

## Failure Mode Analysis for Polymer EL Blue Devices' Lifetime

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### Abstract

We report failure mode observed in polymer EL blue devices, relating with life curve. The modes are analyzed by observing compositional and morphological variation using TEM-EDX, STM, and reverse engineering method as destructive ways, and also investigated mobility changes of hole and electron by measuring transient EL as a nondestructive way corresponding to life curve. We believe that the postulated failure modes in polymer EL devices can present right directions to obtain better performance, especially life time, of polymer devices in material and device structural designing points of view.

### 1. Introduction

Since discovering polymer materials utilizing for electroluminescent(EL) devices in 1990 [1], there's been great efforts pouring into device's performance till now. After more than a decade of such period, we are now on the verge of real application for display. But, in reality, world-wide scientists, engineers, and decision makers does not draw clear picture of future display using polymer materials, especially blue one as a bottle neck due to its relatively short lifetime comparing to red and green.

Considering above, we thought that we are on a situation to figure out what's the cause of short lifetime in polymer EL blue devices. There's been a lot of reports related with lifetime, mostly for green [2] and red polymer devices, less for blue one. [3] As a matter of fact, in spite of reduced number of multilayer, polymer device bears quite a complicated failure modes inside. Thus, even well-known degrading factors are sometimes treated as minor or preventable ones like dark spot. And, degrading mechanism depends highly on materials and device structures. Therefore, it has been pushed us to deeply investigate the failure mechanism/mode of currently developing blue devices in SAIT.

### 2. Experimental

Initially, we prepared polymer EL blue devices like this structure : ITO/PEDOT 50nm/SB1 80nm/BaF<sub>2</sub> 5nm/Ca 3nm/Al 200nm, where SB1 is a SAIT blue material. We approached the failure mode via two ways. The non-destructive way is measure both electron and hole carriers' mobility from transient EL according to life curve. The destructive way is to investigate cross-sectional/compositional variation using EDX filtered TEM and morphology by STM of insoluble layer after reverse engineering.

### 3. Results and discussion

From the beginning of our investigation, we utilized both anode and cathode work functions by choosing appropriate inorganic materials and metals to obtain basic carrier characteristics of SB1 emitting layer. Thus, we found some evidences to know that SB1 was a electron-rich system, which has well band matched cathode structure, and emitting zone was located near PEDOT side. (not in publication)

Fig.1 shows the lifetime curve and its voltage variation. The lifetime curve is not normally observed

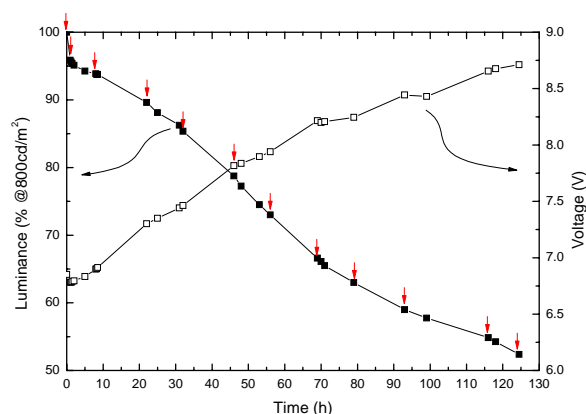


Fig 1. Lifetime curve and its corresponding voltage of a polymer EL blue device. Red arrows indicates points of transient EL measured.

one like a two-exponential curve. The bally part of luminance within 70 hours usually comes from charge unbalance between hole and electron inside emitting materials (SB1), which could be solved by designing device structure.

As indicated by arrows, while we deriving a blue device at constant current with initial luminescence of  $800\text{cd/m}^2$ , we stopped the driving for a few minutes and measured transient EL at different luminescent level. To avoid the effect of residual carrier inside the device due to periodic operation, frequency dependence of peak luminance has been measured and makes us choose 1Hz as a period. We normalized the results with a saturated luminance by varying pulse duration from 10 microsec to 1 msec. Fig. 2 shows the luminescent dependence of transient EL at different position of life curve.

The analysis of the transient EL results followed mostly the previous work done by D. J. Pinner *et al.* [4] Since the recombination zone located near PEDOT and emitting material has an electron-rich property, early stage of luminance within 2 microsec is related with fast-carrier, i.e., hole mobility, and the slow increase of luminescent curve for electron one. With help of Pinner's analysis, we calculated both carriers mobility at the driving filed, logarithmically shown in Fig 3 for assurance.

During operating the device, hole did not changed much of its mobility, even though electron reduced

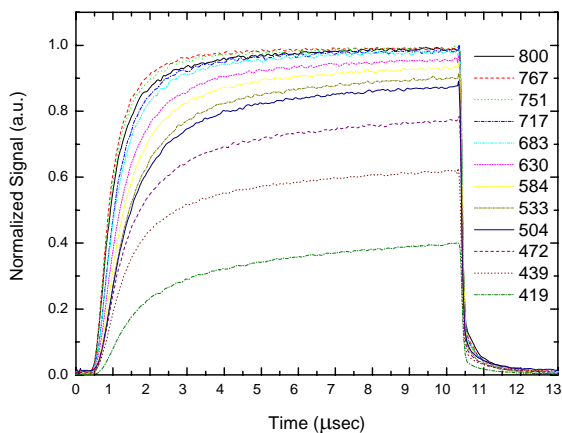


Fig 2. Transient EL signal measuring at different luminescent level along with life curve. The pulse duration is 10 microsec with an applied field of 6V and curve is normalized with saturated luminance.

almost by a order of two up to half luminescent drop. And, interestingly, the curve shape looks like following the lifetime one. In Fig. 1, the luminance slope could be, we think, separated into three regions posting at 30 and 70 hours along the curve. Quite similarly, the electron mobility curve in Fig. 3 has the behavior of varying slope in three different time zones. Thus, we could know that electron mobility is getting reduced by almost double times, affecting on luminescent drop of an operating device.

Even above non-destructive way of looking into device is just a stop-and-go, not an *in-situ* one, those kinds of dynamic failure inside nano-scaled thin film device is not easily investigated for compositional and structural/morphological points of view. So, we adopted reverse engineering analysis for driven (half luminance drop) and undriven pixels in the same devices to compare and find some failure factors.

The samples are de-capped and, with acid solvent, removed cathode. For driven pixels, emitting layer has been dipped into strong solvent like chlorobenzne and chloroform remaining an insoluble layer. Fig. 4 shows photoluminescence images of the sample just without cathode (a) and after dissolved by solvent (b).

As seen clearly in Fig. 4, driven pixels has lower PL intensity and insoluble part within emitting layer thickness. For the overexposed image of (b), other area except insoluble region shows dim PL intensity. It caused from the baking process of emitting layer to make partially insoluble cross-linked layer on top of

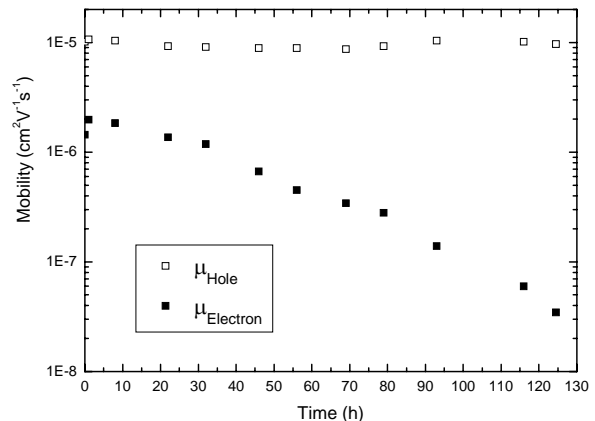


Fig 3. The mobility of both electron and hole according to driving time in logarithmic scale for assurance.

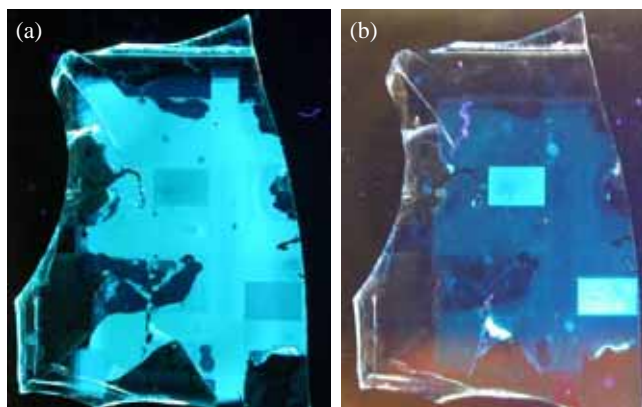


Fig 4. Photoluminescence(PL) images of the polymer EL blue device. (a) ITO/PEDOT/SB1. (b) ITO/PEDOT/Insoluble layer. Driven pixels had less PL efficiency and, in (b), had been overexposed to enhance PL intensity.

PEDOT. With the knowledge of reducing electron mobility higher than hole one, the formation of the insoluble layer on top of hole injecting PEDOT layer represents that degraded emitting polymer has lower stability of electron transporting property than hole one. It could be related with material structure itself.

To obtain more information from reverse engineering, we measured surface morphology of driven and undriven pixels using STM in Fig. 5. Undriven surface has a random distribution of aggregated emitting polymer with some minor orientation. But, insoluble surface of driven pixel shows highly ordered morphology like crystallization between aggregated polymer with reduced distance between them. It looks like a feature of crystallized domain. It could be confirmed by the fact that rms roughness of undriven surface has a value of 1.44 nm higher than 1.36nm from insoluble surface. The insoluble layer is thought to be physically and/or chemically networked system between polymer chains by electro-mechanical and/or –chemical interaction. This networked system had an unwanted behavior of charge transport and light emission. More detailed investigation of insoluble layer will be presented soon or later.

There has been some issues of using PEDOT as a hole injection layer. [5] It had been suggested that sulfur in sulfonic acid, PSS, has a high probability to make the insoluble layer inside emitting polymer due to the sulfur migration or diffusion as told by CDT. In concerning the forming mechanism of insoluble layer,

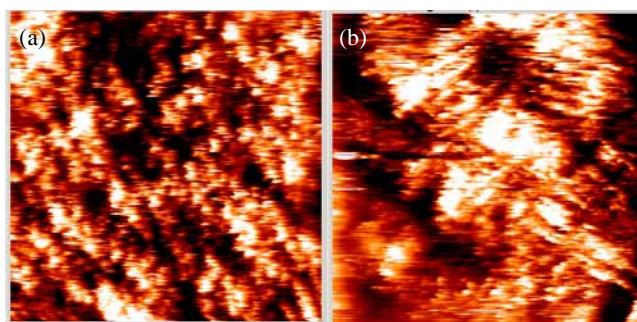


Fig. 5. STM results of undriven (a) and insoluble surface (b) with area of 500nm x 500nm. Lighter means higher altitude of surface. Rms roughnesses are 1.44 nm and 1.36 nm, respectively.

we did compositional observation using EDX filtered TEM for driven and undriven pixels as well. All samples are prepared by FIB for cross-sectional measurements. The scanning has been done from ITO side and calibrated to make zero position at ITO surface.

Fig. 6. gives the direct insight of what's going on compositionally inside polymer EL blue device before and after driving. First, we didn't see any evidence of large difference of sulfur presence inside the emitting polymer layer before and after operation. Experimentally, we already confirmed the relation between the thickness of insoluble layer and the amount of luminance drop. Then, at least, half luminance dropped sample should make almost half of emitting polymer thickness be insoluble. Thus, it surely bring us to conclude that the insoluble forming mechanism via sulfur migration or diffusion into emitting polymer dose not get any more attention as a failure mode in polymer device, rather that PEDOT's functional mechanisms like ITO corrosion due to acidity, higher water uptake, [5] and bad transport property of electron are more plausible story at least for our material and device structure. When we considered above networked insoluble layer, the proposed sulfur migration or diffusion might be hindered to block the process. Second,  $BaF_2/Ca$  layers dose not have clear or definite interface between them. Ba and F has been dissociated in some amount to present Ba-Ca-F in order, which fact had been observed in LiF cathode. [6] And, for driven sample, Ba diffusion into emitting polymer slightly increased. But, it dose not act a major role as a failure mode due to recombination zone located near PEDOT side.

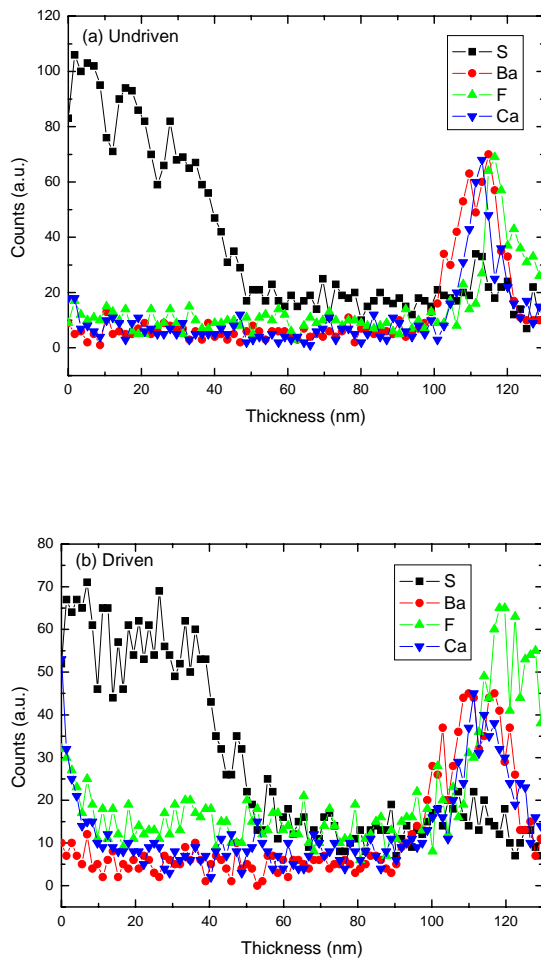


Fig. 6. EDX-TEM results for undriven (a) and driven (b) by scanning oppositely. Zero is ITO surface.

#### 4. Conclusion

We investigated polymer EL blue devices for driving/driven and undriven state with non-destructive and destructive ways.

As a non-destructive way, we measured transient EL along lifetime curve to obtain electron and hole mobility. Interestingly, rather than hole mobility, electron mobility had deeply related with luminance drop. It strongly suggests the electron transport and emission stability of emitting polymer (SB1). Through reverse engineering and observation of surface morphology as a destructive way, insoluble layer showed physically and chemically networked system. The networking between polymer chains possibly induced lowered electron mobility and its related reduced EL efficiency due to unbalanced EL operation.

Finally, as an insoluble layer forming mechanism, we did not, within experimental errors like scanning probe resolution, recognize any sulfur migration or diffusion into emitting polymer and suggest that rather other functional points of PEDOT should be considered to improve device lifetime.

#### 5. Acknowledgements

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#### 6. References

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