Alkali Metal Sources for OLED devices

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Abstract

Electron injection in OLED organic layers is improved by using alkali metals as cathode layer or as dopants inside organic layers. An innovative alkali metal dispensing technology has been developed to overcome handling problems and to ensure controlled and reliable alkali metal layers for OLED.

1. Objectives and background

One of the key issues for organic light emitting diodes (OLEDs) is to achieve high electro-luminescence external quantum efficiency (η_{ext}), high power efficiency (η_E) and long-term stability. These goals imply extremely efficient electron injection and therefore low driving voltage, together with high electron mobility in the organic layer and thus high recombination efficiencies. The cathode structure and the metal-organic interface are the major responsible for the desired performance improvements[1].

In the present work and in broad literature works, deep studies have been carried out on the usage of Li and Cs. Alkali metals incorporation in the OLED structure can be accomplished in two forms:

- ultra-thin layers (Li, LiAl, Li_2O, LiF, Cs, CsAl, CsF and alkali-metal carboxilates) above the electron transport layer (ETL) and capped by an Al back electrode[2,3]
- co-deposition of Li or Cs with an ETL immediately prior to the cathode deposition (also named “alkali metal doping of ETL”)[4-6]

Both configurations have been shown to dramatically reduce the drive voltages and, in the meantime, increase the external quantum efficiency, the overall luminance and the long-term operational stability (Fig. 1).

Moreover, the creation of an electron injection layer (EIL) both by the interlayer between ETL and cathode and by ETL doping, employing transparent cathodes, such as ITO, has been shown excellent improvements in both η_{ext} and η_E also for Top-Emission device architectures (TOLEDs)[7] and for Stacked structures (SOLEDs)[8]. As a side effect of the adoption of Alkali Metals inside the OLED structure, the organic materials experienced longer lifetime and stability due to the reduced electrical stresses.

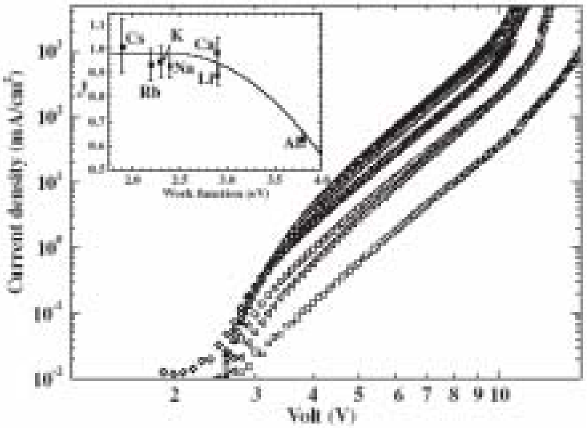

Fig. 1: Current density-voltage (*J*-*V*) characteristics of ITO(110 nm)/α-NPD(50 nm)/Alq3(50 nm)/X(0.5 nm)/Al(100 nm) devices with various cathode metals; X(WF: Work-function) = Cs (1.9eV, Δ), Rb (2.2eV, ▽), K (2.3eV, ☆), Na (2.4eV, ◊), Ca (2.9eV, ◁), Li (2.9eV, ○), and None (3.5eV, □). (Inset) External quantum efficiency (η_{ext})-current density (J) characteristics depending on work-function of inserted cathode metals. It is clearly visible that using Cs a current density of about 100mA/cm^2 is reached at a driving voltage of 6.5 V, compared to a structure without alkali metal where 100 mA/cm^2 are achieved at a value higher than 10 V.[3]

An alkali metal dispenser tool is required for a reliable release of pure Li and/or Cs. Pure Li and Cs, used as buffer layers between ETL and cathode or as dopants inside ETL to create the EIL, exhibited much higher performances than the corresponding fluorine compounds. The present work has been focused on a new available pure Li and Cs source for OLED applications (trade name is “AlkaMax”). In fact, to overcome the high reactivity of alkali metals, which makes difficult their handling and practical exploitation, a suitable dispensers, based on materials extremely stable in air, has been developed: it guarantees a safe and controlled deposition of pure alkali metals.

2. Technologies for dispensing Alkali Metals

Amongst the several possible mechanisms to incorporate the alkali metals within the OLED architecture there are three main techniques referred basically to Li:

1) Li dispensing through crucible
2) Li dispensing through AlkaMax
3) LiF dispensing through crucible.

First, it's worthwhile to underline the main differences between the utility of pure Li and LiF inside the OLED structure, that basically are scientific and technological differences. From the scientific point of view, LiF is an insulator material and to create an active interfacial dipole layer between ETL and cathode its thickness should be extremely low (below 5 Å) and absolutely uniform to prevent shortcuts or electric field stresses within the device. On the other hand, if LiF is well deposited, it can prevent shortcuts between ITO spikes and the cathode and also any reaction between the cathode material and the organic leading to the formation of organo-metallic complexes able to quench the polarons[9]. LiF can act only as interfacial dipole and it is not absolutely able to improve the ETL conductivity and also the recombination probabilities: pure Li, both as interlayer between ETL and cathode and as doping inside ETL, transfers the electron injection inside the bulk organic, creates the gap states and facilitate the electron mobility and finally the recombination efficiency. Moreover Li thickness can vary between 5 Å and 60 Å, without strong constrains about uniformity and planarity. Finally, Li is much more versatile than LiF because it can be adopted in different structures (inter-layer and co-deposition). Anyway many OLED manufacturers exploited the usage of LiF because it is stable in air and easy to be handled.

Therefore, from scientific point of view, Li would be preferable to LiF. But Li still gives rise to several technological problems and AlkaMax can solve all these issues.

3. Results

3.1 Reactivity of alkali metal layers

The creation of an alkali metal layer can be accomplished through conventional physical vapor deposition from a heated crucible. However the alkali metal itself is very reactive and must be handled in inert atmosphere all through the entire process. This is difficult to be achieved since even low traces of humidity, nitrogen and oxygen, cause appreciable degradation of the alkali metal. For example free metallic lithium readily forms LiOH and H_2 reacting with moisture; it also forms Li_3N and Li_2O when heated in presence of nitrogen and oxygen. Furthermore lithium hydroxide readily absorbs CO_2 and water from air. The above cited reactions can also occur during any evaporation cycles leading to several instabilities like splash evaporation, due to reaction at solid-liquid interface, or increased sensitivity to the temperature equilibrium. If such a contamination happens, this reduces the lithium deposition rate and also the lithium total yield in a not controlled way.

An innovative alkali metal dispensing technology has been developed to overcome these problems and ensure OLED alkali metal cathode reliability. This solution allows obtaining a controlled, stable and reproducible evaporation rate.

The Alkali Metal Dispensers (AMD) are able to release Li, Na, K, Rb and Cs. Traditional AMD formats (for laboratory-scale tests) can dispense a few milligrams of alkali metal; new AMD formats (called AlkaMax) to support OLEDs production lines, are able to release a few grams of alkali metals (in particular Li and Cs) throughout the adoption of a very stable form of the alkali metal that can be very easily handled in the fab. environment.

3.2 AMD working principle

The working principle of an AMD is a chemical reaction which involves a precursor of the alkali metal and a metallic alloy: it is extremely stable at room temperature and at standard atmosphere. The alkali metal before evaporation is present in a stabilized form and can be evaporated "on demand": the evaporation could be stopped and re-activated without losing alkali metal yield because the metal not yet consumed remains in its stable form. The additional presence of getter material inside the dispensing material with the Li precursor guarantees pure Li and low operating pressure. In case of Li and Cs the metal obtained is pure and its precursor is non toxic and environmentally friendly.

3.3 AMD configurations for OLED

The alkali metal dispensers have different configuration related to material content and to the production scale-up. Laboratory scale test can be performed with small wires (to evaporate tents milligrams of metal), pilot line test can be carried out with "evaporation boat" (to evaporate hundreds mg up to one gram of metal) and mass production test can run with a bigger evaporation boat called AlkaMax (Fig. 2). The cylindrical configuration will be deepened here: it has been optimised for lithium evaporation in mass production case. The main features are: low outgassing throughput (H_2, CO) during heating, withstand sensitisation (giving corrosion due to chromium carbide precipitation at the grain boundary); withstand embrittlement (due to H2 at high temperature) and feature minimum radiative heating (evaporation chamber, target substrate, Quartz Crystal Microbalance).

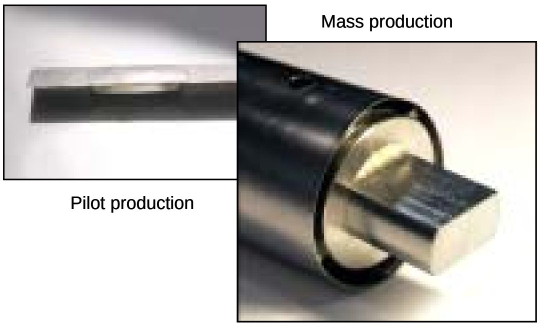

Fig. 2: Alkali Metal Dispensers configurations

AlkaMax container is treated with a firing procedure that enables it to withstand to strong thermal and mechanical stresses. The selected material of the dispenser is SS AISI 304L (140 mm length X 37 mm diameter). The final configuration has been optimized with an external shield [10] which allows obtaining the following improvements during the evaporation stage:

- minimizes the heat exchange with the surrounding elements: very low thermal irradiation on the target and on the QCM. It's essential to avoid heating of the target surface above the glassy temperature of the organic layers deposited on it.
- Reach higher deposition rates at lower current loads, reducing power consumption.

3.4 AMD evaporation test and dispenser usage

A full characterization of dispensing material, dispenser configuration and dispensing process has been carried out in order to optimize the evaporation and deposition dynamics of alkali metals layers. Alkamax was simply mounted to appropriate electrodes and heated by Joule effect. The heating process comprised two steps:

1. Preliminary degassing (around 30-40 minutes) at temperature lower than the starting of evaporation (Fig. 3)
2. Evaporation and deposition controlled on line by means of QCM and/or AAS (Atomic Absorption Spectroscopy)[11]

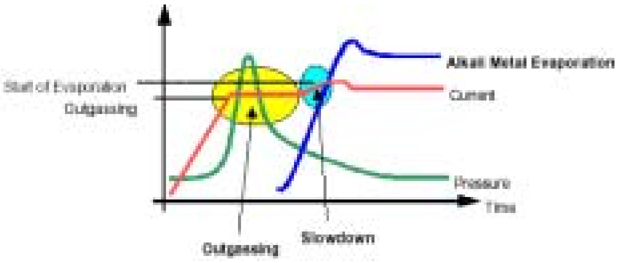

Fig. 3: Outgassing and evaporation from AlkaMax

In case of different evaporations performed with the same dispenser, or in case of need to open the evaporation chamber, it was possible to expose the dispenser to air without contamination of the remaining alkali metal. After each air exposure, a new degassing step was required, in order to remove water vapor attached to the container walls. The deposition rate was continuously adjusted through the closed-loop control. During the long term evaporation the deposition rate obtained was stable and reproducible for several setting in the range 0.05-0.6 Å/s. For example Fig. 4 shows a constant deposition rate of lithium at 0.3 Å/s for 80 hours and the corresponding current applied during evaporation. The control loop acts onto the power supply in order to keep constant rate. The obtained yield was more than 1 gram of Lithium.

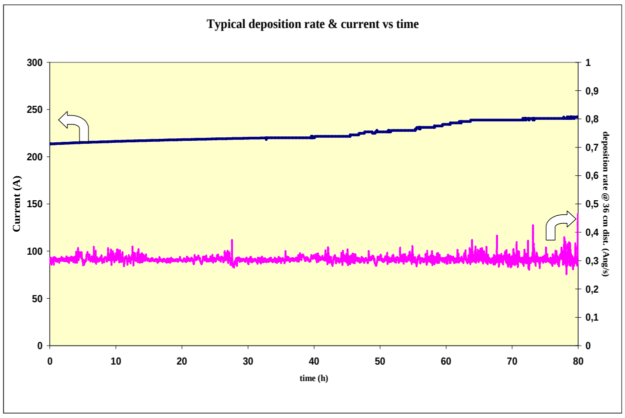

Fig. 4: Evaporation process from Alkamax. Current and deposition rate are monitored over time. Deposition rate is kept constant at 0.3 Å/s.

Generally, the operating voltages and currents applied to obtain Lithium evaporation from the configuration suitable for mass production use are: 0.8-2 V and 170-300 A. The operating temperature of the dispenser does not affect the substrate temperature thanks to the presence of the already described shield. After the preliminary degassing step, the working pressure is below 10^{-6} mbar.

The deposition rate is a function of target-dispenser distance. To obtain the same evaporation rate at different distances, different temperatures (and currents) are required. For example the range 0.2-0.4 Å/s for a distance of about 36 cm between source and target corresponds to a Lithium outgoing flux from the dispenser of about 15 – 35 mg/h. The uniformity of the deposited layer has been verified in case of Li layer. The thickness was set at 200 Å at a distance source-substrate of about 40 cm and the variation was below 15% over a glass substrate with the following dimensions: 300x400 mm (see Fig. 5). Simulations, which consider molecular flow conditions, agree with the quantity measured on the target.

3.5 Monitoring the deposition rate. QCM and AAS.

The detection of deposition thickness and rate is generally performed with a quartz microbalance (QCM). It's also possible to use an in-situ closed-loop control because, in case of Lithium AlkaMax, the variation of the deposition rate F with the temperature T is $\frac{\partial F}{\partial T} \approx 10^{-4} \div 10^{-3}$ Å/sec °C. AlkaMax exploited a much more stable evaporation rate and less sensitive temperature variation, compared to the other dispensing raw materials and dispenser designs. This is mainly due to the adopted alkali metal precursor and also the AlkaMax container design. The low value of first derivative $\delta F/\delta T$ allows an easy tuning of the automatic feedback control on the power supply to heat AlkaMax.

4. Conclusion

In the present work, new alkali metal dispenser material and technology compatible with OLED production are discussed. AlkaMax solution can provide up to a few grams of alkali metals (in particular Li, Cs). The use of a precursor permits to handle a stable and safe product, to obtain a pure alkali metal and to dispense Alkali Metal "on demand" with extremely good operational characteristics and control reliability.

5. Acknowledgments

Our thanks to Prof. C. Adachi and C. Maeda for helpful discussions.

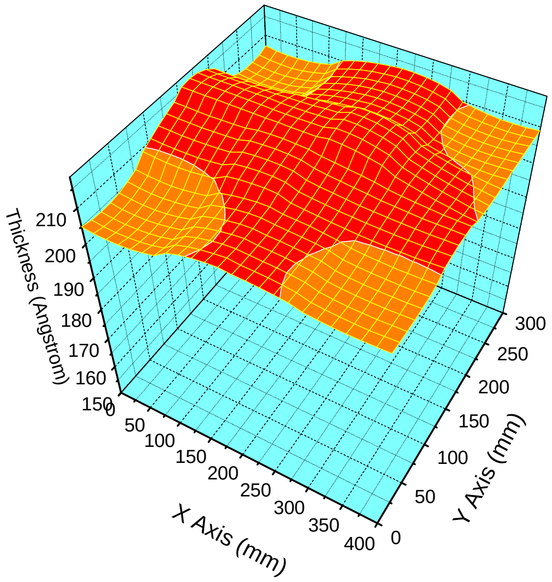

Fig. 5: Surface color plot of the deposition uniformity of Li on Glass substrate 300x400 mm.

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