cost (solution coating) or simple to pattern (printing) they significantly limit the device design possibilities due to the need for orthogonal solvents. Basically, each successive layer cannot use a solvent that dissolves one of the previous layers. As there are a limited number of potential solvent classes, this significantly limits the total number of device layers. It also limits the types of materials that can be used, as not all are readily soluble. For example, Alq is a classic and historically important OLED material with poor solvent solubility. It was one of the two materials originally used by Tang and VanSlyke and the lack of a good solvent was one of the key reasons they used VTE for their device fabrication approach (Tang and Van Slyke 1987; VanSlyke, S. A. 2012, personal communication).

Second, VTE is one of the cleanest methods for depositing materials for a wide range of applications; cleanliness is critical to achieving high performance and long lifetime OLEDs. This cleanliness arises for two reasons. First, high-purity source material is typically used to prevent degradation during evaporation. Because any material to be deposited using VTE must sublime at appropriate pressures and temperatures, zone sublimation refining can be and is usually used to purify source materials. Second, environmental contamination is absent in the high-vacuum environment used in most VTE systems. Most OLED materials are highly sensitive to oxygen and water vapor and, while inert gas environments can be used to provide some protection, high vacuum is typically the best (Aziz and Popovic 2004; Baldacchini et al. 2005). This vacuum environment not only significantly reduces the potential for contamination species, it also helps to minimize particle contamination during device fabrication. The thin layers (10–100 nm typically) used in standard OLED designs are especially susceptible to particulate damage, which lead to shorts. In the vacuum environment, there are no air currents to carry particulates, and they instead drop to the bottom of the chamber. While this does not completely eliminate particulates (for instance, they can be attracted to the surface electrostatically), vacuum does reduce likelihood of contamination (Ouellette 1997).

A final consideration for VTE, while not quite an advantage per se, is that a vacuum deposition step is typically required for electrode deposition. Standard electrode

deposition is usually accomplished using vacuum deposition (either sputtering or thermal evaporation) so that even devices fabricated under atmospheric conditions typically require a vacuum deposition step.

14.2.1 Thermal Evaporation Challenges

Despite all the advantages of VTE described in the previous section, there remain some critical and fundamental disadvantages that have helped limit the penetration of organic devices into more general markets. These disadvantages all revolve around the fact that thermal evaporation of organic materials is difficult to scale up. This is not fundamentally due to the vacuum needs, though the capital costs can present a high barrier to entry, but rather to the organic materials themselves.

The first and most obvious challenge is that most organic materials are very temperature sensitive and rapidly degrade if overheated. This is not generally an issue in low deposition rate research systems where the substrates are small and the rates are low, but for production systems, thermal degradation is usually the limiting factor in scaling both size and throughput. Even though most organic materials are currently thermally purified, they are still large organic molecules and as such have the double (in this case) disadvantage of low vapor pressure and low degradation temperatures. When one compares the typical sublimation temperatures for most relevant organic materials (250–400°C) to the typical degradation temperatures for those materials (300–450°C)—the challenge becomes obvious. Long et al. showed that for typical research deposition rates, Alq has a lifetime orders of magnitude longer than typical deposition times. This is borne out in most OLED work where Alq is considered a very stable and robust material. However, for large area displays or low cost lighting, the deposition rate must be increased by over a factor of 1000 to reduce the cycle times and to cover a larger substrate area. Thus, the overall temperature must be increased to a point where the material begins to degrade after only a few hours. At the high rates needed to achieve acceptable cost targets for OLED-based lighting, the material lifetime is measured in minutes. Table 14.1 shows the relative deposition rates for a nominal 30 nm thick Alq layer on different substrate sizes using typical deposition times.

In order to achieve acceptable system uptimes, it is critical that the temperature of the bulk of the material be reduced and that the evaporative surface area be as large as possible. Specific designs and sources to achieve these simultaneous design criteria will be discussed later in this chapter.

A related challenge is that some materials do in fact start to decompose at temperatures lower than they evaporate, or at least close enough to the evaporation temperature

Table 14.1 Substrate Sizes and Typical Cycle Times for Different Applications Showing the Relative Deposition Rates for a 30 nm Thick Alq Layer

Substrate Class	Size (mm)	Time (s)	Rate (g/h)	Relative Rate
R&D sample	10 × 10	240	0.0021	1
Pilot line	150 × 150	120	0.0142	68
Mobile display	730 × 920	120	1.11	530
Television	2200 × 2400	60	15.1	7200

that degradation is inevitable. As mentioned previously, currently most, if not all, materials go through a zone sublimation thermal purification process during manufacturing where they are evaporated and then condensed in a thermal gradient to improve purity. Almost by definition, if a material survives this process, it can be deposited using VTE at least at some useful rate. However, as chemical processing becomes more precise and the as-synthesized purity of new materials improves, the need for thermal distillation is reduced. As nonthermal purification improves, materials that cannot be successfully evaporated will become viable device materials for low temperature processing such as solution printing.

A second challenge to VTE is that the material utilization is generally low. This is wasteful of expensive material and, furthermore, the wasted material tends to coat up other parts of the deposition system, leading to shorter uptime and higher particle counts. This challenge arises from the fact that the evaporative flux is extremely difficult to direct. Much work has been done on shaped nozzles to improve the fraction of the evaporated flux that hits the substrate surface with only limited success (Keum et al. 2004; Kim et al. 2008, 2011). The challenge is that without a gas flow to entrain the evaporating molecules, the distribution of molecules leaving the evaporative surface have a profile that can be approximated with a cosine function, shown in Equation 14.1 (Ohring 2001).

$$\frac{d\bar{M}_s}{dA_s} = \frac{\bar{M}_e \cos \phi \cos \theta}{\pi r^2} \quad (14.1)$$

In more complex (real world) sources, where the evaporating surface may be at the bottom of a deep and narrow crucible or come through a nozzle with a high aspect ratio, the flux is better approximated by Equation 14.2, where the exponent n is an experimentally determined fitting factor:

$$\frac{d\bar{M}_s}{dA_s} = \frac{\bar{M}_e (n + 1) \cos^n \phi \cos \theta}{2\pi r^2} \quad (14.2)$$

The ideal behavior for the molecular flux would be something collimated like a laser beam, where the flux could be accurately and repeatably directed exactly to the substrate. This corresponds to very high values of the exponent n in Equation 14.2, indicating the flux is highly directional. In practice, though, n can only be varied a small amount, typically between 1 and 3. While increasing n to 2 or 3 is helpful, it still is very small compared to an ideal case, which might someday be possible through the use of baffles and shaped nozzles.

Patterning of thermally evaporated materials, particularly for displays, is done using high precision shadow masks, typically fine metal masks (FMM) to directly pattern the incoming flux during the deposition process (Yotsuya 2005; Kaneko et al. 2006; Matsuura 2012). While this process is relatively straightforward, it is wasteful of material, especially for displays, as most of the evaporated material is deposited onto the mask instead of the substrate and maintaining high precision alignment over large substrates is difficult. This will be covered in more detail in Section 14.6.

Finally, many common organic materials do not melt before evaporating, either because their vapor pressure is sufficiently high at temperatures below their melting point, or because they thermally decompose before melting. Because the evaporating material remains a solid powder, the stability of the flux can be poor for two reasons. First, unlike most liquids, the thermal conductivity of the powder is very low, leading to non-uniform temperature in the source material. Second, the vaporization surface area can change rapidly as the powder depletes, particle sizes change, and particles shift in the deposition boat or crucible. This can be mitigated by adding thermally conductive inert materials, such as ceramic beads, to the powder (CHAOHON TECHNOLOGY CO. 2013).

14.3 Research Scale Deposition

Research scale OLED thermal deposition can be done on systems ranging from simple bell jars with purely manual controls to multichamber systems with fully automated substrate transfer, mask alignment, and transfer and process control. Figure 14.1 shows an example of a part of a research system from Trovato Manufacturing that can be used for material testing and device design. Except for the simplest of systems, typically used to study the deposition process itself or test new materials, most systems have multiple sources to simplify the fabrication of devices containing several different materials. In Figure 14.1, the source flange from a research system contains spaces for 12 thermal boat sources, which will be further discussed in Section 14.4. The panels between the sources prevent cross contamination by preventing material from one source from depositing on another source during normal operation. Also visible in the figure are the quartz crystal monitor (QCM) sensor heads that provide thickness feedback. Depending on the system complexity, layer deposition can be automated using QCM feedback and appropriate control software.

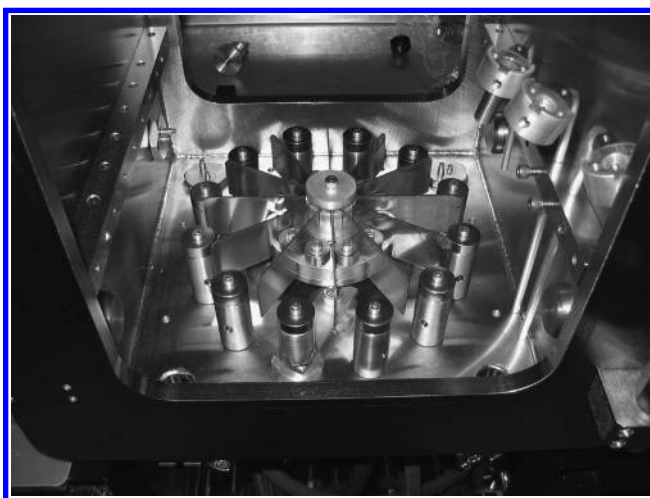


FIGURE 14.1 Source flange for a research system. (Courtesy of Trovato Manufacturing.)

14.4 Production Scale Deposition Systems

Current production OLED systems are primarily used for display fabrication, and as such are based on traditional LCD motherglass sizes to take advantage of existing process lines. Table 14.2 lists the typical glass sizes that have been used in the LCD industry for each generation of display manufacturing, as well as which sizes are being used for OLED manufacturing. Development work has typically been done on smaller production systems because the equipment is readily available, the capital cost fully depreciated and of declining value for LCD fabrication. Current mobile displays are made on either half or full sheets of 4th generation glass (730 mm × 920 mm) and there are several 8th generation (2200 mm × 2400 mm) systems in development for OLED television production.

Production systems come in two basic configurations, cluster, where the chambers are around a central substrate handling robot, (as shown in the photograph in Figure 14.2

Table 14.2 Typical Glass Substrate Sizes for Different Generations of Displays

Generation	Dimensions	Area (m ²)	OLED Application
1	300 mm × 400 mm	0.12	Development
2	400 mm × 500 mm	0.20	Development
3	550 mm × 650 mm	0.36	
4	730 mm × 920 mm	0.67	Mobile displays/lighting
5	1100 mm × 1300 mm	1.43	Lighting/TVs
6	1500 mm × 1800 mm	2.70	
7	1900 mm × 2200 mm	4.18	
8	2200 mm × 2400 mm	5.28	Television
9	2400 mm × 2800 mm	6.72	
10	2850 mm × 3050 mm	8.69	

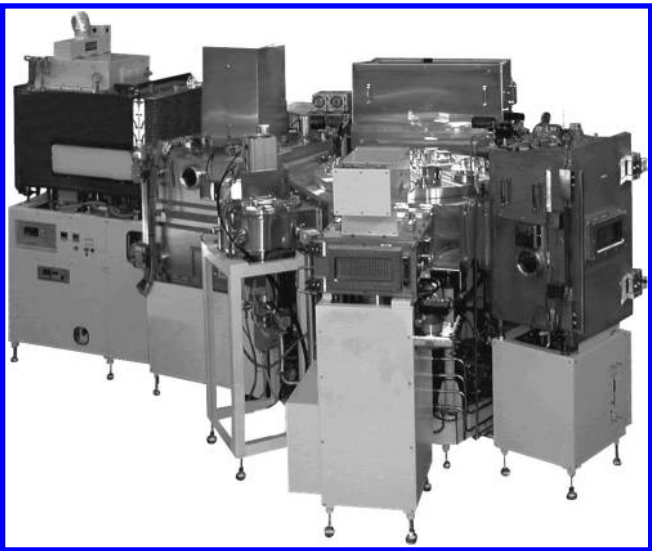


FIGURE 14.2 Cluster deposition system for process development and pilot production. (Courtesy of Tokki Canon.)

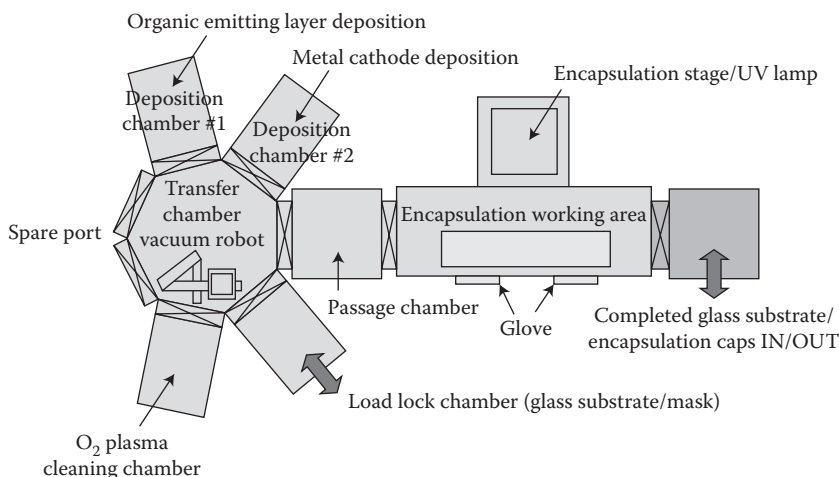


FIGURE 14.3 Cluster production system schematic. (Courtesy of Tokki Canon.)

and the schematic in Figure 14.3) and in-line, where the chambers are in a line and the substrate moves from one end to the other (as shown on the right side of Figure 14.4). Each approach has advantages and disadvantages and the optimal technology often depends on the final product.

Cluster systems use a layout similar to traditional display and semiconductor processing where a central robot is surrounded by an assortment of dedicated process chambers, as shown in Figure 14.3. This approach provides several advantages. First, a cluster tool provides the ability to easily combine multiple process steps into a single system while maintaining a high level of configurability. This enables the system to be optimized for any specific process by adding or removing modules without the need to fundamentally redesign the core hardware. It also enables simple load-balancing, by enabling the addition of multiple process chambers for a slow deposition step. Second, because the chambers are independent and separated by valves, maintenance on an individual chamber can be managed independently without opening the entire system.

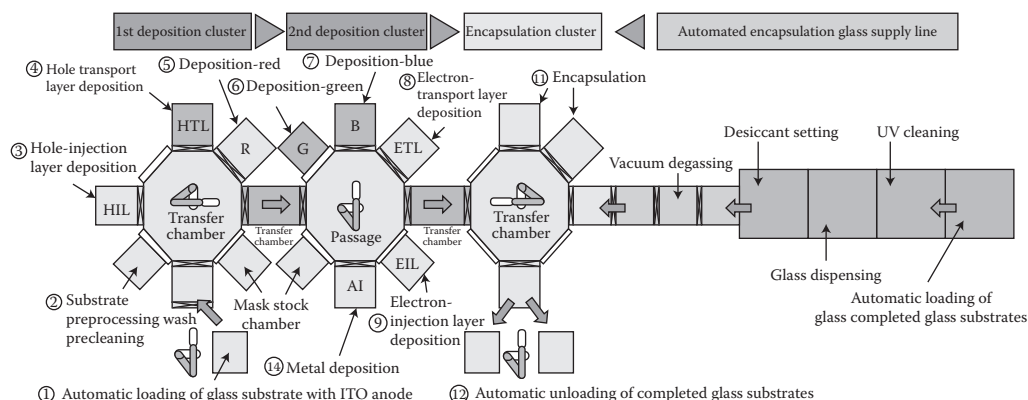


FIGURE 14.4 Hybrid cluster-inline system for higher throughput. (Courtesy of Tokki Canon.)

Third, because the current LCD display industry uses similar equipment for the production of the transistor backplane, the equipment set is well-developed and general purpose components such as substrate cleaning and load locks already exist. However, there are a couple of disadvantages that primarily affect the process cost. First, the cost of the robot and the multiple vacuum management systems, pumps, gauges, valves, and so on, needed add significantly to the overall cost of the system. Second, the transfer from tool to tool requires additional time, reducing the overall throughput of the system. Systems of this type are supplied by Tokki, Ulvac, and K.J. Lesker.

In-line systems use a continuous flow process similar to thin-film photovoltaic and architectural glass coating systems. In these systems, the substrate enters at one end and proceeds through sequential deposition tools, each of which deposits one layer, before emerging fully processed at the end of the line. The primary advantage of this approach is that the throughput to capital expenditure ratio is much better than in a cluster system. The simplified glass transport eliminates the need for the advanced robotic handling, and the straight-line process can reduce the total footprint needed for system installation. The tradeoff for the low cost and high throughput is the lack of configurability, which limits the changes to the device stack that can be made without significant, and expensive, hardware modifications. In addition, the substrate speed is limited by the slowest process. In some cases, for example very thick layers, this can be mitigated by splitting the process into multiple steps, which increases the overall size and cost of the system but enables better cycle time alignment.

Hybrid systems, such as the one shown in [Figure 14.4](#) combine some aspects of in-line (on the right sides) and cluster tools (on the left side) to achieve a balance between configurability and throughput.

14.4.1 Organic Vapor Phase Deposition

An alternate approach to VTE is to use a carrier gas to transport the organic materials from an evaporation zone to a deposition system (Baldo et al. 1998; Shtein et al. 2001; Forrest 2004). This approach has been commercialized by Aixtron AG into a system conceptually similar to those used for Metal-Organic Chemical Vapor Deposition (MOCVD) and uses the ability to easily switch carrier gasses on and off to rapidly control layers (Aixtron 2012). Another advantage of this approach is that very high film thickness uniformity can be achieved across the substrate by careful distribution of the transport gas through a shower-head like distribution system. However, this same distribution can make scaling to very large sizes more difficult as the uniform transport of the carrier gas in a low-vacuum environment becomes challenging as the substrate size increases. Another potential difficulty is that the elevated temperature of the carrier gas needed to prevent premature deposition in the distribution tubing can cause additional material degradation. This can be mitigated by using high gas velocities and reducing transport time as well as by minimizing the heated source volume to reduce the overall time at elevated temperatures.

14.5 Evaporation Source Technology

The key part of any OLED deposition system is the evaporation source itself. For research systems, where the deposition rates are low, uniformity is not a major issue and material

utilization is of limited concern, sources can be very simple evaporation cups or boats. However, for production systems, the design of the source is critical to achieving a cost effective and efficient process.

14.5.1 Point Sources

Point sources are conceptually the simplest evaporation sources, consisting typically of an open crucible surrounded by a heating element. However, they can range in practice from a beaker wrapped in resistive wire to a ceramic or refractory metal crucible heated by a CVD grown pyrolytic boron nitride (pBN) and graphite (pG) heater capable of continuous operation at 1500°C in corrosive environments.

For research systems, the typical source is a simple evaporation boat that holds just a few milligrams or grams of material. Figure 14.5 shows a typical source, consisting of a formed refractory metal, with a small source material area and a cover baffle, from a system designed by Angstrom and located at Pacific Northwest National Laboratory. The baffle serves multiple purposes. First, it helps provide a uniform heating environment for the source material, minimizing hot spots that could cause material degradation. Second, by covering the actual source material, it prevents cross-contamination from flakes and/or particles of material falling from the deposition area located above the source. Finally, as described earlier, most OLED source materials are powders and are not particularly stable during evaporation, so the baffle prevents “spitting” of particles and reduces flux variations to some extent.

More advanced sources provide radiative heat to the top surface of the source material using a perforated or slotted heater. Because most organic materials sublime from powder and have very low thermal conductivity, heating from the top limits evaporation to the top surface, generating flux while reducing thermal damage to the bulk of the

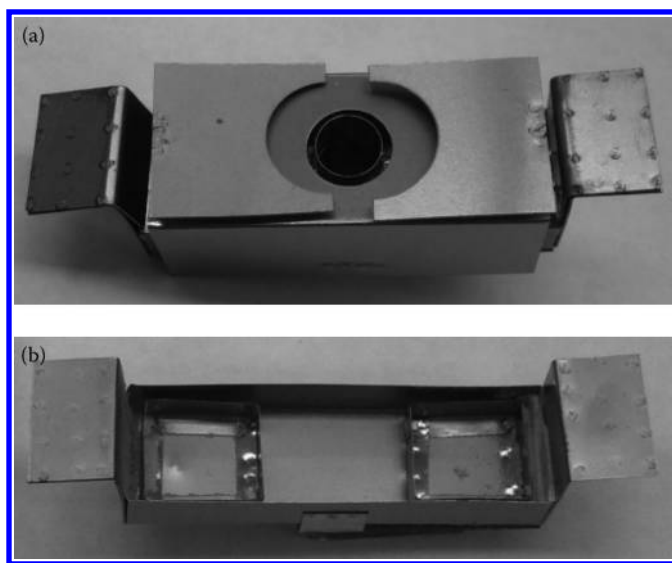


FIGURE 14.5 Research sized boat source shown with (a) cover on and with cover removed, (b) to show the interior of source with pockets at both ends for holding material. (Photo: PNNL.)

source material. Kodak developed such a source for their work on OLEDs using a quartz boat to hold the source material and a refractory metal combination cap and heater with perforated holes to allow the flux to escape. A similar approach is used today in many thermal evaporation sources (Witzman et al. 2001; VanSlyke, S. A. 2012, personal communication).

Even with top heating, point sources are fundamentally limited in operation by the thermal damage to the source material. However, since these sources are typically used for research and small-scale development, this is of limited concern.

14.5.2 Linear Boat Sources

For production on larger substrates, achieving the desired uniformity with point sources becomes infeasible due to the high material efficiency penalty and the large chamber size needed (Conroy et al. 2010a,b, 2011). The logical solution is to use a heated crucible configured as a line source (Krug et al. 1993; Witzman et al. 2001). This is exactly the approach taken by several companies, including Tokki, YAS, and Jusung (Krug et al. 1993; OLED Association 2011; Kim et al. 2011). These sources have similar designs to the point sources, but have a much longer evaporation area, providing a line of flux instead of a point. The flux profile from these sources can be simulated as a line of point sources added together. In fact, some boat sources use a series of nozzles instead of a slot to simplify the source design (Keum et al. 2004). This linear flux profile enables uniform deposition across the width of large glass substrates and either the substrate or the glass can be scanned to provide uniform coverage across the entire substrate.

Linear boat sources have similar material limitations as point sources, with the entire mass of source material being heated during normal operation. Like the point sources, it is possible to heat from the top surface and maintain a gradient from the evaporation zone down to the base of the “charge,” that is, the source material placed in the boat during a deposition run, but the material will still be exposed to potentially damaging temperatures. Because the sources are designed for production, they contain much more material than point sources, typically 100’s of grams (compared to less than a gram for research systems), and are expected to run for longer times, both of which increase the likelihood of material damage. Sources of this type are made by a variety of equipment suppliers, primarily Korean companies such as Sunic, YAS, and Jusung, as well as internally developed sources at the large display manufacturing companies (Kim et al. 2010).

14.5.3 Next Generation Sources

In order to overcome the rate, material lifetime, large area uniformity, and operational uptime challenges that point and boat sources have, different groups have developed a range of novel sources.

Kodak developed an effusion source technology called Variable Injection Source Technology (VIST) (Hamer et al. 2008a,b; Long et al. 2008, 2009). This source was designed to address thermal damage by flash evaporating a small amount of organic material while keeping the bulk cold, and large area deposition by using a distribution nozzle with a carefully tuned flux profile. By evaporating under nonequilibrium conditions, the source enables the coevaporation of materials with different vapor pressure

curves, so hosts and dopants can be evaporated from the same source at the same time. They demonstrated the capability for 20 s cycle time and 70% material utilization for an inline 5G deposition system for solid-state lighting (Tyan 2009). However, the source had challenges with reliably feeding organic powders to the flash evaporator, requiring special processing to achieve the necessary consistency (Long et al. 2009). In the end, the source technology was sold when Kodak exited the OLED business in 2010.

Veeco Instruments has developed a series of sources based on their valved source and linear nozzle technologies developed for the MBE and solar markets (Veeco 2009; Campion 2010). By using a valve to modulate the flux, a more stable deposition rate can be achieved, even when using materials that do not have stable evaporation profiles (Kim et al. 2008; Priddy et al. 2008; Conroy et al. 2010a,b). This ability to control the flux response can be extended to enable reloading the source during brief intervals in operations, effectively increasing the source capacity indefinitely without causing additional material damage. This is done by introducing new material into the crucible and using the valve to keep the flux stable as the powder heats up and comes to equilibrium with the crucible temperature. The nozzles of each source are designed to fit closely together, enabling codoping with multiple materials. The utilization of the source is a function of source–substrate spacing and width of the substrate, with efficiencies approaching 90% for 1 m wide glass and 100 mm source–substrate spacing and nearly 40% for a G4 substrate (730 mm × 960 mm) with a 300 mm source–substrate spacing (Gotthold et al. 2011).

Hitachi Zosen has developed a planar source instead of a linear source, in order to deposit over an entire substrate without moving either the source or the substrate, greatly simplifying the system design and mask alignment. A planar distribution manifold spreads the flux across the entire substrate at once, and multiple materials can be codeposited by interleaving multiple distribution manifolds. The manifolds are supplied from a small, separately heated crucible that can be valved off and vented without breaking vacuum, enabling quasi-continuous operation (Fujimoto 2010). Applied Materials has developed a linear nozzle source to enable the glass to be held in a vertical orientation and uses a distribution nozzle to provide a uniform flux (Hoffmann et al. 2011). Ulvac presented a cell, called the g-cell, that uses a carrier gas to transport a small amount of material to a vaporizer zone and then to a linear nozzle for distribution (Waters 2009).

14.6 Process Control and Feedback

Process control and in situ characterization in OLED thermal evaporation is currently relatively immature compared to many other semiconductor processes and this remains a challenge for high volume manufacturing. An example of a high performance OLED lighting stack (in terms of the combination of efficacy and lifetime) is the tandem hybrid white OLED stack shown in [Figure 14.6](#).

In order to produce a product at high yield, layer thickness and composition must be closely controlled. Typically, layer thickness must be maintained to within $\pm 3\%$ of the aim point, or the color, efficiency, voltage, or lifetime will be out of the specifications for the product. The stack in [Figure 14.6](#) shows 11 organic layers. In order for this product to be manufactured with an economically viable yield, each layer must be in control within specification for $>99\%$ of the time. If each layer were out of specification 10% of the time, the yield for the full device might be expected drop to 31% (device yield = 0.9^{11}). This low

	Cathode
Red and yellow emission	n-type contact layer
	Electron transport layer (ETL)
	Red emitter (phosphorescent)
	Yellow emitter (phosphorescent)
	Hole transport layer (HTL)
Connector	p-type layer
	n-type layer
Blue emission	Electron transport layer (ETL)
	Blue emitter (fluorescent)
	Hole transport layer (HTL)
	Hole injection layer (HIL)
	Anode
	Substrate

FIGURE 14.6 Example of a very high-performance hybrid tandem white OLED architecture with 11 organic layers and two metal/oxide layers.

yield would be difficult to tolerate for displays and would completely eliminate the possibility of cost-effective lighting using thermal evaporation.

14.6.1 Flux Monitoring

The primary technique for flux monitoring in both research and production is a quartz crystal microbalance (QCM) positioned such that the flux from a single evaporation source impinges on the measurement surface. QCMs work by vibrating a small quartz crystal that is exposed to the deposition flux. As material accumulates on the crystal, the resonant frequency shifts. By correlating this shift with the known physical properties of the deposited material, the accumulated mass and deposition rate can be calculated. While this technique works, there are some OLED-specific challenges. First, because organic materials have lower density than most materials the QCMs were developed to measure, the accuracy of the measurements can suffer, especially as the thickness of the accumulated material increases. This is primarily due to the fact that the mechanical properties of organic films are not as well known or as stable with regard to thickness, temperature, and deposition rate as more conventional films such as metals and ceramics.

These issues necessitate the regular replacement of the quartz crystals, which can be done manually or through a reloading system. Manual changes work well for research systems where the deposition chambers are opened regularly and run-to-run variations are less critical. However, this approach is less suitable for production systems where regular system vents cannot be tolerated. Various reloading QCMs are made by the leading sensor manufacturers. For example, Inficon has dual crystal heads (primarily for redundancy) and both 6 and 12 crystal rotatable turret heads designed specifically for long-term operation (Inficon 2013). Colnatec also makes a

multicrystal head design with either 12 or 24 crystals specifically for the OLED and thin-film solar industries.

Another path to extending the operational life is to enable heating of the crystal to remove accumulated material. AVL, now PiezoCryst, has commercialized an orthophosphate-based crystal that can be heated to temperatures up to 800°C without affecting operation. In addition to their multicrystal heads, Colnatec has also developed a heated sensor head/crystal combination suitable for OLED deposition (Colnatec 2013).

Long et al. have developed a flux monitoring gauge that is incorporated into their VIST source (Long et al. 2008). This gauge, a variation on a Pirani gauge (Ellett 1931) modified to run at low temperature, is capable of providing much faster feedback to enable stable flux control from a variable evaporation material. This is not a direct measurement of the flux being delivered to the substrate, but instead is a measure of the pressure inside the source. Under similar operating conditions and source designs, this measurement will correlate linearly with the delivered flux.

Optical absorption of light that passes through the emitted flux plume also has potential as a measurement tool. This has typically been done using atomic absorption (AA) and is especially useful for separating out the fluxes of different materials that are being codeposited. A major issue with this approach is in the name—this is an atomic absorption phenomenon. As such, it works best with discrete atomic species such as In, Ga, and As. In OLED materials, most of the atomic components are the same (i.e., C, N, H, etc.) and the differences are in the elemental ratios and/or structural. A second major issue with AA is that the evaporation process invariably deposits some material all overso that the viewports used to achieve an optical path will coat up with time. This is an issue for all AA applications, not just for OLEDs, and it requires careful system design and operation to achieve reasonable operating times.

14.6.2 Optical Film Measurement

While QCM measurement can provide a key control signal for the film deposition process, it does not measure the performance of the deposited film. Ellipsometry has been used to characterize deposited films providing a range of useful details, including layer thickness, interface quality, and optical constants (Celii 1997). However, the complexity of the data means that the necessary data fitting and modeling can make real-time feedback difficult.

More recent work has focused on using spectroscopic reflectometry from companies such as LayTec (COMEDD 2013) and k-Space Associates (k-space Associates 2012). Several approaches have been developed for the task of determining the important optical parameters of multilayer thin films. One of the most powerful is phase modulated spectroscopic ellipsometry (PMSE) (Celii 1997; Hartmann et al. 2004; Farahzadi et al. 2010). In this method, the incident light is directed through the deposited layer and a photoelastic modulator mounted in the path of the reflected light measures the change in polarization of the reflected light. The polarization change contains information about the amplitude and phase of the reflected wave as it passes through the different components of the stack. While polarization shifts depend on the thicknesses and optical constants (n and k) of the individual layers, it is not possible to obtain these parameters directly from the ellipsometric angles without intensive spectral modeling and fitting

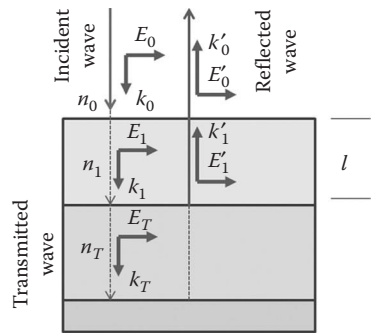


FIGURE 14.7 Normal incidence geometry of spectroscopic reflectance probe for *in-situ* optical constant and thickness measurements. (Courtesy of k-space Associates. 2012. k-Space wins DOE funding for OLED development. Retrieved November 27, 2013, from <http://www.k-space.com/k-space-wins-doe-funding-for-oled-development-2012-06-29>.)

to many unknowns. For this reason, while PMSE is a useful *ex situ* method, it does not lend itself to *in situ* methods that require real-time analysis of the optical data. A more convenient method is spectroscopic reflectance (SR), which also utilizes phase shifts in a light beam as it propagates through the various film layers. The optical geometry of the measurement is schematically shown in Figure 14.7 at normal incidence (the most favorable situation for *in situ* measurements).

Using SR, one can obtain the required information about the optical constants, the layer thicknesses, and interface roughness by modeling the optical response of the stack at different incident wavelengths, and extracting best fit parameters. Layer thickness precision down to 0.1 nm and refractive index uncertainties at the level of a few percent [k-space Associates] have been demonstrated with this approach for OLED multilayer stacks and efficient routines are readily available for this purpose.

14.7 Patterning

In order to make functional devices, organic films usually have to be patterned in some way. The extent and precision of the patterning depends greatly on the application. Whereas lighting might have centimeter scale pixels with 1 mm resolution, mobile displays can have over 400 pixels/inch (ETNews 2012) with micron resolution requirements as shown in Table 14.3.

Table 14.3 Example Resolutions versus Pixel Size and Typical Size Tolerances

Display Type	PPI	Subpixel (μm)	Tolerance (5%) (μm)
Mobile phone (4.8" 1080p)	459	18 × 89	1
Mobile phone (4.1" 720p)	358	42 × 70	2
Tablet (10.1" 1080p)	218	38 × 116	2
Laptop (15" 1080p)	147	57 × 173	3
Monitor (27" 1080p)	82	103 × 311	5
Television (55" 1080p)	40	211 × 634	10

Unlike traditional semiconductors, postdeposition patterning of organics using etching techniques is generally impractical. While the organic layers can be removed by solvents, controlled removal is difficult, and distinguishing between photoresist and the OLED layers is extremely difficult. The one exception is when the organic layer is not directly patterned, but instead the pixel definition is done with the metal contact layer. This is the approach used in some displays, where the individual pixels are white, and then are processed through a color filter. While this approach does not have quite the efficiency and color purity of direct emission, the lack of patterning makes for a dramatically simpler device fabrication. This approach was originally proposed by Kodak (Hatwar et al. 2004; Hamer et al. 2008) and is the method of choice for some large display manufacturing.

14.7.1 Fine Metal Mask

The most direct method of patterning the organic layers when depositing by vapor deposition is the use of shadow masking with FMM. These are thin foils of Invar™ or similar low thermal expansion metals that are typically photochemically etched to produce the pixel pattern. While FMM patterning is conceptually simple and is currently the method used for most OLED display production, there are several significant challenges.

First, because this is a reductive rather than additive approach (like printing), the material utilization for patterned layers can be quite low, especially for the multiple color emissive layers used in displays. Using the coarse approximation that each primary pixel is made up of a red, green, and blue subpixel, then the maximum material utilization for each emissive layer is only 33%, and in real-world applications, where there is spacing between the pixels and each subpixel, the actual utilization can be much lower, closer to 10%.

Second, the stochastic nature of the flux source limits the resolution to which the subpixels can be defined. While this is generally not an issue for lighting or larger displays, it is a key limiting factor for achieving high pixel density in smaller displays. Figure 14.8 shows a schematic of the flux patterns through an etched shadow mask illustrating the issue. Until recently, this has limited displays to <200 PPI, but recent advances

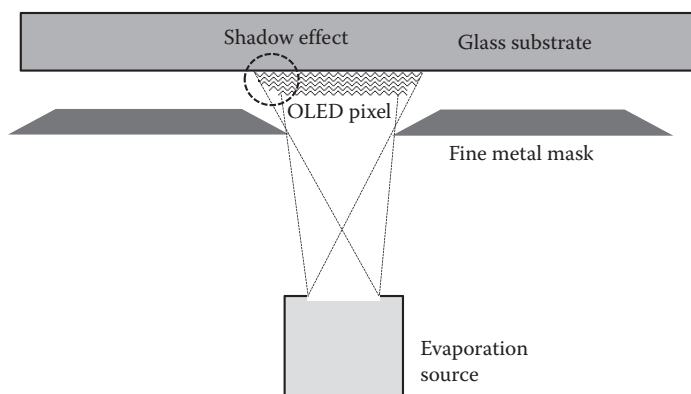


FIGURE 14.8 Schematic of flux pattern through FMM hole. Show beveled edges of a hole, and flux from directly below versus from off angle.

in pattern layout, mask alignment and flux distribution have enabled higher resolution displays (ETNews 2012).

A third problem with FMM is achieving correct alignment and maintaining that alignment during deposition. For larger patterns, physical alignment methods can be used, where the substrate is held in a mount with the masking system that provides for proper registration. Depending on the size of the substrate, this approach can typically be used for alignment down to less than 0.1 mm (100 μm) (Borosan, M. 2012, personal communication). Where higher accuracy is required, such as in display applications, an optical alignment process similar to that used in LCD mask alignment is typically used. This process, while capable of 1 μm registration on Gen 5 (1100 $\times$ 1300 m) substrates, is much more time consuming and can contribute to yield loss, both through errors in registration and through particle generation during the alignment process itself. Once the substrate and mask are aligned, they must be held in alignment during deposition, which is a separate and more difficult issue. It is also clear from the schematic layout in [Figure 14.8](#) that any variation in the mask-substrate spacing could dramatically change the size and edge quality of the masked pattern. In most current processes, the substrate is mounted horizontally and the organic materials are evaporated from below and deposited on the downward facing surface. The orientation limits the number of particulates that could inadvertently land on the substrate before or during evaporation. For smaller substrates, typically <4 G (730 mm $\times$ 960 mm), this approach works well, but for larger substrates, maintaining the spacing between the substrate and the mask becomes much more difficult. For this reason, many conceptual designs for larger FMM-based systems have the substrate oriented vertically, or with a small (<5°) tilt so that the mask can rest gently against the substrate. In this configuration, the mask is often dimpled to provide small contact points with the correct spacing when the mask is laid down on the substrate.

Because VTE is, as its name suggests, a high temperature operation, the thermal loads during the deposition process can be significant. The heat load from the source is directed almost entirely at the FMM, causing both local (right above the source) and broad area heating of the FMM. This heating causes thermal expansion and the potential for misalignment. Because the shadow mask is, by definition, blocking the part of the source from the substrate, the two components heat up at different rates. This is the reason that low thermal expansion alloys are one key to the manufacture of FMMs. [Figure 14.9](#) shows the effect of different temperature differences on the alignment capability for FMMs with a range of substrate sizes. This problem is further compounded by the fact that with each process cycle, a new substrate is introduced, but the mask is typically reused, so there are differences in the cumulative heating of each component.

A final challenge to the FMM process is that the material that is blocked by the mask generally accumulates on it, rather than just reevaporating into the chamber. This leads to build up which can slowly clog the holes in the FMM, reducing the size of the deposited features. If the buildup is sufficiently thick, the deposited material can start to flake off, leading to particulate defects. The exact amount varies greatly with material, deposition conditions, and mask details. Regular mask cleanings and exchanges are required to maintain suitable yields. The exact interval of the cleaning and/or exchanges depends on the structure design, the materials being used and the tolerance of the process for particulates.

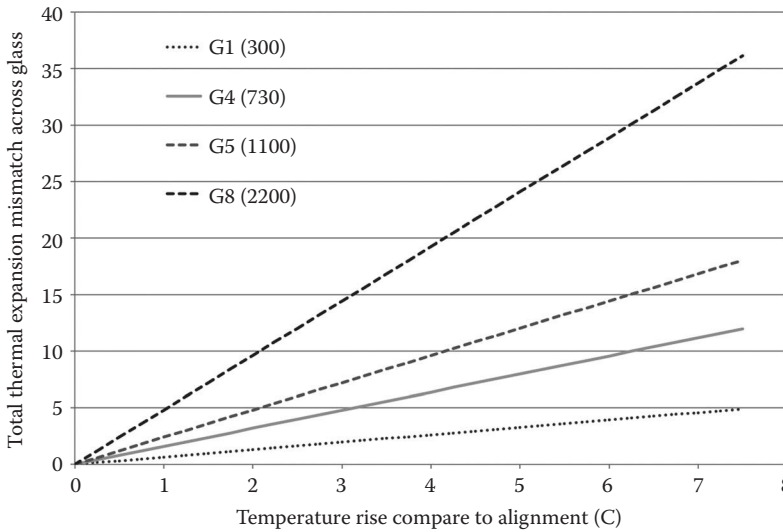


FIGURE 14.9 Alignment mismatch between glass substrate and fine metal mask for different temperature gradients and glass sizes.

A variation on FMM patterning is to use a scanning mask. In this approach, a small, high precision mask is held fixed relative to the source instead of to the substrate. As the substrate is scanned relative to the source, linear patterns or stripes can be produced, which can be used for larger displays or for lighting—where the pixel size can accommodate the lower resolution.

14.7.2 White OLED Plus Color Filter

One approach proposed by Kodak to address many of the shortcomings of FMM patterning for displays is to use individually addressable white pixels matched with a color filter, similar to that used in LCD displays (Hatwar et al. 2004; Hamer et al. 2008). In this approach, the processing is dramatically simplified because only the electrodes need to be patterned, not the organic layers, which completely eliminates the need for shadow masking or post deposition patterning. However, this approach loses some of the efficiency and color purity advantages of direct patterned OLEDs, because white light is generated instead of specific colors. The impact of this can be mitigated by carefully matching the emission colors of the white OLED with the color filters to ensure maximum transmission of the target wavelengths.

14.7.3 Laser-Induced Direct Imaging

Laser-induced direct imaging (LIDI) or laser-induced transfer imaging (LITI) is a novel approach to attempt to address some of the shortcomings of FMM-based patterning (Lamansky et al. 2005). In this process, the organic materials that are to be patterned, typically the emissive layers, are first deposited onto a flexible transparent sacrificial substrate using either traditional thermal evaporation or solution coating.

This sacrificial substrate is then held in close physical proximity to the device substrate and a laser is used to reevaporate the material, leading to deposition on the primary substrate. Because this transfer process is done using a focused laser beam, the material is reevaporated and deposited only where needed.

This process has been proposed as a method for large area display manufacturing, especially for the red and green subpixels, where performance similar to VTE has been demonstrated. However, challenges with yield and blue emitter deposition have limited the impact to date (Kyoon 2009; ETNews 2012).

14.8 Conclusion

Vacuum thermal deposition, while not without its challenges, continues to be a key technology for the deposition of organic light emitting materials for both research and production. While other technologies, such as direct solution printing, are making progress, VTE remains the highest performance and most flexible deposition method. Key challenges must still be overcome to enable lower cost manufacturing. Continued development in the areas of high capacity large area evaporation sources and advanced process monitoring and control will be needed for OLED VTE to expand to address the needs of the broad display and lighting markets.

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