High control Alkali & Alkaline-earth Metal Sources for OLED devices

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Abstract

Electron injection improvement in OLED organic layers can be obtained by their doping or using alkaline-earth or alkali metals as electron injection layers (EIL). Common handling problems can be solved by an innovative metal dispensing technology to ensure controlled and reliable metal layers for OLED. Thickness and deposition rate of EIL during the process have been explored to optimize device performances.

1. Introduction

One of the key issues for Organic Light Emitting Diodes (OLEDs) is to achieve high electro-luminescence external quantum efficiency (η_{ext}) and high power efficiency (η_E). These parameters can be measured by an I-V-L test[1].

Efficient electron injection and high electron mobility in the organic layer can improve the characteristics of the OLED stacks. The electrical I-V characteristic can be modelled considering essentially three regimes[2]: ohmic, trap-charge limited (TCL) and space-charge limited (SCL). This electrical characteristic generates meaningful current from the built-in voltage, given by the difference between the work functions of the anode (ITO) and the cathode (Al). The electrical characteristic can be also limited by the emitted current, whose value is a function of the cathode work function and can be estimated starting from the Richardson-Schottky model.

Alkali metals incorporation in the OLED structure can be accomplished in two forms[3]: 1) ultra-thin layers above the electron transport layer (ETL) and capped by an Al back electrode[4]; 2) co-deposition of Li or Cs with an ETL material immediately prior to the cathode deposition (also named "alkali metal doping of ETL")[5]. As primary objective, we will carry out the comparison of EIL based on Li and Cs layers, with respect to the LiF based technology. The better performances of the former solution have already been demonstrated by Kido[5] and Oyamada[6], showing actual improvements in OLED devices, achieved by using pure Alkali Metals.

In this paper, features related to the process parameters will be deepened. In fact, the improvements can be observed only if the stack is properly designed and the deposition rate is optimized.

2. Experimental

The equipment used in this work is basically a standard prototype machine for producing OLED.
It consists of:
- UV ozone treatment for the ITO-glass sample and glass with cavity plate. This is used to improve the work function of ITO and to clean the samples that are sold by the suppliers with a soft cleaning based on the use of deionized water and Iso-Propyl-Alcohol (IPA).
- vacuum chamber separated in 3 zones:

1. the first one is for vacuum thermal deposition of ETL and HTL with 4 crucibles and 1 QCM (Quartz Crystal Monitor), that will be used to deposit NPD-α and Alq$_3$ (typically at 1 Å/s);
2. the second one is for vacuum thermal deposition of EL (Emission Layer) with 4 crucibles and 3 QCM;
3. the third one is for vacuum thermal deposition of EIL (Cs, Li, LiF) and Al, with 2 couples of connectors for boat, with two QCM.

The vacuum chamber is equipped with a circular sample holder, which can move six groups of four samples and allows the use of masks.

The target is placed at a distance of about 40 cm from the EIL materials boat, while the QCM is placed at about 20 cm.

Moving equipment allows transferring the samples from the evaporation chamber into the glove box, without air exposure (the two chambers are connected by an intermediate vacuum chamber).

The sealing between the front and the back plates takes place in the glove box, using a UV curing machine. The glue is a standard UV curing one and is dispensed by a syringe method onto the back plate.

The standard process requires:

- 5 hours for evacuation of the evaporation chamber until $4 \cdot 10^{-7}$ Torr;
- 2 hours for dummy evaporation of all materials and also EIL (LiF). This dummy evaporation is done keeping the substrate protected by a shutter. In this way, material outgassing can be reduced during the actual process;
- 2 hours for producing one batch (2 samples are typically made for each configuration).

I-V-L standard measuring equipment is used to characterize the OLED's. The electroluminance spectrum is also measured during the I-V-L test.

This work is based on an OLED structure composed of four pixels, bigger than a real one, but with the same typical geometry of the prototypes used by the manufacturing labs for optimization.

QCM calibration is usually done by comparison with another more accurate thickness measuring technique: in our case, α-test (i.e. the profilometer system) has been used.

Our experimental setup has allowed a multivariate analysis of the main system parameters. As for every experimental design, we have identified: main observables at the end of the process, fixed parameters, process and geometry parameters .

The *main observables* are:
- characteristic current density vs. voltage (j-V) in the range j=0÷0.2 A/cm^2 (voltage V=0÷10 Volt);
- current efficiency (η_L) vs. current density.

The *fixed parameters* will be the ETL material (*Alq$_3$*) and the cathode material (*Al*). The *process and geometry parameters* that should be multi-varied in order to obtain the sensitivity and an optimization are the EIL material (Li/Cs/LiF/none), the EIL thickness, the EIL deposition rate (that can have an effect on the interfacial cathode-EIL resistance).

3. Results and discussion

In this paper, we summarize the first part of the results elaboration from the experimental campaign. In fact, the multivariate analysis of the parameters has provided confirmation about the good properties of the SAES Alkali materials, but only part of them published in this paper.

The OLED configurations used for these experiments were NPD(70 nm)/Alq3(50 nm)/SAES metal (various thickness & deposition rate)/Al(200 nm).

The part of the characteristic curve that produces a luminance in the range 100÷3600 cd/m^2 seems to be in the TCL regime, not limited by the injection current because of the low work function, as we will show elaborating the measured characteristics.

The trap-charge limited (TCL) is a transition regime between the ohmic and the space-charge limited (SCL), during which too many charges are injected to allow for ohmic conduction, but not enough charges to fill all trap levels ; the current is governed by the density and energy distribution of the traps:

$$j = N_{LUMO}\mu_n e \left[\frac{\varepsilon\varepsilon_o l \sin(\pi/l)}{eH_t(\pi/l)(1+l)} \right]^l \left(\frac{2l+1}{l+1} \right)^{l+1} \frac{V^{l+1}}{L^{2l+1}} \quad (1)$$

where e is the elementary charge, μ_n the electron mobility in the ETL, n_0 the thermally generated background free charge density, V the applied voltage, d the ETL thickness, N_{LUMO} the density of states in the LUMO-levels, H_t the total trap density (if the trap distribution starts at $E_{LUMO}=0$), ε the dielectric constant and ε_0 the permittivity of free space. The empirical parameter $l > 1$ describes how the concentration of traps changes with energy.

The parameter *l* and the transition between the three conditions depend on the specific process applied and cannot be easily reproduced for different contamination and temperature distribution during the process.

Fig.1 shows the I-V characteristics obtained without EIL and a 1 nm EIL of LiF, Li, Cs. The regression gives an exponent *l* in the range of 7÷7.5, according with the literature[7](6÷8).
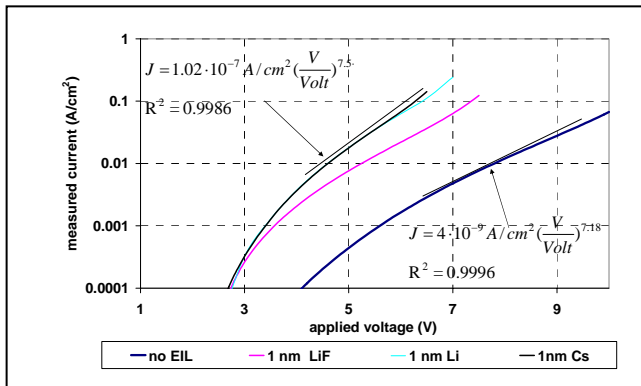
Fig. 1. Characteristic of samples without EIL or with a 1 nm EIL (LiF, Li, Cs).

The main result of the first data analysis is that the main improvement in the use of the Alkali metal is in increasing the mobility parameters μ_N, due to the diffusion of Li and Cs in ETL; this effect is also present in the case of LiF, as expected by SIMS measurements previously published[8].

Evidence of this benefic diffusion for LiF has been given also by UPS[9], explained by different chemical reactions (involving the temperature of the Al layer and the concentration of moisture during the deposition process). Pure Li doping or a pure Li layer can induce Li diffusion. This phenomenon does not depend on moisture contamination during process (a non-controllable parameter) as in the case of LiF; then it should be more stable and reproducible with respect to LiF. First results seem to go in the sense, although the scientific validation will be published in the next future.

The problem associated to Li diffusion is the risk to contaminate the recombination zone (50 Å÷100 Å, above the HTL and Alq₃ layer)[5]. This phenomenon causes quenching of excitons. Then, we must take into account Li diffusion length, that can be extracted through analysis of SIMS data[4] and j – V characteristics. In BCP and CuPc the diffusion length is ~700±100 Å, while in Alq3 it is ~300±100 Å.

In order to explain better this concept, Fig. 2 shows the I-V characteristics of the LiF, Li and Cs compared to the case without EIL. Every point is measured at the same voltage. The linear shape of the plot is indicative of a current increase due to change in resistance more than to the effect of the exponent *l* in equation (1). The TCL characteristics scale by a multiplicative factor that is the mobility ratio (inversely proportional to the resistance of the ETL) .If the variation of exponent *l* were more important, it should give a non-linear plot. The resistance of the ETL has been reduced of a factor 13 for the LiF EIL and 43÷47 for the Cs and Li SAES EIL.

Basing on these considerations, the EIL thickness effect has been evaluated. Thickness of Alkali metal layer has been varied (0.5, 1.0, 1.5 nm).

Fig. 3 shows the I-L characteristics in the case of Li EILs compared to the case without EIL and the standard 1 nm LiF EIL. We observe that:

-Li interlayer gives better results than LiF in terms of current density and luminance
-Current density shows little dependence on Li thickness.
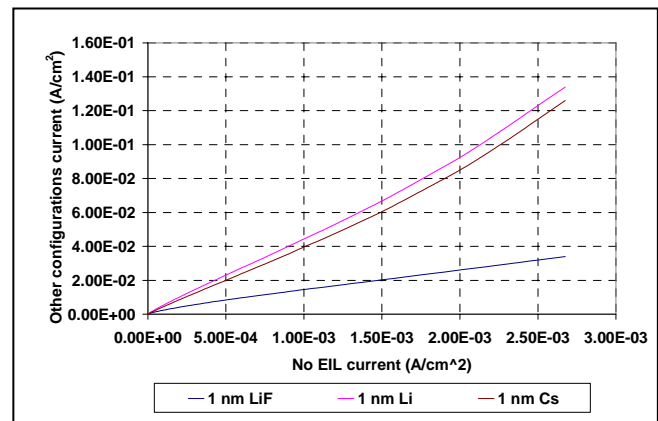
Fig. 2. I-V characteristics of the LiF, Li and Cs against the case without EIL, for different configuration.

Fig.4 shows the same characteristics for the Cs samples. We observe that:

-Cs interlayer gives better results than LiF in terms of current density and luminance
-the optimum thickness is found to be 1 nm.

The kinetic energy of the impinging atoms during the layer generation can be sufficiently high to enable Cs

and Li to diffuse into the ETL, even if no co-evaporation has been done. The change of evaporation rate can change and control the ETL doping.
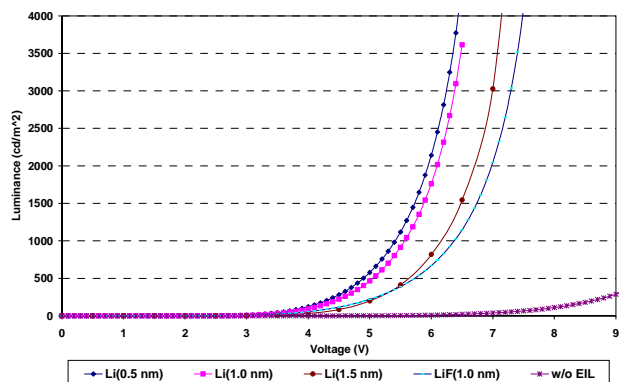

Fig. 3. Characteristic of samples without EIL, with 1 nm thick LiF EIL and with different Li EIL thickness values.
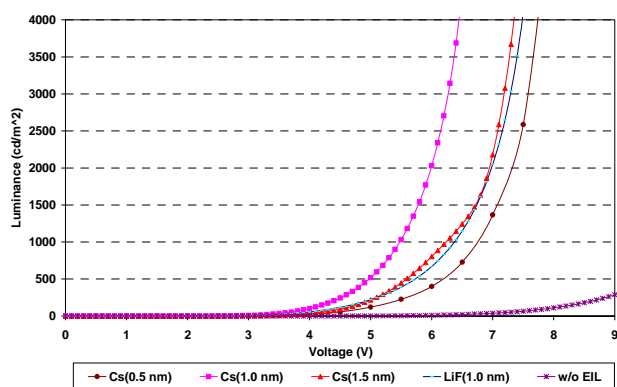
Fig. 4. Characteristic of samples without EIL, with 1 nm thick LiF EIL and with different Cs EIL thickness values.

Fig.5 allows evaluating the resistance ratios of the different solutions:

- 0.4 Å/s vs. 0.2 Å/s deposition rate in the case of Li EIL: the resistance corresponding to the higher deposition rate is one half with respect to the lower deposition rate;
- 0.2 Å/s vs. 0.1 Å/s deposition rate in the case of Cs EIL: the resistance change is not relevant (about 11%). It seems that diffusion of Cs is not caused by the kinetic energy of atoms in the explored range of deposition rate.
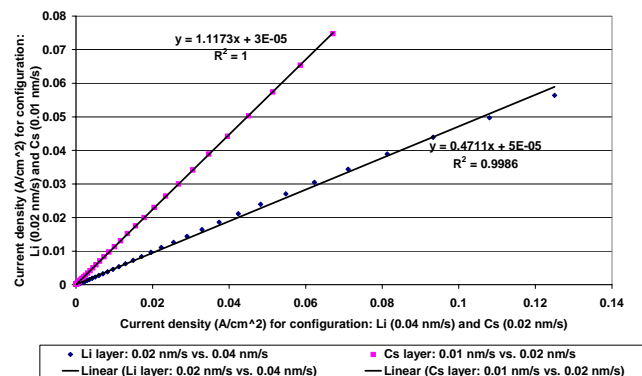
Fig. 5. Evaluation of the ratio between resistance values, changing the deposition rate for the Cs and Li configuration.

4. Conclusions

We have started to explore the effect of different EIL materials on OLED performances. First results show that Li and Cs EIL's are better than LiF solution, provided that thickness and deposition rate are properly set.

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