Ink-Jet Instability Behavior Analysis for Polymer Light Emitting Diodes Fabrication

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Abstract

A polymer light emitting diodes (PLED) is manufactured by thermal bubble ink-jet (TIJ) printing technique. This study is to solve the innate character of ink-jet instability causes the device defect in manufacturing process. Analysis shows that the ink-jet instability occurs at the beginning of each strip pixel because of the mechanical inertia force, the head start-driving instability, and the capillary pressure-driving force effects on drop landing on substrate. The mechanical inertia force generally causes an exponential decay of drop position deviation with the printing distance, and the head start-driving instability makes some nozzles have a critical characteristic in drop landing behavior. Besides, we found different bank pattern at start and end side to regulate the pressure difference will dramatic improve the uniformity of the polymer film in drying. The data shows that converging opening channel of bank pattern got uniform polymer film, and a closing channel of bank pattern made a local defect at both end of strip. By this analysis and improvement, the transient instability can be solved at same time not in conflict. Ink-jet line-width can be very stable and consistence, the line-width average is approximately 95.4 µm and the variation is approximately 2.5%. The printing PEDOT layer and the printing Green-PF layer above said PEDOT layer, it appeared a perfect film distribution in both.

I. Introduction

Polymer organic LED technologies offer many attractive properties for use in a display. The highly efficient light generation at low supply of voltages and the limited thickness of the display are advantageous for mobile applications. Furthermore, the large viewing angle, high contrast and fast switching speed give excellent picture quality for text and video mode operation. The discovery of electro-luminescence in organic molecules and semi-conducting polymers has generated considerable interest in display applications based on these materials.[1]

In past years, many groups have focused on the challenge to overcome the technical hurdles to realize high-resolution passive displays of PLED.[2-6] However, some important technical issues still leave to be resolved for applications, for example, the ink-jet stability control,[7,8] the bank pattern design[9] and the crosstalk issues.[10] Those key processes need more study to complete the full color PLED fabrication.

Figure 1 was a primitive test to verify if the ink-jet process would damage polymer materials. The PF Green polymer was used to exam the deterioration of material through ink-jet process including the thermal damage and evaporation effects. Here the thermal bubble type (TB) and piezoelectric type (PZT) print head was tested. First, the discharged ink solution by TB and PZT were collected then refilled for spin coating to make device. It's observed device performance compared with the origin, or simply spin coating situation, no damage of the material was found for these TB and PZT cases.

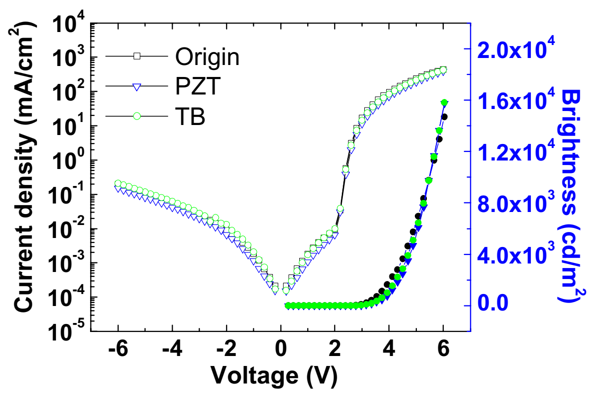


Figure 1. IVB curve

Figure 1 indicated these three different cases have only little difference in its IV curve and luminance. Basically, the difference came from the concentration variation during ink-jet collection process, for the solvent would evaporate and the concentration increases. Eventually, if we operated the collected solution and origin solution in same spin condition, it will have significant thickness difference, and lead to the performance change. The study found, if one re-dilute the collected ink solution to be consist with the origin one, its performance is nearly the same. Although the material damage was not occurred in ink-jet printing, however, the instability phenomenon is still a challenge in fabrication of PLED. This study discussed the ink-jet instability occurring at the beginning of each strip pixel by the mechanical inertia force, the head start-driving energy, and the capillary pressure-driving force effects after drops landing on substrate.

II. Treatment & Fabrication Processes

Ink-jet printing, promises to become more and more important in PLED, especially for full color display. In this study, the ink jet platform developed by OES[11,12] and equipped with the OES-II thermal ink jet print head was used for discharging the hole transport layer PEDOT:PSSA and RGB PF series inks. The orifices diameter is about 40 µm, and the ejection ink drop diameter is near 60µm. To get better printing quality and keep more stable printing condition, the driving waveform is modulated following Cheng et al. (2003) methodology.[13] This waveform modulation includes a preheating function before the main driving waveform to help bubble nucleation, and a intercooling stage follow the main driving waveform to keep the transition phase longer to create strong bubble to accelerate ink jetting velocity and reduce the jetting directional deviation.[14] Table-1 is a tabulation of all the ink-jet fabrication processes.

Table 1. Ink-Jet Fabrication Processes Parameter

Process	Description
Substrate Cleaning	DI Water Flushing IPA Flushing
Plasma Treatment	O_2+CF_4
Ink-Jet Printing	PEDOT in water
Baking PEDOT	200°C
Ink-Jet Printing Blue	PF Blue, co-solvent
Ink-Jet Printing Red	PF Red, co-solvent
Ink-Jet Printing Green	PF Green, co-solvent
Post Baking	90°C

During these processes, sometimes the baking process is used for improving the device performance. Liu et al (2001)[15] found the annealing affect the polymer morphology, and the orientation of dipole moments and the degree of interchain are subjected to change, thereby varying the optical and electrical properties of polymer thin films as well as device performance. The effects of annealing show a tradeoff between hole-injection efficiency and PL efficiency. Two approaches have been demonstrated to yield high performance PLEDs. The first one is to optimize the annealing temperatures, i.e., annealing the polymer film at a temperature close to but slightly less than the *Tg*, can dramatically increase the EL efficiency for the single layer device. In the second approach a very thin polymer film, annealed at a temperature much higher than the *Tg*, improves hole-injection efficiency.

III. Results and Discussion

Three major innate characters of ink-jet instability causing the device defect in manufacturing process were found. They are the mechanical inertia instability at print head acceleration and deceleration, the head start-driving energy instability, and the capillary pressure-driving force effects on drops landing on substrate. Below are the detail observations.

Driving Stability

Two key factors dominate the jetting behavior of thermal printing head, the waveform and driving voltage. It needed appropriate waveform modulation and the starting voltage operation range for certain ink discharging, like PEDOT and PF.

Figure 2 operated the driving voltage at different pulse width. A CCD displayed drop image and a printing system discharged ink drop were constructed and triggered by a synchronous pulse signal. The definition of the starting voltage is the ink began to can be observed, and the stable voltage is the drops remained steady with fixed pulse width as Fig. 3(a). Two instabilities occurred in observation. In Fig. 3(b), the drops didn't remain steady and they appear shaking. In Fig. 3(c), the puddling behavior is caused by insufficient driving energy causing ink coalesce on the nozzle surface. From Fig. 2, it suggested stable voltage started with pulse width greater than 2.8 µs, its stable region has approximately a 3V range. It was calculated in energy equation (1):

$$E=PW*V^2/R \tag{1}$$

where E is driving energy, PW is pulse width, V is driving voltage, R is head resistance. The stable start energy is the stable start energy is relatively low in pulse width between 3.4µs and 4.4µs, propose that pulse width region is between 3.4µs and 4.4µs. The ratios of stable voltage and begin voltage is between 1.14 and 1.35.

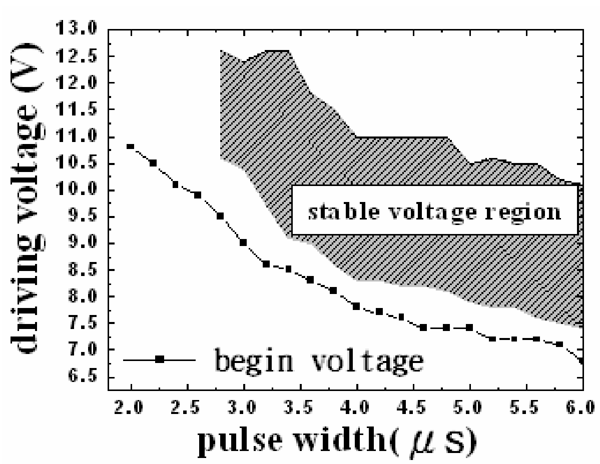
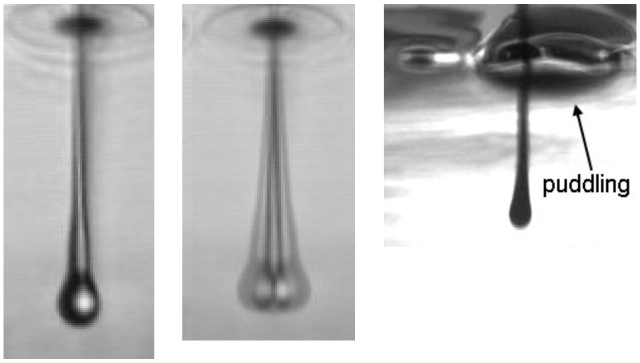


Figure 2. Driving voltage operated at different pulse width. Stable voltage started with pulse width greater than 2.8µs, its stable region approximately 3V.



(a) (b) (c)

Figure 3. (a)-(c) Observation of ink break-off behavior leave from nozzle. (a) Stable operation (b) Instable operation (c) Pudding on nozzle plate during operation.

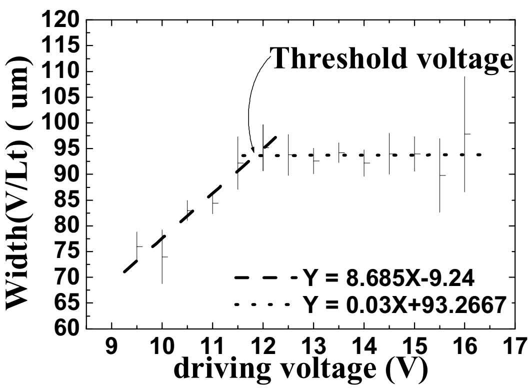


Figure 4. Ink-jet wire width for different driving voltage. Threshold voltage is 11.84V, ink-jet wire width will not increase after threshold voltage.

To find the correction of ink drop size with driving condition, we operated at different stable voltage range with the same printing pattern, to form a line after printing. Figure 4 show the ink-jet line width for different driving voltage. That ink-jet printing parameter was fixed pulse width (4 µs) as the suggestion in Fig. 2, and the driving voltage ranged between 9.5 to 17. The data show when the voltage is over 11.84V threshold value, the ink-jet line width stop growing and remain the same. Over than 15.5V, the ink-jet behavior started to be unstable, and large standard deviation appeared. This observation was very important for fabricating device, and it suggested a stable and consistence operation condition to reduce the drop-to-drop variation.

Figure 5 verified the repeat printing and its deviation in line width as operated in Fig. 2 and Fig. 4 suggestion. The ink-jet printing parameter was fixed pulse width (4µs) and driving voltage (12V). Ink-jet line-width is very stable and consistence, the line-width average is approximately 95.4µm and the variation is approximately 2.5%, the region of width between 92µm and 97µm is approximately 95.45%.

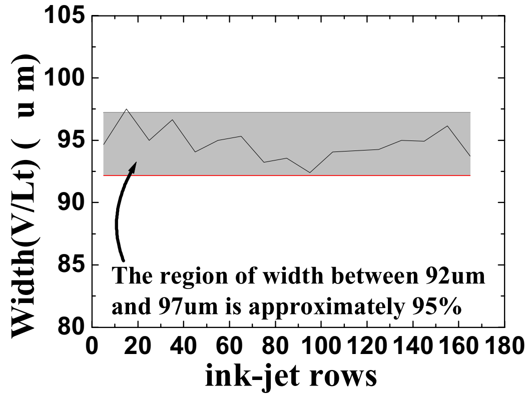


Figure 5. Ink-jet line-width for ink jet rows. Ink-jet line-width is very stable, its width is 95.4 µm.

Mechanical Inertia Affects on Instability

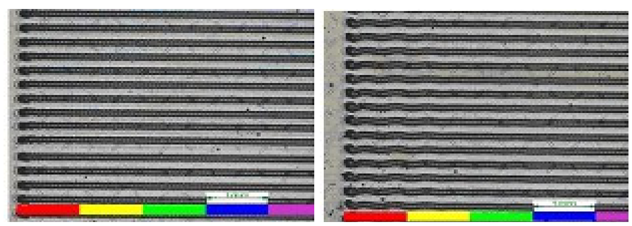


Figure 6(a) 10RPS/S *Figure 6(b) 100RPS/S*

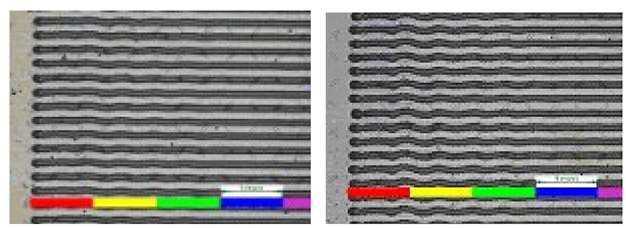


Figure 6(c) 300RPS/S *Figure 6(d) 600RPS/S*

Figure 6. (a)-(d) inertia force instability for different acceleration:10 (a), 100 (b), 300 (c), 600 (d) rps/s, it is minimum to oscillate at 10rps/s.

Figure 6(a)-(d) changed the acceleration speed from 10-600 rps/s to observe the inertia force instability acting on the print head. Printing direction was from left side (start printing) to right side (stop printing) for each strip. For each condition, the print head was operated at same driving energy and drop overlay distance. In Fig. 6(a), it was found small oscillation behavior occurred at left end of strip. With the acceleration speed increasing, obvious oscillation in left side presented, and its amplitude scaled up with the acceleration speed. The oscillation and damping frequency were related with the print head and its carriage weight, and different acceleration speed will affect different oscillation distance to get stable. When the acceleration is 10 rps/s in Fig. 6(a), it was found the influence of transient oscillation not obvious.

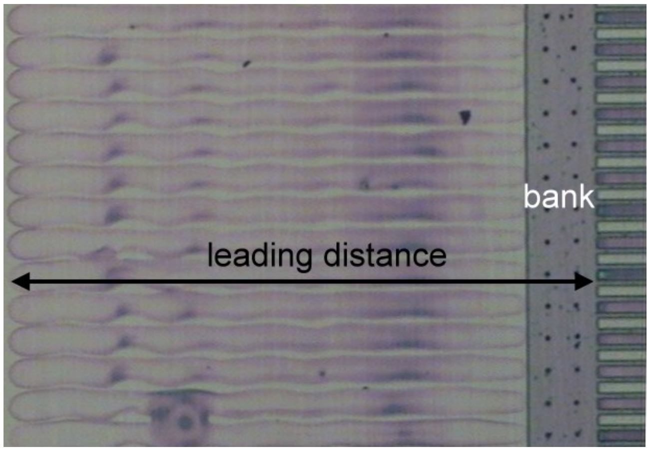


Figure 7. A 4mm leading distance is operated at 600 rps/s to keep stable into trench

Follow in Fig. 6(a)-(d) observation, generally, it was about 4mm leading distance to get stable for acceleration speed of 600 rps/s. It implies that when one operates at different acceleration speed, the leading distance should be different to insure the start of each strip is in stable, as in Fig. 7.

Shrinking Behavior in Trench

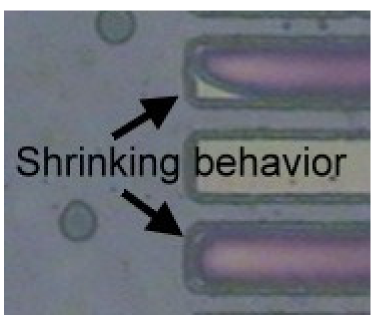


Figure 8. Shrinking behavior occurred at left end of strip.

After printing, it's found that the non-uniform wettability behavior occurred at each end of trench. This shrinking behavior occurs will make omission at both end of trench, and leakage current increase. The major reason is that the etching and developing were not perfect near the corner, and when the drop is drying, the pressure difference by capillary force shrinks from the corner, as shown in Fig. 8. To solve the defect at corner, in this study, a novel bank pattern was designed.

Open Channel Design

The open channel design concept included a converging-diverging variation in channel width. By controlling the ratio of throat width over channel width, and the converging-diverging part length, one can modulate the flowing behavior according to different solvent ink. For example, high evaporation ink needs narrower throat width to attract ink flow, and low one is in wider throat width. This converging-diverging design will balance the flow direction toward to open end to against the capillary shrinking force, to keep from the defect at end.

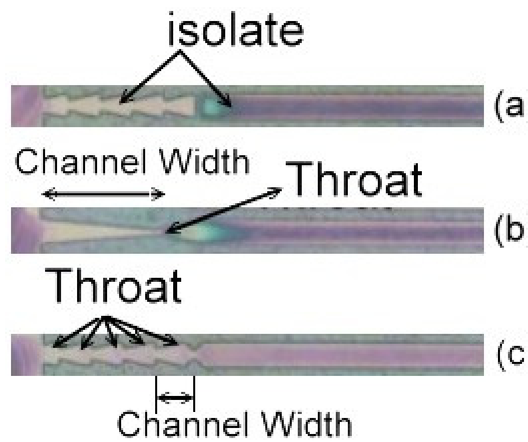


Figure 9(a)-(c). Three different bank designs for PEDOT ink-jet testing. (a) Isolated end. (b) Open end with small throat width and large diverging length. (c) Open end with large throat width and small diverging length.

Figure 9(a)-(c) compared three different bank channel design, they were isolated end design in Fig. 9(a), where the channel isolated from pixel, it was clearly found the corner existed shrinking behavior. In Fig. 9(b) and (c), an open boundary of the channel end were adopted at different throat/channel width ratio. It was found that small throat/channel width ratio limits the ink flowing toward the end, and it still has defect near the corner, as in Fig. 9(b), the throat must greater than 20μm. And for optimal controlling of the throat/channel width ratio, as in Fig. 9(c), a uniform perfect PEDOT film was feasible. Here we concluded that the throat/channel width ratio depends on the viscosity and evaporation characteristics. To control the flowing rate by this throat/channel width ratio, accumulation and shrinking behavior can be significantly improved.

IV. Conclusion

Three different instability behaviors were disclosed and solved in this paper. First, the driving waveform setting at a certain threshold value can reduce the variation behavior in line width, the ink-jet line-width is very stable and consistence, the line-width average is approximately 95.4 μm and the variation is approximately 2.5%. Secondly, the mechanical inertia instability can be solved by a leading distance pre-printing operated before ink-jet printing at the start of a trench. And finally, after printing, the corner defect can be improved by an opening converging-diverging bank design. Those transient instabilities can be solved at same time without conflict. In Fig. 10 (a)-(b), use the new open channel design, and a leading distance pre-printing to avoid transient instability. As shown in Fig. 10(a) for PEDOT layer and Fig. 10(b) for a Green-PF layer on said PEDOT layer, it appeared a perfect film distribution in both.

Figure 10(a). Ink-jet PEDOT on ITO in trench

Figure 10(b). Ink-jet Green-PF on the PEDOT /ITO in trench.

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Biography

C. F. Sung received his Master degree in engineering and system Science from National Tsing Hua University in 2003. He is now a process integration & verify engineer in the printing technology division, Opto-Electronics and Systems Laboratories of Industrial Technology Research Institute at Taiwan. His work has primarily focused on the industrial ink-jet printing processes development, especially in PLED (polymer light emitting diodes), OTFT device fabrication by ink-jet printing. E-Mail : buttonsong@itri.org.tw